# Mechanisms of Inorganic Reactions

Summer symposium of the
Division of Inorganic Chemistry
of the American Chemical Society
at the University of Kansas,
Lawrence, Kan., June 21-24, 1964

**Jacob Kleinberg,** *Symposium Chairman*

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# FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications.

# PREFACE

The Summer Symposium on "Mechanisms of Inorganic Reactions" was held in June 1964 at the University of Kansas in Lawrence, under the direction of Professor Jacob Kleinberg. It was sponsored by the Inorganic Chemistry Division of The American Chemical Society. Following the suggestion of the Division, the symposium was patterned after the Faraday meetings and was devoted almost entirely to discussion. Thus, this conference was an experiment to see if this type of meeting would be more valuable than that usually held.

Attendance was limited to 160 speakers, discussion leaders, and participants. In order for others in this and related fields to read the papers and the discussion, the entire meeting was recorded on tape and by the shorthand reporters, Suddreth, Hostetler, Lewis, and Shipley (Kansas City). The statements of the participants were sent to each individual for correction, modification, or deletion and then compiled with the papers into this book.

I wish to express my appreciation to John Bauman and R. T. M. Fraser for their extensive assistance in preparing the program and this manuscript. The authors, discussion leaders, and participants were exceptionally helpful during the conference and in the prompt modification and return of their papers and comments. The success of the conference was due in large part to the excellent preparations of Jacob Kleinberg and the University of Kansas staff.

R. KENT MURMANN

University of Missouri
January 1965

# The Role of Ion Association in the Substitution Reactions of Octahedral Complexes in Nonaqueous Solution

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**The kinetics of replacing X in complexes of the type [Co $en_2$ A X]$^{+n}$ have been reviewed. The rate dependence on the concentration of the entering reagent varies from first-order to zero-order and reflects the preassociation equilibria of the reagents and not the molecularity of the actual substitution. The nature, stoichiometry, and equilibrium constants of these ion aggregates have been discussed in terms of competition between solvent and solute for a position in the inner solvation shell of the complex. It is proposed that, although the kinetic behavior does not reflect the substitution mechanism, there are circumstances in which it is possible to distinguish between a unimolecular mechanism and a borderline bimolecular mechanism in which the entering group does not contribute to the enthalpy of the transition state.**

In molecularity studies of substitution at an octahedral transition metal ion, the reactions of cobalt(III) complexes with ethylenediamine, of the type, [Co $en_2$ A X]$^{+n}$, have provided much of the data. It was realized early that the choice of solvent was important since water, in which these compounds are conveniently soluble, interfered in studying the reactivity of the entering group. The only reactions observed were, (a) the displacement of a ligand by water (Aquation), (b) the displacement of coordinated water by an anion (Anation), and (c) the displacement of a ligand by hydroxide. In each case an important entity of the reaction was solvent molecule or its lyate ion. Therefore, any kinetic interpretation was either equivocal or impossible. In the solvolytic reaction, the zero-order with respect to

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*Paper presented by Cooper H. Langford.

solvent is not related to the molecularity. In the anation reaction, extensive mass-law retardation by water will lead to a second-order kinetic form for a unimolecular reaction (*4*). In the base hydrolysis reaction, it is not possible to tell whether the hydroxide in the product entered as such, or came in as water in a base-catalyzed solvolysis.

It was obvious, therefore, that alternative solvents should be used. The first problem was to be certain that direct substitution was occurring. Replacement of one ligand by another has been shown to be a two stage process (*6*),

$$cis\text{-}[\mathrm{Co\ en_2\ NO_2\ Cl}]^{+} + \mathrm{H_2O} \rightarrow cis\text{-}[\mathrm{Co\ en_2\ NO_2\ H_2O}]^{+2} + \mathrm{Cl^-}\ (Aquation)$$

$$cis\text{-}[\mathrm{Co\ en_2\ NO_2\ H_2O}]^{+2} + \mathrm{SCN^-} \rightarrow cis\text{-}[\mathrm{Co\ en_2\ NO_2\ NCS}]^{+} + \mathrm{H_2O}\ (Anation)$$

The relative reaction rates and the stability of the aquo complex make it possible to identify the aquo complex as an intermediate and study the individual acts separately. However, if the solvento complex were less stable and the anation rate much faster than the solvolysis, it would not be possible to observe this intermediate, and the process would be kinetically indistinguishable from a unimolecular dissociative process. Both processes would exhibit overall first-order kinetics and the usual mass-law retardation and other competitive phenomena characteristic of an extremely reactive intermediate.

This problem requires a modified approach which Gray (*16*) has solved in the case of substitution in square planar complexes. He uses the fact that bases, like hydroxide, substitute very slowly but will immediately deprotonate, and hence stabilize, a protonic solvento intermediate. This elegant approach cannot be applied to the octahedral cobaltammines whose reaction rate with such bases is very high.

Our alternative approach has been to synthesize the solvento intermediate and then study its reactions in isolation. We thereby hope to show that its reactivity and steric course is inconsistent with the postulate stating that it is an intermediate in the substitution reactions. Complexes of the type *cis*- and *trans*-$[\mathrm{Co\ en_2\ CH_3OH\ Cl}]^{+2}$ (*7*), and *cis*-$[\mathrm{Co\ en_2\ (CH_3)_2SO\ Cl}]^{+2}$ (*32*) have been prepared. We have shown in the first case that the lability of the coordinated methanol does not sufficiently explain the nonappearance of the solvento complex in the reactions of *cis*- and *trans*-$[\mathrm{Co\ en_2\ Cl_2}]^{+}$ in methanol unless it is not an intermediate in the reaction. In dimethyl sulfoxide solution, *cis*- and *trans*-$[\mathrm{Co\ en_2\ Cl_2}]^{+}$ have been shown to isomerize to an equilibrium mixture that also contains the solvento intermediate (*32*). Detailed kinetic studies indicate that about 80% of the time isomerization goes via the solvento intermediate. But this is not a rate-determining solvolysis, rather a temporary diversion of the intermediate of a dissociative reaction. Watts (*33*) has recently prepared the dimethylformamide complex, $[\mathrm{Co\ en_2\ DMF\ Cl}]^{+2}$ and has shown that it cannot be an intermediate in the isomerization of *cis*- and *trans*-$[\mathrm{Co\ en_2\ Cl_2}]^{+}$ in dimethylformamide.

In this paper we will discuss the substitution reactions of complexes of the type, $[\mathrm{Co\ en_2\ A\ X}]^{+n}$ in nonaqueous solvents and will show how the general conditions that apply here can be extended to aquation and other solvolytic reactions, and to the base hydrolysis reaction.

Brown, Ingold, and Nyholm (*9*, *10*, *11*) were the first systematically to study substitution in octahedral complexes in methanol solution. They observed two types of behavior in the reaction between *cis*-[Co $en_2$ $Cl_2$]$^+$ and a variety of anions: (a) reagents of low nucleophilicities, e.g., $NCS^-$, $Cl^-$, $Br^-$ and $NO_3^-$, entered at a common rate that was independent of their nature and concentration and (b) reagents such as $CH_3O^-$, $N_3^-$ and $NO_2^-$ were more reactive and entered at a rate that increased with increasing concentration. These observations were interpreted in terms of a dual mechanism but were later challenged successfully by Basolo, Henry, and Pearson (*26*, *27*). They showed that all the reagents, except methoxide, entered at a common rate, and that the enhanced reactivity observed for azide and nitrite by Brown *et al.* was caused by the solvolytic disturbance caused by these basic anions. Basolo *et al.* also showed that the true reaction rate between *cis*-[Co $en_2$ $Cl_2$]$^+$ and $N_3^-$ in methanol depended somewhat upon [$N_3^-$] at low concentrations. But it reached a maximum, concentration-independent rate at higher concentrations. This behavior was ascribed to ion association between the reagents, the free ion being somewhat less reactive than the ion pair.

We have recently completed a study of the isomerization, racemization, and chloride exchange rates of *cis*-[Co $en_2$ $Cl_2$]$^+$ in methanol in the presence of only small quantities of chloride. We found that the rate depended upon chloride concentration when it was low and became independent of chloride concentration in the higher region studied by Brown *et al.* The rate constants are plotted in Figure 1 as function of chloride ion concentration (*8*). These observations are very similar to those of Basolo *et al.* for the substitution by azide and can be explained in the same way, i.e., by invoking ion association. The kinetic curves can be reproduced by an ion association constant, $K$, for the equilibrium,

$$\textit{cis}\text{-[Co en}_2\text{ Cl}_2]^+ + \text{Cl}^- \overset{K}{\rightleftarrows} \textit{cis}\text{-[Co en}_2\text{ Cl}_2]^+ \cdots \text{Cl}^-$$

having a value of 250/mole at 35°C. Even though ion association causes spectrum changes in the region around 3000A., spectrophotometric estimations are unreliable since the change in absorption is small. The relationship between the various rate constants gives the steric course of the chloride substitution. This is reported in Table I.

**Table I. The Steric Course of Substitution of Chloride in cis-[Co en$_2$ Cl$_2$]$^+$ and in its Chloride Ion Pair in Methanol at 35°C.**

| | $k_{c\to t}$ × *10³/min.* | $k_{rac.}$ × *10³/min.* | $k_{exch.}$ × *10³/min.* | % *trans* | % *cis*$_{inv.}$ | % *cis*$_{ret.}$ |
|---|---|---|---|---|---|---|
| free ion | 3.2 | 4.6 | 4.6 | 70 | 15 | 15 |
| ion pair | 7.1 | 8.2 | 8.2 | 86 | 8 | 8 |

Notice the similarity of steric courses in the substitution reactions of the free ion and the ion pair, and the complete loss of optical activity for every act of substitution.

In the isomerization reactions of *cis*- and *trans*-[Co $en_2$ $Cl_2$]$^+$ in dimethylformamide and dimethylacetamide, the equilibrium isomer ratios depend upon the concentration of chloride. This has been interpreted in terms of ion association, and the equilibrium constants have been computed (*31*). The dependence of the isomerization rate upon the chloride concentration was interpreted in terms of the different reactivities of the free ion and the ion pair. Preliminary chloride exchange experi-

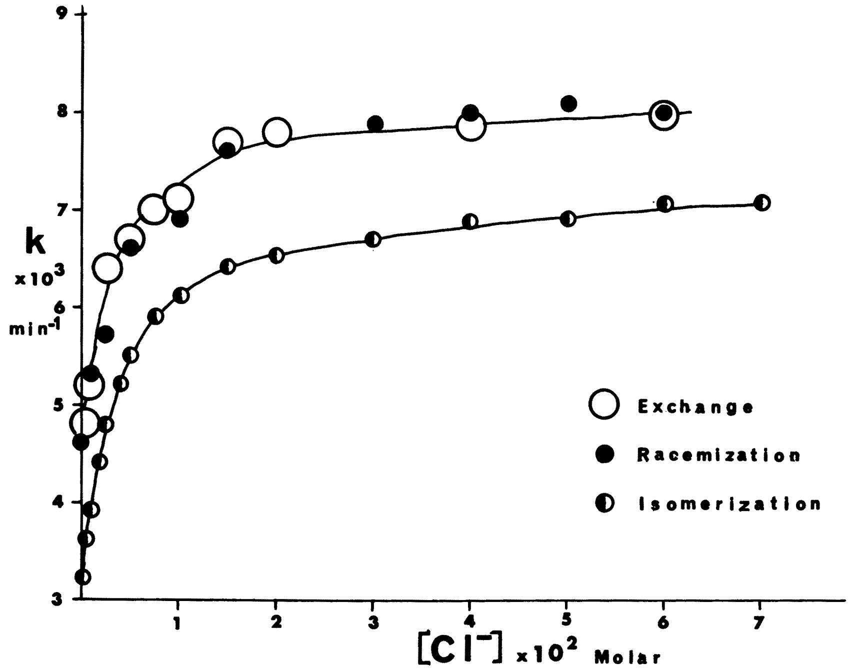


*Figure 1. First-order rate constants for the reactions of* (+)D-cis-[*Co en$_2$ Cl$_2$*]$^+$ *in methanol at 35°C. plotted as a function of the chloride concentration.*

ments indicated that the rate difference was due to a difference in the rate of substitution and not just to a change in the steric course.

The rate constants for the reactions of the free ions and chloride ion pairs of the *cis*- and *trans*-[Co en$_2$ Cl$_2$]$^+$ complexes in methanol, dimethylformamide, and dimethylacetamide are in Table II. The dots indicate that the information could not be derived from the published data—not that these quantities are insignificant.

**Table II. Ion Association Constants and First-Order Rate Constants for Chloride Exchange of Isomerisation of cis- and trans-[Co en$_2$ Cl$_2$]$^+$**

| | $K_{,}$/ mole | $K_t$/ mole | $k_{,}$/ min | $k_t$/ min | $k_{,.IP}$/ min | $k_{t.IP}$/ min |
|---|---|---|---|---|---|---|
| Methanol (35°C.) | 250 | . . . | 0.0046 | 0.00032* | 0.0082 | . . . |
| Dimethylformamide (60°C.) | 1800 | 30 | . . . | 0.003 | 0.008 | 0.093 |
| Dimethylacetamide (60°C.) | 1700 | . . . | 0.0017 | 0.0003 | 0.0041 | . . . |

* Data from Pearson (*26*) measured at 25°C.

By combining the data for the chloride exchange of *cis*-and *trans*-[Co en$_2$ Cl$_2$]$^+$ in methanol (*26, 27*) with the known fact that no cis isomer could be detected at equilibrium, it was possible to determine that the steric course of chloride exchange in the trans isomer is almost entirely retentive. This is in direct contrast to the steric courses of the reactions in dimethylformamide, dimethylacetamide, and dimethyl sulfoxide (*32*), where chloride exchange or solvolysis of the trans complex gives mainly the cis isomer. No satisfactory explanation has yet been given for this observation.

It is easy to argue that the behavior of the $[Co\ en_2\ Cl_2]^+$ isomers is not surprising. The correlation of aquation rates of complexes of the type, $[Co\ en_2\ A\ Cl]^{n+}$ with the electron displacement properties of the nonparticipating ligand, A, has led to the belief that ligands able to donate a second pair of electrons to the metal can thereby stabilize the 5-coordinate intermediate and hence promote a unimolecular reaction (*2*, *18*, *24*). Chlorine is such a ligand, C̈l—Co–:–Cl, and the essentially first-order kinetic form could be used as evidence for a unimolecular mechanism, once the ion association pre-equilibrium effects for the displacement of chloride under the electron-displacing influence of the other chlorine atom have been taken into account.

Consequently, it was interesting to study the reactions of compounds of the type, $[Co\ en_2\ NO_2\ X]^{+n}$, where the displacement of X under the electron-displacement influence of $NO_2$ was thought to take place bimolecularly. The amount of interest is reflected in the amount of work that has been published. At first sight, there appears to be little agreement between the observations of the different workers in the field. Ašperger (*3*) found that the rate of replacement of chloride in *cis*- and *trans*-$[Co\ en_2\ NO_2\ Cl]^+$ by thiocyanate in methanol solution was independent of the concentration of thiocyanate for the cis isomer, and had a mixed zero- and first-order dependence for the trans complex. Langford and Tobe (*23*) found a first-order rate dependence of thiocyanate entry into *trans*-$[Co\ en_2\ NO_2\ Br]^+$ in sulfolane upon $[SCN^-]$; but they observed that chloride reacted much more rapidly, and a limiting, chloride independent rate was reached as $[Cl^-]$ was increased. Langford and Langford (*22*) showed that the rate of replacement of chlorine in *trans*-$[Co\ en_2\ NO_2\ Cl]^+$ by thiocyanate in dimethylformamide was independent of the anion concentration.

Langford (*21*) has recently reported some anation reactions of *trans*-$[Co\ en_2\ NO_2\ H_2O]^{2+}$ in sulfolane and we have studied similar reactions over a wider range of solvent (*17*). The data for this reaction are in Figure 2, where two apparent types of behavior are characterized. Thiocyanate enters at a rate that is independent of anion concentration in all three solvents, acetone, dimethylformamide, and sulfolane. The rate is only slightly dependent upon the nature of the solvent but covers a tenfold change in rate constant. However, for a bimolecular substitution at a tetrahedral carbon atom such a solvent change would alter the reaction rate by many powers of ten. Nitrate has a similar kinetic behavior but the rate is 15% greater than that of thiocyanate. Chloride and bromide have an entirely different kinetic form. At relatively low anion concentration the rate has a mixed zero- and first-order dependence on the anion concentration. But as this increases, a limiting rate is attained. This rate is almost the same in acetone and sulfolane.

Conductiometric studies showed that ion aggregates exist under these conditions. In dimethylformamide, the association between one dipositive cation and two anions, bromide or thiocyanate, was almost complete when stoichiometric amounts of anion and cation were mixed, even in dilute solution. But there was no tendency for a third anion to be added to the assembly. In acetone, thiocyanate saturated the ion aggregate at the 2:1 composition and did not add further to it. But chloride

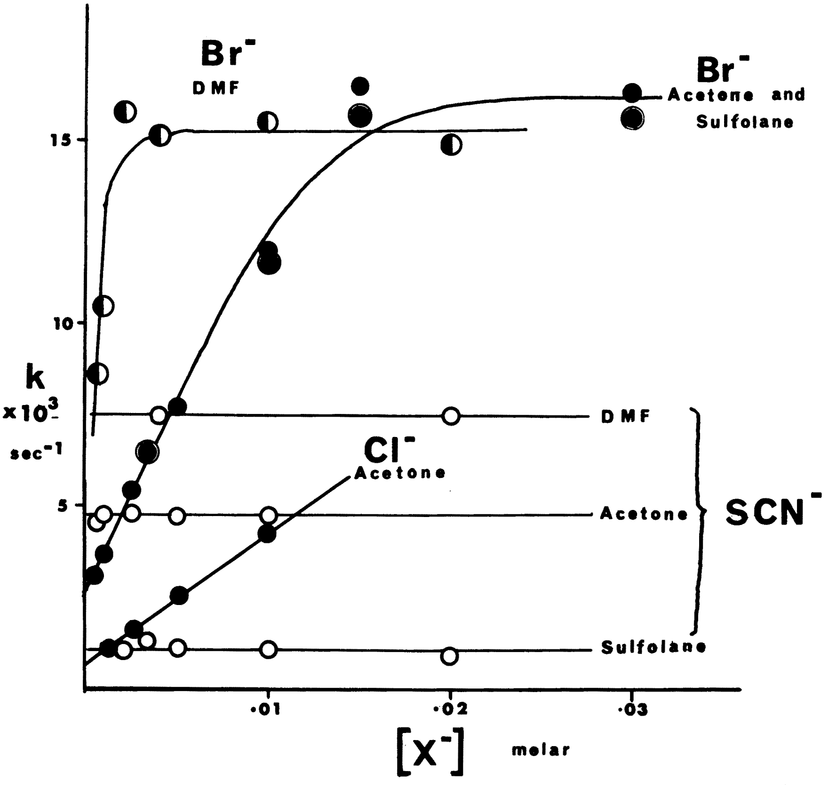


*Figure 2. Pseudo first-order rate constants for the replacement of the water in* trans-[*Co en*$_2$ *NO*$_2$ *H*$_2$*O*] (*ClO*$_4$)$_2$ *by Cl*$^-$, *Br*$^-$, *and SCN*$^-$ *in nonaqueous solvents at 25°C. as a function of anion concentration.*

and bromide ions added on to the neutral 2:1 aggregate, *trans*-[Co en$_2$ NO$_2$ H$_2$O]$^{+2}$ ··· 2Br$^-$, to form the negatively charged 3:1 aggregate, *trans*-[Co en$_2$ NO$_2$ H$_2$O]$^{+2}$ ··· 3Br$^-$.

Consequently, all the data in Figure 2 can be explained in terms of the different reactivities of the various aggregates. The insensitivity of the rate of thiocyanate entry to the thiocyanate concentration simply shows that, over the whole concentration range studied, the substrate was always in the form of the ion triplet. The rate dependence on the chloride or bromide concentration represents the change in the distribution of the substrate between the 2:1 and the 3:1 aggregate as the anion concentration is increased.

A general pattern emerges for all of the nonaqueous substitution reactions of the [Co en$_2$ A X]$^{+n}$ cations. In every case there is a limiting rate at a sufficiently high anion concentration. Sometimes this limit may have been passed at the lowest anion concentration studied, in which case the rate would appear to be quite independent of the reagent concentration. In other cases it may not be possible to attain a high enough anion concentration to detect the limiting rate. In the limit the rate would appear to depend linearly upon anion concentration.

What is the significance of this general behavior? It is easy to assume mistakenly that the similar, overall kinetic form of these non-aqueous reactions of the cobaltammines indicates a similar mechanism. Since the rates are not directly proportional to the reagent concentrations, it is easy to assume that this is a unimolecular reaction.

The limiting reaction rate can be explained in terms of the pre-equilibrium association between the cationic and anionic species. The complex, in solution, can interact quite specifically with its environment. In the absence of other interfering solute particles, this environment will consist of solvent molecules forming the solvation shell. When we consider the cations of the type, $[\mathrm{Co\ en_2\ A\ X}]^{+n}$, we find that there is considerable attraction for certain anions, often exceeding any simple electrostatic prediction. The evidence for this type of association ranges from kinetic and equilibrium studies to spectrometry and conductivity measurements. These interactions lead to forming ion aggregates which can be regarded as species in which anions occupy positions in the inner solvation shell of the complex ion. They can be called "intimate ion aggregates" in the Winstein sense of the word (*34*) or "outer sphere" complexes in the Taube sense (*29*).

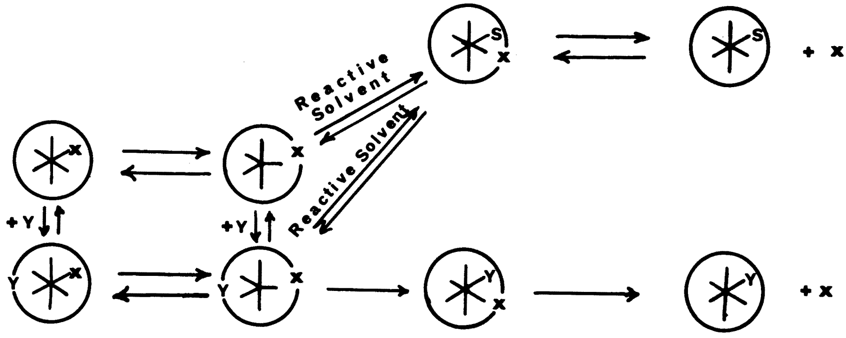
Since the attraction between the complex cation and the anions is balanced by the repulsion between the anions and by the solvent's ability to solvate the anions, there must be a maximum number of anions that can be accommodated in the aggregate. This number must depend upon the nature and charge of the cation, the nature and charge of the anion, and the nature of the solvent. There is no reason to believe that the number is limited by charge cancelling in the aggregate. Neutral reagent species can likewise preassemble in the solvation shell but they lack the initial electrostatic advantage. Although they may be affected by differential solvation effects, in appropriate circumstances, they can replace completely the original solvent so that their effect may be more pronounced in the long run.

Since movement within the solvation shell in these complexes is relatively sluggish, it is postulated that a complex remains activated only long enough to react with its immediate environment, the inner solvation shell. In the reaction with anionic species, a situation can be reached in which nearly all of the substrate is in the form of the maximum ion aggregate. Any increase in the anion concentration in the bulk solvent will not change the immediate environment of nearly all the substrate and, therefore, will not effect the reaction rate. In this way a limiting rate can be independent of the concentration of added anionic reagent, irrespective of the actual mechanism of the actual act of substitution.

Furthermore, I suggest that these reactions can be regarded as rearrangement processes of the aggregate whereby an inner sphere ligand changes place with an outer sphere ligand. Consequently, each aggregate can be assigned its own first-order rate constant for its rearrangement. Any dependence of rate upon anion concentration arises from changes caused in distributing the substrate between the various possible aggregates. For example, in the reactions described in Figure 2, the rate dependence on bromide concentration in acetone arises from the transformation of the 2:1 aggregate into the 3:1 species. The limiting rate corresponds to all of the substrate being in the form of the higher aggregate and is equal to its rearrangement rate.

This concept cannot use kinetics to elucidate the mechanism. This then raises the question of applying the molecularity concept to processes that involve rearranging a previously assembled aggregate of reagents. What is probably more important is distinguishing between the possibilities once we accept their existence. The conceptual distinction can be made by considering the timing of the bond-making and bond-breaking processes. If bond making and breaking are synchronous, the process is clearly bimolecular. If bond breaking precedes bond making, the mechanism is unimolecular with a five-coordinate intermediate. If bond making occurs first, the process will be associative with a seven-coordinate intermediate.

A possible way to distinguish the mechanism in the actual act of substitution is outlined in Figures 3 and 4. Here the solvation shell is represented by a circle around the complex, and any ion aggregate is represented by an anion in the circumference. The unimolecular reaction of the free ion requires a slow dissociation to give the five-coordinate intermediate. The departing group is then held for a short while within the solvation shell. Three possible fates await this intermediate: (1) a solvent molecule enters the intermediate from the solvation shell and solvolysis occurs. This is the normal behavior in water and happens quite often in dimethyl sulfoxide; (2) the leaving group may re-enter the coordination shell and thus no net substitution or exchange has occurred. This act is observable in the sense of being a type of mass-law retardation; (3) the intermediate will last long enough for an ion of reagent $Y^-$ to take a position in the solvation shell and then enter the coordination shell to give substitution.



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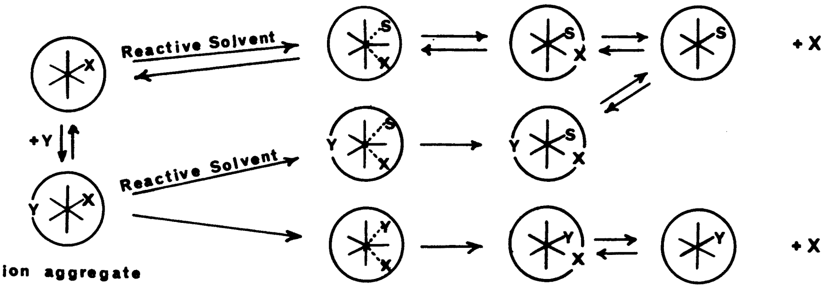
In terms of orientation within this aggregate, the leaving group, X, will hold a position in the solvation shell which is not very different from its position in the original octahedron. The consequences of this have already been discussed in connection with the steric course of unimolecular aquation (*13*). But in the general content of this reaction it means that the position taken up by the entering reagent $Y^-$ will be similar in the ion aggregate which is obtained in this way to that obtained after the initial dissociation of the ion pair formed with the octahedral complex. In other words, it is of little consequence whether, in the ion aggregate involving the five-coordinate intermediate, X has left the coordination shell before or after Y has



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entered the solvation shell. Similar steric courses of substitution in the free ion and the ion pair would result and actually have been observed.

The unimolecular reaction of the ion aggregate follows a similar course and the intermediate faces the same three possibilities for reaction. The rate of bond fission will not necessarily be the same as that of the free ion because the solvation environment has changed. We see this effect in the ion pair-catalyzed solvolytic reactions (*1*). In addition, since the reagent Y is in position before the five-coordinate intermediate is formed, the path by which X re-enters the coordination shell becomes less probable as a result of more effective competition by Y, and the rate is increased.

The bimolecular process is depicted in Figure 4, where the free ion has little choice in its reaction, being surrounded only by solvent molecules. If it can undergo solvolysis, then one of these molecules will attack; if not, there will be no reaction. The ion aggregate contains suitable reagents in the inner solvation shell, and the bimolecular reaction can take place, either by solvolysis or by anion attack.

How then can we distinguish kinetically between these two possible mechanisms? One possibility is to study the reactions under conditions where most of the substrate is in the free ion form. If the solvolytic reaction did not interfere, a first-order rate dependence on anion concentration would be observed if the reaction were bimolecular since only the ion pair can be involved in the substitution.

$$[R - X]^{+n} + Y^- \overset{K}{\rightleftarrows} [R - X]^{+n} \cdots Y^- \quad \text{ion pair}$$

$$[R - X]^{+n} \cdots Y^- \xrightarrow{k} [R - Y]^{+n} \cdots X^- \quad \text{(bimolecular)}$$

$$\text{Rate} = k[R - X^{+n} \cdots Y^-]$$

and

$$[R - X^{+n} \cdots Y^-] = K[R - X^{+n}][Y^-]$$

If only a small part of the complex and $Y^-$ are engaged in ion association, then these true concentrations will be approximately equal to the concentrations of added material and,

$$[R - X^{+n}] = [\text{complex}] \text{ and } [Y^-] = [\text{anionic reagent}]$$

so that,

$$\text{Rate} = kK[\text{complex}][\text{anionic reagent}]$$

In other words, the rate decreases to zero as the concentration of anionic reagent decreases to zero.

The reactions of the free ion and the ion pair contribute to the unimolecular reaction.

$$[R - X]^{+n} \xrightarrow{k_1} [R]^{(n+1)+} \cdots X^- \xrightarrow[\text{fast}]{+\,Y^-} [R - Y]^{+n} \cdots X^-$$

$$[R - X]^{+n} + Y^- \overset{K}{\rightleftarrows} [R - X]^{+n} \cdots Y^-$$

$$[R - X]^{+n} \cdots Y^- \xrightarrow{k'} [R - Y]^{+n} \cdots X^- \quad \text{(unimolecular)}$$

Then,

$$\text{Rate} = k_1[R - X^{+n}] + k'[R - X^{+n} \cdots Y^-],$$

which, under the conditions discussed above gives,

$$\text{Rate} = \{k_1 + k'K[\text{anionic reagent}]\}\ [\text{complex}].$$

Hence, the rate will remain finite as the concentration of the anionic reagent approaches zero.

This approach applies only when we are certain that the substrate is mainly in the form of the free ion at the lowest anion concentrations. This is true in the chloride exchange of *cis*-[Co en$_2$ Cl$_2$]$^+$ in methanol and we can safely conclude that the mechanism is unimolecular (*8*, *9*, *10*, *11*, *26*, *27*). This condition did not exist when we studied the displacement of water in *trans*-[Co en$_2$NO$_2$H$_2$O]$^{+2}$ by anions where, because of the large ion association constants, none of the substrate was in the free ion form under reaction conditions. However, in the reaction between *trans*-[Co en$_2$ NO$_2$ Br]$^+$ and thiocyanate in sulfolane, the substrate was mainly in the free ion form. The observed second-order kinetic form was fully consistent with assigning a bimolecular mechanism to the rearrangement of the ion pair.

Is it possible to distinguish the mechanism by the extent to which the rearrangement rate of the ion aggregate depended upon the nature of the entering anion? Small differences would be expected for an S$_N$1 mechanism since the presence of anions in the solvent shell would exert a "solvent effect" upon the rate of bond fission. In addition, the nature and location of the anions in the aggregate will determine the extent of the competition with the return processes and hence, affect the observed rate. If the reactivity difference of the entering nucleophiles were large (i.e., several powers of 10), as in the case of bimolecular substitution at tetrahedral carbon (*15*) and octahedral silicon (*25*), one would not hesitate to assign a bimolecular mechanism.

However, if, as has been suggested (*23*), the activation energy is collected mainly by the complex and the function of the entering group is to be present when the complex is activated, one would not expect the rate of this type of bimolecular process to be greatly sensitive to the nature of the entering group. This might explain Langford's (*20*) observation that solvolysis of Co(III) ethylenediamine complexes is far less sensitive to the solvent ionizing power than unimolecular solvolyses of tetrahedral carbon compounds; but, he also points out that the Co–X bond in the ground state is much more ionic than the C–X bond and hence there is a smaller difference in the solvation of the ground state and the transition state.

At present, although the unimolecular mechanism has been adequately demonstrated for complexes of the type [Co $en_2$ $Cl_2$]$^+$, the bimolecular mechanism postulated for complexes of the type, [Co $en_2$ $NO_2$ X]$^{+n}$ (*2*, *18*, *24*) is by no means certain. If it does exist, it is conceptually different from bimolecular substitution at platinum (II) and tetrahedral carbon. There is, as yet, no reason definitely to assign a unimolecular mechanism to their reactions and much more work will be necessary before any final conclusion can be drawn. It is interesting to note that, in going from solvolytic aquation to substitution reactions in noninterfering solvents, we still have not been able to apply kinetics directly to relate molecularity to order. Although in water the kinetic form reflected the permanent unchangeable solvent environment, the nonaqueous work shows no relationship between the controllable concentration of the reagent in the bulk solvent and the composition of the kinetically important environment of the complex. The kinetic approach is again useless, and one must use the more equivocal approaches which were applied to aquation.

The concept of preassembly as a requirement for substitution may throw light upon the vexed question of the mechanism of the base hydrolysis reaction. It has long been known that complexes of the type, [Co $en_2$ A X]$^{+n}$ can react rapidly with hydroxide in aqueous solution. The kinetic form is cleanly second-order even at high hydroxide concentrations, provided that the ionic strength is held constant. Hydroxide is unique in this respect for these complexes. Two mechanisms have been suggested. The first is a bimolecular process; the second is a base-catalyzed dissociative solvolysis in which the base removes a proton from the nitrogen in pre-equilibrium to form a dissociatively labile amido species (*5*, *19*, *30*).

Without discussing the relative merits of the two mechanisms it is interesting to point out the information that does not readily fit either mechanism: (1) the high reactivity of hydroxide is peculiar to certain Co (III) and Ru (III) complexes and the analogous complexes of Pt (IV), Rh (III), and Ir (III) appear to have little or no excess lability in the presence of hydroxide; (2) in many cases, the great reactivity difference between water and hydroxide comes mainly from the activation entropy and not the activation energy (*12*).

All of this suggests that the ion association explanation may be applied here to an essentially bimolecular (or associative) phenomenon. Considering the difference between hydroxide and any other reagent in water, apart from its basicity, one concludes that its mobility must play an important part. Whereas all the other reagents must be in a suitable position within the solvation shell before they can enter the complex, the hydroxide ion, by means of a Grotthus chain proton transfer, can be transmitted to any position where it is needed while the complex becomes activated. It can therefore be looked upon as an unsaturatable ion aggregate with hydroxide fully "delocalized" about the complex. Consequently, we do not observe any departure from the first-order dependence upon hydroxide concentration. This contribution to the reactivity will appear in the activation entropy rather than in the enthalpy term.

In conclusion, this extreme importance of preassociation of reagents appears to be peculiar to the cobaltammine systems and may very well arise from some property of the N–H bond (*27*). Recent work on the substitution reactions of [Co $diars_2$ $Cl_2$]$^+$ (diars = *o*-phenylenebis(dimethylarsine)) in methanol shows that, even in the case of the cis complex, there is absolutely no kinetic effect in isomerization, in chloride exchange or in thiocyanate substitution which can be assigned to ion association (*28*). Conductivity studies suggest that no association occurs (*14*).

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# Discussion

**Cooper H. Langford:** I don't pretend to be a chemically satisfactory substitute for Martin Tobe, but I thought it might be useful for me quickly to summarize some of the main conclusions contained in his paper. Perhaps I may also accept Kent Murmann's invitation to add just one or two things that have interested us recently which follow Dr. Tobe's suggestions concerning the importance of preassociation.

The interest in nonaqueous solutions for studying substitution reactions of the amminecobalt(III) systems began very obviously from the difficulties caused by participation of the solvent in reactions in aqueous solution. There was hope that perhaps there would be some cases in nonaqueous solvents where the kinetics would be, in a straightforward way, diagnostic of the molecularity of the reaction. The notion that the entering group might appear in the rate law (some entering group other than the solvent) and lead to a clear cut decision on the role of the entering group in the reaction, was one of the motivations for doing nonaqueous work.

As work has progressed in Dr. Tobe's hands, a new ambiguity has appeared in the kinetics for nonaqueous systems. One does find substitution reactions whose kinetics depend on the concentrations of entering anions; but, in almost all cases, detailed analysis reveals that this dependence can be accounted for by keeping track of the nature of ion aggregates, or outer sphere complexes formed. The complicated rate laws found are rather easily sorted out if one can obtain some data about the equilibrium between different ion aggregates and assign correct substitution rates for each of the various outer sphere complexes. Certainly some very interesting things do emerge from considering these systems. Dr. Tobe has found in several systems that reaction stereochemistries in the outer sphere complexes, or ion aggregates, are similar to the stereochemistries of the reactions of the free ions. I am not sure that this has been thoroughly explained, and perhaps it is an interesting point for this discussion.

Careful consideration of the outer sphere complexes does lead to an understanding of circumstances under which something definite about the molecularity of substitution reactions might be said. It becomes clear, that in order to understand the molecularity of a substitution reaction, one must find data for the concentration region of an entering or anionic group, where it is possible to measure reaction of the free ion. If one can proceed to sufficiently low concentration of the entering group so that the predominant species in solution are the free complex ion and the 1:1 outer sphere complex, an appropriate extrapolation can lead to molecularity determination. As I understand Dr. Tobe's point of view, if there is no pathway independent of the entering group, the reaction should be described as bimolecular in character, but if there is a pathway completely independent of the entering group, the reaction may be unimolecular. Now, of course, one must say, "may be unimolecular," because the same difficulty that arises in aqueous solution arises in these solvents. The complex may be reacting with the solvent to form an intermediate solvo complex, and this possibility has to be resolved before one can decide about the molecularity of the substitution process.

This is another of the very interesting contributions in Tobe's paper. Tobe has studied substitution reactions of the dichloro-bis(ethylenediamine)cobalt(III) ion in methanol, reported the preparation of the supposed solvo intermediate that would be required, and studied the rate of the chloride anion entry into this supposed solvo intermediate. He reports that the lability of methanol in this complex is insufficient to allow the complex to be an intermediate in a substitution process of the dichloro complex. Yet it is possible to obtain, in the case of the dichloro–chloride exchange, a term in the rate law for the free ion. This leads to the conclusion that, in fact, one has a genuinely unimolecular substitution process.

If there is no pathway independent of the chloride, that is, if extrapolation to very low chloride concentration of chloride exchange reaction led to a zero intercept and no free ion pathway, then we would have a bimolecular reaction. This definition of bimolecularity only requires chloride to be a component of the second coordination sphere for chloride exchange to occur.

A quibble in designating the molecularity appears. The process might be considered unimolecular if one considers the second coordination sphere as part of the complex in this single species; it might be considered bimolecular if one prefers to consider the chloride as exterior to the complex—and the aggregate two particles. But it is quite possible that the reaction mechanism is not different in any important way from the reaction mechanism that leads to a clear cut unimolecular pathway. Let's imagine an intermediate, in the sense of transition state theory, that has a minimum potential energy surface with "weak" bonds to both chlorides in the outer coordination sphere. We could have an intermediate in the sense of transition state theory but it would not be kinetically detectable, because it might react so rapidly that its second coordination sphere could not rearrange in the time for its reaction. Then, of course, it would never appear in the rate law at all.

One wonders if we are looking, in some sense, in the right direction by attempting to analyze these reactions with a notation that designates molecularity rather than focusing attention on the energetic role or lack of energetic role of the entering group. Dr. Tobe points out that a large body of the studies on the amminecobalt(III) systems can be interpreted successfully from a point of view suggesting that the reactions require preaggregation of the reactants (the original complex and the entering group), but that the activation energy for the substitution derives largely within the original complex and is not significantly reduced by participation of the entering group.

I think Dr. Tobe's paper clearly suggests that concepts developed in connection with reactions in nonaqueous solvents, preassociation, and its importance for reaction, may have important applications in studying reactions in aqueous solution. In that context I would like to offer a few thoughts on the more or less classic reaction of water with the chloropentamminecobaltic ion.

The forward reaction, the replacement of chloride by water, was studied quite some years ago. Although there has been some interest in the reverse reaction, the replacement of water by chloride, no detailed studies have been published to date.

On the general question of the anation reaction of the aquo complex by various anions, there is a little more information. In particular, of course, there are a few cases where one may identify rates of the same sort that are discussed in the paper on nonaqueous systems–i.e., rates of interchange between outer and inner sphere ligands.

In the case of sulfate and dihydrogen phosphate where the ion pair association constants have been clearly identified, the anation rates are known for the 1:1 outer sphere complex. These rate values vary somewhat, and this perhaps indicates participation of the entering group. But there may be another way to interpret what is going on. These two rates of anion entry are smaller than the rate of water exchange of the aquopentammine complex. In fact, the univalent anion enters the complex from the outer sphere at approximately one-eighth of the rate of water exchange, and the divalent anion enters the complex from the outer sphere about twice as fast.

Perhaps these results could be interpreted by adopting a model where the entering group does not participate in the activation process at all but that when the bond from the cobalt to the water is sufficiently well broken, whatever group is in place (statistically), falls in. From this point of view the number eight (as a magic number) for the number of molecules in the second coordination sphere is not entirely unreasonable.

We have some preliminary experiments on the rate of chloride entry in the aquopentammine complex over a range of chloride concentrations, which perhaps also can be incorporated into a picture of this kind.

If we plot the observed rate *vs.* the concentration of sodium chloride of less than $0.10M$ to $2M$, the rate in the low concentration region depends on the chloride concentration. The reaction is approximately second-order. (This is without controlling the ionic strength.) Slightly above $0.10M$ there is a definite change of slope, and the reaction rate is less sensitive to chloride concentration. Perhaps here again the change of slope represents the formation of the 1:1 outer sphere complex, and in this region the additional rate increase is caused by additional chloride association with the ion. If we extrapolate the high chloride portion of the curve to zero, the intercept is again approximately one-eighth of the water exchange rate, or in pretty close agreement to the rate of entry of dihydrogen phosphate.

At this point I am not sure that I am prepared to defend this interpretation. But I suggest that these results indicate that perhaps Dr. Tobe's concept of preassociation should be seriously considered in accounting for reaction process in aqueous solution which have been regarded more in terms of the dissociative process.

**Ralph G. Pearson:** I would like to say a few things in connection with the ideas brought out by Dr. Tobe's paper. First, the thing that impressed me very much was the fact that just as in an aqueous solution, for these octahedral complexes (at least the amminecobalt(III) systems) we find that the rate of the reaction is remarkably independent of the nature and concentration of the incoming group. This has, of course, led many people to discuss a reaction path in which bond making was relatively unimportant, and bond breaking led bond making to a substantial degree.

I would be interested in any comment from the audience about the chronological development of this concept. As far as I can remember, in 1958 a number of people simultaneously brought this idea forward. Roughly, it was that if we are going to replace a coordinated chlorine by something, then just as Tobe's diagram represents, we would have a mechanism in which lengthening of the cobalt—chlorine bond would be the critical step. We have to supply activation energy from within the complex, an extreme vibration, so that eventually this cobalt—chlorine bond becomes greatly lengthened and is on the verge of breaking. But I feel that for many cases of the normal substituents on cobalt it would be quite impossible for this chlorine just to leave and for a five-coordinated intermediate to remain behind.

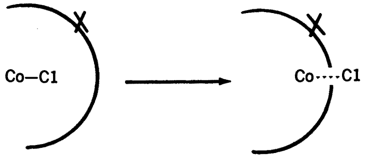

*Figure A. Solvent assisted dissociation, or SAD mechanism; X-solvent molecule or other ligand in second coordination shell.*

Also, rearrangement in many cases would be difficult because of the crystal field stabilization effects. But it could be possible that somewhere, when this bond had lengthened sufficiently, this group X could slip in; and as Dr. Langford indicated, we would then have an intermediate, or transition state, or something which would have these two groups partially bonded.

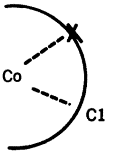

*Figure B. Partial bonding of X and Cl groups*

Then in water solution it seems that this X group is water, almost universally. But this would account for the general independence of the reaction rate on the nature of this X group.

This is the mechanism which has been called the solvent assisted dissociative mechanism, or the SAD mechanism. I think the name "interchange mechanism" might be a good one, perhaps better than the SAD mechanism.

In 1958, as I remember it, Fred Basolo and I, Arthur Adamson and Henry Taube, and H. R. Hunt came out with this mechanism basically, stressing slightly different features. Then Dr. Tobe joined the bandwagon with this mechanism in 1959, and the term "solvent assisted dissociation" was coined by Wallace and his group in Canada in 1961. That is the story as I see it at the present time

I would like to show some figures to set up some background and language.

| *Base* | $K_A$ | $k$ |
|---|---|---|
| $OH^-$ | $1 \times 10^{-16}$ | $1.7 \times 10^{3}\ M^{-1}\ \text{sec.}^{-1}$ |
| $O_2H^-$ | $1 \times 10^{-12}$ | $8.0 \times 10^{4}$ |
| $NH_2NH_2$ | $4 \times 10^{-9}$ | 33 |
| $HPO_4^{-2}$ | $7 \times 10^{-8}$ | $3.2 \times 10^{-2}$ |
| $NH_2OH$ | $2 \times 10^{-6}$ | 1.2 |
| $F^-$ | $2 \times 10^{-5}$ | $1.7 \times 10^{-3}$ |
| $NO_2^-$ | $4 \times 10^{-4}$ | $8.8 \times 10^{-3}$ |
| $H_2O$ | 55 | $4.9 \times 10^{-6}$ |
| $I^-$ | — | $3 \times 10^{-4}$ ? |

*Figure C. Rate constants for base-catalyzed hydrolysis of $Si(acac)_3^+$*

Figure C shows an extreme case of the dependence of a substitution reaction rate on the nature of the incoming group. This happens to be the hydrolysis of the trisacetylacetonate complex of silicon(IV), cationic species, which Kirchner studied first—the rate of racemization or rate of dissociation. We studied the base-catalyzed rate of dissociation and showed that a large number of anions and nucleophilic groups, in general, would catalyze in the dissociation process. We found that the reaction rates were actually for a second-order process, so these units are liters per mole per second. But the reaction rate did vary over an enormous range—in this case, about a factor of $10^9$—and this is typical of the sort of variation in rates of reaction (that you can get) for processes that seem to be $S_N2$ bimolecular displacement processes.

The mechanism, incidentally, for this acetylacetonate case is not unambiguous and it is possible that nucleophilic attack occurs at the ligand ring in one of the carbonyl groups.

You will notice in this case that the nucleophilic reactivity constants—these rate constants—vary roughly with the basicity. Hydroxide ion is almost the most powerful nucleophilic reagent because it is the strongest base that can exist in aqueous solution. Water is the weakest nucleophilic reagent, simply because anything weaker than water is not detectable in an aqueous solution. So this number is the lower limit for nucleophilic reactivity.

For other nucleophiles such as iodide—really one can't decide whether there is a nucleophilic rate constant for iodide or not, because you have to have enormous concentrations of iodide to detect a rate constant of this value. So this number here is really just an upper limit to what the reactivity of iodide is.

Notice—and I want to make a point of this—the hydrogen peroxide anion is a better nucleophilic reagent than the hydroxide ion by a factor of about 50, even though hydrogen peroxide is a stronger acid than water by a factor of about $10^4$. We convert water to the same units as hydrogen peroxide.

This is an example of what John Edwards and I call the alpha effect. I think it is valuable because it does enable us to generate quite easily a very powerful nucleophilic reagent in water, this hydrogen peroxide anion.

This particular nucleophilic reactivity series which we find for silicon(IV) is not necessarily characteristic of what one would expect to find for all different metal ions. And in fact, we know in the case of platinum(II), where $S_N2$ reactions seem to occur quite commonly, that we get quite a different nucleophilic reactivity series. The variation in rates for platinum(II) is almost as large as this. I don't know that an actual range of $10^9$ has been covered yet, but the order of the different nucleophiles is quite different.

The next two figures introduce some terminology about hard and soft that I am pushing at the moment, because I think it is useful. Daryle Busch suggested this to me one time and I picked it up and found it useful.

| *Hard Bases* | *Soft Bases* |
|---|---|
| $OH^-$, $F^-$ | $I^-$, $R_2S$, $R_3P$ |
| $SO_4^{-2}$, $PO_4^{-3}$ | CO, $CN^-$, RCN |
| $CH_3COO^-$, $RO^-$ | $C_6H_6$, $C_2H_4$ |
| $Cl^-$, $NH_3$ | $H^-$, $R^-$ |

*Figure D. Examples of some hard and soft bases*

We define a hard base simply as one that is not very polarizable. It usually means also that the basic atom is one of high electronegativity and not very easily oxidized. The typical hard bases would be oxygen atom ligands and fluoride ion, with chloride ion and ammonia certainly not as hard as those, because chloride is more polarizable than fluoride, and ammonia is more polarizable than water.

By soft bases I mean highly polarizable bases. This usually means not only large atoms such as iodide and sulfur, but also unsaturated systems such as the nitriles, the olefins, the aromatics, and the alkyl and hydride ions which are known experimentally to be highly polarizable. Soft bases are of low electronegativity and easily oxidized.

Figure E shows the corresponding entries in the case of the acids which coordinate to these various bases, forming our familiar coordination compounds in some

| *Hard Acids* | *Soft Acids* |
|---|---|
| $H^+$, $Mg^{+2}$, $Al^{+3}{}_b$ | $Cu^+$, $Pt^{+2}$, $Hg^{+2}$ |
| $Cr^{+3}$, $Si^{+4}$, $As^{+3}$ | $RS^+$, $I^+$, $HO^+$ |
| $BF_3$, $PRO_2{}^+$, $RSO_2{}^+$ | $I_2$, nitrobenzene, quinones |
| $R_3C^+$, $RCO^+$ | O, Cl, $R_3C$ |
| HX (hydrogen bonders) | Metal atoms |

*Figure E. Examples of some hard and soft acids*

cases, or perhaps other types of complexes, such as charge transfer complexes, in other cases.

We define the hard acids simply as those of low polarizability. They would be of small size and high positive charge. The soft acids would be those of high polarizability, large size, and low positive charge. As you can see, there are many other acids besides metal ions which can be classified in this way.

Now as far as metal ions are concerned, this classification is identical with—in fact I use the same operational definition as that which Chatt, Ahrland, and Davies use. Hard acids would be Class A metal ions and soft acids would be Class B metal ions; but I don't think Class A and Class B mean quite the same thing as hard and soft, because hard and soft have wider applicability in that you can discuss other systems as well. And furthermore, I think bases can be classified as hard and soft, and then one has this very useful rule that hard acids like to combine with hard bases, and soft acids like to combine with soft bases. This is just an empirical observation—various theories can be put forward to account for it—but it is a fact, and the reason we should be aware of it is because if we are looking at kinetics, if we are looking at reaction rates, then we should remember that our substrate, that is, the complex which is going to lose a group, will provide the acid site. The metal atom will be the electrophilic center or the acid site. Depending upon whether that is a hard acid site or a soft acid site, we will expect that nucleophiles, either highly basic towards the proton (the proton is the key hard acid, the prototype hard acid) or else the polarizability phenomenon will be important—one or the other. For silicon(IV) it seems that basicity is important, for platinum(II) it seems that polarizability or low electronegativity is important. So we expect to get different nucleophilic orders, certainly.

I want to say something about the end of Dr. Tobe's paper on base hydrolysis. The University College School has been feuding with some of us on this side of the ocean regarding the mechanism of base hydrolysis of cobalt pentammines for some years, and they are extremely ingenious at coming up with alternative explanations for all of the conclusive experiments that we seem to do. However, I am strongly of the opinion that much of this resembles the clouds of black ink that the cuttlefish is said to emit when it is escaping from some pursuer.

$$Co(NH_3)_5Cl^{+2} + OH^- \rightarrow Co(NH_3)_4NH_2Cl^+ + H_2O$$
$$Co(NH_3)_4NH_2Cl^+ \rightarrow Co(NH_3)_4NH_2{}^{+2} + Cl^-$$
$$Co(NH_3)_4NH_2{}^{+2} + H_2O \rightarrow Co(NH_3)_5OH^{+2}$$

*Figure F. $S_N1CB$ Mechanism*

Figure F shows the conjugate base mechanism for base hydrolysis. Dr. Tobe suggests essentially that in base hydrolysis, the hydroxide ion occupies a unique position for one of several reasons. Perhaps the hydroxide ion is hydrogen bonded to an NH group, and that is the reason why it is special. Why other anions wouldn't be bonded to an NH group escapes me. The other thing is that perhaps the hydroxide ion can penetrate to a reaction site very quickly by a "Grotthus" chain mechanism. In other words, we might always have water close to chloride ion, which is going to be a leaving group; then as the cobalt—chlorine bond stretches, that water molecule might instantaneously be converted to a hydroxide ion by a proton transfer mechanism. I think this sort of thing can indeed happen, and it is certainly worthwhile considering the possibilities of rapid proton removal converting a weakly nucleophilic water to a strongly nucleophilic hydroxide ion.

Incidentally, I should say that the thermodynamic data on cobalt(III) indicates that it is a hard acid, but just barely so, and one might say borderline. It is a little harder than tetrahedral carbon and alkyl halides. So hydroxide ion in that sense would be expected perhaps to be a good nucleophilic reagent, as hard acids would like hydroxide ion.

The alternate mechanism which opposes the hydroxide ion as actually being the group that slips in either an $S_N2$ mechanism or some variation of an $S_N2$ mechanism is, of course, the conjugate base mechanism proposed by Garrich in 1937. The loss of a proton, with the amido group acting as a powerful activator owing to $\pi$-bonding, would be the first step. Unimolecular dissociation then occurs forming a five-coordinated intermediate which has some moderate kinetic stability, at least under suitable circumstances. Then water is picked up by this five-coordinated intermediate, followed by rearrangement of protons and the attainment of the final product.

Fred Basolo and I have come up with at least three critical tests of this particular mechanism to distinguish it from an $S_N2$ mechanism. One critical test is based on the fact that this mechanism requires acidic protons, whereas other straightforward displacement mechanisms certainly would not require such acidic protons. Admittedly, the concept of hydroxide ion binding to an NH group also requires acidic protons.

By now a great many studies of such complexes have been made, and Dr. Tobe reports one himself, the diarsine complex. For all those cases involving an unidentate leaving group, the rate of the hydrolysis under basic conditions is no different from the rate of hydrolysis under acid conditions. As far as I can tell, for unidentate ligands, at least where the results perhaps are a little less unambiguous compared to chelate leaving groups, the requirements of a conjugate base mechanism have stood up to tests even on the side of the opposition.

The second critical test of this conjugate base mechanism is based on the fact that this five-coordinated intermediate, if indeed it exists, would not always have to react with the solvent, though the solvent would be what it would react with under most circumstances. We have run this type of base hydrolysis in the presence of many anions of high concentration, and the only thing that we can find is the hydroxo complex; so at least in water solution, water seems to be what this five-coordinated intermediate picks up. But in dimethylsulfoxide it certainly is possible to throw in various anions, and since dimethylsulfoxide is not as good as water in coordination, other nucleophiles may react. We do find in dimethylsulfoxide that a base, such as hydroxide ion, speeds up the rate of base hydrolysis; but the product, instead of being a hydroxo compound, is the complex corresponding to whatever anion we have added, such as nitrite ion, azide ion, and thiocyanate ion.

It is interesting that Taube and Green have done this same experiment essentially in water. I said that we couldn't do this experiment in water because water always was the reactant and not other added anions. But Taube and Green very cleverly took advantage of the fact that an isotope discrimination factor for oxygen-18 such as the ratio of oxygen-18 to oxygen-16 in water is not the same as the ratio in hydroxide ion. This in effect labels the hydroxide ion and distinguishes it from water, in spite of the fact that rapid proton transfer is occurring. Green and Taube showed that in base hydrolysis in aqueous solution, the hydroxo complex that they obtained had an oxygen ratio such that the hydroxo group must have been derived from water and not from hydroxide ion. This experiment seems to me to be pretty unequivocal and, in fact, the exact analog of the experiment that we did in dimethylsulfoxide.

The third test of the conjugate base mechanism that we put forward was based on the idea that the first step should be written as an equilibrium, and the reaction rate should show specific hydroxide ion catalysis. If this is indeed in equilibrium, and deuterium exchange studies say that it must be, then the rate of the reaction must depend on the hydroxide ion concentration, and on nothing else.

This is experimentally what is found, of course; but then it makes one wonder if $S_N2$ mechanisms exist when one never gets any effect of any other added nucleophile. We did what I thought was the extreme thing to distinguish between $S_N1CB$ mechanisms and $S_N2$ mechanisms. We added hydrogen peroxide to the solution of hydroxide ion and cobalt chloropentammine. Now, if it were an $S_N2$ reaction, the argument would be that the anion hydrogen peroxide in every case that has been tested—and there are about a dozen of them—is anywhere from 35 to 10,000 times more reactive than the hydroxide ion as a nucleophilic reagent. So, if there is any $S_N2$ character to this reaction, it seems to us that we should have gotten some increase in rate. On the other hand, because of the fact that hydrogen peroxide is a stronger acid than water, adding hydrogen peroxide, of course, cuts down the hydroxide ion concentration drastically. This draws the equilibrium way back to the left, and hydrogen peroxide should decrease the rate of the reaction. At $1M$ hydrogen peroxide, in fact, one should get a decrease in the rate of the reaction by a factor of 150. Here we had either the possibility of an increased reaction rate, or a decreased reaction rate both by a factor of a 100 or so. I hardly need to say, that the reaction rate decreased by a factor of 100.

It seems to me that we have given this particular reaction mechanism as many tests as possible.

Now, let me dispose of, I hope, Tobe's argument that perhaps a Grotthus chain transfer mechanism is involved. The argument would be that the hydroxide ion can appear anywhere by being generated from water by a proton transfer. I admit this, but the very simple thing is, if hydroxide ion can generate hydroxide ion by a proton transfer, why can't all other bases generate hydroxide ion by a proton transfer? If all one needs to cause a rapid reaction of cobalt complex is to be able to create hydroxide ion on demand by a proton transfer, any base will do this; and the hydrogen peroxide anion, in fact, may do it better than the hydroxide ion, from the viewpoint of rate, not equilibrium.

But we know from many experiments done by many workers that no other base in the case of the typical pentamminecobalt or chloramminecobalt systems—no other base shows any kinetic effect at all that I am aware of. It seems to me absolutely incredible that only the hydroxide ion would be privileged to indulge in proton transfer, and that all other bases would be excluded.

In the acid hydrolysis of the pentamminecobalt complexes where you have a leaving group, such as nitrato or bromo, H. Taube and A. Haim came out with some very interesting work, with which I am sure you are all familiar. They suggested that the five-coordinated pentamminecobalt species was formed which then discriminated between various nucleophilic reagents, sometimes reacting with water, sometimes with thiocyanate ion. In fact, they were able to measure these nucleophilic discrimination factors in a number of cases, and they were able to correlate different types of reactions in which the pentamminecobalt would be generated in different ways.

I was shocked when I saw this paper because we have been of the opinion for a long time that this pentamminecobalt species is much too high in energy to exist for a long enough time to discriminate between different nucleophilic reagents. In fact, even in the base hydrolysis where we have a strongly activating amido group it doesn't seem possible to get discrimination in water solution.

There are some simple tests of this hypothesis of Haim and Taube. All we have to do is to carry out acid hydrolysis of one of these typical complexes in the presence of a large amount of an anion. Then we should go directly to the anionic complex according to Haim and Taube. I felt that we would not form any large amount of the anionic complex, because the pentamminecobalt intermediate is not formed, and instead we would go to the aquo complex and then from the aquo complex to the thiocyanate complex, or whatever it might be.

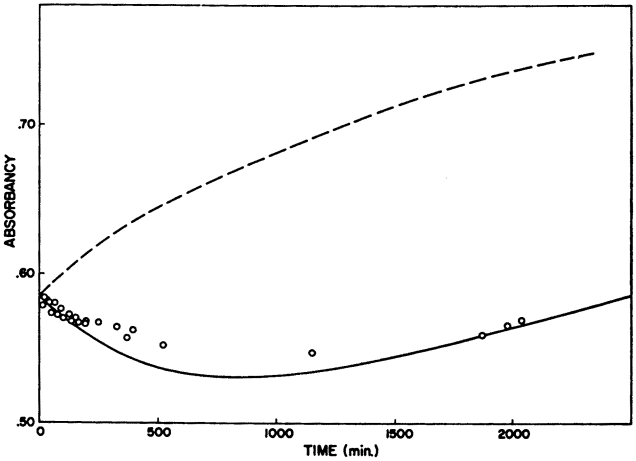

*Figure G. Plot of absorbancy vs. time for aquation of* $[Co(NH_3)_5NO_3](NO_3)_2$ *(0.01M) in the presence of 0.50M NaSCN;* $H^+ = 0.02M$. *Upper curve calculated for mechanism involving a five-coordinate intermediate. Lower curve calculated for mechanism involving conversion to* $Co(NH_3)_5H_2O^{+3}$ *which subsequently reacts to form* $Co(NH_3)_5NCS^{+2}$. *Points are experimental. (Inorg. Chem.* **3**, *1334 (1964).*

Figure G shows the results of the following reaction.

$$[Co(NH_3)_5NO_3]^{+2} \xrightarrow[NCS^-]{0.5M} [Co(NH_3)_5(H_2O)]^{+3} + NO_3^-$$

This is the optical density plotted against the time for an experiment in which we took the nitratopentamminecobalt complex in the presence of 0.50$M$ thiocyanate ion since the competition ratio for thiocyanate ion and for water had been determined by Haim and Taube. Knowing the optical densities of all the possible reactants and products, we could calculate what the optical density should be as a function of time according to the mechanism of Haim and Taube. This calculation depends upon a rate constant for the aquation of the nitrato complex which we took from the literature. But one should get a continuously increasing optical density because the thiocyanate complex has a higher optical density than anything else.

However, if reaction went by way of aquation to an aquo complex and then anation of the aquo complex to the thiocyanato, and we knew this rate constant, then the optical density would do the following: since the aquo complex has a lower extinction coefficient than the nitrato, the density would drop first and then eventually rise, and of course the two curves would come together eventually.

The experimental points here follow the predictions of the second mechanism very closely, and I would say that not more than 2% of thiocyanate complex is formed directly. Taube and Haim's prediction would be 14%.

We have done the same experiment, incidentally, for the bromopentammine and the results are precisely the same. You will recall that Langford mentioned that also in the hydrolysis of the chloropentammine there was no mass law retardation such as would be predicted from the mechanism of Haim and Taube.

**Arthur W. Adamson**: I would like to say that two years ago I had the privilege of a year's visit at University College London and that Dr. Tobe and C. K. Ingold represented an island of England in the Australian Sea.

I want to fill in some of the discussions we had at UCL on what I was calling the cage mechanism, to add still another to the list of names. I think it is better than the SAD mechanism. But the point that I think is essential to the general idea is that which comes out of the following set of numbers. If one considers a bimolecular gas phase reaction, and let's say 0.01$M$ reagents, one can expect a molecule to experience something like $10^9$ collisions per second.

The situation is different with solutions, where the reactant molecules must diffuse together. For the same 0.01$M$ concentration of A and B reactants, the frequency with which either makes a diffusional encounter with the other will be about $10^7$ per second. They will then undergo about 100 collisions or vibratory impacts before diffusing away, so that it is the pattern rather than the total number of collisions that is different from the gas phase case.

If, now, 20 or 30 kcal. of energy of activation are needed for reaction, one supposes in the gas phase situation that the colliding molecules must have this amount of kinetic energy or of available internal energy between them. The approximate picture is then that of simultaneous assembly of the energy and of the components of the transition state. In the case of a liquid phase situation, however, it is unlikely that a molecule having accidentally acquired this sort of energy will be able to retain it for more than a few vibrational periods. In the above illustration, a reactant spends about $10^{-7}$ seconds or about $10^5$ vibrational periods between encounters and about a hundred such periods during an encounter. It seems clear that only if the needed activation energy happens to arrive while reactants are undergoing an encounter will there be much chance of reaction.

The approximate picture provided by the cage mechanism is then one of a preassembly of the reactants by diffusional encounters (whose duration may be lengthened if attractive forces or chemical bonding ability is present) with subsequent arrival of the energy of activation.

The central argument, namely that excess energy cannot be held for long times compared to vibrational periods, is supported by our own work on photochemistry. Here, large amounts of energy are delivered to a complex ion and more often than not, escape as vibrational or thermal energy without any reaction's occurring. Were it possible for such energy to be retained between encounters, photochemical quantum yields should always be very high.

One important implication of the cage mechanism is that those reactions should be favored for which there is a high probability for the reactants to be in each other's vicinity or cage. Hence, the prevalence of aquation reactions and the importance of ion pairs as intermediates in anation reactions. I think it is very interesting that John Bailar's examples of stereospecificity involve rather drastic changes in the immediate environment around the complex since concentrated systems were used in the one set of cases, and dilute ones, in the other.

Dr. Pearson has been somewhat blunt. I think the $S_N$ designations of reactions have constituted a kind of wasteland, in that there has been too much tendency to make distinctions without real differences and too much pigeonholing of reactions by label. The effect has been to reduce rather than enhance understanding.

**Martin Tobe:*** I would like to take this opportunity of putting on record my thanks to Dr. Cooper Langford for the excellent way in which he rose to the occasion and presented my paper.

I want to take issue with Prof. Pearson on two points from his supplementary lecture. I see that he does not like a dissociative mechanism in which the five-coordinate intermediate has a finite existence. I am not quite sure whether he is attacking this concept on energetic grounds but, if he is, we are harking back to the arguments used against Dr. Ingold in the thirties when he proposed the now accepted unimolecular mechanism for certain substitution reactions at tetrahedral carbon. We must remember now, as then, that when there is sufficient separation between reaction center and the leaving group, the gain in solvation energy of the forming components overcompensates the energy required to stretch the bond further and finally break it. Thus, if Dr. Pearson is happy to stretch the metal—ligand bond to its critical distance, he should not be surprised if it "comes apart in his hands." As has been pointed out many times, the transition state for a unimolecular process still has a partial bond between the reaction center and the leaving group and should not be confused with the intermediate of lower coordination number, which is somewhat more stable. The incoming reagent enters this intermediate and not the transition state. We really need a five-coordinate intermediate to explain why we have stereochemical change in certain reactions.

The so called "solvent assisted dissociation" mechanism in which reagent Y (which may or may not be solvent) slips in when the bond between the metal and

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* These comments added after the conference by invitation.

the leaving group is stretched beyond a critical length, is identical in concept to the process that I have described for the reactions of the $(Coen_2AX)^{+n}$ complexes, where $A = NO_2$, $NH_3$, and CN, the quasi bimolecular reaction. It is sterile to argue about the words used to describe it as long as there is general agreement about the picture itself. This type of process most certainly explains the observation that these complexes undergo substitution with complete retention of configuration. The mechanism is probably general for the substitution reactions of analogous Rh(III) and possibly Cr(III) complexes where retention of configuration on substitution appears to be the general rule.

For my second point, I want to comment on Prof. Pearson's reaction to the minor comment that the conjugate base mechanism does not explain a number of important observations on the base hydrolysis reaction, and the imaginary feud to which he refers. For a number of years, we have accepted that a classical bimolecular mechanism is unlikely in the substitution reactions of the amminecobalts, but we feel that the uniqueness of the hydroxide reaction cannot be attributed to a naive $S_N1$*CB* mechanism either. Neither mechanism can explain adequately the rapidly accumulating data (coming mainly from the group at Northwestern University) which show that the special reactivity of the lyate ion is peculiar only to certain Co(III) and Ru(III) complexes. While one may still be in the dark as to precisely what it is that hydroxide does when it presents itself to the complex, I still think that it is reasonable to attribute, as I have done in the paper, a great deal of its specificity to the fact that it is mobile through the solvent shell (which is in accord with the observation of large positive entropies of activation). Dr. Pearson's "demolition charge" for the Grotthus chain hypothesis clearly failed to explode, possibly because it was a little wet. In the solvent system that he uses for the hydroperoxide experiment it is very unlikely that the solvation shell of the complex contains any hydrogen peroxide molecules. There is therefore no chance of a hydroperoxide ion's presenting itself for reaction. (If the reaction were carried out in 100% hydrogen peroxide, I have no doubt that the results would be startling!) Hydrogen peroxide, being a stronger acid than water would monopolize most of the Grotthus chains (which is saying much the same as "hydrogen peroxide reduces the concentration of hydroxide") and so leads to a reduction of rate (which is precisely what was observed).

## 2

# Mechanisms of Substitution Reactions of Cobalt (III) Cyanide Complexes

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**A review has been made of the kinetic data for the substitution reactions of the $Co(CN)_5X^{-3}$ ions, where X refers to any one of various ligands. The evidence suggests that the pentacoordinate $Co(CN)_5^{-2}$ is generated as a reactive intermediate in the substitution of water in $Co(CN)_5OH_2^{-2}$ by various nucleophiles and in the aquation of the various $Co(CN)_5X^{-3}$ ions. Preliminary studies indicate that the intermediate detected by the scavenger action of $Br^-$ and $SCN^-$ in the reaction of $HNO_2$ and $Co(CN)_5N_3^{-3}$ is a different species than the one discussed above.**

The results below consist of kinetic studies of the following reactions: *a*) the substitution of water in $Co(CN)_5OH_2^{-2}$ by various nucleophiles (*3*, *7*) including $H_2O^{18}$, b) the aquation (*3*, *7*) of $Co(CN)_5X^{-3}$, where $X^-$ represents one of a variety of nucleophiles, c) the scavenger (*3*, *7*) action of $SCN^-$ for the reactive intermediate generated in the acid-catalyzed aquation of $Co(CN)_5N_3^{-3}$, and d) the scavenger action (*5*) of $Br^-$ and $SCN^-$ for the reactive intermediate formed in the reaction of $Co(CN)_5N_3^{-3}$ with $HNO_2$, a process which produces $Co(CN)_5OH_2^{-2}$ in the absence of scavengers.

### *Anation of $Co(CN)_5OH_2^{-2}$*

All experiments were carried out at constant ionic strength and constant cation concentration, a restriction designed to minimize medium effects (*10*, *11*). Negatively charged nucleophiles were introduced into the solution as sodium salts, and the ionic strength was adjusted to the desired value by addition of the appropriate amount of $NaClO_4$. In the presence of a large excess of a nucleophile, $X^-$, the rate of formation of $Co(CN)_5X^{-3}$ is characterized at each concentration of $X^-$ by a pseudo-first-order rate constant, *k*, the numerical value of which may be evaluated from the slope of the linear plot of log $(D_\infty - D_t)$ *vs.* time, where $D_t$ and $D_\infty$ are the molar absorbancies of the solution after a reaction time *t*, and after a time long enough for the system to approach equilibrium, respectively. Numerical values of *k* were obtained for each nucleophile at a number of $X^-$ concentrations.

The formation of $Co(CN)_5X^{-3}$ by a rate-determining bimolecular reaction of $Co(CN)_5OH_2^{-2}$ and $X^-$ would imply that in the absence of medium effects the ratio $k/(X^-)$ should be a constant, independent of the $X^-$ concentration, for any given nucleophile. However, in experiments at unit ionic strength, it was found that the quantity $k/(X^-)$ decreased with increasing $X^-$ concentration, with the deviation from constancy generally increasing with increasing reactivity of the nucleophile. This behavior is illustrated in Figure 1, a plot of *k vs.* $X^-$ for two typical nucleophiles, $N_3^-$ and $Br^-$. For each nucleophile the point at $(X^-) = 0$ represents the aquation rate of $Co(CN)_5X^{-3}$, the appropriate intercept for either an $S_N1$ or $S_N2$ mechanism. The points for $Br^-$, a rather unreactive nucleophile, define a straight line to within the limit of error of the measurements. By contrast, the points for the much more reactive $N_3^-$ fall on a curve with the limiting slopes, corresponding to the dotted lines in the figure, having the numerical values of $80 \times 10^{-5}$ and $38 \times 10^{-5}$ at zero and $1.0M$ $N_3^-$, respectively. Other nucleophiles, to be discussed below, show an analogous behavior.

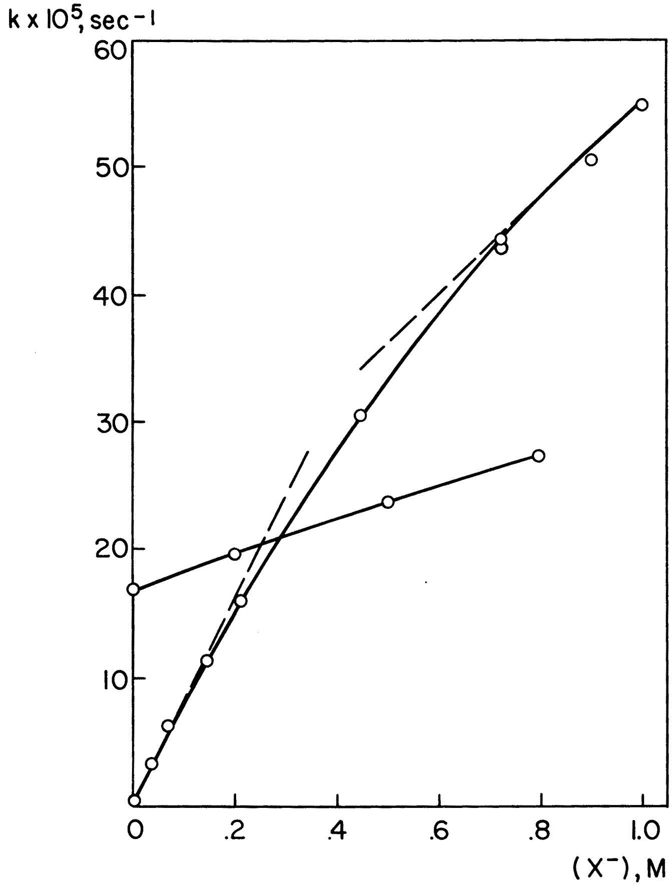

*Figure 1. Pseudo first-order rate constants vs. anion concentration at 40°C. and ionic strength 1.0M*

Curvature in a plot of $k$ *vs.* ($X^-$) suggests that the substitution reaction under consideration is occurring by a limiting type of $S_N1$ mechanism in which $X^-$ is reacting with a reactive intermediate, formed from $Co(CN)_5OH_2^{-2}$ and having a life time long enough to distinguish between various nucleophiles in the solution. In the reaction sequence below, which will be adopted in the following discussion of mechanisms, the proposed reactive intermediate has been assigned the formula $Co(CN)_5^{-2}$ and is regarded as a five-coordinate Co(III) complex of unspecified geometry.

$$Co(CN)_5OH_2^{-2} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(CN)_5^{-2} + H_2O \tag{1}$$

$$Co(CN)_5^{-2} + X^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Co(CN)_5X^{-3} \tag{2}$$

The forward and reverse paths of Reactions 1 and 2 serve to define the rate constants $k_1$, $k_2$, $k_3$, and $k_4$, the symbols placed over or under the appropriate arrows, with the exception that the concentration of water is included in $k_2$ in the customary fashion.

If we assume that the activity coefficients of $X^-$ and $H_2O$ are independent of the $X^-$ concentration at any given ionic strength, then the usual steady state treatment leads, without further approximation, to Equation 3, a relationship between the pseudo first-order rate constant and the other kinetic parameters.

$$k = \frac{k_1(X^-) + k_2k_4/k_3}{k_2/k_3 + (X^-)} \tag{3}$$

When the reverse of Reaction 2, the aquation of $Co(CN)_5X^{-3}$, is relatively slow, as it is for $N_3^-$ and $SCN^-$, then $k_1(X^-) \gg k_2k_4/k_3$ and the omission of the second term in the numerator of Equation 3 is a valid approximation. Equation 3 may be rearranged and written as Equation 4, a form which indicates more clearly that $k_1 - k_4$ and $k_2/k_3$ may be evaluated from the intercept

$$\frac{1}{k - k_4} = \frac{1}{k_1 - k_4} + \frac{k_2/k_3}{(k_1 - k_4)(X^-)} \tag{4}$$

and the ratio of slope to intercept in a plot of $1/(k - k_4)$ *vs.* $1/(X^-)$. Values of $k_4$ are listed in Table IV. When $k_1(X^-) \gg k_2k_4/k_3$, then $k_4$ may be omitted from the denominator of each of the terms of Equation 4, and $k_1$ and $k_2/k_3$ may be evaluated from a plot of $1/k$ *vs.* $1/(X^-)$.

The inverse plots of $1/(k - k_4)$ *vs.* $1/(X^-)$ for the nucleophiles $N_3^-$, $SCN^-$, $I^-$, and $Br^-$ are presented in Figure 2, with the points representing the data at 40°C. and unit ionic strength. Only the data at concentrations above $0.1M$ have been included in order to provide an adequate expansion of scale, so that the region near the intercept may be clearly visible. Any reasonable straight line drawn through the points in Figure 2 for $N_3^-$, $SCN^-$, and perhaps $I^-$, where the data are somewhat less reliable, would seem to require a nonzero intercept, the characteristic feature of a limiting $S_N1$ mechanism. The two points for $Br^-$ are included only to indicate the relative position of the points, all of which lie on a straight line, but with a slope so great that the intercept is poorly defined and the zero value could equally well have been chosen.

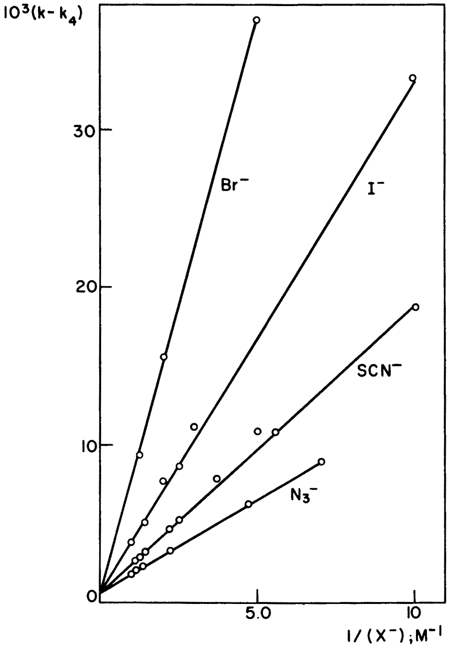

*Figure 2. A plot of $10^3/(k-k_4)$ vs. the reciprocal of the anion concentration for data obtained at 40°C. and ionic strength 1.0M*

The intercept on the ordinate in Figure 2 corresponds to a numerical value of $k_1$ of 1.60 x $10^{-3}$/sec. In physical terms, the rate constant $k_1$ represents the rate constant for generation of $Co(CN)_5^{-2}$ from $Co(CN)_5OH_2$. It also represents the rate constant for formation of $Co(CN)_5X^{-3}$ by a hypothetical nucleophile so efficient in its scavenger action that it would be able to capture all of the $Co(CN)_5^{-2}$ generated in Reaction 1 before reaction with water could occur.

The ratio of slope to intercept for the various lines in Figure 2 leads to numerical values of $k_2/k_3$ of 1.90, 2.95, 5.15 and 10 for $N_3^-$, $SCN^-$, $I^-$, and $Br^-$, respectively. These numbers represent the relative efficiencies with which water competes with the various nucleophiles for $Co(CN)_5^{-2}$, the competing reactions being Reaction 2 and the reverse of Reaction 1. In comparing the relative efficiencies of water as a scavenger for $Co(CN)_5^{-2}$ with that of a given nucleophile, it might be somewhat more realistic to define the rate of the reverse of Reaction 1 as equal to $k_2[Co(CN)_5^{-2}]$ $[H_2O]$, a change which would formally correct for the water concentration. If this procedure were adopted, all of the values of $k_2/k_3$ would be divided by 52, the approximate concentration of water in the system. However, any correction which may be applied to the ratio $k_2/k_3$ in an effort to correct for the water concentration is, at best, a rather arbitrary one. The water molecule entering the coordination sphere of the $Co(CN)_5^{-2}$ ion may well be part of a highly ordered solvation shell, and the reverse of Reaction 1 a multimolecular process involving the synchronized action of a number of water molecules (*8*).

**Experimental.** In order to study the nucleophilic properties of $I_3^-$, it was necessary to add excess $I^-$ to the solutions to prevent precipitation of $I_2$. The rate of formation of $Co(CN)_5I^{-3}$ was followed spectrophotometrically after the $I_3^-$ in aliquots of the solution taken at suitable time intervals was reduced to $I^-$ by arsenite ion. A typical set of experiments was carried out at 40°C. and unit ionic strength, with all solutions containing 0.5*M* $I^-$ and variable $I_3^-$ at a maximum concentration of 0.28*M*, the approximate upper limit imposed by solubility restrictions. The results are presented in Figure 3 as a plot of $k'$, the symbol used for the pseudo first-order rate constant for this system, *vs.* $1/(I_3^-)$. It is apparent that $I_3^-$ is a remarkably efficient nucleophile, with a reaction rate considerably greater than that found for $I^-$ at comparable concentrations. The points in Figure 3 also show detectable deviation from linearity. despite the limited range of $I_3^-$ concentration which was available.

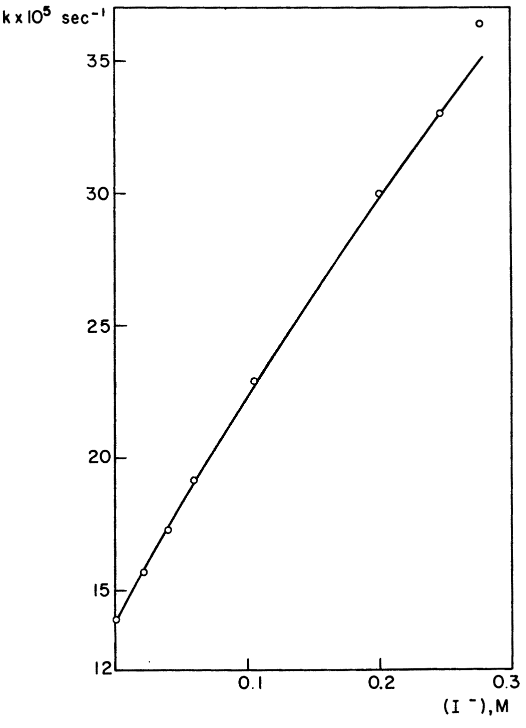

*Figure 3. Pseudo first-order rate constant vs. $I_3^-$ concentration at 40°C. and ionic strength 1.0M*

As the discussion below will indicate, the interpretation of the $I_3^-$ data is somewhat more ambiguous than that of the systems considered above. An obvious mechanism, which adequately represents the data, may be based on Equations 1, 2, 5, and 6.

$$Co(CN)_5^{-2} + I_3^- \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Co(CN)_5I^{-3} + I_2 \qquad (5)$$

$$I_2 + I^- \xrightarrow{K} I_3^- \qquad (6)$$

The steady state treatment coupled with the microscopic reversibility restriction yields Equation 7.

$$k' = k + \frac{\dfrac{k_2k(\mathrm{I_3^-})}{k_3(\mathrm{I^-})}}{\dfrac{k_3}{k_5}\left[\dfrac{k_2}{k_3} + (\mathrm{I^-})\right] + (\mathrm{I_3^-})} \tag{7}$$

In Equation 7 the symbols $k'$ and $k$ are used to represent the pseudo first-order rate constant for the $\mathrm{I_3^-}$ system, the pseudo first-order rate constant for the $0.5M$ solution not containing $\mathrm{I_3^-}$. Inspection of Equation 8, obtained by rearranging Equation 7, shows that $k_3/k_5[k_2/k_3 + (\mathrm{I^-})]$ may be evaluated from the ratio of slope to intercept in a plot of $1/(k' - k)$ *vs.* $1/(\mathrm{I_3^-})$.

$$\frac{1}{k' - k} = \frac{1}{k_2k/k_3(\mathrm{I^-})} + \frac{\dfrac{k_3}{k_5}\left[\dfrac{k_2}{k_3} + (\mathrm{I^-})\right]}{k_2k(\mathrm{I_3^-})/k_3(\mathrm{I^-})} \tag{8}$$

The position of the solid line in Figure 3 has been drawn using the resulting value of $k_3/k_5 = 0.31$. The numerical value of the ratio $k_2/k_5 = 0.61$ implies that $\mathrm{I_3^-}$ is a somewhat more reactive nucleophile than $\mathrm{I^-}$ or any of the other species so far considered. The possible significance of this result will be discussed below.

At this point it is necessary to consider several possible sources of ambiguity in interpretation of the $\mathrm{I_3^-}$ data. First, it should be noted that $\mathrm{I_2}$ may form an addition complex (*2*, *9*) with $\mathrm{Co(CN)_5I^{-3}}$, just as it does with alkyl iodides in nonaqueous solution. (Experiments bearing on this question are in progress.) Fortunately, the presence of such a complex would not alter the numerical values of the kinetic parameters. Secondly, there is the possibility that Reaction 5 is a trimolecular process, with the $\mathrm{I_2}$ and $\mathrm{I^-}$ reactants adding to $\mathrm{Co(CN)_5^{-2}}$ at separate stages of the reactant.

$$\mathrm{Co(CN)_5^{-2}} + \mathrm{I_2} + \mathrm{I^-} \underset{k_6}{\overset{k_5'}{\rightleftharpoons}} \mathrm{Co(CN)_5I^{-3}} + \mathrm{I_2} \tag{9}$$

This formulation, which is kinetically indistinguishable from that given by Equation 5, would require that the numerical value of 0.31 be assigned to the quantity $k_3K/k_5'$, where $K$ is the association constant for $\mathrm{I_3^-}$ formation. Finally, it should be emphasized that nothing is known about the geometry of the activated complex generated by either Reaction 5 or 9. To be more specific, the $\mathrm{I_2}$ molecule may be bonded to $\mathrm{I^-}$, to a cyanide ligand, or to the $t_{2g}$ electrons of the Co(III) ion.

In weakly acidic solutions the various anation reactions are not pH dependent. However, when formation of $\mathrm{Co(CN)_5OH^{-3}}$ becomes appreciable in alkaline solution, there is a marked decrease in rate. The anation reaction of $\mathrm{N_3^-}$ was studied in some detail in this pH region. Typical results are given in Table I.

Two alternate $\mathrm{S_N1}$ reactions must be considered for the reaction in basic solution. The first alternative assumes that $\mathrm{Co(CN)_5OH^{-3}}$ is completely unreactive and that at any given pH, $\mathrm{N_3^-}$ reacts only with that fraction of the complex present as $\mathrm{Co(CN)_5OH_2^{-2}}$. In this formulation the pH and azide ion dependence of the pseudo first-order rate constant is given by Equation 10.

**Table I. Rate of Formation of $Co(CN)_5N_3^{-3}$ at 40°C.**

Ionic strength 1.0*M*, pH 6.4

| $[Co(CN)_5OH_2^{-2}]$, $M \times 10^4$ | $(N_3^-)$, $M$ | $10^4 \times k/(N_3^-)$, $M^{-1}$ sec.$^{-1}$ | $k \times 10^5$, sec.$^{-1}$ | $k \times 10^5$ sec.$^{-1}$ (calcd.) |
|---|---|---|---|---|
| 0.86 | 0.0355 | 9.30 | 3.30 | 2.95 |
| 1.72 | .071 | 8.80 | 6.25 | 5.78 |
| 6.89 | .142 | 7.89 | 11.2 | 11.2 |
| 6.89 | .212 | 7.48 | 16.1 | 16.0 |
| 5.32 | .45 | 6.78 | 30.5 | 30.6 |
| 2.83 | .45 | 6.82 | 30.7[a] | 30.6 |
| 1.00 | .45 | 6.85 | 30.8[a] | 30.6 |
| 5.67 | .725 | 6.14 | 44.5[a] | 44.4 |
| 7.50 | .725 | 6.03 | 43.7 | 44.4 |
| 5.68 | .90 | 5.61 | 50.5[b] | 51.5 |
| 5.70 | 1.0 | 5.48 | 54.8[b, c] | 55.2 |

[a] In these experiments the $Co(CN)_5OH_2^{-2}$ was prepared by hydrolysis of $Co(CN)_5Br^{-3}$.
[b] Unbuffered perchloric acid solutions at pH 6.7.
[c] In this experiment the $Co(CN)_5OH_2^{-2}$ was prepared by acid hydrolysis of $Co(CN)_5N_3^{-3}$.

$$k = \frac{k_1(H^+)\,(N_3^-)}{[(k_2/k_3 + (N_3^-)]\,[K_a + (H^+)]} \qquad (10)$$

In equation 10 $K_a$ refers to the acidity constant of $Co(CN)_5OH_2^{-2}$. It has the numerical value of 2.0 x $10^{-10}$ at 40°C. and unit ionic strength. In the second of the two alternative mechanisms, the further assumption is made that $Co(CN)_5^{-2}$ may also be generated by Reaction 11.

$$Co(CN)_5OH^{-3} \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} Co(CN)_5^{-2} + OH^- \qquad (11)$$

(In deriving Equation 10 and 11 the aquation rate of the reaction product $Co(CN)_5N_3^{-3}$ has been neglected. This is a valid approximation which somewhat simplifies the form of the equations and helps to clarify the physical significance of the various kinetic parameters.)

When Reaction 11 is included in the mechanism, the expression for the rate constant is given by Equation 12.

$$k = \frac{[k_1(H^+) + k_1'K_a]\,(N_3^-)}{[(k_2/k_3) + (k_2'/k_3)\,(OH^-) + (N_3^-)]\,[K_a + (H^+)]} \qquad (12)$$

Equation 10 does not provide an adequate representation of the data. First, the rate constants calculated using this equation for experiments carried out at a pH greater than 10 are 15–20% smaller than the experimentally determined values. A second, and perhaps more compelling point is that Equation 10 does not correctly predict the dependence of rate upon $N_3^-$ concentration in the more alkaline solutions. In qualitative terms what is observed is that the points in a plot of $k$ *vs.* $(N_3^-)$ approach linearity as the alkalinity of the solution is increased. A plot of the data in Table II obtained at pH 10.1 exhibits much less curvature than that presented in Figure 1. In a similar plot of the data in Table III obtained at a hydroxide ion concentration of 9 x $10^{-3}M$ there is no detectable deviation from linearity.

The data under consideration all agree well with the predictions of Equation 11. To test the validity of this equation, it is necessary to evaluate the new kinetic parameters $k_1'$ and $k_2'/k_3$. From inspection of the equation values of $[K_a + (H^+)]/$

**Table II. Rate of Formation of $Co(CN)_5N_3^{-3}$ at 40°C.**

pH 10.1, $\mu = 1.0$
$[Co(CN)_5OH_2^{-2}] = 6.44 \times 10^{-4}$ *M*

| $(N_3^-)$, *M* | $10^4k/(N_3^-)$, $M^{-1}$ sec.$^{-1}$ | $k \times 10^5$, sec.$^{-1}$ | $k \times 10^5$ sec.$^{-1}$ (calcd.) |
|---|---|---|---|
| 0.18 | 2.67 | 4.81 | 4.64 |
| .27 | 2.49 | 6.72 | 6.80 |
| .45 | 2.36 | 10.6 | 10.8 |
| .72 | 2.29 | 16.5 | 16.2 |
| .90 | 2.19 | 19.7 | 19.5 |

**Table III. Rate of Formation of $Co(CN)_5N_3^{-3}$ at 40°C.**

$(OH^-) = 0.009$ *M*, and $\mu = 1.0$
$[Co(CN)_5OH_2^{-2}] = 6.44 \times 10^{-4}$ *M*

| $(N_3^-)$, *M* | $10^5k/(N_3^-)$, $M^{-1}$ sec.$^{-1}$ | $k \times 10^5$ sec.$^{-1}$ | $k \times 10^5$ sec.$^{-1}$ (calcd.) |
|---|---|---|---|
| 0.19 | 2.37 | 0.43 | 0.42 |
| .45 | 2.29 | 1.03 | 1.04 |
| .90 | 2.28 | 2.05 | 2.05 |

$[k_1(H^+) + k_1'K_a]$ and of $(k_2/k_3) + k_2'/k_3)$ $(OH^-)$ may be obtained from the intercept and the ratio of the slope to the intercept in the linear plots of $1/k$ *vs.* $1/(N_3^-)$. Use of the data of Tables II and III and the previously evaluated quantities $k_1$, $k_2/k_3$, and $K_a$, we obtain $K_1' = 6.5 \times 10^{-4}$/sec. and $k_2'/k_3 = 3.0 \times 10^3$. The excellent agreement between theory and experiment may be seen by referring to Tables I, II, and III where experimental values of $k$ may be compared with those calculated from Equation 11.

Inspection of the numerical values of the kinetic parameters indicates that Reaction 11 is somewhat less efficient than Reaction 1 as a generating source for $Co(CN)_5^{-2}$. A more surprising result is the large value of $k_2'/k_3$, an indication of the efficiency with which $OH^-$ competes with water for capture of $Co(CN)_5$. Comparison of the value of $k_2'/k_3$ with the $k_2/k_3$ values cited suggests that the mechanism of reaction of $OH^-$ with $Co(CN)_5^{-3}$ differs from that of other nucleophiles. Quite possibly the capture of $OH^-$ is facilitated by a Grotthus chain mechanism involving proton transfer through the solvation sphere of the $Co(CN)_5^{-2}$ ion. The observation that $OH^-$ competes so favorably with water implies that the water reaction has either a rather appreciable activation energy, or an unfavorable activation entropy (or both). It is presumably these factors which enable other nucleophiles to compete with water, even when the latter is present at a much higher concentration.

Our discussion of the reaction mechanism in alkaline solution has assumed that the bimolecular reaction of $Co(CN)_5OH^{-3}$ and $N_3^-$ does not provide an important path for formation of $Co(CN)_5N_3^{-3}$.

$$Co(CN)_5OH^{-3} + N_3^- \rightarrow Co(CN)_5N_3^{-3} + OH^- \qquad (13)$$

Fortunately, there is an experimental test of the validity of this assumption. In the discussion of the aquation reactions, to be presented below, it will be shown that the aquation rate $Co(CN)_5N_3^-$ in alkaline solution is pH independent, clearly indicating that the reverse of Reaction 13 is unimportant. Consequently, the microscopic reversibility restriction requires no appreciable formation of $Co(CN)_5N_3^{-3}$ by Reaction 13.

After completion of the experiments at unit ionic strength, exploratory studies were carried out at much higher nucleophile concentrations, despite the possible uncertainty involved in interpretation of the physical significance of such data. The results of anation studies using $N_3^-$ and $SCN^-$ at 20°C. and an ionic strength of 5.0 are presented in Figure 4 as a plot of $k$ *vs.* the $X^-$ concentration. The points show a very pronounced deviation from linearity, as Equation 3 would predict, and and in the $N_3^-$ system the rate becomes almost zero-order in $N_3^-$ above a concentration approximately 3.0*M*. The inverse plots, based on Equation 4, yielded a value of $k_1 = 51 \times 10^{-5}$ sec.$^{-1}$ and $k_2/k_3$ values of 3.0 and 5.0 for $N_3^-$ and $SCN^-$, respectively. The position of the curves in Figure 4 were calculated using these numerical values of the kinetic parameters. The data for the $SCN^-$ system conform closely to the predictions of Equation 4. However, the observed deviations from linearity in the $N_3^-$ system are somewhat more pronounced than the theory would predict.

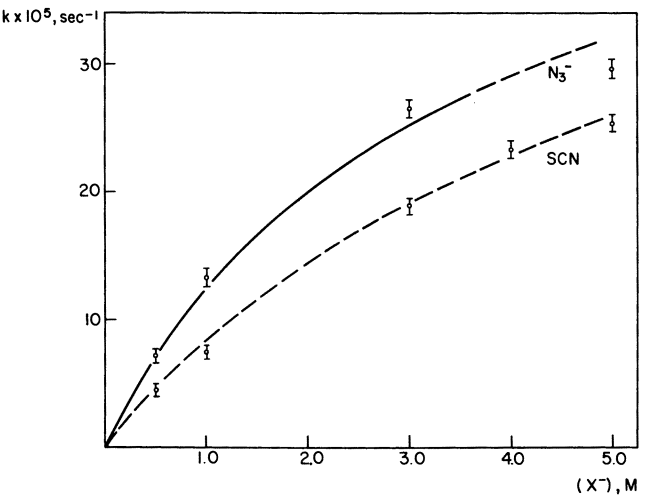

*Figure 4. Pseudo first-order rate constants vs. anion concentration at 20°C. and ionic strength 5.0M*

More recently, unpublished studies (*6*) have been completed in the $Br^-$ system at 20°C. and at an ionic strength of 5.0. The results obtained at 0.5, 1.0, 3.0, and 5.0*M* $Br^-$ may be adequately represented by the Equation, $k = [1.2 \times 10^{-5} + 4.9 \times 10^{-5} (Br^-)]$/sec. The interpretation of the constant $1.2 \times 10^{-5}$/sec. presents no problem since it would represent a not unreasonable value for $k_4$, the rate constant for solvolysis of $Co(CN)_5Br^{-3}$. However, the linear dependence of $k$ upon the $Br^-$ concentration is not in agreement with calculations based on the value of $k_1$ cited above. It should probably be concluded, as kineticists generally have in the past, that there is considerable uncertainty in the interpretation of kinetic data obtained at so high an ionic strength. Apart from this note of caution, no very useful generalization may be drawn because of the very limited amount of analogous data in the chemical literature.

Before concluding the discussion of the anation reaction, some consideration should be given to alternative formulations of the reaction mechanism. In particular, there is the question whether the reaction might not be proceeding by an $S_N2$ mechanism, with the decrease in $k/(X^-)$ with increasing $(X^-)$ merely representing a medium effect arising from the replacement of $ClO_4^-$ by $X^-$. Medium effects could be attributed either to the usual long range interaction of ions, or to ion pairs, or triplets having the formulas $Co(CN)_5OH_2^{-2} \cdot X^-$, or $Co(CN)_5OH_2 \cdot Na^+ \cdot X^-$. Driving force for the formation of ion pairs presumably would arise from hydrogen bonding of the sort $Co\text{-}OH_2 \cdot \cdot X^-$ or from electrostatic interaction of $X^-$ with an incompletely shielded Co(III) ion.

It does not seem to us that long range interaction provides a very plausible explanation of the data. In a reaction of two negative ions both theory and experiment seem to indicate that the value of the rate constant is not sensitive to the nature of the negative ions in the solution as long as the positive ion environment is held constant (*11*). If the rate law for the $N_3^-$ system were formulated in terms of the Brönsted–Bjerrum equation, the data of Figure 1 would require that the activity coefficient ratio change by a factor of two when the medium is changed from $1.0M$ $NaN_3$ to $1.0M$ $NaClO_4$. Further, the data would require the rather unlikely coincidence that large changes in the activity coefficient ratios occur only with reactive nucleophiles.

An explanation based upon ion pairing would require that a substantial fraction of the $Co(CN)_5OH_2^{-2}$ be associated with $X^-$ ions. In view of the unfavorable electrostatic interaction of two anions, it hardly seems likely that extensive ion pairing would occur.

It is interesting to consider whether an $S_N1$ mechanism might have been anticipated in the present system. In organic systems the presence of a highly electronegative cyano substituent would tend to favor an $S_N2$ rather than an $S_N1$ mechanism. The presence of a single cyano ligand in a positively charged complex ion appears to have similar mechanistic consequences. However, when the number of cyano ligands is increased to five, the accumulation of negative charge probably produces a relatively high electron density at the cobalt atom, despite the tendency for $\pi$-bonding to spread the charge throughout the ligand sphere. Such an accumulation of negative charge at the cobalt atom should lead to a relatively weak $Co\text{–}OH_2$ bond, a weakly acidic complex, and a relatively favorable activation energy for an $S_N1$ reaction path. The observed pK of the complex and the comparatively rapid water exchange are consistant with this view.

For a limiting type of $S_N1$ mechanism, it is also necessary that the energy of the reactive intermediate be appreciably lower than that of the preceding activated complex. In the present system, it can perhaps be argued that the decrease in coordination number from six to five is accompanied by an increase in bond angles and a decrease in electrostatic repulsion of the negative ligands. However, it is difficult to assess the importance of this electrostatic argument since the changes in bond angles and coordination number also imply important changes in bond energies. Finally, as we have suggested above, it is quite probable that the nature of the solvation sphere plays an important role in determining the life time of the reactive intermediate. Entry of a water molecule into the solvation sphere of the $Co(CN)_5^{-2}$ intermediate by a complicated synchronized motion of a number of water molecules obviously represents a process which might have a quite unfavorable enthalpy and entropy of activation.

### *Rate of Exchange of $Co(CN)_5OH_2^{-2}$ with $O^{18}$ Labelled Water*

A quite conclusive test of the validity of the mechanism based on Equations 1 and 2 would be provided by an accurate measurement of the exchange rate of the water in $Co(CN)_5OH_2^{-2}$ with $H_2O^{18}$ labelled solvent, a project which unfortunately has not yet been completed. If the proposed mechanism is valid, the rate constant for water exchange should equal $k_1$, the rate constant for formation of $Co(CN)_5^{-2}$ from $Co(CN)OH_2^{-2}$. Further, the rate of water exchange and the rate of $Co(CN)_5X^{-3}$ formation should be competitive processes, with the water exchange being inhibited in the presence of a reactive nucleophile.

Exchange data would also test the validity of an alternative mechanism in which the reactive intermediate is formulated as the seven coordinate $Co(CN)_5(OH_2)_2^{-2}$ complex.

$$Co(CN)_5OH_2^{-2} + H_2O \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} Co(CN)_5\,(OH_2)_2^{-2} \qquad (14)$$

$$Co(CN)_5\,(OH_2)_2^{-2} + X^- \underset{k_4}{\overset{k_3'}{\rightleftharpoons}} Co(CN)_5X^- + 2\,H_2O \qquad (15)$$

The anation data presented above could equally well be interpreted in terms of such a mechanism. However, if the water molecules in the complex formed in Equation 14 become equivalent, a plausible, although not inevitable, consequence of the mechanism, then the predicted rate constant for water exchange would equal $k_1/2$.

Earlier attempts to measure the water exchange were based on an analytical procedure involving precipitation of the partially labelled $Ag_2Co(CN)_5OH_2$ dehydration, and analysis of the dehydrated water for $O^{18}$ content. Attempts to obtain quantitative data were frustrated by a silver ion induced exchange process which occurred with extreme rapidity, even when the precipitation was carried out in aqueous methanol at −50°C. However, by varying the $O^{18}$ content of the medium used in precipitating $Ag_2Co(CN)_5OH_2$, it was possible to draw the tentative conclusion that the exchange rate constant had a numerical value approximately equal to that of $k_1$. More recently, alternate separation procedures have been developed, and it is hoped that exchange data will soon become available. A study of the catalyzed exchange induced by various Lewis acids will also be undertaken.

The aquation of the various $Co(CN)_5X^{-3}$ complexes must occur by a reaction path which is merely the reverse of that followed in the anation. If the proposed mechanism for the anation reaction is valid, the reverse of Reactions 1 and 2 may be used to describe the equation. In any given experiment the rate of approach to equilibrium may be characterized by a first-order rate constant $k$ which is related to the other kinetic parameters by Equation 3. When $k_2k_4/k_3 \gg k_1(X^-)$, as it is in the aquation of $Co(CN)_5Br^{-3}$ in the absence of added $Br^-$, then the aquation proceeds to completion, and $k$ equals $k_4$.

The aquation reactions of the other complexes do not proceed to completion, even in the absence of added $X^-$. Under these conditions two alternative methods may be used to evaluate $k_4$. In the first method $k_4$ is obtained from a study of the initial rate of aquation in the time interval when the anation reaction may be neglected. In the second method the aquation is studied in alkaline solution where the formation of $Co(CN)_5OH^{-3}$ tends to drive the reaction to completion.

In all of the systems so far investigated the aquation rate has been found to be pH independent in alkaline solution, at least up to 0.1$M$ OH$^-$, the largest concentration investigated. It may be noted that this behavior is entirely analogous to that of trityl chloride and other organic halides which undergo solvolysis by well established S$_N$1 mechsnisms. (*8*)

Numerical values of $k_4$ and $K$, the equilibrium constant for $Co(CN)_5X^{-3}$ formation, have been assembled in Table IV. In the three cases where temperature coefficient data is available, it can be seen that the relative values of $k_4$ are determined by the differences in both $\Delta H$ and $\Delta S$. A comparison of $k_4$ and $K$ indicates that an increase in $K$ is accompanied by a decrease in $k_4$. For any given nucleophile $k_4$ and $K$ may be related by the expression $K = k_1k_3/k_2k_4$. This latter expression has been used to calculate the numerical values of $K$ for the SCN$^-$ and $N_3^-$ systems where equilibrium data is not available.

**Table IV.**

| $X^-$ | $T$, °C. | $10^7k_4$ sec.$^{-1}$ | $\Delta H$ | $\Delta S$ | $K$ | $\frac{k_1k_3}{k_2k_4}$ |
|---|---|---|---|---|---|---|
| $N_3^-$ | 40 | 5.5 | | | | |
| | 60 | 80 | 27.3 | −0.6 | | 1530 |
| SCN | 40 | 3.7 | | | | |
| | 60 | 78 | 31.1 | 11.5 | | 1460 |
| $I^-$ | 40 | 74 | | | | |
| | 69.9 | 4950 | 29.7 | 12.5 | 39 | 42 |
| $Br^-$ | 40 | 1680 | | | 0.88 | 0.95 |

The rapid anation reaction observed in the presence of $I_3^-$ implies that $I_2$ should be a very efficient catalyst for the aquation of $Co(CN)_5I^{-3}$. Qualitative observations confirm this prediction, but a careful study of the catalyzed aquation has not yet been completed. A study of the catalysis by other halogen molecules and Lewis acids will also be undertaken in future work.

### *Acid-Catalyzed Aquation of $Co(CN)_5N_3^{-3}$*

In acidic solution the aquation of $Co(CN)_5N_3^{-3}$ was found to be acid-catalyzed. In the absence of anions other than $ClO_4^-$, the only reaction products were $Co(CN)_5OH_2^{-2}$ and $HN_3$. Typical results obtained at unit ionic strength and 40°C. are presented in column 2 of Table V as pseudo first-order rate constants.

**Table V. Acid-Catalyzed Aquation of $Co(CN)_5N_3^{-3}$.**

$t = 40°C., \mu = 1.0$

| $(H^+)$ | $10^5k$, sec.$^{-1}$ | $10^5k$ sec.$^{-1}$ calcd.[a] |
|---|---|---|
| 0.0042 | 5.90 | 6.15 |
| .0084 | 12.1 | 12.1 |
| .0168 | 23.5 | 23.5 |
| .0336 | 43.2 | 43.6 |
| .0364 | 47.2 | 47.0 |
| .0505 | 64 | 61 |
| .091 | 94 | 95 |
| .166 | 132 | 140 |

[a] Calculated using Equation 17.

The mechanism of the acid-catalyzed aquation may be formulated in terms of Equation 16 and 17.

$$Co(CN)_5N_3^{-3} + H^+ \overset{K}{\rightleftharpoons} Co(CN)_5N_3H^{-2} \tag{16}$$

$$Co(CN)_5N_3H^{-2} + H_2O \xrightarrow{k_a} Co(CN)_5OH_2^{-2} + HN_3 \tag{17}$$

As we shall show below, Reaction 17 does not occur in a single step, but this complication may be ignored for the moment. If we assume that Reaction 16 is rapidly reversible and the Reaction 17 is rate-determining, then it may readily be shown that the expected dependence of $k$ upon hydrogen ion concentration is given by Equation 18.

$$k = \frac{k_aK(H^+)}{1 + K(H^+)} \tag{18}$$

In Equation 18, $K$ and $k_a$ are the equilibrium constant and first-order rate constant for Reactions 16 and 17, respectively. The constants $k_a$ and $K$ may be evaluated by using Equation 18 and the data given in columns 1 and 2 of Table V. The procedure involves obtaining $1/k_a$ and $K$ from the intercept and the ratio of intercept to slope in the linear plot of $1/k$ *vs.* $1/(H^+)$ and leads to $k_a = 3.2 \times 10^{-3}$ sec.$^{-1}$ and $K = 4.7$. The excellent agreement between theory and experiment may be seen by comparing the experimental and calculated values of $k$ given in Table V.

Major results were obtained when the acid-catalyzed aquation was carried out in solutions containing $SCN^-$ ions. By carrying out the spectrophotometric analyses at appropriate wave lengths, it was possible to follow simultaneously the rate of disappearance of $Co(CN)_5N_3^{-3}$ and the rate of formation of $Co(CN)_5OH_2^{-2}$. It was found that the presence of $SCN^-$ did not influence the rate of disappearance of $Co(CN)_5N_3^{-3}$. However, both $Co(CN)_5OH_2^{-2}$ and $Co(CN)_5NCS^{-3}$ appeared as reaction products, even in time intervals so short that the $Co(CN)_5NCS^{-3}$ could not have been formed by reaction of $Co(CN)_5OH_2^{-2}$ and $SCN^{-3}$. Data illustrating these experimental results are presented in Table VI. The pseudo first-order rate constants for the disappearance of $Co(CN)_5N_3^{-3}$ are listed in column 3 under the heading $10^5$ $k_{380}$ sec.$^{-1}$, the subscript 380 indicating that the spectrophotometric measurements were carried out at $\lambda = 380$ m$\mu$ where $Co(CN)_5OH_2^{-2}$ and $Co(CN)_5NCS^{-3}$ have identical molar absorbancy indices. Within the limit of error these rate constants agree with those of Table V. By contrast, the pseudo first-order rate constants in column 4 of Table VI, which measure the initial rate of appearance of $Co(CN)_5OH_2^{-2}$, show a distinct decrease in magnitude in the presence of added $SCN^{-2}$ because of the parallel formation of $Co(CN)_5NCS^{-3}$. To indicate more clearly the nature of the studies, the results of a single experiment are presented in more detail in Figure 5.

**Table VI. Acid-Catalyzed Aquation of $Co(CN)_5N_3^{-3}$ at 40°C.**

$\mu = 1.0$, in the presence of $SCN^-$

| *($H^+$)* | *($SCN^-$)* | *$10^5$ $k_{380}$, sec.$^{-1}$* | *$10^5$ $k_{278}$, sec.$^{-1}$* | *$10^5$ $k_{278}$ sec.$^{-1}$, calcd.* |
|---|---|---|---|---|
| 0.019 | 0 | . . . | 94 | . . . |
| .092 | 0.50 | 96 | 83 ± 3 | 85 |
| .091 | .70 | 94 | 80 ± 3 | 76 |
| .091 | .90 | 91 | 66 ± 4 | 69 |
| .166 | 0 | 133 | 132 | . . . |
| .166 | 0.40 | 132 | 121 ± 5 | 116 |
| .166 | .80 | 133 | 104 ± 4 | 104 |

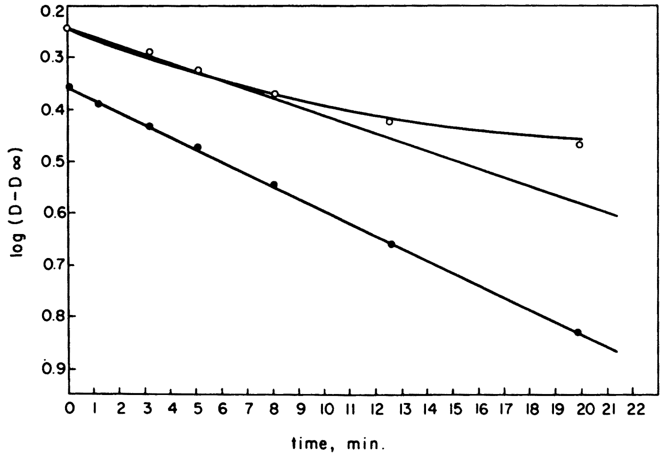

*Figure 5. An experiment illustrating the change in stoichiometry in the presence of thiocyanate ion; ● and ○ represent measurements at 380 and 278 mμ, respectively; the dotted line represents our evaluation of the initial slope.*

The data of Table IV strongly suggest that water and SCN⁻ are reacting in a competitive fashion, with a reactive intermediate generated in or after the rate-determining step of the acid-catalyzed aquation. Equations 19, 20, and 21 represent a plausible mechanism for generation of the reactive intermediate, assumed to be $Co(CN)_5^{-2}$, and its competitive reactions with water and SCN⁻.

$$Co(CN)_5N_3H^{-2} \xrightarrow{k_a} Co(CN)_5^{-2} + HN_3 \quad \text{rate-determining} \tag{19}$$

$$Co(CN)_5^{-2} + H_2O \xrightarrow{k_2} Co(CN)_5OH_2^{-2} \tag{20}$$

$$Co(CN)_5^{-2} + SCN^- \xrightarrow{k_3} Co(CN)_5NCS^{-3} \tag{21}$$

If we assume that the chemical properties of the $Co(CN)_5^{-2}$ generated in Reaction 19 are identical with those of Reaction 1, then the measured value of $k_a$ and the previously tabulated value of $k_2/k_3 = 2.95$ may be used to calculate $k_{278}$, the rate constant for formation of $Co(CN)_5OH_2^{-2}$ at various SCN⁻ concentrations. The calculation was carried out using Equation 22, an equation which was derived in the appendix of our original publication (*7*).

$$k_{278} = \frac{kk_2/k_3}{(SCN^-) + k_2/k_3} \tag{22}$$

The excellent agreement between the calculated and experimental values of $k_{278}$ listed in Table VI would seem to provide strong support for the proposed $S_N1$ mechanisms.

The kinetic parameters obtained in the absence of SCN⁻ are of some inherent interest. The acid-catalyzed aquation of ligands which are conjugate bases of weak acids has been observed in a number of other systems (*1*), but previous studies frequently provide a value only for the product $k_aK$. The numerical values of $k_a$ and $K$ are therefore of some inherent interest. Both $Co(CN)_5N_3H^{-2}$ and $Co(CN)_5N_3^{-3}$ appear to undergo solvolysis by an $S_N1$ mechanism. The large increase in lability caused by addition of the proton to the azide ligand is given by the ratio $k_a/k_4 = 5800$.

It is interesting to compare the acidity constant of $Co(CN)_5N_3H^{-2}$ with that of $HN_3$. The addition of $Co(CN)_5^{-2}$ to the latter species increases the acidity constant by a factor of approximately $5 \times 10^3$. The acidity constant of $Co(CN)_5OH_2^{-2}$ is larger than that of $H_2O$ by a factor of $2 \times 10^5$. The somewhat different behavior of the two pairs of acids is not particularly surprising, since the structures of $Co(CN)_5OH_2^{-2}$ and $Co(CN)_5N_3H^{-2}$ are quite different.

### *Reaction of $Co(CN)_5N_3^{-3}$ and $HNO_2$*

An attempt was made to generate $Co(CN)_5^{-2}$ by the rapid reaction of $Co(CN)_5N_3^{-3}$ and $HNO_2$, a process (*4*) which yields only the products listed below in the absence of anions other than $ClO_4^-$.

$$Co(CN)_5N_3^{+3} + HNO_2 + H^+ \rightarrow Co(CN)_5OH_2^- + N_2 + N_2O \quad (23)$$

It was hoped that an intermediate in Reaction 23, perhaps $Co(CN)_5N_4O^{-2}$, would contain the nitrogen atoms in a very weakly bonded ligand, a situation which would favor ligand expulsion and generation of $Co(CN)_5^{-2}$. The procedure designed to detect the presence of $Co(CN)_5^{-2}$ involved studying the rate and stoichiometry of the reaction in the presence of added $Br^-$ and $SCN^-$; this method of approach is entirely analogous to that adopted in the study of the acid-catalyzed aquation of $Co(CN)_5N_3^{-3}$. However, the results were somewhat more complex than those obtained in the latter system. At concentrations of $Br^-$ or $SCN^-$ in the range of $0.01M$, the stoichiometry of the reaction remained that given by Equation 23, the expected result at this low scavenger concentration. However, the presence of either $Br^-$ or $SCN^-$ was found to increase the reaction rate, quite possibly because of the appearance of a new reaction path involving NOX, a rather common feature of $HNO_2$ reaction mechansims.

When the concentration of $Br^-$ or $SCN^-$ was increased from $2.0M$ to $5.0M$, an increase in rate and the expected scavenger action were both observed, with $Co(CN)_5Br^{-3}$ or $Co(CN)_5NCS^{-3}$ appearing as reaction products. It can be concluded that these latter products were formed by reaction of $Br^-$ or $SCN^-$ with a reactive intermediate, since there was no correlation between the change in rate and the change in stoichiometry caused by the presence of the scavengers. However, an analysis of the stoichiometry data leads to values of $k_{H_2O}/k_{X^-}$ which are two to three times smaller than the corresponding values of $k_2/k_3$ obtained from the anation studies. Preliminary results are summarized in Table VII.

Several alternative interpretations may be suggested to explain the above results. First, it is possible that the scavenger ions are reacting, not with $Co(CN)_5^{-2}$, but with some other reactive intermediate such as the species $Co(CN)_5N_4O^{-2}$ mentioned above. Secondly, there is the possibility that $Co(CN)_5^{-2}$ is generated in both the acid-catalyzed aquation and the $HNO_2$ reaction, but that the two reactions may produce different isomeric forms of $Co(CN)_5^{-2}$, one form

**Table VII. Competition of $X^-$ and $H_2O$ for the Intermediate Generated in the $Co(CN)_5N_3^{-3}$–$HNO_2$ System**

| *t* | *μ* | $k_{H_2O}/k_x$ |  |
|---|---|---|---|
|  |  | *Br⁻* | *SCN⁻* |
| 20 | 5.0 | 15 – 7.7[a] | 3.7 |
| 40 | 1.0 | 33 | 6.7 |

[a] Values at 1.0, 3.0, and 5.0 *M* ($Br^-$) are 15, 12 and 7.7, respectively.

perhaps being trigonal bipyramidal and the other tetragonal pyramidal. As a third and somewhat less plausible explanation, it might be assumed that anation Reaction 1 and 2 actually proceeded by two parallel reaction paths, one corresponding to the mechanism discussed above, and the other to a bimolecular $S_N2$ process. This situation would lead to an incorrect assignment of $k_2/k_3$ values. However, this explanation would seem to be ruled out by the fact that identical values of $k_2/k_3$ were obtained in two different systems, the anation reaction and the acid-catalyzed aquation of $Co(CN)_5N_3^{-3}$.

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RECEIVED April 3, 1964.

# Discussion

**Wayne K. Wilmarth:** It is a pleasure to report the work carried out by Albert Haim and Robert Grassi dealing with substitution reactions of the pentacyanocobalt(III) complexes.

In the paper, we explore the possibility of interpreting these results in terms of a limiting type of $S_N1$ mechanism with an intermediate which has a proposed lifetime sufficient to discriminate between various nucleophiles present in the system.

I had hoped that we might have more work to report at this time, and while we have carried out certain other studies, in the main, they do not change greatly the conclusions of the paper. I think, therefore, in harmony with the philosophy of the Faraday Society, that I will merely conclude the talk at this point and attempt to answer pertinent questions.

**Richard G. Yalman**: John Bailar pointed out that in the early days there were some 30-odd proposals for a Walden rearrangement. As I look at the papers today and their different mechanisms it seems that we are trying to establish, for the most part, single mechanisms to describe—and that's all we are doing, we are describing things here—a wide variety of systems. What I am suggesting is that when we look at the pentammine system, we are looking at the pentammine system. When we are looking at the pentacyano system, we are looking at the pentacyano system. When we look at the bisethylenediamine system, we are looking at the bisethylenediamine system. It does not follow that any of these systems may have related mechanisms.

I would even say that to try to look at a system and then analyze our data in terms of the proposal of the authority figures is probably doing ourselves a disservice. This is not to say that these do not serve as wonderful guide lines, and that perhaps we will end up using those mechanisms, but I do have a word of caution.

Another point which I would like to bring up is the importance of what I will call "off-site" reactions. We have already touched on this today in our discussions of other sphere association.

I think in the current paper, Dr. Wilmarth's paper worked on by Dr. Haim, the acid catalysis of the aquation of the azide system is an example of what I call an "off-site" reaction. The attachment of hydrogen to nitrogen, which is three atoms away from the cobalt atom bringing about a weakening of the cobalt nitrogen bond and—if I remember the figures correctly—a 3500-or 5800-fold increase in the rate of aquation.

For those who are turning toward biological applications, it is the "off-site" reactions which I think are going to be more important than the on-site reactions which have been the subject of the previous discussion.

Another example is the increase in the aquation of the iodidopentacyano system in the presence of the tri-iodide ion. Again, this is what I would call an "off-site" or OSR reaction.

A third example is the reaction of nitrite with the azide complex. I don't want to discuss this more. I think that Carl Brubaker would like to talk about this.

I wish to point out that these reactions were studied in either neutral or acidic solutions where the cyanide cobalt system is really unstable thermodynamically. I raise the question about oxidation-reduction in the iodo complex. This wasn't mentioned in the paper. It seems to me it would provide an alternate path which might increase the reaction rates in the case of the iodide complex.

I have touched on some of the peripheral matters.

**Carl H. Brubaker, Jr.**: I agree with Dr. Yalman that this represents a very complete piece of work, and I think, the majority of the conclusions are fairly clear cut. There is not much that can be added aside from speculation. I would hope that a little later Prof. Wilmarth or others will speculate about the structures of this transition state species, or several species of the pentacyanocobaltate(II) that are supposed to be the transition state complex, or an intermediate.

I also hope that someone would comment regarding Dr. Yalman's comments about the reaction between the nitrite ion and the azido complex. One finds that the scavenging activity of—I believe it was bromide and thiocyanate—is much more effective in the presence than in the absence of nitrite in the azide system. The statement is made toward the end of the paper that the enhanced scavenging activity of thiocyanate or bromide might be the result of more ready attack by thiocyanate or bromide on the product of the reaction between the nitrite and the azido complex, in other words, a thing designated as perhaps being an $N_4$ or an $N_4O$ group; or the pentacyanocobaltate species in this case might be isomeric with another entirely different species. I wonder if it woulden't be worthwhile to speculate as to why one might expect that a different species would result following the elimination of an $N_4O$, or whatever the fragments are, and why one might expect that this $N_4O$ unit might be so much more efficiently displaced by thiocyanate or bromide. In fact, I think it might be worthwhile to discuss the possible structure of this pentacyanocobaltate.

**Dr. Wilmarth:** With respect to the reaction of the azido complex and nitrous acid, since this work was done by Dr. Haim, I think he should comment if he cares to do so.

In addition, I think workers in Dr. Taube's lab have studied in some detail the reaction of a number of azido complexes with nitrous acid, and it might be interesting to have a few comments on this work.

**Henry Taube:** I think that Dr. Wilmarth and his co-workers have presented excellent evidence for the existence of a genuine pentacoordinated intermediate in the cyano system. The result reported by them that the intermediate generated by the spontaneous reaction is different from that which may be generated by the reaction of HONO with $Co(CN)_5N_3^{+3}$ casts doubt on some of the conclusions which Dr. Haim and I reached on the reaction of nitrous acid with the azidopentaamminocobaltic ion. In addition, you will remember that some of the results which Ralph Pearson mentioned also cast doubt on our conclusions.

I want to enlarge a little on the theme of looking for genuine intermediates. I do not know how to understand the results of Dr. Pearson and co-workers, but at the same time I believe evidence for the existence of intermediates in the cationic species is accumulating. I would like to offer a suggestion relating to the work which Dr. Pearson has cited and then mention some additional evidence by D. Loeliger which fits in well with the results of A. Sargeson, and with those of others. The results *in toto* support the assumption that pentacoordinated intermediates are formed in some systems.

Dr. Pearson presented data on the optical density observed when the nitratocobaltic complex reacts with thiocyanate ion, and there is nothing to object to in these results. But I think one might be concerned abcut the theoretical curve calculated using the competition ratio in a table which Haim and Taube presented in the journal.

An important point in this work which must be kept in mind is that the reaction of HONO with $(NH_3)_5CoN_3^{+2}$ often implicates the ligand, X. Though in some instances it was shown that the formation of the product $(NH_3)_5CoX^{+2}$ was not related to the contribution to the total reaction by the path $(NH_3)_5CoN_3^{+2}$ + HONO + $X^-$, this was not done in all cases. In any individual case, the possibility exists that a species NOX in removing $N_3^-$ places $X^-$ on Co(III). The mere fact that $(NH_3)_5CoX^{+2}$ is formed is no proof that an intermediate $(NH_3)_5Co^{+3}$ is formed; any proof rests rather on demonstrating that the ratio, $((NH_3)_5CoX^{+2})/((NH_3)_5CoOH_2^{+3})$ is linear in $(X^-)$ and on finding the same competition ratio in more than one system. In our work, the variation of competition ratio as a function of ($X^-$) was tested only in a few cases, and our results in any event were not very precise. For the system with $X^- = NCS^-$ the competition ratio was found not to be independent of ($X^-$), and this itself is evidence that there is a complication in this reaction; the complication may be that there is a strong component from $(NH_3)_5CoN_3^{+2} + NOX$ where $X^-$ is inserted when azide ion leaves (as $N_2 + N_2O$).

R. B. Jordan, having learned about the work of Pearson and Moore, has become interested in the issues and has searched for the formation of $(NH_3)_5CoBr^{+2}$ when $(NH_3)_5CoNO_3^{+2}$ reacts in the presence of $Br^-$. His observations suggest that the bromo complex does appear initially, but on calculating the competition ratio finds it to be less by a factor of about 2 than that reported by Haim and myself. Jordan has done only a single experiment on this. The subject is obviously worth going into in some detail, but at this point I am neither prepared to say that Jordan's result supports the conclusions which Dr. Haim and I reached, nor that it does not.

Dr. Loeliger has been studying the changes in configuration which accompany substitution in acid solution. The relevance of these experiments to our present concern is this: if intermediates are formed which have properties independent of how they are formed, then changes in geometry should be independent of how the net substitution is brought about. Some of the data which Loeliger has obtained together with those of others are shown in the following table.

**Configuration Changes Accompanying Spontaneous and Assisted Aquation**

| *Assumed Intermediate* | *Method of Formation* | % *trans Product* |
|---|---|---|
| *trans*-Co $en_2N_3^{+2}$ | *trans*-Co $en_2(N_3)_2^+ + HNO_2$ | 100[a] |
| *trans*-Co $en_2N_3^{+2}$ | *trans*-Co $en_2(N_2)_2 + Hg^{+2}$ | 100[a] |
| *trans*-Co $en_2N_3^{+2}$ | *trans*-Co $en_2N_3Cl^+ + Hg^{+2}$ | 100[a] |
| *trans*-Co $en_2H_2O$ | *trans*-Co $en_2N_3H_2O^{+2} + HNO_2$ | 60 ± 5[a] |
| *trans*-Co $en_2H_2O$ | *trans*-Co $en_2ClH_2O^{+2} + Hg^{+2}$ | 60[b] |
| *trans*-Co $en_2H_2O$ | *trans*-Co $en_2(H_2O)_2^{+3} + H_2O$ | 65[c] |

[a] Experiments by D. Loeliger.
[b] Sargeson, A. M., *Australian J. Chem.*, **17**(3), 385 (1964).
[c] Kruse, W., Taube, H., *J. Am. Chem. Soc.*, **83**, 1280 (1961).

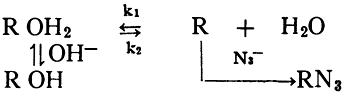
The observations in which configuration is retained (100% trans product) are only of limited usefulness. The experimental results are not refined enough to distinguish between 99.0, 99.9 and 99.99% formation of the trans product, yet these numbers correspond to a variation in the product ratios by a factor of 100. However in several instances, product ratios in the range of 0.1 to 10 have been observed. and if a particular product ratio in this range is maintained while the means of forming the aquo product is altered, this observation can be regarded as significant. One of the most interesting observations is that involving *trans*-$Coen_2H_2O^{+3}$ as the presumed intermediate. The extent of isomerization, within experimental error is the same whether the diaquo product is formed by the reaction of *trans*-$Coen_2N_3H_2O^{+2}$ with $HNO_2$ or of *trans*-$Coen_2ClH_2O^{+2}$ with $Hg^{+2}$. In the oxygen isotopic studies with *trans*-$Coen_2(H_2O)_2^{+3}$ two kinds of measurements where made: the exchange of oxygen into *trans*-$Coen_2(H_2O)_2^{+3}$ and the rate of change of the trans form to the cis, which involves incorporating one solvent oxygen for each cis ion formed. If it is assumed that both processes involve a common intermediate, *trans*-$\mathrm{Coen_2H_2O^{+3}}$, which is picking up a molecule of solvent either retains configuration or changes to the cis form, a number corresponding to the retention of the trans configuration can be calculated which, within experimental error, is the same as for the other two systems. The results suggest that the leaving group does not influence the geometric course of the reaction, and this in turn, suggests that a common intermediate is formed which has lost memory of how it was formed.

**Michael Anbar:** I would like to ask two or three questions pertaining to this paper. First, according to this paper, the hydroxyl complex is formed also according to the same $S_N1$ mechanism, as far as I could understand, which means that the proton transfer, going from the aquo to a hydroxide, is slower than a dissociation of the aquo complex to form the pentacyano complex. Could this be corroborated by some independent method of looking at the rate of proton exchange? In other words, the reaction exchange and the oxygen exchange should be at the same rate, according to this mechanism, if I understood it right.

The other question concerns the catalytic effect of iodine on the iodination of the pentacyano complex. Did you ever observe the same effect of $I_2$ say on the substitution of bromide, or thiocyanate as well?

A third question is whether you have observed any specific cationic effect in changing, at your high concentrations, from sodium to potassium or to another alkali metal—i.e., whether this has any effect on the rate. There is one more comment. You mentioned an $S_N1$ mechanism referring to organic chemistry. A few years ago we published results on the hydrolysis of fluoroborate ions where exactly the same mechanism was postulated (*J. Phys. Chem.* **64,** 1896 (1960)). Fluoroborate ions undergo hydrolysis in the alkaline region independent of $OH^-$ concentration; and again this very high increase in the rate of the $S_N1$ mechanism by protonation occurs. $HBF_4$ undergoes again an $S_N1$ cleavage, but the rate of hydrolysis is accelerated by several orders of magnitude.

**Dr. Wilmarth:** First, with respect to the effect of acidity, if I understand you correctly, you are not quoting the mechanism we proposed.



$$\begin{array}{lcl} \mathrm{R\,OH_2} & \underset{k_2}{\overset{k_1}{\rightleftarrows}} & \mathrm{R} + \mathrm{H_2O} \\ \uparrow\downarrow \mathrm{OH^-} & & \Big\lfloor \xrightarrow{\mathrm{N_3^-}} \mathrm{RN_3} \\ \mathrm{R\,OH} & & \end{array}$$

In acid solution it is assumed that the aquapenta-cyano ion reacts to form an intermediate, and that the intermediate may react with water, or may be picked up by a scavenger such as azide ion to form products. It is also assumed that the complex, which has a pK of 9.8 is in equilibrium with ROH, the predominant species in akaline solution. The decision that we had to make was whether the decrease in rate occurred because ROH was a completely inert species, or whether ROH also underwent an $S_N1$ mechanism as well as this. It was our conclusion that the evidence favored two parallel $S_N1$ mechanisms.

With respect to the general iodine catalysis or hydrogen catalysis, this subject is still under investigation, and possibly the mechanism is more complicated than we have indicated in the paper. We do know, among other scattered observations, that the iodopentacyano complex reacts in time of mixing with aqueous bromine to give the bromopentacyano complex. There is some suspicion that the hypoiodous acid would also catalyze the solovolysis of iodopentacyano complex, so that a rather careful pH dependence will be required to determine more accurately the possible mechanisms.

We know relatively little about the effect of change in positive ion in the system, but we think that the rate would probably be fairly sensitive to this. The only definite information we have involves recent studies of the substitution of water by pyridine, a neutral nucleophile, and a rather efficient one. Here there is perhaps a 20 or 30% difference in rate depending on whether we are working in 1*M* sodium ion or 1*M* pyridinium ion. The rate is faster in the pyridinium ion solution.

Interestingly, the plot of *k vs.* pyridine concentration does not curve to the extent that we would expect. Possibly this represents a general difficulty in attempting to study neutral nucleophiles.

In the study of a nucleophile such as azide, it is possible to replace perchlorate with azide even to 1*M* concentration without an appreciable change in the amount of water or the activity of water in the system; but by the time one has reached 1*M* pyridine, 78 grams of pyridine, the medium has changed rather substantially, and the reverse path involving water may be substantially effected.

**Arthur Adamson:** I think Dr. Wilmarth and co-workers have probably supplied the better available evidence for the pentacoordinated intermediate in a cobalt substitution reaction.

However, I think that again it is possible to treat these data, as I think also that Dr. Taube noted, in terms of the solvent cage picture and in terms of the idea that the reactants have preassembled before the activation energy arrives.

Specifically, I am not sure that it's always safe to assume that because one species is neutral, or because the two are like in charge, that one will therefore not have ion association or any appreciable preference towards association.

It has been observed that ion-pairing constants are different for analogous Cr(III) and Co(III) complexes. This indicates that the nature of the complex and not just the overall charge is important. There is a question as to just how far out, for example, appreciable *d*-electron density may be present; whether there may be, in fact, a good deal of coordination possible in the second coordination sphere so that one has forces favoring association which are not just electrostatic. Thus associations could provide kinetic intermediates even in these systems.

**Jack Halpern:** I would like to comment further on the question that Dr. Anbar raised about the possibility of generating the pentacyanocobalt(III) by electron transfer from pentacyanocobalt(II).

Shuzo Nakamura at the University of Chicago has been looking into this possibility. The reaction in question is

$$Co(CN)_5^{-3} \xrightarrow{-e^-} Co(CN)_5^{-2}$$

It has been known for some time, as a result of the work of Prof. Adamson and others, that cobalt(II) forms a stable pentacyano complex in aqueous solution. However there have been some questions raised about the structure of this species particularly as to whether it is a truly pentacoordinated species or whether there is a loosely held water molecule.

When one examines the oxidation of $Co(CN)_5^{-3}$ by complexes of the pentamminecobalt(III) type, several types of behavior are observed. By far the strongest preference appears to be for $Co(CN)_5^{-3}$ to capture a sixth ligand from the oxidant as in the inner sphere electron transfer reaction:

$$Co(NH_3)_5Br^{+2} + Co(CN)_5^{-3} \rightarrow Co(CN)_5Br^{-3} + \sim$$

The reaction proceeds with a rate constant in excess of $10^9$ $M^{-1}$ $sec.^{-1}$ approaching the diffusion controlled limit and implying that substitution of a sixth ligand into the coordination shell of $Co(CN)_5^{-3}$ is an extremely rapid process.

Now, if one oxidizes $Co(CN)_5^{-3}$ with an oxidizing agent such as $Co(NH_3)_6^{+3}$ which cannot supply a bridging ligand, so that inner sphere electron transfer is precluded, then by far the strongest preference of the $Co(CN)_5^{-3}$ under these conditions is, if at all possible, to pick up a sixth cyanide from the solution and thus to form $Co(CN)_6^{-3}$ as the product.

The kinetics of this reaction are first-order in free $CN^-$ as well as in $Co(CN)_5^{-3}$ and $Co(NH_3)_6^{+3}$. This behavior persists down to extemely low $CN^-$ concentration. $CN^-$, even in very small concentration, is the preferred ligand to complete the coordination shell.

If one really forces the issue by going to extremely low cyanide concentrations, the reaction becomes exceedingly slow, to the point where the results are almost unreliable. Under these conditions the formation of some $Co(CN)_5OH_2^{-3}$ as a reaction product is detectable, and we have attempted to see whether this might arise through the pentacoordinated cobalt(III) intermediate $Co(CN)_5^{-2}$ by doing this in the presence of ions such as $N_3^-$. However, we do not observe any pickup of $N_3^-$ under these conditions consistent with the discrimination pattern reported by Haim and Wilmarth. We thus concluded that the $Co(CN)_5^{-2}$ reported by them is not formed under any conditions in the oxidation of $Co(CN)_5^{-3}$.

There are two inferences that need to be drawn here. One concerns the extremely high rate for these inner sphere oxidations, coupled with our failure to form $Co(CN)_5OH_2^{-2}$ under any but most extreme conditions. I think this argues very strongly against the suggestion that $Co(CN)_5^{-3}$ is actually an aquo complex (-i.e., $Co(CN)_5OH_2^{-3}$). If it were, it is hard to understand why it fails to undergo direct oxidation to $Co(CN)_5OH_2^{-2}$, which is a perfectly stable species when generated in other ways.

The other inference relates to the fact that it also appears to be very difficult even under conditions where one has slowed down all the alternate paths, to convert $Co(CN)_5^{-3}$ by direct oxidation to a species which is identical to the $Co(CN)_5^{-2}$ species of Dr. Haim and Dr. Wilmarth. This suggests that the two species must be structurally very different, so that the transformation of one to the other does not occur readily, but rather that $Co(CN)_5^{-2}$ prefers to expand its coordination shell by capturing a sixth ligand before transferring an electron.

It seems likely the structure of the $Co(CN)_5^{-3}$ is trigonal bipyramidal, whereas the structure of the $Co(CN)_5^{-2}$ is square pyramidal.

**Dr. Brubaker:** I have been interested personally in the work that has come from Australia in the last year by Betts and Winfield and others on the oxidation also of the pentacyano with oxygen. Here they find the oxygen binds a proposed intermediate species which may be a monoperoxo monomer, which this group scavenges very well for the pentacyanocobalt(II) and forms the familiar decacyano-μ-peroxyldicobalt(III) complex. So in this case too, the oxidant sticks, not water.

**Anthony Poe:** I would like to comment on the relative nucleophilic character towards active intermediates and the fact that it has been said that the differences between the nucleophilic characters of anions are rather small.

We would have thought the same thing after some studies of the competition between chloride, bromide, and iodide for some rhodium(III) complexes, because we found that the ratios of the rate constants at 50°C. were very nearly 1:1:1. However, when activation energies were measured, we found that these produce a much bigger discrimination. In fact, the activation energy for the addition of iodide to our reactive intermediates is no less than 6 kcal. greater than the activation energy for addition of chloride and bromide.

None of these experiments on reactive intermediates has been done over a range of temperatures. At least, I think that is true. It would be interesting to see whether this would produce a bigger discrimination between the various nucleophiles than is given by the rate constants.

**Dr. Wilmarth:** We would be interested in having better temperature coefficient data for $\frac{k_2}{k_3}$, but it would require experiments of extreme accuracy to obtain any information of interest here. One would be dealing with a ratio of slopes to intercepts in plots at two temperatures to obtain this information.

**Dr. Yalman:** In connection with that, do you want to comment on the fact that the entropy change to the azide aquation is markedly different from that for the thiocyanate and the iodide? It is quite possible that the difference is more apparent than real.

**Dr. Wilmarth:** I don't have any real explanation for this, but I believe that the difference is real. Since the structure of the two ions is different, it seems that the $\Delta S^*$ values might differ.

**Albert Haim:** Regarding these questions of the reactions of the azido complexes with nitrous acid, there are two systems that I have tried to explore: the azidopentammine-cobalt(III) complex and the azidopentacyanocobalt(III) complex.

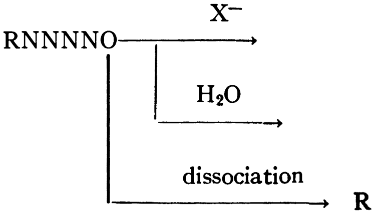
We have treated these complexes with nitrous acid in the presence of various anions, and we tried to obtain information on the kinetics and stoichiometries of the reactions. It is clear that the kinetics of the reactions of nitrous acid with either azidopentamminecobalt(III) or azidopentacyano-cobalt(III) are extremely sensitive to the presence of anions other than perchlorate. In regard to the kinetic sensitivity, we can indicate by a plus sign that both of these reactions are extremely sensitive to the presence of anions other than perchlorate.

| | *Sensitivity of Kinetics* | *Sensitivity of Stoichiometry* |
|---|---|---|
| $Co(NH_3)_5N_3^{+2} + HNO_2$ | + | – |
| $Co(CN)_5N_3^{-3} + HNO_2$ | + | – |

The other question is the sensitivity of the stoichiometry of the reaction. If there is nothing but nitrous and perchloric acids in these systems, the products of these reactions are the corresponding aquo complexes. If one has, in addition, the anion $X^-$ at sufficiently high concentration of $X^-$, one detects some X-pentamminecobalt-

(III) or some X-pentacyanocobalt(III). But the sensitivity of the stoichiometries to the added anion is very small, and we can indicate this by a minus sign. I think that the only conclusion that one can reach from this type of data is that there is an intermediate in the system.

Now the question is, what is this intermediate? This is what the argument has been about. As we suggest in the paper, there are various possible intermediates. The first one that comes to mind is, by analogy to the reaction of free azide ion with nitrous acid which has been studied by kinetic and tracer studies, the intermediate RNNNNO formed by addition of $NO^+$ to the azide. Now the question is, what is the fate of this intermediate in the present systems? It can react with $X^-$, it can react with $H_2O$; or it can dissociate to give the intermediate, R. The point that needs to be established is which, if any, of these alternatives is correct, and if more than one is correct, what are the relative contributions. That is, the possible discrimination of the RNNNNO intermediate for $X^-$ and $H_2O$ may be different from the possible discrimination of the pentacoordinated intermediate for $X^-$ and $H_2O$. In addition to the question of intermediates of different stoichiometry, (RNNNNO and R) there is the question of the geometry of the pentacoordinated intermediate. At this point it would be only speculation to say what the geometry of this pentacoordinated intermediate is. However, it is possible, that in different reactions, different geometries might be obtained.



# 3

# The Kinetics and Mechanism of Formation of Metal Complexes

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**Kinetic data for the formation of metal complexes obtained by various methods show that the complex formation of ML from metal ion, M, and ligand, L, can be described in terms of a rapid pre-equilibrium, involving formation of an outer sphere complex $M(H_2O)L$, which then loses water in the rate-determining step of inner sphere complex (ML) formation. The formation rate is affected by electron configuration and oxidation state of M, the charge of the entering ligand, as well as ligands, including $OH^-$, already present. The metal–water exchange process is probably important in determining the rate of polymerization and formation of intermediates in redox processes.**

The classification of metal complex reactions as "labile" and "inert" by Taube (*121*) was based essentially on literature of qualitative observations. In the last decade or so this situation has changed dramatically, as even a cursory examination of the Tables will show.

This account is concerned with the rate and mechanism of the important group of reactions involving metal complex formation. Since the bulk of the studies have been performed in aqueous solution, the reaction will generally refer, specifically, to the replacement of water in the coordination sphere of the metal ion, usually octahedral, by another ligand. The participation of outer sphere complexes (ion pair formation) as intermediates in the formation of inner sphere complexes has been considered for some time (*122*). Thermodynamic and kinetic studies of the slowly reacting cobalt(III) and chromium(III) complexes (*45*, *122*) indicate active participation of outer sphere complexes. However, the role of outer sphere complexes in the reactions of labile metal complexes and their general importance in complex formation (*33*, *34*, *41*, *111*) had to await modern techniques for the study of very rapid reactions. Little evidence has appeared so far for direct participation of the ligand in the formation of octahedral complexes. If an S$_N$1 mechanism for inner sphere substitution is assumed, the reaction can be formulated in a general manner as follows:

$$\begin{tikzcd}
(1)\ M(H_2O)_6^{+a} \arrow[rr, shift left, "+L^{-b}(k_{13})"] \arrow[d, shift right, "{-H_2O\ (k_{12})}"'] & & M(H_2O)_6^{+a}\cdot L^{-b}\ (3) \arrow[ll, shift left, "-L^{-b}(k_{31})"] \arrow[d, shift right, "{-H_2O\ (k_{34})}"'] \\
(2)\ M(H_2O)_5^{+a} \arrow[u, shift right, "{+H_2O\ (k_{21})}"'] \arrow[rr, shift left, "+L^{-b}(k_{24})"] & & M(H_2O)_5^{+a}\cdot L^{-b}\ (4) \arrow[u, shift right, "{+H_2O\ (k_{43})}"'] \arrow[ll, shift left, "-L^{-b}(k_{42})"] \arrow[d, shift right] \\
 & & M(H_2O)_5L^{+(a-b)}\ (5) \arrow[u, shift right]
\end{tikzcd}$$

The importance of individual steps would be expected to vary with the particular system studied. It is extremely difficult (if even meaningful) to distinguish the fine mechanism of the reaction. If the pentacoordinate species (Reaction 2) has a similar affinity for most nucleophiles (*51*, *53*, *84*), or if the outer sphere association (Reaction 3) is weak and incomplete, then in either case, second-order kinetics for the formation reaction may be observed. For calculated values see Hammes and Steinfield (*56*). Experimentally, the outer-sphere association constant for the reaction of $Co(NH_3)_5H_2O^{+3}$ with $SCH^-$, $SO_4^{-2}$ and $H_2PO_4^-$ at moderate ionic strengths is in the range 2–12 (*51*). That for $Co(NH_3)_6^{+3}$ with $NH_3$ is 0.2 (*75*) and for $Cr(H_2O)_6^{+3}$ with $SO_4^{-2}$ is 12 (*45*). The rate constant would be close to the value for water exchange with either $M(H_2O)_6^{+a}$ or $M(H_2O)_6^{+a}\cdot L^{-b}$, since little difference would be expected. If the route of Reactions (1) (2) (4) is chosen, the water exchange rate constant would be modified by a factor $k_{24}/k_{21}(H_2O)$; whereas with the sequence of Reactions (1) (3) (4) the factor would be $k_{13}/k_{31}$, the outer sphere association constant. The importance of outer sphere complexes is minimized when reactants of similar charge sign are involved (–e.g., in the reactions of $Co(CN)_5H_2O^{-2}$ with anions (*53*); whereas for oppositely charged reactants, mechanism (1) (3) (4) prevails if the pentacoordinated intermediate is unstable (–i.e. as long as $k_{21}$ $(H_2O) \gg k_{31}$, since usually $k_{13} \geq k_{24}$ and $k_{34} \approx k_{24}$).

The data in the tables have been obtained by various methods (*18*, *46*) including electrochemical, electric field, sound absorption, nuclear magnetic and electron paramagnetic resonance, temperature and pressure jump, flow and classical kinetic studies for the slower reacting ions (often from isotopic exchange data). In nonaqueous solution studies (Table II) rates can be reduced to the easily measurable range by working at low temperatures, a simple idea first exploited in this field by Bjerrum and Poulsen (*14*). Many of the formation rate constants cited are from "direct" measurements; some have been obtained by combining dissociation rate constants with the appropriate thermodynamic constants where possible.

### *Nontransition Metal Ions*

Results for alkali and alkaline earth ions with a great variety of ligands have been reported in previous papers (*35*, *40*). For these ions, substitution of water molecules from the inner coordination sphere generally is very rapid. Thus, for $Li^+$, $Na^+$, and $K^+$ ions, $k \sim 5 \times 10^7$, $5 \times 10^8$ and $1 \times 10^9$ sec.$^{-1}$ respectively (*39*, *40*). Except for $Be^{+2}$ and $Mg^{+2}$ the overall process is almost diffusion controlled and therefore, can be measured only by special techniques (–e.g., sound absorption). Complexes containing multidentate ligands depend slightly on the number of ligands to be substituted. For $Mg^{+2}$, substitution is about three orders of magnitude slower than for $Ca^{+2}$. $Be^{+2}$, again, is several orders of magnitude slower, depending somewhat on the proton affinity of the ligand to be substituted (internal hydrolysis). In all other cases the invariance of the rate with respect to the nature of the substituting ligands (apart from charge effects in ion pairing) is striking. For details of the mechanisms see references (*35*, *40*).

The correlation found between rate data and physical properties, such as charge and radius, for these metal ions has led to some predictions (*35*) concerning the rate behavior of the tervalent earth metal ions. Aluminum(III) and gallium (III) appear to fit very well into this scheme. A different behavior, however, was found for the series $Sc^{+3}$, $Y^{+3}$, $La^{+3}$ and the lanthanides (*48*). The rates are higher than for bivalent ions of the same size and show some irregularities, which apparently are caused by differences in coordination numbers. These studies are still in progress; they show that charge and size of the metal ion are not sufficient for a full description of the behavior, even in the case of noble gas-like electron configurations. This is not surprising perhaps, since the correlation between metal ion size and rate (for a given charge and coordination type) is not simple; several force interactions contribute to structure and stability of the coordination compound.

### *Transition Metal Ions*

The bulk of the systematic work has been carried out so far in this area. Even then most of it refers to the first period, and data for the second and third periods are needed. The predominance of hydroxo and polynuclear cationic species with this latter group will undoubtedly complicate the measurements.

**Bivalent Metal Ions.** The relative reaction rates of the vanadium(II)–zinc (II) series have been discussed often (*8*, *34*, *35*, *40*, *41*, *111*). The important features, which are well shown by examination of Table I, are:

(i) relative slowness of reaction of the $d^3$ and $d^8$ systems. Preliminary results for the reaction of vanadium(II) indicate that this ion reacts more slowly than even nickel(II) with thiocyanate ion and with dipyridyl (*74*).

(ii) extreme rapidity of reaction of the $d^9$ system shown by copper (II), due to a combination of Jahn-Teller labilization of the apical positions as well as rapid changes within the coordination structure (*35*). There is some evidence that when rapid interconversion of equatorial and axial positions in the coordination sphere of copper is prevented–e.g., by using polyaminecopper(II) ions, then equatorial water is substituted with a rate constant similar to that for nickel ions (*103*). The mechanisms the argument is based on are complex, however, and further experimental work on this interesting problem is needed. There is no indication in the table data for such slow reactions. The $d^4$ (high spin) system might also be expected to show such extremely rapid rates because of Jahn-Teller effects, and indeed chromium(II) behaves like copper(II) ultrasonically in reactions which occur rapidly with $SO_4^{-2}$ ion (*39*). However, much slower rates have been found for substitution with multidentate ligands (*74*), and these probably refer to substitution in the equatorial positions.

(iii) rapid rates of reaction of $d^{10}$ ions–e.g., mercury(II); the rate constants and activation energies suggesting diffusion-controlled processes (*36*, *37*, *92*). Zinc(II) ion also is faster than expected from its radius, when compared with $Mg^{+2}$ and $Ca^{+2}$ ions. The possibility that substitution in octahedral complexes is indirect and proceeds through active species of lower coordination number,–e.g., tetrahedral, can be dismissed by the recent demonstration that the rates of conformational interconversion are too slow (~0.1 seconds) to allow such catalytic effects (*35*, *110*).

The amount of data available for nickel(II) allows some generalizations, although it must be remembered, that with the variety of experimental techniques and conditions, little reliance should be placed on small differences in separate values. Second-order rate constants range from $2 \times 10^5$ (HEDTA$^3$) through $3 \times 10^3$ ($NH_3$) to a value as low as 3.5 ($H_3te^{+3}$), a variation understandable in terms of the proposed mechanism.

**Tervalent Metal Ions.** Once again the general similarity of rate constants for a particular metal is striking. Although Schmidt and Taube (*105*) have estimated the values of the first-order loss of water from the outer-sphere complexes, $Co(NH_3)_5H_2O^{+3} \cdot H_2O$, $Co(NH_3)_5H_2O^{+3} \cdot SO_4^{-2}$ and $Co(NH_3)_5H_2O^{+3} \cdot H_2PO_4^-$ (Table I) and suggested a kinetic influence of the incoming group, the differences are certainly not large. The dramatic increase in the water lability in changing from a low to a high spin cobalt(III) complex is evidenced by the fact that flow methods must be used to measure the reaction rate between $Co^{+3}$ and $Cl^-$ ion (*23*). In moderate acid concentrations (0.1*M*) the rate of the chromium(III) and cobalt(III) complexes considered in the table appear to be influenced little by pH. With the iron(III) system the rate behavior suggests that $Fe(OH)^{+2}$ reacts more rapidly than $Fe^{+3}$ with $Cl^-$, $Br^-$ and $SCN^-$; but with ligands which protonate in weak acidity ($X = SO_4^{-2}$, $F^-$ and $N_3^-$) ambiguity of interpretation is possible. In the acid independent path, reactants may be considered to be $Fe^{+3}$ and $X^-$, or $Fe(OH)^{+2}$ and HX (*106*). If the latter formulation is used, rate constants for all reactions of $Fe(OH)^{+2}$ are in the $3 \times 10^3$ to $3 \times 10^5$ $M^{-1}sec.^{-1}$ range and for those of $Fe^{+3}$, 4–127 $M^{-1}sec.^{-1}$, once again emphasizing the small role of the ligand. The rate constants in the table are presented on this basis (*106*).

## *General Conclusions*

It has been tacitly assumed in this discussion that the second-order formation rate constants measure the simple water substitution process. Although this must apply when unidentate ligands replace coordinated water, a composite process could describe the replacement by multidentate ligands. However, consideration of rate constants for successive formation and dissociation processes suggests that the overall rate of complex formation with flexible bidentate (and probably multidentate) ligands such as diamines, dipyridyl, glycine is probably determined by the rate of expulsion of the *first* water molecule from the metal aqua ion (*56*, *80*, cf. *3* and *84*).

It is clear that with these metal ions the role of water exchange is paramount. Even activation parameters, where available, agree with those for the water exchange process. We can, therefore, suggest that the high activation energies for dissociation of $Fe(phen)_3^{+2}$ and $Fe(dipy)_3^{+2}$, of the order of 30 kcal./mole, must indicate that the formation of these ions from the bis species be unusually highly exothermic ($\sim$ 20 kcal./mole), and this is indeed observed (*4*). In some cases the coordinated water is apparently weakened by having several charged donor atoms also attached to the metal (–e.g., $CN^-$ or $EDTA^{-4}$), or even only one hydroxide group. However, this charge effect is not present for other ligands. Detailed studies (*78*) show that it is not the overall charge, but local charge density at the ligands present in the coordination sphere (or binding strength relative to $H_2O$) which is the more decisive factor. (These results will be presented by Margerum (*78*).) Important effects of coordination groups on water lability are shown by the rate constant for the reaction of $M(terpy)^{+2}$ with terpyridine, M = Fe, Co, and Ni, being some 200 times larger than for the formation of the mono species (*62*). The experimental results are not accurate or clear enough yet to allow definite conclusions about the water exchange rate when a magnetic change occurs in the formation reaction–e.g., $Fe(CN)_5H_2O^{-3} \rightarrow Fe\ (CN)_6^{-4}$, and some quantitative data are required here.

We can now make sensible guesses as to the order of rate constant for water replacement from coordination complexes of the metals tabulated. (With the formation of fused rings these relationships may no longer apply. Consider, for example, the slow reactions of metal ions with porphyrine derivatives (*20*) or with tetrasulfonated phthalocyanine, where the rate determining step in the incorporation of metal ion is the dissociation of the pyrrole N–H bond (*104*).) The reason for many earlier (mostly qualitative) observations on the behavior of complex ions can now be understood. The relative reaction rates of cations with the anion of thenoyltrifluoroacetone (*113*) and metal-aqua water exchange data from NMR studies (*69*) are much as expected. The rapid exchange of $CN^-$ with $Hg(CN)_4^{-2}$ or $Zn(CN)_4^{-2}$ or the very slow $Hg(CN)^+$, $Hg^{+2}$ isotopic exchange can be understood, when the dissociative rate constants are estimated. Reactions of the type $M^{+a} + L^{-b} \rightleftharpoons ML^{+(a-b)}$ can be justifiably assumed rapid in the proposed mechanisms for the redox reactions of iron(III) with iodide (*47*) or thiosulfate (*93*) ions or when copper(II) reacts with cyanide ions (*9*). Finally relations between kinetic and thermodynamic parameters are shown by a variety of complex ions since the dissociation rate constant dominates the thermodynamic stability constant of the complex (*127*). A recently observed linear relation between the rate constant for dissociation of nickel complexes with a variety of pyridine bases and the acidity constant of the base arises from the constancy of the formation rate constant for these complexes (*87*).

The metal ion–water exchange process must be important in areas other than those of simple metal complex formation. For example, the discharge of nickel ion at a mercury cathode is probably controlled, not by diffusion, but by rearrangement of the water coordination shell. The estimated rates and heat of activation for this agree with the idea that this, in turn, is related to the water exchange process (*66*). Then too, the dimerization rate of metal hydroxy species may be controlled by water exchange. The reaction

$$2FeOH^{+2} \rightarrow Fe_2(OH)_2^{+4}$$

has a rate constant 4.5 × $10^2$ $M^{-1}$sec.$^{-1}$ at 25°C. (*124*), and this is similar to the water exchange value for $FeOH^{+2}$ (~5 × $10^2$ sec.$^{-1}$ (*22*)). The rate constant for the formation of $Cu_2(OH)_2^{+2}$, $Sn_2(OH)_2^{+2}$, $Ce_2(OH)_2^{+6}$ and other similar species could thus be predicted once the water exchange rate has been determined. It will be interesting to see if the facts confirm this idea. The formation of other binuclear species might also be controlled in this way. As examples we can cite the formation of $Mg_2F^{-2}$ from $Mg^{+2}$ and $MgF^{-4}$ ($k = 1.6 \times 10^6$ $M^{-1}$sec.$^{-1}$ at 25°C.); while the formation of an intermediate in the reaction of Co(EDTA) $(H_2O)^{-2}$ with $Fe(CN)_6^{-3}$ occurs at a rate one would expect for the replacement of water from the cobalt(II) coordination sphere (*2*). Halpern and Orgel (*54*) have discussed the possibility that in certain redox reactions the formation of a bridged intermediate (rather than electron transfer within the intermediate) may be the rate-controlling step. The second-order rate constants for (a) $Fe^{+2}$ – $FeN_3^{+2}$ exchange (*17*) (2 × $10^3$ $M^{-1}$sec.$^{-1}$ at 0°C.) and (b) Co(EDTA) $(H_2O)^{-2}$ with $IrCl_6^{-2}$ (*32*) (4 × $10^3$ $M^{-1}$sec.$^{-1}$ at 22°C.) suggest that with these reactions, formation of bridged intermediates via water exchange may indeed control the process. This point may be generally important.

Apparently future work lies in the investigation of some of the interesting effects mentioned above and other metal ions. In addition, more systematic studies in nonaqueous solvents are required, the paucity of data here being obvious from Table II. What little evidence we have indicates that here too, solvent release from the metal ion may play an important role in forming metal complexes. Already, interesting effects of small amounts of water on labilizing coordinated methanol have been observed (*77*, *112*).

## *Guide to Tables*

1. *Metal Ion.* In general, coordinated solvent is omitted.

2. *Ligand.* Some 50 different ligands are included. These are arranged in order of decreasing negative charge for the reactions with a particular metal ion. The following abbreviations apply: $HF^{-5}$ protonated metal phthalein (*26*); $ATP^{-4}$ adenosine triphosphate; $ADP^{-3}$ adenosine diphosphate; $EDTA^{-4}$ ethylenediaminetetraacetate; $PDTA^{-4}$ propylenediaminetetraacetate; $NTA^{-3}$ nitrilotriacetate; $IDA^{-2}$ iminodiacetate; $G^-$ glycine; $GG^-$ diglycine; $GGG^-$ triglycine; py pyridine; IM imidazole; en ethylenediamine; te.C-tetramethylethylenediamine; phen 1,10-phenanthroline; dipy 2,2′-dipyridyl; terpy 2,2′,2″-terpyridyl; ptn 1,2,3-triaminopropane; PAD pyridine-2-azodimethylaniline; trien triethylenetetramine; te tetraethylenepentamine; p(–penten) N,N,N′,N′-tetra-(2-aminoethyl)ethylenediamine.

3. *Rate Constant.* The logarithms of second-order rate constants (expressed as $M^{-1}$sec.$^{-1}$) are given for 25°C. unless otherwise indicated. These are rounded off to the nearest 0.1 unit. The ionic strengths are often 0.1–0.2 *M*.

4. *E.* The energies of activation are given to the nearest kcal./mole.

5. *Method.* When rapid techniques are involved the following abbreviations apply: F, flow; TJ, temperature jump; PJ, pressure jump; E, electrochemical; NMR, nuclear magnetic resonance; ESR, electron spin resonance; SA, sound absorption; EF, electric field. Classical methods for investigating kinetics are not specified unless low temperatures (LT) have been used.

## Table I. Kinetic Data for the Formation of Metal Complexes in Aqueous Solution at 25°C.

I. Nontransition metal ions

| *Metal Ion* | *Ligand* | *Log Rate Constant* | *Method* | *Reference* |
|---|---|---|---|---|
| $Li^{+}$ | $TP^{-5}$ | $9.0^{b}$ | SA | (*39*) |
| | $EDTA^{-4}$ | $7.7^{ab}$ | SA | (*39*) |
| | $NTA^{-3}$ | $7.7^{ab}$ | SA | (*39*) |
| | $IDA^{-2}$ | $8.4^{ab}$ | SA | (*39*) |
| $Na^{+}$ | $TP^{-5}$ | $>9.3^{b}$ | SA | (*39*) |
| | $EDTA^{-4}$ | $7.7^{ab}$ | SA | (*39*) |
| | $NTA^{-3}$ | $7.9^{ab}$ | SA | (*39*) |
| | $IDA^{-2}$ | $8.4^{ab}$ | SA | (*39*) |
| $K^{+}$ | $TP^{-5}$ | $>9.7^{b}$ | SA | (*39*) |
| | $EDTA^{-4}$ | $7.9^{ab}$ | SA | (*39*) |
| | $NTA^{-3}$ | $8.2^{ab}$ | SA | (*39*) |
| $Rb^{+}$ | $TP^{-5}$ | $>9.7^{b}$ | SA | (*39*) |
| | $EDTA^{-4}$ | $8.1^{ab}$ | SA | (*39*) |
| | $NTA^{-3}$ | $8.4^{ab}$ | SA | (*39*) |
| $Cs^{+}$ | $TP^{-5}$ | $>9.7^{b}$ | SA | (*39*) |
| | $EDTA^{-4}$ | $8.3^{ab}$ | SA | (*39*) |
| | $NTA^{-3}$ | $8.5^{ab}$ | SA | (*39*) |
| $Be^{+2}$ | $SO_4^{-2}$ | $2.0^{ab}$ | SA | (*41*) |
| $Mg^{+2}$ | $HF^{-5}$ | 6.2 | TJ | (*26*) |
| | $ATP^{-4}$ | 7.1 | TJ | (*30*) |
| | $HATP^{-3}$ | 6.5 | TJ | (*30*) |
| | $ADP^{-3}$ | 6.5 | TJ | (*38*) |
| | $HADP^{-2}$ | 6.0 | TJ | (*38*) |
| | $SO_4^{-2}$ | $5.0^{ab}$ | SA | (*41*) |
| | $CrO_4^{-2}$ | $5.0^{ab}$ | SA | (*41*) |
| | $S_2O_3^{-2}$ | $5.0^{ab}$ | SA | (*41*) |
| $Ca^{+2}$ | $HF^{-5}$ | 8.8 | TJ | (*26*) |
| | $ATP^{-4}$ | $\geqslant 9.0$ | TJ | (*30*) |
| | $ADP^{-3}$ | $\geqslant 8.4$ | TJ | (*38*) |
| | $IDA^{-2}$ | $8.4^{ab}$ | SA | (*39*) |
| | $CrO_4^{-2}$ | $\geqslant 7.7^{ab}$ | SA | (*39, 40, 41*) |
| | $G^{-}$ | $8.6^{ab}$ | SA | (*39*) |
| $Sr^{+2}$ | $IDA^{-2}$ | $8.5^{ab}$ | SA | (*39*) |
| $Ba^{+2}$ | $IDA^{-2}$ | $8.9^{ab}$ | SA | (*39*) |
| $Pb^{+2}$ | $HEDTA^{-3}$ | 9.3 | E | (*16, 116, 117*) |
| | $HNTA^{-3}$ | 8.2 | E | (*72*) |
| $Al^{+3}$ | $SO_4^{-2}$ | $\sim 0.0^{a}$ | PJ | (*10*) |
| | $H_2O$ | $<1.0^{a}$ | F | (*6*) |

II. Bivalent transition metal ions

| *Metal Ion* | *Ligand* | *Log Rate Constant* | *E* | *Method* | *Reference* |
|---|---|---|---|---|---|
| $V^{+2}$ | $SCN^{-}$ | $1.6^{b}$ | | | (*74*) |
| | dipy | $-0.5$ | $\sim 15$ | | (*74*) |
| $Cr^{+2}$ | dipy | $\sim 2.0$ | | | (*74*) |
| $Mn^{+2}$ | $NTA^{-3}$ | 8.7 | | E | (*72*) |
| | $HNTA^{-2}$ | 5.3 | | E | (*72*) |
| | $SO_4^{-2}$ | $6.6^{ab}$ | 6 | SA | (*41*) |
| | | $\sim 8.0^{ab}$ | | ESR | (*59*) |
| | $Cl^{-}$ | 7.2 | 9 | ESR | (*59*) |
| | $H_2O$ | $7.5^{a}$ | 8 | NMR | (*111*) |
| $Fe^{+2}$ | $SO_4^{-2}$ | $6.0^{ab}$ | | SA | (*41*) |
| | $H_2O$ | $6.5^{a}$ | 8 | NMR | (*111*) |
| | phen | 5.9 | | F | (*11*) |
| | terpy | 4.7 | 9 | F | (*62*) |
| $Fe(phen)_2^{+2}$ | phen | $5.8^{c}$ | | | (*67, 129*) |
| $Fe(dipy)_2^{+2}$ | dipy | $5.6^{c}$ | | | (*67, 129*) |

| | | | | | |
|---|---|---|---|---|---|
| $FeG_2$ | $G^-$ | 4.6 | 10 | NMR | (*95*) |
| $Fe(CN)_5^{-3}$ | $CN^-$ | ~0.0 | | | (*44*) |
| $Co^{+2}$ | $EDTA^{-4}$ | ≈9.0 | | E | (*114*) |
| | $HEDTA^{-3}$ | 7.0$^d$ | | E | (*114*) |
| | | 6.6 | | | (*76*) |
| | $HP_3O_{10}^{-4}$ | 8.6 | | TJ | (*55*) |
| | $HP_2O_7^{-3}$ | 6.3 | | TJ | (*55*) |
| | $SO_4^{-2}$ | 5.3$^{ab}$ | 6 | SA | (*41*) |
| | $GG^-$ | 5.7 | | TJ | (*56*) |
| | $SCN^-$ | >4.0 | | F | (*27*) |
| | $H_2O$ | 6.0$^a$ | 8 | NMR | (*111*) |
| | IM | 5.1 | | TJ | (*56*) |
| | phen | 5.5 | 11 | F | (*62*) |
| | | 5.2$^c$ | 10 | | (*4, 43, 67*) |
| | PAD | 4.6$^d$ | 10 | TJ | (*128*) |
| $Co(IM)^{+2}$ | IM | 5.0 | | TJ | (*56*) |
| $Co(en)_2^{+2}$ | en | 6.3$^c$ | | NMR | (*88*) |
| | | 6.8$^c$ | | NMR | (*95*) |
| $Co(phen)_2^{+2}$ | phen | 5.6$^c$ | 13 | | (*4, 43, 67*) |
| $CoG^+$ | $G^-$ | 6.3 | | TJ | (*56*) |
| $Co(GG)^+$ | $GG^-$ | 5.0 | | TJ | (*56*) |
| $CoG_2$ | $G^-$ | 6.0 | | TJ | (*56*) |
| | | 6.3$^c$ | | NMR | (*95*) |
| $Ni^{+2}$ | $HEDTA^{-3}$ | 5.3 | | | (*81*) |
| $Ni^{+2}$ | $HPgO_{10}^{-4}$ | 6.8 | | TJ | (*55*) |
| | $HP_2O_7^{-3}$ | 6.3 | | TJ | (*55*) |
| | | 4.0$^e$ | | E | (*119*) |
| | $H_2EDTA^{-2}$ | 3.3 | | | (*81*) |
| | | 2.3$^e$ | | E | (*119*) |
| | $SO_4^{-2}$ | 4.2$^{ab}$ | 8 | SA | (*41*) |
| | $C_2O_4^{-2}$ | 4.9 | 15 | F | (*91*) |
| | $HC_2O_4^-$ | 3.7 | 15 | F | (*91*) |
| | $GG^-$ | 4.3 | | TJ | (*56*) |
| | $GGG^-$ | 3.9 | | TJ | (*56*) |
| | $SCN^-$ | 3.7 | 9 | F | (*27*) |
| | $H_2O$ | 4.4$^a$ | 12 | NMR | (*111*) |
| | $NH_3$ | 3.4$^c$ | 10 | F | (*84*) |
| | $N_2H_4$ | 3.4 | | F | (*84*) |
| | py | 3.7 | 13 | F | (*84*) |
| | IM | 3.7 | | TJ | (*56*) |
| | en | 4.6$^{ce}$ | 12 | | (*3*) |
| | phen | 3.4 | 10 | | (*7, 79*) |
| | | 3.6$^c$ | 13 | | (*4, 42, 67*) |
| | | 3.6 | 14 | F | (*62*) |
| | 2–Mephen | 2.7$^c$ | | | (*42, 68*) |
| | 5–Mephen | 3.2$^c$ | | | (*42, 83*) |
| | dipy | 2.8$^c$ | 14 | | (*4, 42*) |
| | terpy | 3.1 | 13 | F | (*62*) |
| | PAD | 3.6 | | TJ | (*128*) |
| | enao | 4.4 | | | (*90*) |
| | $Henao^+$ | 0.6 | | | (*90*) |
| | $Hen^+$ | 2.8 | | F | (*86*) |
| | $Htrien^+$ | 4.0 | | | (*80*) |
| | $H_2trien^{+2}$ | 2.0 | | | (*80*) |
| | $H_2te^{+2}$ | 2.5 | | | (*80*) |
| | $H_3te^{+3}$ | 0.5 | | | (*80*) |
| $Ni(NH_3)_5^{+2}$ | $NH_3$ | 5.5$^c$ | 5 | NMR | (*64*) |
| $Ni(p)(H_2O)^{+2}$ | $H_2O$ | 3.3$^{acef}$ | | F | (*85*) |
| $Ni(IM)^{+2}$ | IM | 3.6 | | TJ | (*56*) |
| $Ni(IM)_2^{+2}$ | IM | 3.4 | | TJ | (*56*) |
| $Ni(en)_2^{+2}$ | en | 4.1$^{ce}$ | 8 | F | (*3, 98*) |
| $Ni(phen)^{+2}$ | phen | 3.5$^c$ | 14 | | (*4, 67, 129*) |
| $Ni(phen)_2^{+2}$ | phen | 2.5$^c$ | 15 | | (*4, 67, 129*) |
| $Ni(dipy)_2^{+2}$ | dipy | 3.6$^c$ | 13 | | (*43, 67, 129*) |
| $Ni(ptn)(H_2O)_4^{+2}$ | $H_2O$ | 3.1$^{acf}$ | | F | (*85*) |

| | | | | | |
|---|---|---|---|---|---|
| $NiG^+$ | $G^-$ | 4.8 | | TJ | (*56*) |
| $Ni(GG)^+$ | $GG^-$ | 3.6 | | TJ | (*56*) |
| $Ni(GGG)^+$ | $GGG^-$ | 3.8 | | TJ | (*56*) |
| $NiG_2$ | $G^-$ | 4.6 | | TJ | (*56*) |
| $Ni(GG)_2$ | $GG^-$ | 3.5 | | TJ | (*56*) |
| $Ni(GGG)_2$ | $GGG^-$ | 3.2 | | TJ | (*56*) |
| $Ni(SCN)_3^-$ | $SCN^-$ | $\approx 5.8^{c}$ | | NMR | (*64*) |
| $Cu^{+2}$ | $HEDTA^{-3}$ | 9.5 | 8 | E | (*118*) |
| | | $7.9^{e}$ | | E | (*1*) |
| | $H_2EDTA^{-2}$ | $5.6^{e}$ | | E | (*1*) |
| | $SO_4^{-2}$ | $>7^{ab}$ | | SA | (*41*) |
| | $CH_3COO^-$ | $8.4^{ab}$ | | SA | (*39*) |
| | $H_2O$ | $8.3^{a}$ | 5 | NMR | (*111*) |
| | $NH_3$ | $\sim 7.3^{cg}$ | | F | (*126*) |
| | te | $\sim 9.3^{ce}$ | 4 | | (*126*) |
| | PAD | $8^{ad}$ | | TJ | (*128*) |
| $Cu(te)^{+2}$ | te | $\sim 8.3^{ce}$ | 5 | | (*126*) |
| $Cu(en)_2^{+2}$ | en | 6.8 | 5 | NMR | (*25*, *89*) |
| | | 6.3 | 7 | NMR | (*95*) |
| $CuG_2$ | $G^-$ | $\sim 7$ | 6 | NMR | (*95*) |
| $Zn^{+2}$ | $HEDTA^{-3}$ | $\sim 9$ | | E | (*16*) |
| | $CH_3COO^-$ | $7.5^{ab}$ | | SA | (*39*) |
| | $SO_4^{-2}$ | $7.5^{ab}$ | | SA | (*39*) |
| | $Cl^-$ | $7.4^{ab}$ | | SA | (*39*) |
| | $Br^-$, $I^-$ | $\sim 5.7$ | | NMR | (*60*) |
| | PAD | $6.6^{d}$ | | TJ | (*128*) |
| $ZnX^+$ | $Br^-$, $I^-$ | $\sim 5.7$ | | NMR | (*60*) |
| $ZnX_2$ | $Br^-$, $I^-$ | $\sim 5.7$ | | NMR | (*60*) |
| $ZnBr_3^-$ | $Br^-$ | 7.9 | | NMR | (*60*) |
| $ZnI_3^-$ | $I^-$ | 6.8 | | NMR | (*60*) |
| $Cd^{2+}$ | $HEDTA^{-3}$ | 9.6 | | E | (*120*) |
| | | 8.9 | | E | (*73*) |
| | $NTA^{-3}$ | 10.3 | | E | (*72*) |
| | $HNTA^{-2}$ | 5.9 | | E | (*72*) |
| | | 6.5 | | E | (*94*) |
| | $SO_4^{-2}$ | $>8^{ab}$ | | SA | (*39*) |
| | $CH_3COO^-$ | $8.4^{ab}$ | | SA | (*39*) |
| | $Cl^-$ | $8.6^{ab}$ | | SA | (*39*) |
| | $Br^-$ | 9.1 | | NMR | (*60*) |
| | $I^-$ | $\sim 9.7$ | | NMR | (*60*) |
| | $CN^-$ | 9.6 | | E | (*29*) |
| | PAD | $\sim 7.0^{d}$ | | TJ | (*128*) |
| $CdBr^+$ | $Br^-$ | 8.1 | | NMR | (*60*) |
| $CdCl_2$ | $Cl^-$ | 8.0 | $\approx 5$ | SA | (*123*) |
| $CdBr_2$ | $Br^-$ | 7.1 | | NMR | (*60*) |
| $Cd(CN)_2$ | $CN^-$ | 10.6 | | E | (*71*) |
| $CdCl_3^-$ | $Cl^-$ | 9.6 | | SA | (*123*) |
| $CdBr_3^-$ | $Br^-$ | 7.1 | | NMR | (*60*) |
| $CdI_3^-$ | $I^-$ | $\sim 8.6$ | | NMR | (*60*) |
| $Cd(CN)_3^-$ | $CN^-$ | 8.2 | | E | (*49*) |
| | | 7.9 | | E | (*50*) |
| $Hg^{+2}$ | $Cl^-$ | $9.3^{ab}$ | | SA | (*39*) |
| $HgCl^+$ | $Cl^-$ | $\sim 9.8$ | | EF | (*36*) |
| $HgBr_2$ | $Br^-$ | 9.7 | | NMR | (*60*) |
| $HgBr_3^-$ | $Br^-$ | 9.0 | | NMR | (*60*) |
| $HgI_3^-$ | $I^-$ | 8.8 | 2 | NMR | (*92*) |
| | | $5.3^{c}$ | | | (*24*, *33*) |
| $Hg(CH_3)OH$ | $SO_3^{-2}$ | $5.4^{h}$ | | TJ | (*37*) |
| | $Cl^-$ | $4.0^{h}$ | | TJ | (*37*) |
| | $Br^-$ | $5.3^{h}$ | | TJ | (*37*) |
| | $I^-$ | $6.8^{h}$ | | TJ | (*37*) |
| | $SCN^-$ | $5.3^{h}$ | | TJ | (*37*) |

| | | | | | |
|---|---|---|---|---|---|
| III. Tervalent transition metal ions | | | | | |
| $V^{+3}$ | $SCN^-$ | 1.8[b] | | | (*74*) |
| V(IV) | $SO_4^{-2}$ | 3.2[a] | | PJ | (*108*) |
| $Cr(H_2O)_6^{+3}$ | $SO_4^{-2}$ | −5.7 | 28 | | (*45*) |
| | $SCN^-$ | −5.7 | 26 | | (*99*) |
| | $H_2O$ | −4.7[a] | 27 | | (*65*) |
| | | −2.9[aj] | | | (*65*) |
| | phen | −2.5[j] | | | (*13*) |
| $Cr(NH_3)_5(H_2O)^{+3}$ | $Cl^-$ | −5.7 | 25 | | (*58*) |
| $Cr(H_2O)_5Cl^{+2}$ | $Cl^-$ | −6.0 | | | (*70*) |
| $Cr(C_2O_4)_2(H_2O)_2^-$ | $C_2O_4^{-2}$ | −3.9 | 23 | | (*57*) |
| $Cr(C_2O_4)_2(H_2O)_2^-$ | $HC_2O_4^-$ | −4.2 | 22 | | (*57*) |
| $Cr(SCN)_5(H_2O)^{-2}$ | $SCN^-$ | −5.0 | | | (*101*) |
| $Fe^{+3}$ | HF | 1.1 | 9 | F | (*100*) |
| | $Cl^-$ | 1.0 | 17 | F | (*21*) |
| | $Br^-$ | 1.3 | | F | (*82*) |
| | $SCN^-$ | 2.1 | 13 | F | (*12*) |
| | $HN_3$ | 0.6 | | F | (*106*) |
| | | <0.8 | | TJ | (*19*) |
| | $H_2O$ | 0.6[a] | | NMR | (*22*) |
| $FeOH^{+2}$ | $SO_4^{-2}$ | 5.5 | | F, PJ | (*28*, *125*) |
| | $HSO_4^-$ | 5.1 | | F | (*28*) |
| | HF | 3.5 | | F | (*100*) |
| | $Cl^-$ | 4.0 | | F | (*21*) |
| | $Br^-$ | 4.4 | | F | (*82*) |
| | $SCN^-$ | 4.0 | | F | (*12*) |
| | $N_3^-$ | 5.3 | 1 | TJ | (*19*) |
| | $HN_3$ | 3.9 | | F, TJ | (*19*, 106) |
| | $H_2O$ | 2.6[a] | 1 | NMR | (*22*) |
| $Co^{+3}$ | $Cl^-$ | +1.5 | | F | (*23*) |
| $Co(NH_3)_5(H_2O)^{+3}$ | $SO_4^{-2}$ | −5.7[a] | | | (*122*) |
| | $H_2PO_4^-$ | −6.1[a] | | | (*105*) |
| | $H_2O$ | −5.2[a] | 27 | | (*63*) |
| $Co(HEDTA)H_2O$ | $H_2O$ | −3.6[af] | 26 | | (*31*) |
| $Co(HPDTA)H_2O$ | $H_2O$ | −3.6[af] | 26 | | (*109*) |
| $Co(EDTA)H_2O^-$ | $H_2O$ | −3.4[adf] | 25 | | (*107*) |
| $Co(PDTA)H_2O^-$ | $H_2O$ | −2.7[af] | | | (*109*) |
| | | −3.3[adf] | | | (*109*) |
| $Co(EDTA)OH^{-2}$ | OH | −4.4[af] | ~19 | | (*107*) |
| $Co(PDTA)OH^{-2}$ | OH | −3.6[af] | 15 | | (*109*) |
| $Co(CN)_5(H_2O)^{-2}$ | $H_2O$ | −2.9[ak] | | | (*53*) |
| | $N_3^-$, $SCN^-$ | −3.3[ab] | | | (*53*) |
| $Rh(H_2O)_6^{+3}$ | $H_2O$ | −4.7[aj] | | | (*97*) |
| $Rh(H_2O)_5OH^{+2}$ | $H_2O$ | −2.5[aj] | | | (*97*) |
| $IrCl_5(H_2O)^{-2}$ | $Cl^-$ | −4.3[m] | | | (*102*) |

**Table II. Kinetic Data for Solvent Exchange and Formation of Complexes of Bivalent Transition Metal Ions in Methanol at 25°C.**

| *Metal Ion* | *Ligand* | *Log Rate Constant* | *E* | *Method* | *Reference* |
|---|---|---|---|---|---|
| $Fe(dipy)_2^{+2}$ | dipy | ~4.0[e] | <16 | LT | (*15*) |
| $Co(CH_3OH)_6^{+2}$ | $CH_3OH$ | 5.0[a] | 14 | NMR | (*77*) |
| $Co(CH_3OH)_4(H_2O)_2^{+2}$ | $CH_3OH$ | 6.3[a] | | NMR | (*77*) |
| $Ni(CH_3OH)_6^{+2}$ | $CH_3OH$ | 3.3[a] | | NMR | (*96*) |
| | | 3.8[a] | 11 | NMR | (*77*) |
| $Ni(CH_3OH)_6^{+2}$ | py | 3.5 | | LT | (*14*) |
| $Ni(CH_3OH)_6^{+2}$ | en | <4.4[e] | | LT | (*15*) |
| $Ni(CH_3OH)_4en^{+2}$ | en | 4.4[e] | | LT | (*15*) |
| $Ni(CH_3OH)_2en_2^{+2}$ | en | 4.8[e] | 13 | LT | (*15*) |
| $Cu^{+2}$ | $CH_3OH$ | 4.0[a] | | NMR | (*96*) |
| | en | 11.7[a] | 4 | LT | (*15*) |

## *Footnotes to Tables I and II*

[a] Rate constant in sec.$^{-1}$ units. The water exchange values for the labile bivalent metal ions are for the reaction $M(H_2O)^{+n} + H_2O \rightarrow M(H_2O)^{+n} + H_2O$ for the NMR studies and for the outer sphere to inner sphere $M(H_2O)X \rightarrow MX + H_2O$ for the sound absorption measurements. For the tervalent metal ions, $k = 6 \times 0.693/t_{1/2}$ (exch).

[b] 20°C.

[c] Calculated from reverse (dissociation) rate constant and thermodynamic data.

[d] 15°C.

[e] 0°C.

[f] In this process coordinated water or hydroxy is eliminated by the "free" donor group of quinquedentate-acting (*p*), (EDTA) or (PDTA) or bidentate-acting (ptn). Thus an intramolecular substitution completes the chelation.

[g] Copper chelates with diamines dissociate *about* 200–400 times more rapidly than the corresponding nickel complex. If the same situation pertains with the monoammonia complex, an estimated dissociation rate constant, with thermodynamic data, yields the value shown.

[h] 10°C.

[i] Forming *cis* or *trans* $Cr(H_2O)_4Cl_2^+$.

[j] 60°C.

[k] 40°C.

[m] 50°C.

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# Discussion

**Dale Margerum:** Ralph Wilkins has mentioned the interesting effect of terpyridine on the subsequent substitution reaction of the nickel complex. I would like to discuss this point—namely the effect of coordination of other ligands on the rate of substitution of the remaining coordinated water. However, before proceeding we should first focus attention on the main point of this paper–which is that a tremendous amount of kinetic data for the rate of formation of all kinds of metal complexes can be correlated with the rate of water substitution of the simple aquo metal ion. This also means that dissociation rate constants of metal complexes can be predicted from the stability constants of the complexes and the rate constant of water exchange. The data from the paper are so convincing that we can proceed to other points of discussion.

The work of G. Hammes and J. Steinfeld (*3*) showed the effect of glycine and imidizole coordination on subsequent rates of substitution of nickel (Figure A).

These are the rate constants for aquo nickel ion reacting with glycine, for $Nigly^+$ reacting with glycine, for $Ni(gly)_2$ reacting with glycine, etc. The calculated $k_o$

| *Glycine* | Observed $k_n$ $M^{-1}$ *sec.*$^{-1}$ | Calculated $k_o$ (*sec.*$^{-1}$) |
|---|---|---|
| $n = 1$ | $1.5 \times 10^4$ | $0.9 \times 10^4$ |
| $n = 2$ | $6.0 \times 10^4$ | $1.2 \times 10^5$ |
| $n = 3$ | $4.2 \times 10^4$ | $4.0 \times 10^5$ |
| *Imidazole* | | |
| $n = 1$ | $5.0 \times 10^3$ | $1.6 \times 10^4$ |
| $n = 2$ | $4.3 \times 10^3$ | $1.6 \times 10^4$ |
| $n = 3$ | $2.4 \times 10^3$ | $1.1 \times 10^4$ |

*Figure A. Rate constants of Ni complex reactions (3)*

value corrects for ion pairing and is believed to correspond to the rate of water loss from the nickel ion. When one glycine is coordinated to nickel, the water substitution increases by a factor of 10, and when two glycines are bound there is a further increase in the rate constant.

On the other hand, with imidazole the three rate constants are essentially the same. The conclusion drawn was that as the charge of the metal complex is reduced, the water substitution becomes easier.

In general, it has often been suggested that the reduction of charge of a metal complex leads to faster substitution of coordinated water. This has been observed with $FeOH_{aq}^{+2}$ *vs.* $Fe_{aq}^{+3}$ and other species.

During the past year, in association with Manfred Eigen in Gottingen, Germany, I examined a number of substitution reactions of nickel to see if there was indeed a direct relationship between the charge of a complex and its rate of water substitution. The temperature jump method was used to measure the rate of substitution of $NH_3$ for water with various complexes.

$$ML(H_2O)_x + NH_3 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} ML(H_2O)_{x-1}NH_3 + H_2O$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$OH^- + HInd. \rightleftharpoons Ind.^- + H_2O$$

$$1/\tau = k_{21} + k_{12}(\bar{C}_{ML} + \bar{C}_{NH_3})$$

The reaction is coupled to an indicator color change which is much faster than the metal substitution step. L refers to the multidentate ligands which were employed to avoid multiple relaxations; $\tau$ is the relaxation time.

$$NiL + NH_3 \xrightarrow{k_{12}} NiLNH_3$$

| *L* | *Coordinate Groups* | *Charge of Complex* | $k_{12}$, $M^{-1}$ *sec.*$^{-1}$ |
|---|---|---|---|
| Gly | 1*N*, $1COO^-$, $4H_2O$ | +1 | $1 \times 10^4$ |
| IDA | 1*N*, $2COO^-$, $3H_2O$ | 0 | $6 \times 10^3$ |
| NTA | 1*N*, $3COO^-$, $2H_2O$ | −1 | $6 \times 10^3$ |
| HEEDTA | 2*N*, $3COO^-$, $1H_2O$ | −1 | $\sim 1 \times 10^3$ |
| EDTA | 2*N*, $3COO^-$, $1H_2O$ | −2 | $1.5 \times 10^3$ |
| Dien | 3*N*, $3H_2O$ | +2 | $7 \times 10^4$ |
| Trien | 4*N*, $2H_2O$ | +2 | $6 \times 10^3$ |
| Tetren | 5*N*, $1H_2O$ | +2 | $<10^3$ |

*Figure B. Rate of substitution of $NH_3$ for $H_2O$ with various complexes*

Using different ligands for L permitted the charge of the complex to be varied from +2 to −2. The constant $k_{12}$ is the second-order rate constant not corrected for ion-dipole association. However, a direct comparison can be made of the −2 and +2 rates as well as the −1 and +1 because $NH_3$ is neutral and the outer sphere attraction should be approximately the same for the same absolute charge on the complex.

The result for glycine is comparable to that of Hammes and Steinfeld and the water dissociation rate constant is probably about 10 times $k_{12}$. As the charge decreases from +1 to −2 there is a decrease in the $k_{12}$ value rather than the very large increase which would be expected if a charge decrease made the coordinated water much more labile. In fact, the rate drops more or less in order of the statistical number of coordinated water available for substitution. On the other hand, with the +2 polyamines the dien complex shows a substantial increase in rate of water substitution. The individual coordinated water appears to be about 100 times more labile than in $Ni_{aq}^{+2}$.

A comparison with the glycine work suggests that it is the nitrogen coordination rather than the carboxylate coordination which accelerates the water substitution of the metal complex. It appears that three nitrogens coordinated to Ni(II) gives a labile system which is diminished by having four or five nitrogens coordinated.

It is interesting that Dr. Wilkins' data for the terpyridine system, also with three nitrogens bonded to Ni(II), gives a much more labile complex.

I believe it is too early to say exactly what factors affect the rate of water loss from metal complexes. However, I believe this work shows that reduced charge does not necessarily give a more labile complex. Groups which are more strongly coordinated (supply a greater electron density) may have the greatest influence.

**Jack Halpern:** What is the rate constant for the aquo ion in this series for comparison?

**Dr. Margerum:** An experimental comparison with the aquo ion was not made in this series because nickel hydroxide would precipitate. However, the Niglycine$^+$ data provides a reference point which suggests all the $k_{12}$ values can be multiplied by a factor of about 10 to give the first-order constant for water dissociation.

**Daniel L. Leussing:** We have here the summary of some excellent work. The picture that emerges is that of a ceiling limited by the rate of water discharge from the metal ion. I have no criticism of this concept. We understand much more about these systems than we did a few years ago. However, I would like to make a few suggestions which might contribute to this second generation of theories as it were. Already the results of Norman Sutin for redox systems have shown that not only do the energies of the initial reactants play a part but also the energies of the products. In other words, the free energy of the reaction actually affects the rate constant, and it seems to me that in the present theories a good deal of what is known in a particular system about the stability of the complex ion itself has been neglected. A case in point would be the very low rate of formation of the complex between the protonated ethylenediamine and nickel. The rate constant here is about a factor of 1000 less than that for the unprotonated ethylenediamine nickel reaction. This isn't understandable in terms of a mechanism in which the rate of water loss is the only governing step. We know, of course, that this complex is very weak, and it seems as though this fact must be taken into account.

As far as dissociation rates are concerned, a picture has emerged in which the ends of the ligand operate more or less independently; however, here again stabilities and factors that determine the stabilities of the complex ions have to enter into a more complete picture.

In Figure C we have a comparison of some studies on tris(ethylenediamine)-nickel(II) and tris(phenanthroline)nickel(II).

| | *log $k_d$ sec.$^{-1}$* | *$K_f$ intrinsic* |
|---|---|---|
| $Ni(en)_3^{+2}$ | 1.95 | 4.8 |
| $Ni(en)_2^{+2}$ | 0.72 | 5.7 |
| $Ni(en)^{+2}$ | −0.84 | 6.3 |
| $Ni(phen)_3^{+2}$ | −5.11 | 7.9 |
| $Ni(phen)_2^{+2}$ | −4.74 | 7.5 |
| $Ni(phen)^{+2}$ | −5.00 | 7.2 |

*Figure C. Dissociation rates of tris(ethylenediamine)nickel(II) and tris(phenanthroline)nickel(II)*

We find that in looking at the data for the ethylenediamine we have more or less normal behavior; the highest complex dissociates with the fastest rate, and as the complexity of the ion decreases the rate constant falls off. With phenanthroline, however, we find that the highest complex is actually the slowest to dissociate. The bis complex is the fastest, and once again we have a decrease with the mono complex.

A parallel in this behavior can be seen in the stepwise formation constants of these complexes after a correction is made for statistical effects. The tris(ethylenediamine)nickel ion is much less stable than the mono(ethylenediamine)nickel ion. But with phenanthroline, as the degree of complexity increases, the intrinsic stability also increases. There are important changes in the nature of the complexes as the ligand number is increased in the phenanthroline series. This behavior can be observed once again in the positions of the first *d–d* transition. With ethylenediamine the first band occurs at 10,300 cm.$^{-1}$; with tris(ethylenediamine) 11,200 cm.$^{-1}$. With the mono(phenanthroline)nickel ion the first ligand field band actually lies at a lower energy than with ethylenediamine. However, when the highest complex is formed the well known strong ligand field effect of phenanthroline is observed. In the lower complexes, phenanthroline acts as a fairly hard molecule, and in the higher complexes it acts as the soft molecule as Prof. Pearson might say.

An inconsistancy also appears to exist in situations where two different types of groups are coordinated—e.g., Ni(II)—glycinate. From NMR studies Prof. Pearson has proposed a model in which the carboxylate in this complex is more easily dissociated than the amine group. However, Prof. Wilkins proposes when one end of a bidentate ligand is detached, the other end behaves as a unidentate ligand which accordingly dissociates at a characteristically more rapid rate. It would seem that these models would lead to a predicted stability of the Ni(II)—glycinate complex of the order of that for a unidentate ligand, contrary to the facts. Here again it seems necessary to consider the ligand as a whole rather than focusing attention on the individual dentate groups.

**Dr. Halpern**: I want to comment on two points. The first relates to the suggestion made by Dr. Wilkins that substitution may be rate determining in some redox processes.

Of course, in inner sphere bridged electron transfer reactions, one of the steps in the mechanistic sequence is the substitution of one of the complexes into the coordination shell of the second. Thus, if the electron transfer process that follows is fast enough, the substitutional step may become rate determining. I am not sure that there is any clear cut evidence that this is the case for any systems actually examined. I did cite a case of a bridged electron transfer reaction that proceeded with a rate constant of $10^9$—i.e.,

$$Co(CN)_5^{-3} + Co(NH_3)_5Br^{+2} \rightarrow Co(CN)_5Br^{-3}$$

But this is a rather special case, in that the complex to which the bond was being formed is pentacoordinated, so that entry into the coordination shell does not involve the displacement of another ligand.

In the case of the reduction of pentaminecobalt(III) complexes by $Cr^{+2}$ which Prof. Taube has studied, some fast rates are now turning up. John Candlin has just completed measurement of the rates of reduction of the halopentamminecobalt(III) complexes by $Cr^{+2}$ and determined that the rate constants lie in the range $10^6$ to $10^7$ $M^{-1}$sec.$^{-1}$. This must be getting close to the substitution rates of the pentamminecobalt halide into the coordination shell of the $Cr^{+2}$. Although it would be helpful to have more information about substitutional rates of $Cr^{+2}$ to compare with these numbers, I think we are getting close to this limit in some of these systems.

My other question concerns the general theme of the effect of ligands in the coordination shell of a metal ion on the rate of water displacement. I refer particularly to the effect of hydroxide as a ligand,—i.e., to the effect of hydrolysis of metal ions on the substitution of water.

It appears from some of the systems observed that $OH^-$ is very efficient in promoting the substitution of water by other ligands, particularly in the case of ions such as $Fe^{+3}$ and $Be^{+2}$. I was interested to see some of the results presented here which suggest that some of these effects don't correlate with the overall charge, because I think there is also other evidence that the effect of hydroxide transcends that which can be ascribed to charge. For example, in the case of iron(III) complexes, I think there are some data on the effect of $Cl^-$ on substitution and the effect is much smaller, as I recall, than that of $OH^-$. This suggests that $OH^-$ plays a special role or exerts a specific effect, and I wondered whether someone would care to comment further on this point. It is conceivable that the role of $OH^-$ is related to the special labilizing effect of the $NH_2^-$ group in the $S_N1CB$ mechanism. In connection with this there is one other point which is a little troublesome; namely, that it seems difficult to ascribe the effect of hydroxide as being caused by weakening of the binding of the residual waters. If this were so, one would expect this to occur also in the subsequent hydrolysis constants. If the binding of the remaining waters were weakened, one would expect their hydrolysis constants to fall off.

In the few cases where successive hydrolysis constants have been determined with some reliability—e.g., $Fe^{+3}$ and $Sc^{+3}$—it seems that there is practically no decrease in going from the first to the second hydrolysis constant. This argues against hydroxide's having a strong weakening effect on binding or coordinated water.

**Dr. Margerum:** Although it argues against it, there is rather direct kinetic evidence that in the iron case, at least, it does increase the rate of substitution.

**Dr. Halpern:** This could be used in stabilizing, say an activated complex. The point about the hydrolysis observation is that this refers to the octahedral complex, whereas the explanations that have been offered for the effect of amide in the conjugate base mechanism are concerned, not with weakening of the binding, but with stabilizing a five-coordinated intermediate. I wondered if the role of the hydroxide in promoting water substitution might be of the same nature.

**Leonard Katzin:** I want to make two comments, one on this last point in relation to the point that Dr. Margerum made about substituents. Chromium(III) in the hexahydrated state is quite resistant to penetration of the coordination shell by nitrate ion. Yet if one takes the violet chromium nitrate hexahydrate in solid state and treats it with liquid tributylphosphate, within a matter of minutes one gets chromium compound in solution by the mechanism of substituting tributylphosphate for water. So this reaction is fast. This initial solution is violet Within the space of an hour or two it is green. And we have had for some years now infrared evidence that this color change is accompanied by penetration of the nitrate ion into the coordination sphere (*4*). So this again is a matter of the substituent's changing the relationship of the water.

In this particular case there is something which bears on what Dr. Halpern said—namely, that tributylphosphate and its analogs are such strong donors that I think they upset what is the normal distribution of bonding energy in the cation. Perhaps hydroxyl does the same thing. The pentacyano substances that were mentioned this morning undoubtedly do the same sort of thing, which can then lead to other sorts of changes, either change in the rate of loosening, or change of substituents, or even a change in coordination number. This brings me to a comment that Dr. Wilkins made which again ties in with some of this morning's work. With the rare earths he mentioned that the rates are fast. With the rare earth salts one has a multitude of coordination states, even for the same coordination number. I think this sort of thing is a factor in some of these kinetic effects and is a place at which equilibrium chemistry and kinetic chemistry may come together. With respect to the pentacyano I believe there are verified copper situations in which there is a coordination number of five, I believe, in a bipyrimidal arrangement and so on. And if one thinks of the ordinary effects in transition elements as between tetrahedral and octahedral coordination, for instance, in which the determining factor is the nature of the ligand, then it is clear that many of these things must be extremely dependent on the particular ligand and the energy with which it is bound.

**Carl Brubaker:** I want to comment again that we are working with uranium(IV) as a reducing agent and reductions involving uranium(IV) in the presence of tartaric acid. Regardless of whether we are carrying out net reductions or exchange with uranyl, we find that the rate-controlling step appears to be the formation of a uranium(IV) tartrate complex.

**Arthur Adamson:** If I may, I would like to mention a reaction that I think is an example of substitution which paves the way for a redox reaction, and yet is not a case of the charge following the oxidant into the coordination sphere. This is the reaction of ferrocyanide with cobaltous EDTA.

$$\mathrm{Co(EDTA)^{-2} + Fe(CN)_6^{-3} \rightleftharpoons Co(EDTA)^{-1} + Fe(CN)_6^{-4}}$$

The final product is ferrocyanide and cobaltic EDTA, but this goes through an intermediate which can be isolated, and which is an adduct of these two. Dr. Wilkins tried this system out in his rapid flow rate system and found a rate of association which was about right for substitution rates on a cobaltous ion. So this seemed to be a case where perhaps the nitrogen end of a cyanide was able to coordinate into a cobaltous complex, with either concomitant or subsequent charge transfer. Yet no transfer of ligand occurs in the overall reaction.

One point I would like to ask Dr. Wilkins about is this: about 15 years ago Rodzinski published in a Russian journal an interesting experiment which I could never duplicate; I wonder if you could comment on it in the light of current work. He took aqueous silver nitrate and alcoholic silver nitrate, equal volumes, equal concentrations. He mixed these rapidly, and immediately after mixing added aqueous sodium chloride with enough chloride to precipitate about a third of the total silver. The alcoholic silver nitrate was labelled, and he reported that the activity of the silver chloride produced indicated that most of the silver precipitated had come from the alcoholic silver nitrate. Do you think, in the light of current information on solvent exchange rates, that it is possible for silver ion to have retained the memory of its original solvent environment* long enough for this to show up in the labelling of the precipitate?

**Ralph Wilkins:** It was really thinking about the cobalt(II) EDTA—$Fe(CN)_6^{-3}$ system that gave me the idea, although I realize that I wasn't the first, that in certain redox processes—and this is very important, only in certain ones, the substitution was rate controlling. I have also carried out some temperature jump experiments on the system at 0°C. using freshly prepared solutions of reac tants, and observed some relaxation effects which are ascribed to this reaction. They are in the order of a few milliseconds, so it looks as though the flow and the temperature jump experiments are in reasonable agreement. These rates are anticipated for cobalt(II) substitution. We also know now that with EDTA complexes of bivalent metals, these almost certainly contain quinquedentate EDTA. Therefore, there is a water free and you would expect the water perhaps to be substituted by the ferrocyanide. It might be interesting to see if there are other cases, other metal EDTA complexes with ferrocyanide which give intermediates and for which the rates can be measured, and to show that these also conform to this pattern—that the water substitution is dominating the formation of the intermediate in the redox reaction.

As far as the second point is concerned, we know very little about the substitution rates of silver ion, although we would guess they are pretty fast. Therefore, I think that this is one of those observations which no one will be able to repeat.

**Arthur C. Wahl:** Could I comment on this point? I tried to repeat this experiment in 1940 and found no evidence for slow exchange (7).

**Ralph Pearson:** I would like to go back a couple of questioners and answer Dr. Halpern's question. I would certainly like to believe that the accelerating effect of the hydroxyl group is caused by $\pi$-bonding's stabilizing a five-coordinated intermediate with a trigonal bipyrimidal structure.

Just the other day I was reviewing the fine paper by Dr. Sutin and his coworker on the anation reactions of the ferric ion, where the accelerating effect of

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* Original wording (drunken condition).

the hydroxyl group shows up very nicely. In that paper Dr. Sutin pointed out that you could interpret the data for the anation reaction involving weak anions in two ways. You could either consider the reaction to be between the aquo ferric ion and the anion of the weak acid, or between the hydroxy complex—the ferric ion and the undissociated molecule. At first I wasn't inclined to believe this latter interpretation. For one thing I would like to think of this five-coordinated intermediate as being a long-lived, reasonably stable sort of species, perhaps showing a great deal of discrimination in its reactions with various potential nucleophiles. Interpreting the data in one way gives large discrimination factors; whereas, interpreting the data in terms of reaction with the hydroxyl complex and the undissociated molecule of the weak acid, doesn't give very large discrimination factors.

I was in doubt about this, but then I looked over Dr. Wilmarth's paper again and it occurred to me that he has data there for calculating the reaction rate of the cobaltpentacyano five-coordinated species with the hydrozoaic acid molecule. Fortunately, he has measured all the pertinent information so that we can unambiguously get the rate constant of a true five-coordinated intermediate. We can get the rate constants for the reaction of the five-coordinated intermediate with both azide ion and with hydroazoic acid. The interesting result is that $HN_3$ is slightly more reactive than $N_3^-$ so the neutral molecule is a better nucleophile for this particular case. I think really that perhaps Dr. Sutin's suggestion that it is the neutral molecule reacting in this anation of the ferric ion is the correct explanation, and you just don't get much discrimination in this case. You have such a high energy species, I would have to say, that even though it may be stabilized by $\pi$-bonding, it is not going to give any large discrimination effect.

**Gunther Eichhorn:** I want to mention briefly two recent studies concerning the relative reactivity of metal ions in what presumably are substitution reactions.

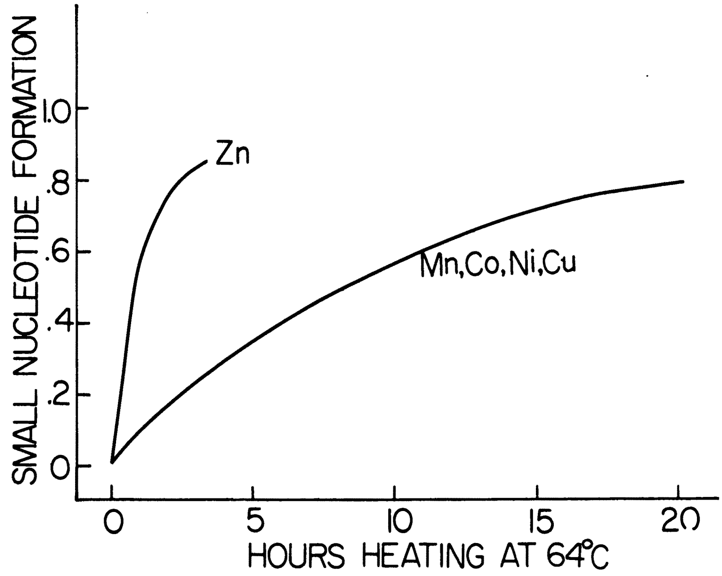


*Figure D. Plot of formation of various small nucleotide complexes vs. hours of heating at 64°C.*

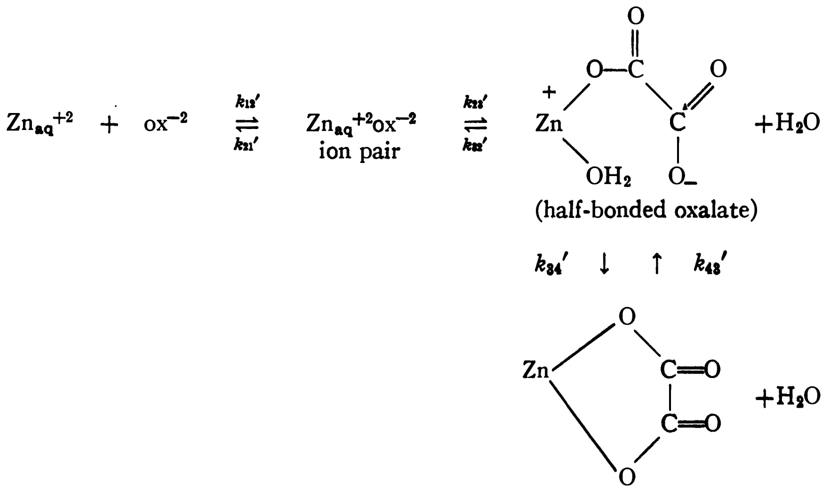
In one of these studies we have observed the metal-catalyzed degradation of polynucleotides, in which ribose—phosphate bonds are broken in a polymer in which phosphate and ribose groups alternate. This degradation reaction turned out to be a rather striking illustration of the effect, discussed by Fred Basolo and Ralph Pearson (*1*), of the very high reactivity of $d^{10}$ ions. A plot of the formation of small nucleotide complexes from the high molecular weight polynucleotides revealed that zinc reacted very rapidly, and that other divalent metal ions of the first transition series (Mn, Co, Ni, Cu) reacted very much more slowly (Figure D).

The second study is relevant to a discussion in the paper by Dr. Wilkins of instances in which the relative rates are related to stabilities. We have come across a very striking example of such a relationship in the activation of the enzyme ribonuclease by metal ions. In Figure E the activity is plotted *vs.* concentration of metal ion added to the enzymatic reaction mixture. In the absence of metal the activity is as indicated by the straight line in the center of the figure. It can be seen that a list of the transition metals in the order of concentrations giving maximum activity corresponds rather neatly with the Irving–Williams series.

**Dr. Margerum:** I want to develop briefly another point directly related to the dissociative mechanism—namely the opening of a chelate ring.

Consider the parallel reactions between zinc ion and acetate ion and between zinc ion and oxalate ion.

$$Zn_{aq}^{+2} + Ac^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{ion pair}}{Zn^{+2}(OH_2)Ac^-} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ZnAc^+ + H_2O$$



Maass and Eigen have shown for the zinc acetate system $k_{23} = k_{32} = 3.2 \times 10^7$ sec.$^{-1}$ The rate of loss of water from zinc equals the rate of loss of a carboxylate group from zinc. This means that the ion pair and inner sphere species of zinc acetate are present in solution in equal amounts. If we now examine the zinc oxalate system we see that we have similar rate steps.

The ratio of rate constants $k_{34}'/k_{43}'$, if the same dissociative mechanism holds, should be approximately one, because this too is the ratio of water loss to the loss of a carboxylate group. This would mean that zinc oxalate would be a mixture of the ion pair, the one-bonded and the two-bonded species. However, I think most

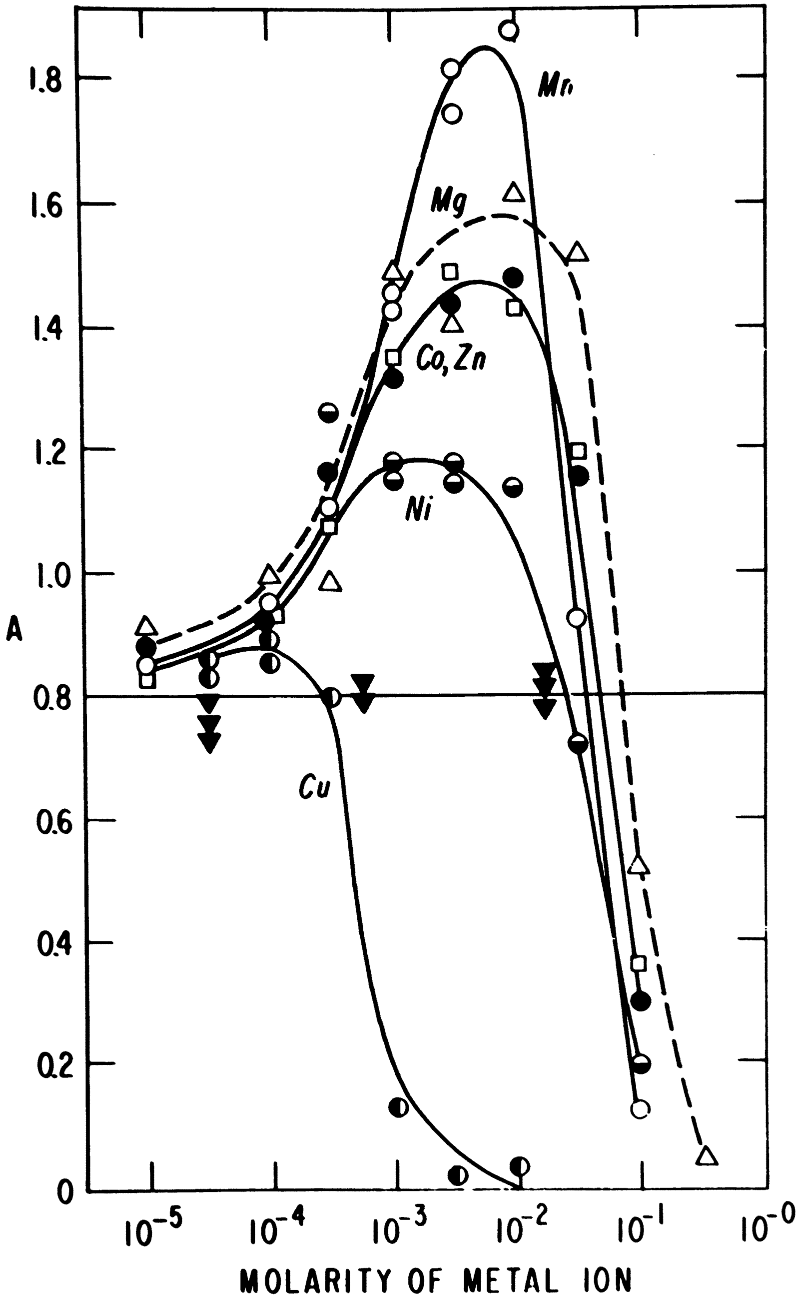


*Figure E. Activation of ribonuclease by metal ions* of you would agree that this is not going to be the case—that, in fact, the chelate form will be preferred. There is much chemical evidence to support the latter statement with oxalate complexes. Furthermore, the stability constant of zinc oxalate is much higher (it varies from $10^{3.7}$ to $10^5$, depending on one's preference of experimental results) than can be accounted for by ion-pair formation and equal energies for the one-and two-bonded oxalate. Hence, it is clear that from the kinetic viewpoint the rate constant $k_{43}'$ must be much less than $k_{34}'$. This says that opening the chelate ring must have a greater barrier than breaking a monodentate ligand, and it must also have a greater barrier than closing the chelate ring. In the case of zinc oxalate this means that the chelate bond cleavage is a factor of $10^2$ to $10^3$ less than the cleavage of the nonchelate group. This factor might be attributed to the necessary rotation of the chelated ligand but the problem arises as to why such a rotational barrier should not operate for closing the ring as well as opening the ring. Furthermore, if minimal energy paths of rotation were permissible the chelate effect would, in general, be much less than is actually the case.

Returning to the dissociative mechanism for substitution reactions permits a crude picture of the oxalate reaction between the one-bonded and two-bonded forms.

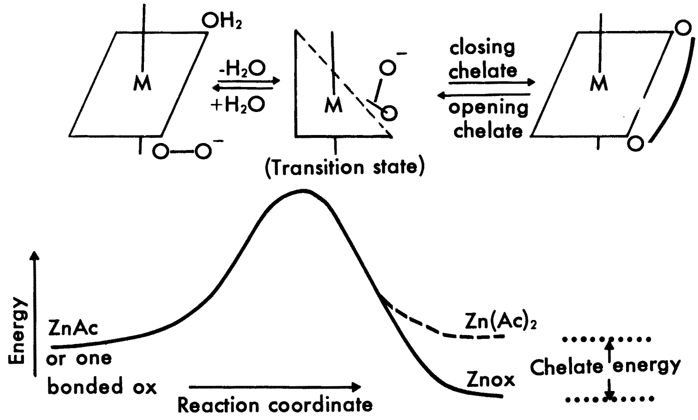
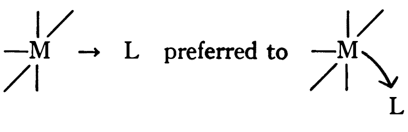


*Figure F. Opening and closing of chelate ring in transition state; plot of energy vs. reaction coordinate for ZnAc or a one-bonded ox.*

I propose that the reason a chelate bond is so much more difficult to break is that the minimum energy path for the dissociation of a ligand from a metal is a linear displacement rather than an angular displacement.



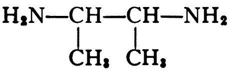
Another example of preferred linear displacement in ring openings can be found in the study of the hydrolysis of sultones (*2*). For a chelate ring to open it must have an angular displacement with a minimum arc to avoid the repulsions from other groups, etc. This means that almost all the possible rotational barriers of the chelate molecule will be encountered in opening the ring. Opening the chelate ring thus involves the unfavorable energy transition from a six- to five-coordinate species, the rotational barrier of the chelate, and any additional energy owing to lack of linear displacement. Water can add rapidly to this transition state to give the one-bonded species. If we examine the reverse process we find that water can be displaced linearly to reach the same transition state, and now the closing of the chelate ring is energetically downhill, so that despite the rotation, etc. the energy of the system decreases as the ring closes. Therefore, the opening of a chelate ring has an energy barrier which is not as important in the closing of a chelate ring.

The following results of the rate constants for the opening of en chelates can be understood by this mechanism (*8*).

| *Chelate* | *k, sec.*$^{-1}$ |
|---|---|
| Nien$^{+2}$ | 0.15 |
| Nibn$^{+2}$ | 0.020 |
| Ni-N-tetraMeen$^{+2}$ | 0.14 |
| Cuen$^{+2}$ | ~115 |
| Cubn$^{+2}$ | 4.56 |
| Cu-C-tetraMeen | 0.80 |
| Cu-N-tetraMeen | 38.5 |

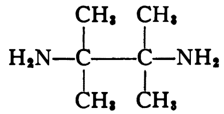
en = ethylenediamine

bn =



$H_2N-\underset{CH_3}{CH}-\underset{CH_3}{CH}-NH_2$

C-tetraMeen =



$H_2N-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-NH_2$

N-tetraMeen =

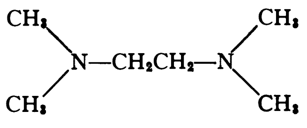


*Figure G. Rate constants for ring opening*

The C-substituted chelates provide higher rotational barriers to ring openings giving smaller values of *k*. Furthermore, C-tetraMeen forms a thermodynamically more stable complex with Cu than does en.

Larger chelate rings should be easier to open and of course they are known to have a smaller thermodynamic chelate effect.

**Richard Yalman:** It seemed to me that decreasing rates with increasing number of ligands could be explained statistically, but increasing the number of negative groups around the central ion weakens the bond between the central metallic ion and water, and a displacement reaction occurs. That is very intriguing. For example, I should be able to carry out a reaction involving zinc more rapidly in the presence of acetate. This suggestion was made to me a year ago by Robert Connick when I was investigating the incorporation of zinc in the porphyrins, in an acetate buffer. When I increased the acetate concentration I did find an increase in the rate of zinc incorporation, which seemed to fit very nicely with some of the things that have been said here. But subsequently I found that this was caused by a reaction between acetate and the porphyrin itself. Here we have a case where the prophyrin was labilized by an adduct between the porphyrin and acetate rather than the zinc's being labilized by formation of the zinc acetate complexes. Oddly enough, formate had no effect here.

In another set of experiments in alkaline solution it seems that with three hydroxides zinc reacts rather rapidly with porphyrins, but with four hydroxides it doesn't react nearly as rapidly. And if you replace the hydroxide by cyanides, you can stop the reaction altogether. I think this goes back to the remarks I made this morning, that each system may have its own particular mechanism.

**Anthony Poe**: Some recent data which we have obtained suggest another possible mechanism for formation reactions. In studies of the anation of *trans*-$Rhen_2BrOH_2^{+2}$ by chloride at an ionic strength of $1.5M$ (maintained with $NaClO_4$) and at 45°C., the graph of the pseudo first-order rate constant plotted against ($Cl^-$) curved down at high values of ($Cl^-$). A plot of $1/k_{obs}$ against $1/(Cl^-)$ gave a straight line as would be expected for a mechanism involving dissociation of a water molecule leading to a five-coordinate intermediate for which both water and chloride compete (cf. Wilmarth *et al.*, this volume). A first-order rate constant, $k_{-w} = 4 \times 10^{-3}$ sec.$^{-1}$, was found for the dissociation of water. However, when $ClO_4^-$ was replaced by $NO_3^-$ as the "inert" anion the rates were up to 30% slower and the curvature of the $k_{obs}$ *vs.* ($Cl^-$) plot was considerably lessened. A dependence on the nature of the "inert" anion would not be expected for this mechanism. The curvature cannot be explained by preassociation of chloride and complex ions. This would have to be much larger than is expected for 2:1 electrolytes of this type and no spectrophotometric evidence for it was obtained.

The data can be explained, however, by a general anionic catalysis in which the anions encourage the removal of the water molecule from the primary coordination sphere, presumably by hydrogen bonding. The anion does not have to be the one which will eventually enter the complex, and the results suggest that $ClO_4^-$ is better than $NO_3^-$ at abstracting the water molecule, with $Cl^-$ probably even less effective.

Such a mechanism was postulated by R. Plane and H. Taube (*5*) in discussing the $Cr(H_2O)_6^{+3}$—$H_2O$ exchange which was found to be linearly dependent on anion concentration. With this linear dependence no distinction is possible between an association mechanism, in which the associated anion has a generally labilizing effect on the complex, and the abstraction mechanism in which the anion acts specifically to remove a particular water molecule. W. Plumb and G. Harris (*6*) have found that the $Rh(H_2O)_6^{+3}$–$H_2O$ exchange is also dependent on ($ClO_4^-$) over a wide concentration range. In both of the above studies the ionic strength varied directly with the anion concentration and the behaviour has been ascribed to this (*6*).

Because of the curvature observed in our case a distinction between these two mechanisms is possible since association can be studied independently to see whether it is large enough to account for the curvature. In the abstraction mechanism, the curvature is caused by the competition between the perchlorate or nitrate ions, which can help complex formation only by abstracting a water molecule, and the chloride ions, which are essential for eventual formation of the complex and which can also help in the abstraction of the water molecule.

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# 4

# Substitution Reactions of Square Planar Complexes

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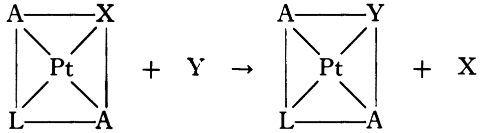
**Kinetic studies show that substitution reactions of square planar complexes generally take place by a displacement mechanism. A two-term rate law is obtained where one term (the solvent path) is zero-order in reagent and the other term (the reagent path) is first-order in reagent concentration. The rate of replacement of a group is very sensitive to the nature of the ligand opposite to it in the coordination sphere (trans effect). Increased steric hindrance in the complex is accompanied by a decrease in its rate. Reagents vary markedly in their reactivities towards these substrates, and it is found that the polarizability of the reagent is more important than basicity in determining its reactivity. These effects and others are discussed on the basis of the proposed mechanism of reaction.**

Square planar complexes are generally of the low-spin $d^8$ type. This includes the four-coordinated complexes of Ni (II), Pd(II), Pt(II), Au(III), Rh(I) and Ir(I). The best known and most extensively studied are the compounds of Pt(II). The kinetics and mechanisms of substitution reactions of these systems have been investigated in considerable detail. Studies on complexes of the other metal ions are rather limited, but the results obtained suggest that their reaction mechanism is similar to that of the Pt(II) systems. This paper briefly surveys some of the available information, and presents the current view on the mechanism of substitution reactions of square planar complexes.

## *Platinum (II)*

**Trans Effect.** The $\alpha$-(cis) and $\beta$-(trans) forms of $[Pt(NH_3)_2Cl_2]$ were discovered more than a century ago. Since then there has been a continued interest in the chemistry of Pt(II) complexes. Most of the work has dealt with the syntheses and properties of many compounds. On the basis of these qualitative observations the now well recognized (although less well understood) trans effect phenomenon was postulated. This phenomenon is best described with reference to equation (1). The trans effect is a property of the substrate and should be discussed in the section on the nature of the substrate. It is treated separately here because of its emphasis in the literature of Pt(II) chemistry.



(1)

The influence of ligands A on the reactivity of X is small, but L has a pronounced effect, called trans effect, on the replacement rate of X. Qualitatively, the labilizing influence of L decreases in the order:

$$C_2H_4 \sim NO \sim OCO \sim CN^- > R_3P \sim H^- \sim SC(NH_2)_2 > CH_3^- > C_6H_5^- > SCN^- > NO_2^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O. \quad (2)$$

Several theories have been proposed to explain this trans effect, but at present only the polarization and the π-bonding theories are commonly used.

The trans effect of metal complexes was the subject of a recent review (*6*). Further details can be obtained from this review. It will suffice here to describe briefly the two theories and to give some data to show the relative magnitude of the trans effect. Grinbergs polarization theory explains the trans effect of ligand L as resulting from its polarization of Pt(II) so that the opposite Pt–X bond is weakened. This then is responsible for the more rapid replacement of X. Some x-ray studies show that the Pt–X bond is longer when it is opposite a good trans labilizing ligand. Infrared data provide additional evidence for a weakening of the Pt–X bond.

The π-bonding theory explains why ligands such as $C_2H_4$, CO and $PR_3$ have an extremely large trans labilizing influence. The theory suggests that the presence of a π-bonding ligand has a greater stabilizing influence on the five-coordinated transition state than on the four-coordinated ground state. Because of π-bonding with L, the withdrawal of electron density from the vicinity of the entering Y and leaving X promotes the displacement of X. Both x-ray and infrared data available show that the Pt–X bond is also often weakened in these systems. This implies that the donation of electrons from Pt(II) to L by π-bonding results in L having a greater tendency to return electrons to Pt(II) via σ-bonding.

Some kinetic data on the trans effect are now available. More detailed systematic studies are needed, but quantitative information does provide the magnitude of the trans labilizing ability of various ligands for substitution reactions in these systems. For complexes of the type $[PtNH_3LCl_2]^-$, where the leaving $Cl^-$ is trans to L, the trans effect order of L is approximately (*28*),

$$C_2H_4 : NO_2^- : Br^- : Cl^- = > 100 : 9 : 3 : 1$$

The increase in reaction rate is accompanied by a decrease in activation energy. The reaction rates of trans $[Pt(PEt_3)_2LCl]$ with pyridine show the approximate trans effect order (*3*).

$$\mathrm{Cl^-}:p\text{—}\mathrm{CH_3OC_6H_4^-}:p\text{—}\mathrm{ClC_6H_4^-}:\mathrm{C_6H_5^-}:\mathrm{CH_3^-}:\mathrm{PEt_3}:\mathrm{H^-} =$$

$$1 : 32 : 38 : 40 : 165 : 10{,}000 : 10{,}000$$

The large trans labilizing ability of $H^-$ is explained on the basis of the polarization theory, whereas the $\pi$-bonding theory is involked to account for the large effect of $PEt_3$.

**Rate Law and Mechanism of Reaction.** Only about ten years ago kinetic investigations on these systems were reported. This research was done independently in the laboratories of Prof. Grinberg in Russia, Prof. Martin at Iowa State University and ours at Northwestern University. The initial studies showed that the rates of reaction such as (1) are first-order in substrate concentration but either first-order or zero-order in reagent concentration. Subsequently, more detailed studies have shown that the reaction rates obey rate law (3), where $k_s$ is a first-order rate constant for

$$\text{Rate} = k_s[\mathrm{PtA_2LX}] + k_y[\mathrm{PtA_2LX}][\mathrm{Y}] \qquad (3)$$

a solvent-controlled reaction and $k_y$ is a second-order rate constant for reaction with Y. Such a rate law was first reported by Rich and Taube (*22*) for the exchange of chloride ion with $[\mathrm{AuCl_4}]$, and it was suggested that this may be a general rate expression for square planar complexes. In experiments containing an excess of Y, the pseudo first-order rate constant, $k_{obs}$, is related to the individual rate constants by equation (4). Linear plots of $k_{obs}$ *vs.* [Y] are obtained and

$$k_{obs} = k_s + k_y[\mathrm{Y}] \qquad (4)$$

have the same nonzero intercepts $k_s$, but different slopes $k_y$ for different Y (Figure 1). This rate law applies for all of the square planar systems investigated, except the sterically hindered Pd(II) complex described later.

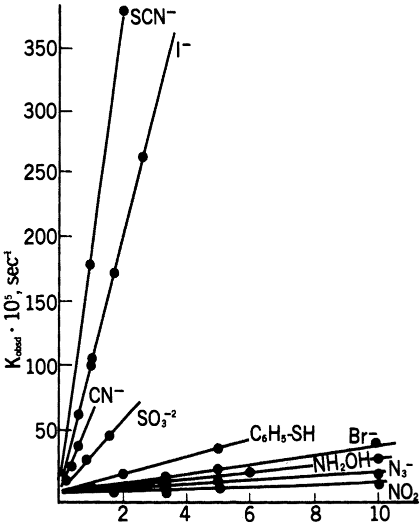


*Figure 1. Rates of reaction of trans-$[Pt(py)_2Cl_2]$ with various nucleophiles in methanol at 30°C.*

Both the solvent-controlled path and the direct reagent path appear to involve an expansion in coordination number of the metal as shown in Figure 2. A more detailed representation would include in the substrate coordinated solvent and/or reagent, at greater distances on the *z* axis above and below the *xy* plane. The geometry of the five-coordinated species is not known, but perhaps it has a trigonal bipyramidal or a tetragonal pyramidal structure. Either structure permits substitution with configuration retention, and this is found experimentally.

**Nature of the Substrate.** Data gathered from several sources provide information on the effect of certain changes in the platinum(II) substrate on the reaction rates. These results are summarized here with specific reference to the effect of (1) charge on the complex, (2) the nature of the departing ligand, (3) steric hindrance of other ligands, and (4) basicity and $\pi$-bonding of other ligands.

The effect of charge on reaction rates of platinum(II) complexes is best illustrated by the results of the excellent investigations of Professor Martin (*23*) and his students on the series of complexes from anionic $[PtCl_4]^{-2}$ through $[Pt(NH_3)_3Cl]^+$. The rate constants for aquation, replacement of the first chloride ion, and for direct exchange of radiochloride ion are shown in Table I. The most striking feature of these data is the small variation in aquation rate constants of the series, for substrates varying in charge from $-2$ through $+1$. This argues against a simple dissociative mechanism ($S_N1$) where charge separation is important. It supports the displacement process ($S_N2$) shown in Figure 2 where both charge separation and charge neutralization are important. Because of these compensating opposing effects a change in charge on the complex does not greatly alter its reactivity. It is significant that for the six-coordinated systems where charge separation is important, the complex charge can effect the reaction rate. Thus, the aquation rate of trans $[Co(NH_3)_4Cl_2]^+$ is approximately 1000 times faster than that of $[Co(NH_3)_5Cl]^{+2}$. Finally, the results also show that $Cl^-$ relative to $H_2O$ is a better reagent for zero valent and cationic substrates than for anionic complexes. This may be expected on the basis of the negative charge on chloride ion, but that would not account for its being a better reagent towards *trans*-than *cis*-$[Pt(NH_3)_2Cl_2]$. Reagent reactivity is described later.

**Table I. Rate Constants for the Hydrolysis and Chloride Exchange of Chloroammineplatinum (II) Complexes.**

Temp. 25°C. $\mu = 0.318M$

| *Complex* | $10^5 k_{H_2O}$ *sec.*$^{-1}$ | $10^5 k_{Cl^-}$ $M^{-1}$ *sec.*$^{-1}$ |
|---|---|---|
| $[PtCl_4]^{-2}$ | 3.9 | <3 |
| $[PtNH_3Cl_3]^-$ | 3.6 | <3 |
| *cis*-$[Pt(NH_3)_2Cl_2]$ | 2.5 | ~3 |
| *trans*-$[Pt(NH_3)_2Cl_2]$ | 9.8 | 78 |
| $[Pt(NH_3)_3Cl]^+$ | 2.6 | 7 |

[a] Data from Tucker *et. al.* (*23*).

Regardless of the reaction mechanism one should expect the reaction rates for a series of analogous substrates to vary with changes in the nature of the leaving group. Meaningful results can best be obtained if the other three ligands are the same and only $X^-$ changes, as in complexes of the type $[Pt\ A_3X]^+$. One such study has been made (*4*) where $A_3$ is diethylenetriamine, and the data are given in Table II. The reaction rates decrease with increasing Pt–X bond strength. This result

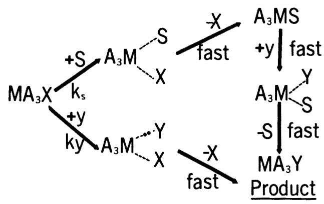


*Figure 2. Bimolecular displacement mechanism for substitution reactions of square planar complexes. $k_s$ is the rate constant for the solvent path and $k_Y$ is the rate constant for the direct reagent path.*

does not indicate the reaction mechanism. Earlier work (*5*) on the exchange of $X^-$ with $[PtX_4]^{-2}$ showed that the rate of exchange for different $X^-$ ligands decreased in the order $CN^- > I^- > Br^- > Cl^-$. The stabilities of these complexes also decrease in this order. However, the exchange rates are not directly comparable in this series because of the different trans effects of $X^-$ and because of its reagent reactivity differences.

An increase in steric hindrance in the substrate is accompanied with a decrease in reaction rate (Table III). This result is in accord with a reaction that requires an expansion of coordination number. By contrast, the dissociative reactions of cobalt (III) complexes show a steric acceleration (*5*) It is noteworthy that steric retardation for alkyl substituted phenyl complexes of the type $[Pt(PEt_3)_2$ phenyl Cl$]$ is much greater for the cis than for the trans isomers. Examining molecular models suggests that this is expected, providing the active intermediates have trigonal bipyramidal structures. For tetragonal pyramidal structures the steric hindrance would be about the same for the two isomers. Also note that if the top and bottom of the square plane are completely blocked, then the complex behaves like an octahedral system. The reaction mechanism changes to a dissociative process, as discussed in the section on Pd(II).

**Table II. Rates of Replacement of $X^-$ in $[Pt(dien)X]^+$ with Pyridine (0.0059*M*) in Water at 25°C.**

| $X^-$ | $10^5 k_{obs.}$ $sec.^{-1}$ | $X^-$ | $10^5 k_{obs.}$ $sec.^{-1}$ |
|---|---|---|---|
| $NO_3^-$ | fast | $N_3^-$ | 0.083 |
| $Cl^-$ | 3.5 | $SCN^-$ | 0.030 |
| $Br^-$ | 2.3 | $NO_2^-$ | 0.0050 |
| $I^-$ | 1.0 | $CN^-$ | 0.0017 |

[a] Data from Basolo *et. al.* (*4*).

Information on the effect of the $\sigma$-bonding (basicity or inductivity) or $\pi$-bonding properties of ligands in cis positions to the leaving group is as yet fragmentary. The relative rates of methanolysis of *trans*-$[PtA_2Cl_2]$ for A-piperidine: triethylphosphine-pyridine are $1.2{:}{\sim}10^{-2}{:}1$. Piperidine is a good $\sigma$-bonding ligand and triethyl: phosphine a good $\pi$-bonder. The rates of solvolysis differ, and this difference varies with changes in reagent for the direct displacement path, as is mentioned in the section on reagent reactivity.

**Table III. Steric Factors in Substitution Reactions of Platinum (II) Complexes in Ethyl Alcohol.**

| *Compound* | *Reagent* | *Temp. °C.* | *k, sec.$^{-1}$* |
|---|---|---|---|
| *cis*-$[Pt(4\text{-ampy})_2Cl_2]$[a] | $^{36}Cl^-$ | 25 | $1.1 \times 10^{-5}$ |
| *cis*-$[Pt(\alpha\text{-pic})_2Cl_2]$[a] | $^{36}Cl^-$ | 25 | $4.8 \times 10^{-7}$ |
| *cis*-$[Pt(PET_3)_2(\text{phenyl})Cl]$[b] | pyridine | 0 | $3.8 \times 10^{-2}$ |
| *cis*-$[Pt(PET_3)_2(o\text{-tolylCl}]$[b] | pyridine | 0 | $8.7 \times 10^{-5}$ |
| *cis*-$[Pt(PET_3)_2(\text{mesitylCl}]$[b] | pyridine | 0 | $4.2 \times 10^{-7}$ |
| *trans*-$[Pt(PET_3)_2(\text{phenyl})Cl]$[b] | pyridine | 25 | $3.3 \times 10^{-4}$ |
| *trans*-$[Pt(PET_3)_2o\text{-tolylCl}]$[b] | pyridine | 25 | $6.7 \times 10^{-6}$ |
| *trans*-$[Pt(PET_3)_2\text{mesitylCl}]$[b] | pyridine | 25 | $1.2 \times 10^{-6}$ |
| $[\text{PtdienCl}]^+$[c] | $Br^-$ | 25 | $1.0 \times 10^{-4}$ |
| $[\text{PtEt}_4\text{dienCl}]^+$[d] | $Br^-$ | 80 | $8.5 \times 10^{-6}$ |

[a] Data from Pearson *et. al.* (*20*).

[b] Data from Basolo *et. al.* (*3*).

[c] Data from Basolo *et. al.* (*4*).

[d] $Et_4dien = (C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$. The complex is a pseudo-octahedron and reacts by a dissociation process. See discussion for palladium(II). Data from R. Wanguo, private communication.

**Effect of Solvent.** The effect of solvent on the rate of chloride ion exchange with *trans*-$[Pt(py)_2Cl_2]$ has been studied in some detail (*20*). Some of the results of this investigation are shown in Table IV. The rates of solvolysis bear no relation to dielectric constants or general solvating properties of the solvents. The results are best correlated with the coordinating properties of the solvent. The solvent $CH_3NO_2$ is particularly interesting because it is not a good coordinating solvent, but yet it provides an effective path for chloride ion exchange. This is attributed to its $\pi$-bonding ability which allows *d*-orbital electrons on the platinum to delocalize into a vacant *p*-orbital on the nitrogen. A similar explanation is used to account for the increase in exchange rate following the addition of either $CH_3COOH$ or $H_3BO_3$. These substances do not form stable platinum (II) complexes, but behave as catalysts in these reactions because of their electrophilic properties.

**Table IV. Effect of Solvents on the Rates of Chloride Ion Exchange with *trans*-$[Pt(py)_2Cl_2]$ at 25°C.**

| *Solvent*[b] | *k$_s$ sec.$^{-1}$* | *Solvent*[c] | *$k_{Cl^-}$ $M^{-1}$ sec.$^{-1}$* |
|---|---|---|---|
| $H_2O$ | $3.5 \times 10^{-5}$ | $CCl_4$ | $10^4$ |
| $(CH_3)_2SO$ | $3.8 \times 10^{-4}$ | $C_6H_6$ | $10^2$ |
| $CH_3NO_2$ | $3.2 \times 10^{-5}$ | *m*-cresol | $10^{-1}$ |
| $C_2H_5OH$ | $1.4 \times 10^{-5}$ | *tert*-$C_4H_9OH$ | $10^{-1}$ |
| *n*-$C_3H_7OH$ | $4.2 \times 10^{-6}$ | EtOAc | $10^{-2}$ |
| $CH_3NO_2(CH_3COOH)$[d] | $4.0 \times 10^{-4}$ | $(CH_3)_2CO$ | $10^{-2}$ |
| $C_2H_5OH(H_3BO_3)$[e] | $5.3 \times 10^{-5}$ | $HCON(CH_3)_2$ | $10^{-3}$ |

[a] Data from R. Pearson *et. al.* (*20*).

[b] For these good solvents, the exchange proceeds by the solvent path at $[Cl^-]$ between 0.001 and 0.007*M*.

[c] For these poor solvents the exchange proceeds by the direct displacement path.

[d] For a solution of 2.2*M* $CH_3COOH$ in $CH_3NO_2$.

[e] For a solution of 0.075*M* $H_3BO_3$ in 90% ethanol and10% water.

There is considerable evidence that the solvent path, $k_s$, is not a dissociative process, but involves a direct displacement by the solvent. This is supported by the following observations: (1) the values of $k_s$ are invariant with changes in the net charge on the complex, (2) the values of $k_s$ decrease with increase in steric hindrance,

(3) the values of $k_s$ roughly parallel the coordinating ability of the solvent, (*4*) the value of $k_s$, when the solvent is water, is just the expected value for the reaction of water acting as a nucleophilic reagent compared to other nucleophiles and (5) competition reactions between $OH^-$ and $X^-$ for $[PtdienX]^+$ show that $k_s$ is not affected by adding a considerable amount of $X^-$ to the solution (14).

**Reagent Reactivity.** One of the most interesting aspects of substitution reactions of square planar complexes is that the reaction rates depend on the nature of the reagent. This permits a thorough investigation of the factors responsible for reagent reactivity towards these substrates. Note that this has not been possible for the reactions of most six-coordinated metal complexes, since their rates do not depend on the reagent.

Recently, extensive investigations have been made of the reaction of *trans*-$[Pt(py)_2Cl_2]$ in methanol solution with a variety of reagents, Y (*8*). The values of $k_Y$ are given in Table V. Less complete but similar results are available for the substrates $[PtdienBr]^+$, *trans*-$[Pt(piperidine)_2Cl_2]$ and *trans*-$[Pt(PEt_3)_2Cl_2]$. Also shown in this table are the basicities, the polarizabilities and the estimated oxidation potentials of the various nucleophiles. Excellent reviews (*11*) (*12*) have been written which consider the contributions of these factors to the nucleophilic character of different reagents towards various substrates. The LFER equation of Brönsted (*9*) is a correlation of the rates of nucleophilic displacement on hydrogen with the basicities of the neuclophiles. Instead, for platinum (*II*) complexes basicity clearly is not an important factor in nucleophilic strength (*12*). Polarizability is a dominant factor. Edwards (11) has called attention to the empirical correlation with $E^\circ$ values, since these are a measure of a reagent's tendency to release electrons in solution. It appears that a polarizable (soft) substrate reacts best with a polarizable (soft) nucleophile and a "nonpolarizable" (hard) substrate prefers a "nonpolarizable" (hard) nucleophile (*19*).

Belluco (8), following the suggestion of Edwards, has correlated values of $E^\circ$ and estimated values of $E^\circ$ with log $k$ values for the reaction of three Pt(II) sub-

**Table V. Properties of Reagents and Rates of Nucleophilic Displacement on the Substrate *trans*-$[Pt(py)_2Cl_2]$ in Methanol at 30°C.**

| *Nucleophile, Y* | $pK_a$ | $P$ | $E^{\circ a}$ | $10^3 k_y M^{-1}$ *sec.*$^{-1}$ |
|---|---|---|---|---|
| $H_2O(CH_3OH)$ | −1.7 | 0.000 | −2.60 | $1 \times 10^{-5}$[c] |
| $^{36}Cl^-$ | (−5) | 0.389 | −1.36 | 0.45 |
| $C_6H_5N$ | 5.3 | | −1.40 | 0.55 |
| $NH_3$ | 9.3 | | −0.76 | 0.47 |
| $NO_2^-$ | 3.35 | | −0.87 | 0.68 |
| $N_3^-$ | 4.72 | | −1.02 | 1.55 |
| $NH_2OH$ | 5.98 | | | 2.9 |
| $N_2H_6$ | 8 | | | 2.93 |
| $Br^-$ | (−6) | 0.539 | −1.09 | 3.7 |
| $C_6H_5SH$ | | | | 5.7 |
| $I^-$ | (−7) | 0.718 | −0.535 | 107 |
| $SCN^-$ | 0.5 | | −0.77 | 180 |
| $SO_3^{2-}$ | 7.2 | | −0.026 | 250 |
| $SeCN^-$ | | | (>−0.535) | 5150 |
| $C_6H_5S^-$ | (~7) | | (~+0.3) | 6000 |
| $S{=}C(NH_2)_2$ | −0.94 | | +0.42 | 6000 |
| $S_2O_3^{2-}$ | 1.5 | | +0.28 | ~9000 |

[a] The $E^\circ$ values are for $Y^-_{aq.} = \frac{1}{2} 2Y_2{}^+{}_{aq.} + e_{aq.}$

[b] Data from U. Belluco (*8*).

[c] Value of $k_s$ in sec.$^{-1}$.

strates with several nucleophiles. The linear plots (Figure 3) show a relationship between the free energy for reaction and the parameter $E^\circ$. Also interesting is that for the substrates *trans*-[$PtA_2Cl_2$], the slope of the line is greater for A = $PEt_3$ than for A = py or pipyridine. This suggests that Pt(II) is more electrophilic in the $PEt_3$ system than in the other two substrates. This is in accord with the π-bonding tendency of phosphine ligands in these systems.

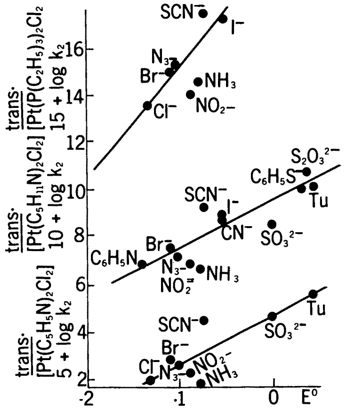


*Figure 3. Rates of reaction of Pt(II) substrates in methanol at 30°C.*

**Table VI. Effect of Charge and of π-Bonding of Pt(II) Complexes on the Reactivity of the Nucleophile $Cl^-$ and the Biphile $NO_2^-$.**

| | $10^3k_y M^{-1}$ *sec.*$^{-1}$ | |
|---|---|---|
| *Complex* | *$Cl^-$* | *$NO_2^-$* |
| [$PtdienH_2O$]$^{+2}$[a] | $1.0 \times 10^3$ | $0.56 \times 10^3$ |
| [PtdienBr]$^{+}$[a] | 0.88 | 3.7 |
| *trans*-[$Pt(C_5H_{11}N)_2Cl_2$][b] | 0.93 | 2.0 |
| *trans*-[$Pt(py)_2Cl_2$][b] | 0.45 | 0.68 |
| *trans*-[$Pt(PEt_3)_2Cl_2$][b] | 0.029 | 0.022 |

[a] Data from H. Gray (*13*). Temp. 25°C.
[b] Data from U. Belluco (*8*). Temp. 30°C.

Note that reagents may also vary in relative reactivity towards different substrates. For example, the reactivity $NO_2^- > Cl^-$ towards [PtdienBr]$^+$ is reversed for [$PtdienH_2O$]$^{2+}$ as shown in Table VI. Likewise, $NO_2^-$ is a poorer reagent than $Cl^-$ towards a Pt(II) substrate containing a good π-bonding ligand such as $PEt_3$; but $NO_2^-$ is a better reagent than $Cl^-$ towards systems containing good σ-bonding ligands such as piperidine. These results can be explained in terms of $NO_2^-$ behaving as a biphilic reagent. Thus, in addition to σ-bonding, $NO_2^-$ can π-bond by vacating a *p*-orbital and accepting *d*-orbital electrons from Pt(II). This will be more important for a substrate where the nonbonding *d*-orbitals are in an expanded state relative to one with contracted *d*-orbitals. Ligands that increase the electron density on Pt(II) or anionic complexes will enhance the reactivity of a biphilic reagent.

**Activation Energy Parameters.** Values of $\Delta H\ddagger$ and $\Delta S\ddagger$ for some reactions of Pt(II) complexes are shown in Table VII. More data are needed, but apparently the activation enthalpy is larger and the entropy less negative for the solvent path ($k_s$) than for the reagent path ($k_y$) in these reactions. The negative activation entropy for aquation is reasonable because, in going from reactants to activated complex, there is an increase in charge. This results in the "freezing" of solvent molecules around the incipient ions. The unexpected result is the negative entropy found for the direct displacement reaction between a cationic complex and an anionic reagent. Such a charge neutralization process is expected to release (or "melt") "frozen" solvent and result in an increase in entropy. Since the entropy of activation is negative, this suggests an increase in polarity in going from ground state to transition state and/or the activated complex imposes stringent stereochemical requirements on the entering and leaving groups.

**Table VII. Activation Energy Parameters for Some Reactions of Pt(II) Complexes.**

| *Complex*[a] | $\Delta H‡$, *kcal.* | $\Delta S‡$, *e.u.* |
|---|---|---|
| $[PtCl_4]^{-2}$ | 21 | −8 |
| $[Pt(NH_3)Cl_3]^-$ | 19 | −15 |
| *cis*-$]Pt(NH_3)_2Cl_2]$ | 20 | −14 |
| *trans*-$]Pt(NH_3)_2Cl_2]$ | 20 | −11 |
| $[Pt(NH_3)_3Cl]^+$ | 18 | −18 |
| $[Pt(dien)Cl]^{+}$[b] | 14 | −23 |
| $[Pt(dien)Cl]^{+}$[c] | 10 | −30 |
| $[Pt(dien)Cl]^{+}$[d] | 10 | −28 |
| *trans*-$]Pt(PEt_3)_2Cl_2]$[e] | 15 | −30 |
| *trans*-$]Pt(C_5H_{11}N)_2Cl_2]$[e] | 14 | −25 |

[a] Data are for the replacement of one $Cl^-$ by $H_2O$. From D. S. Martin, *et. al.*, J. Am. Chem. Soc., **77**, 2965 (1955); *80*, 536 (1958); *83*, 2457 (1961); Inorg. Chem., **1**, 551 (1962); *2*, 562 (1963).
[b] For the replacement of $Cl^-$ by $Br^-$, W. H. Baddley (*2c*)
[c] For the replacement of $Cl^-$ by $I^-$, W. H. Baddley (*2c*).
[d] For the replacement of $Cl^-$ by $SC(NH_2)_2$. W. H. Baddley (*2c*).
[e] For the replacement of one $Cl^-$ by $NO_2^-$. U. Belluco, private communication.

**Other Observations.** Recent communications by Haake report two different, interesting observations. First, the rate constants for reaction (5) are nonlinear in concentration of $NO_2^-$ (*16*). This was explained in terms of a rapid preassociation

$$cis\text{-}[Pt(NH_3)_2NO_2Cl] + NO_2^- \rightarrow cis\text{-}[Pt(NH_3)_2(NO_2)_2] + Cl^- \qquad (5)$$

equilibrium (*5*) followed by the rate-determining displacement step (*6*). Spectroscopic evidence was also

$$cis\text{-}[Pt(NH_3)_2NO_2Cl] + NO_2^- \overset{\text{fast}}{\rightleftharpoons} [Pt(NH_3)_2(NO_2)_2Cl]^- \qquad (6)$$

$$[Pt(NH_3)_2(NO_2)_2Cl]^- \xrightarrow{\text{slow}} cis\text{-}[Pt(NH_3)_2(NO_2)_2] + Cl^- \qquad (7)$$

obtained supporting the "five-coordinated" intermediate. This mechanism corresponds to that referred to as a "dissociation" mechanism (*5*).

The other interesting observation (*17*) is that the reaction of *cis*-$[PtA_2Cl_2]$, where $A_2$ = en, 2py or bipy, with dithiooxamide to yield *cis*-$[PtA_2(ditoa)]^{+2}$ shows the following relative rates for changes in $A_2$: en = 1.4, 2py = 1, bipy = 90. These results were rationalized on the basis of a strong trans effect resulting from aromaticity in the platinum-$\alpha$-diimine chelate ring in the bipy complex. This may result from the $p_z$-orbitals on the nitrogens overlapping with the $d_{xz}$- and $d_{yz}$- orbitals on the platinum (complex in $xy$ plane) to produce an aromatic system with eight π-electrons in the five-membered ring. Thus, there would be a low electron density on the chloride side of the complex and a large trans effect. This may also account for $[Pt(tripy)Cl]^+$ reacting approximately 1000 times faster than $[Pt(dien)Cl]^+$ (*4*).

### *Palladium (II)*

Detailed investigations on the kinetics and mechanisms of reactions of square planar palladium (II) complexes are largely lacking. However, enough data exist to show that the reactions of palladium (II) complexes are much faster than those of platinum (II), and that the two systems react by the same type of mechanism. Some of the data available are given in Table VIII along with the same information on platinum (II) and nickel (II) for comparison (*3*). The results show an approximate relative order of reactivity for analogous complexes of the triad as follows:

$$Ni(II):Pd(II):Pt(II) = 10^6:10^5:1$$

It was observed recently that the reaction of $[Pd(dien)Cl]^+$ with several good reagents at millemolar concentrations and 25°C. is too fast to measure by a stopped-flow method (*2b*). Therefore, we decided to investigate a similar sterically-hindered complex which we expected to react slower. In fact, the complex $(Pd(Et_4dien)Cl]^+$, where $Et_4dien = (C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$ reacts with an approximate 5 minute half life at room temperature. Its rates of reaction with different reagents as a function of reagent concentration are plotted in Figure 4. This shows that for the reagents $Br^-$ and $I^-$ the reaction rate is independent of reagent concentration. Instead the rate of reaction with hydroxide ion is dependent on its concentration. These results are reminiscent of reactions of cobalt (III) ammines which show the same behavior (*5*). An examination of the molecular model of $[PdEt_4dienCl]$ shows that the four ethyl groups completely block the top and bottom of the planar complex and give it the appearance of an octahedral complex. Thus, because of this and because its substitution reactions resemble those of octahedral complexes, it is called a pseudo-octahedral complex.

Since a direct displacement process characteristic of reactions of square complexes seems unlikely, it would appear that in such sterically-hindered systems the reaction proceeds by a dissociative process similar to that found for six-coordinated

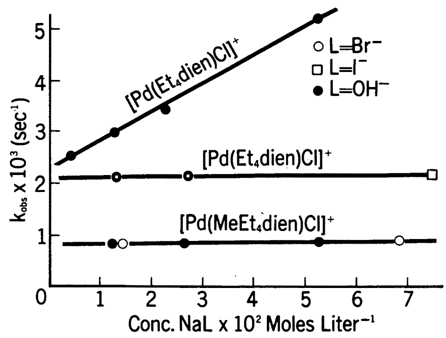


*Figure 4. Rates of reaction as a function of reagent concentration, 25°C.*

complexes. The special dependence on $OH^-$ concentration can result from the presence of an N–H hydrogen which permits an $S_N1CB$ mechanism, (*7*, *8*, *9*).

$$[PdEt_4dienCl]^+ + OH^- \xrightleftharpoons{\text{fast}} [PdEt_4dien\text{-}H)Cl] + H_2O \qquad (8)$$

$$[Pd(Et_4dien\text{-}H)Cl] \xrightarrow{\text{slow}} [Pd(Et_4dien\text{-}H)]^+ + Cl^- \qquad (9)$$

$$[Pd(Et_4dien\text{-}H)]^+ + H_2O \xrightarrow{\text{fast}} [PdEt_4dienOH]^+ \qquad (10)$$

**Table VIII. Rates of Reaction of Some Analogous Ni(II), Pd(II) and Pt(II) Complexes at 25°C.**[a]

| *Complex*[b]: | $k_{obsd.}$ *sec.*$^{-1}$ |
|---|---|
| $[Pt(dien)Cl]^+$ | $7.0 \times 10^{-6}$ |
| $[Pd(dien)Cl]^+$ | fast[c] |
| $[Pt(dien)SCN]^+$ | $6.2 \times 10^{-8}$ |
| $[Pd(dien)SCN]^+$ | $4.2 \times 10^{-2}$ |
| $[Pt]Et_4dien)Cl]^+$ | $8.6 \times 10^{-6}$ |
| $[Pd(Et_4dien)Cl]^+$ | $2 \times 10^{-3}$[d] |
| *Complex*[e] | $k_s$ *sec.*$^{-1}$ |
| *trans*-$]Ni(PEt_3)_2(o\text{-tolyl})Cl]$ | $3.3 \times 10^{1}$ |
| *trans*-$]Pd(PEt_3)_2(o\text{-tolyl})Cl]$ | $5.8 \times 10^{-1}$ |
| *trans*-$]Pt(PEt_3)_2o\text{-tolylCl}]$ | $6.7 \times 10^{-6}$ |
| *trans*-$]Ni(PEt_3)_2\text{mesitylCl}]$ | $2.0 \times 10^{-2}$ |
| *trans*-$]Pt(PEt_3)_2\text{mesitylCl}]$ | $1.2 \times 10^{-5}$ |

[a] Data from (*2*, *3*, *4*).
[b] Rates are for the reaction with 0.001*M* py.
[c] Too fast to measure by the stopped flow method, therefore $t_{1/2} < 10^{-3}$ sec.
[d] For these pseudo-octahedral complexes the reaction rate is independent of the reagent. The value for Pt(II) is at 80°C.
[e] The solvent is ethanol and the reaction is the replacement of $Cl^-$ by py.

Supporting this is the observation that the reaction rate of $[Pd(MeEt_4dien)Cl]^+$ (which contains no N–H, having instead a methyl group on the center nitrogen) with $OH^-$ does not depend on its concentration (Figure 7).

Pearson and Johnson (*21*) have thoroughly investigated the reaction of $[Pd(acac)_2]$, where acac = acetylacetonate ion, with the solvent water and with a variety of reagents. The reactions involved are rather complicated, involving the step-wise opening of the chelate rings and replacement of the chelate with solvent or reagent. One interesting point is that the nucleophilic reactivity of various reagents increased in the order

$$H_2O \sim OH^- < Cl^- < Br^- < I^- < SCN^-.$$

This is the same order as that characteristic of reactions of Pt(II) complexes. Note again that $OH^-$ is not a good reagent.

### *Nickel (II)*

Nickel (II) complexes containing groups of high ligand field strength are often square planar low-spin $d^8$ systems. Many of these are chelate compounds, but several systems of the type $[Ni(PR_3)_2X_2]$ are also known. For the latter complexes no detailed kinetic studies have been reported. The data in Table VIII show that these nickel (II) complexes react much more rapidly than the complexes of platinum (II). It is not known whether the same two-term rate law applies to these nickel (II) systems, nor do we know the reagent reactivities toward these substrates. Such questions, and many others await investigation and possible answer.

Murmann (*18*) has investigated the reaction of some amineoximatonickel (II) complexes with EDTA as well as isotopic ligand exchange with the amineoximes. These systems are rather complicated, but the replacement rate of the chelate ligand does show the typical two term rate law (*22*). It was also observed that the reaction rate is catalyzed by the addition of other substances such as ammonia, ethylenediamine and oxalate ion.

### *Gold (III)*

One of the earliest studies of the kinetics of substitution reactions of square planar complexes is that of the $Cl^-$ exchange of $[AuCl_4]^-$ (*22*). A two-term rate law was found for the exchange rate and it was suggested that this may prove to be general behavior for square complexes.

Baddley (*2*) has recently completed an investigation of the reaction rate of $[Au(dien)Cl]^{2+}$ and/or its conjugate base $[Au(dien\text{-}H)Cl]^+$ with the reagents $Br^-$, $I^-$, $SCN^-$, $N_3^-$ and $OH^-$. The reactivities of the nucleophiles toward the gold (III) substrates increase in the order

$$H_2O \sim OH^- < N_3^- < Br^- < SCN^- < I^-.$$

This is the same order as that for the similar Pt (II) complexes. Likewise, the reactions of Au (III) obey the same rate law as do reactions of Pt (III), and apparently, the gross features of the reaction mechanisms are the same for both. However, the Au(III) complex reacts approximately $10^4 \times$ faster than that of Pt (II). For the replacement of $Cl^-$ in $[Au(dien)Cl]^{+2}$ by $Br^-$ the direct displacement path predominates over the solvent path to a much greater extent than the analogous reaction of $[Pt(dien)Cl]^+$. Apparently, for reactions of Au(III) systems bond-making is more important than bond-breaking. Thus, the cation $[Au(dien)Cl]^{+2}$ reacts about 100 times faster than the anion $[AuCl_4]^-$. Likewise, the complex $[Au(dien)Cl]^{+2}$ reacts faster than its conjugate base $[Au(dien\text{-}H)Cl]^+$. This agrees with charge neutralization being more important than charge separation in the transition state.

### *Rhodium (I) and Iridium (I)*

There is considerable current interest in the Rh(I) and Ir(I) complexes of the type $[M(PR_3)_2COCl]$ because of their ability reversibly to add either oxygen or hydrogen (*25*). Wojcicki (*26*) found that the exchange rate of carbon monoxide with $[Rh(P(C_6H_5)_3)_2COCl]$ is too fast to measure by conventional techniques. He and Gray (*27*) also found that the chloride ion and the phosphine exchange very rapidly. Since the substrate is extremely stable, these results provide an excellent example of a very labile but thermodynamically, extremely stable system (*24*). Recent studies have been extended to $[Rh(CO)_2(p\text{-anisidine})Cl]$ and $[Ir(CO)_2(p\text{-toluidine})Cl]$ (*27*). Both compounds exchange CO at −80°C. with the same second-order rate constant of 2 $M^{-1}$sec.$^{-1}$ and both CO's in the compound exchange at the same rate. Direct evidence that these bimolecular displacements proceed by a trigonal bipyramidal intermediate is provided by the isolation of the five-coordinated compounds [$Ir(PPh_3)_2(CO)_2Cl$] (*1*) and the Rh(I) and Ir(I) compounds [$M(PPh_3)_3(CO)H$] (*7*).

Cramer (*10*) has recently reported the most interesting observation, that in the compound $\pi$-$C_5H_5Rh(C_2H_4)_2$, the ethylene rotates with the coordination bond axis with an energy barrier to rotation of 6 kcal. His NMR studies also showed that the coordinated ethylene in this compound does not exchange with $C_2D_4$ during 5 hours at 100°C. Instead, exchange between [$Rh(C_2H_4)_2(acac)$] and $C_2D_4$ is very rapid, the average lifetime for coordinated ethylene is less than $10^{-4}$ second at 25°C. Furthermore the exchange rate depends on the concentration of ethylene. It is suggested that a rapid, low energy, bimolecular process is possible because this substrate is a low-spin $d^8$ system and has a vacant orbital of low enough energy to accommodate the two electrons of an entering nucleophile. Instead, the cyclopentadienyl system has attained a rare gas configuration and is inert. However, this does not explain the rapid CO exchange of $\pi$-$C_5H_5Rh(CO)_2$.

## Conclusions

It always seems appropriate to conclude by saying that more research is needed. However, it is also true that there is already a considerable amount of information on substitution reactions of square complexes, and it is gratifying that much of this can be explained in terms of current theories. The reactions are bimolecular, and perhaps this is largely because of the geometry of the square planar systems which readily allow an expansion of coordination number. Six-coordinated complexes, regardless of electronic structure, appear to react primarily by a dissociative process. No doubt the electronic structures of these systems are important and are responsible for the colors and other properties of metal complexes. However, this overemphasis on electronic structure has somewhat detracted from the fact that steric factors can also be important, sometimes most important. Surely steric factors predominate in the complex [$Pd(Et_4dien)Cl]^+$ which behaves like an octahedral complex and not like one of its low-spin $d^8$ relatives. Finally, reagent reactivity in square planar substrates in a function of polarizability and not basicity. This is in accord with the generalization that soft acids prefer soft bases.

## Acknowledgment

I wish to thank Dr. W. H. Baddley, Dr. D. A. Johnson, Dr. U. Belluco, Dr. A. Wojcicki, Dr. H. B. Gray, Professor R. G. Pearson and Professor A. Turco for providing me with results of some of their investigations prior to publication. Our research on square planar complexes is supported in part by the U. S. Atomic Energy Commission under grant At(11–1)–1087 and in part by the National Institutes of Health grant RG–7488.

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# Discussion

**Fred Basolo:** Prior to opening this paper for discussion I wish to make some changes pertaining to the section on reagent reactivity towards platinum(II) complexes. Although there is a rough correlation between the nucleophilic properties of different reagents and their $E^\circ$ values, there are a few reagents that do not adhere well to this correlation. For this reason other attempts have been made to find better methods of correlating the rate data in these systems. One method was to use the charge transfer spectra of the complexes $[Co(NH_3)_5Y]^{+2}$ where $Y^-$ is the reagent. Another was to use the pK data for the formation constants of $CH_3HgY$ for the reaction of the soft acid $CH_3Hg^+$ with the nucleophile $Y^-$. These methods gave results that were about the same as using $E^\circ$ values.

Since none of these attempts were satisfactory, it was decided finally to use the rate constants for the complex *trans*-$[Pt(py)_2Cl_2]$ with various nucleophiles as standards. This procedure is essentially that of Swain and Scott (7) except that a different reference substrate is used. The nucleophilic reactivity constants, $n_{\mathrm{Pt}}$, are defined by the equation

$$\log k_{\mathrm{Y}}/k_{\mathrm{S}} = n_{\mathrm{Pt}}$$

where $k_{\mathrm{Y}}$ and $k_{\mathrm{S}}$ refer to the rate constants for the reaction of *trans*-[Pt(py)$_2$Cl$_2$] in methanol at 30°C. Values of $n_{\mathrm{Pt}}$ for some reagents are given in Figure A. A plot

| *Y* | $n_{Pt}$ | *Y* | $n_{Pt}$ |
|---|---|---|---|
| $H_2O$ | $0^a$ | $Br^-$ | 2.79 |
| $OH^-$ | $<1^b$ | $I^-$ | 4.03 |
| $Cl^-$ | 1.65 | $SCN^-$ | 4.26 |
| $NH_3$ | 1.67 | $SO_3^{-2}$ | 4.40 |
| py | 1.74 | $SeCN^-$ | 5.71 |
| $NO_2^-$ | 1.83 | $C_6H_5S^-$ | 5.78 |
| $N_3^-$ | 2.19 | $SC(NH_2)_2$ | 5.78 |
| $N_2H_4$ | 2.47 | $S_2O_3^{-2}$ | 5.95 |

[a] Value for $CH_3OH$.
[b] Value for $CH_3O^-$.

*Figure A. Some nucleophilic reactivity constants (2)*

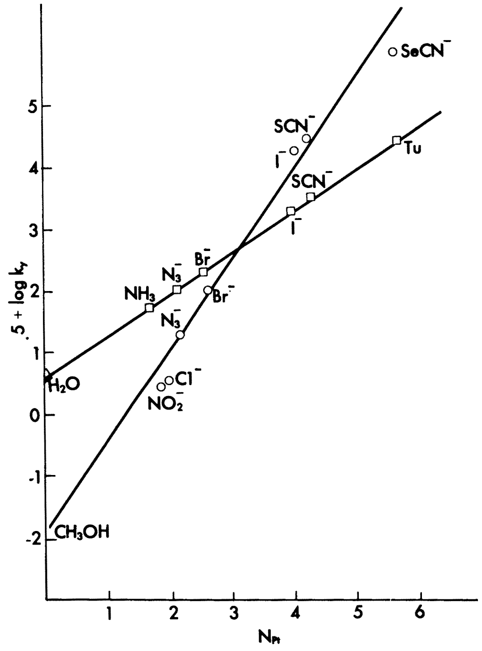


*Figure B. Correlation of the rates of reaction of Pt(II) complexes with the standard trans-[Pt(py)$_2$Cl$_2$] for different nucleophiles; the circles are trans-[Pt(py)$_2$Cl$_2$] in methanol at 30°C.; the triangles are [Pt(en)Cl$_2$] in water at 35°C* of log $k_Y$ for other Pt(II) complexes against $n_{Pt}$ gives reasonably good straight lines as is shown in Figure B. This supports the linear free energy relationship

$$\log k_Y = s\, n_{Pt} + \log k_S.$$

The constant $s$ depends on the nature of the complex. It is a nucleophilic discriminating factor. A large value of $s$ means that the complex is very sensitive to change in the nature of the nucleophilic reagent. Values of $s$ and of log $k_S$ for several Pt(II) complexes were found from the slopes and intercepts of straight lines such as Figure B by the use of a least-squares analysis. These values are given in Figure C. It is interesting to note that there is an inverse correlation between $s$ and $k_S$. This is reasonable if we interpret $k_S$ as a measure of the "intrinsic" reactivity of the complex. That is, it is the rate constant for the poorest nucleophilic reagent whose effect can be measured in any solution. This places the maximum burden on the complex to reach the activated complex for reaction. Thus, a complex of high intrinisic reactivity will not be very discriminating in its reactions with different nucleophiles, and $s$ will be small. For a more complete discussion of this see Belluco, *et.al.* (*2*).

| *Complex* | *log $k_S$* | *s* |
|---|---|---|
| *trans*-$[Pt(PEt_3)_2Cl_2]$[a] | −6.83 | 1.43 |
| *trans*-$[Pt(AsEt_3)_2Cl_2]$[a] | −5.75 | 1.25 |
| *trans*-$[Pt(SeEt_2)_2Cl_2]$[a] | −4.67 | 1.05 |
| *trans*-$[Pt(pip)_2Cl_2]$[a] | −4.56 | 0.91 |
| $[Pt(en)Cl_2]$[b] | −4.33 | 0.64 |
| $[Pt(dien)Br]^{+}$[c] | −4.06 | 0.75 |
| $[Pt(dien)Cl]^{+}$[b] | −3.61 | 0.65 |
| $[Pt(dien)H_2O]^{+2}$[c] | −0.44 | 0.44 |

[a] Values of $k_s$ sec.$^{-1}$ in methanol at 30°C.
[b] Water solution at 35°C.
[c] Water solution at 25°C.

*Figure C. Nucleophilic discrimination parameters, s, and solvolysis constants, log $k_S$, for several Pt(II) complexes (2)*

**Don S. Martin:** I want to make some modifications in the data presented by Dr. Basolo. These results were originally reported by me and my group of students. It is the Table I that is quoted in the paper which indicates quite strikingly and correctly, I think, that charge on the ion does not affect the rate of solvation, the replacement of a chloride ligand with platinum(II) with water.

We are modifying the system for the trichloroammine complex for which the rate constant is given in Table I. This is the one complex, of course, which has two different kinds of chloride ligands. This feature makes the system a good deal more complicated, which I guess is my apology for why the number in the table is incorrect.

To indicate the complexity, Figure D shows the reactions that are possible for the first and second aquations or acid hydrolyses.

The trichlorcammine can have either a *cis*-chloride replaced by water to give the *cis*-aquo complex, or it can have the *trans*-chloride replaced, and then each of these two isomers in turn can hydrolyze further. They will each lead to a common *cis*-diaquo species, and the *cis*-dichloroaquoammineplatinum(II) will also lead to a possible *trans*-diaquo isomer.

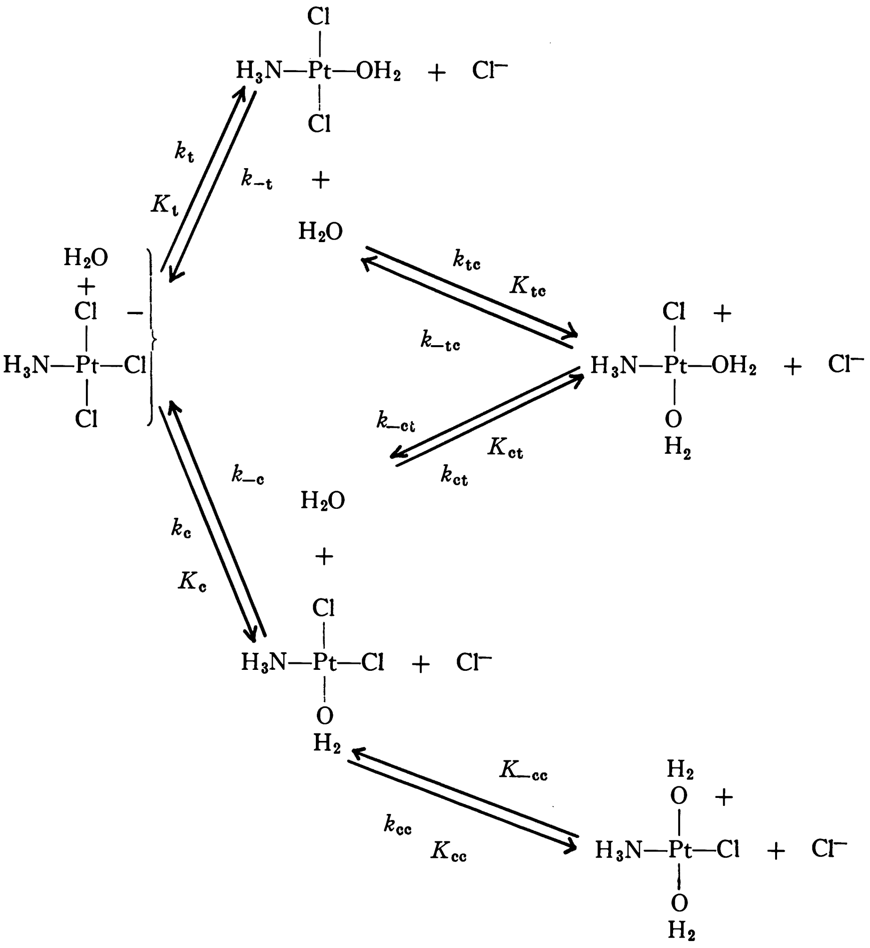


*Figure D. Complete reaction scheme for the first and second acid hydrolyses of $[Pt(NH_3)Cl_3]^-$*

You can measure the equilibria in this system by effectively titrating the acidic hydrogens on these waters, and the equilibrium measurements show—I don't want to get involved in the details of the measurements—but they show that starting with approximately a $0.01M$ ion concentration, gives comparable quantities of what must be the sum of these two isomers. This is what titration determines. Their combined concentrations must be roughly equal to the trichloro species and the concentration of the diaquo species will be very small.

It appears that one of these rate constants ($k_c$ or $k_t$) is 10 times as large as the other; and anyone who has worked in platinum chemistry will say, of course, that chloride has a greater trans effect than ammonia. These are both weak trans directors, but one would expect the fast reaction site to be the *cis*-chlorides; in other words, the chloride which is trans to a chloride, the cis-diaquo isomer, is the one which should be formed rapidly.

Moreover, the equilibrium constant for the formation of this isomer is one-tenth of the equilibrium constant for the trans isomer. Consequently, when this aquation occurs the cis is formed predominately first, but at equilibrium the system is predominately trans.

I do want to indicate that in considering the kinetics, although a high concentration of the diaquo species is not formed, their formation is presumably the path which leads to what looks like a first-order isomerization reaction. In other words, there is a reversible interconversion of the cis and trans isomers which has to be expressed kinetically.

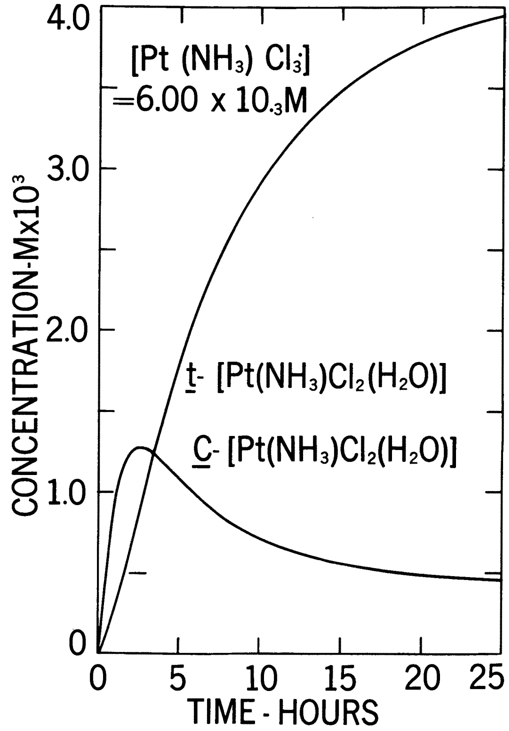


*Figure E. Calculated concentration of the isomers of [$Pt(NH_3)Cl_2(H_2O)$] during acid hydrolysis*

Figure E shows the actual concentration of the isomers that we calculate now from the rate constants as they have been determined. First, the cis isomer is formed; at equilibrium there will be ten times as much as the trans isomer.

The rate constant for the formation of the cis, the number that should be in the table now is 5.6 x $10^{-5}$ sec.$^{-1}$. The value of the rate constant for the formation of the trans isomer is 0.62 x $10^{-5}$ sec.$^{-1}$. With the six rate constants for this particular system of the chloroammineplatinum(II) complexes I would like to indicate a correlation that can now be made.

The rate constant alone for the tetrachloro complex is 4 x $10^{-5}$ sec.$^{-1}$ To be fair, it should be divided by the number of equivalent chlorides, –i.e., by *n*. Since there are four chlorides the number $1.0 \times 10^{-5}$ applies. Then, taking a factor, which comes from substituting a *trans*-chloride by an ammonia, reduces the rate constant by 0.5; this gives the expression $0.5^m$, where $m$ is the number of ammonias which are trans to the chloride being replaced. Therefore, $m$ will be either zero, or one in this series of complexes. If ammonia is put in cis to the chloride, the reaction is faster by a factor of 2.4. Raising that to a power equal to the number of ammonias cis to the chloride being replaced gives the formula:

$$k/n = 1.0 \times 10^{-5}\,(0.5)^m\,(2.4)^k$$

where $n$ is the number of equivalent chlorides undergoing acid hydrolysis

$m$ is the number of ammonias trans to the chloride (0 or 1)

$k$ is the number of ammonias cis to the chloride (0, 1, or 2)

This formula will give all six of these acid hydrolysis constants to within 20%. I think the interesting thing, and perhaps the heresy of it, is that the effect of the ammonia going in cis to the group which is being replaced, has a larger kinetic effect than in the trans group. Consequently, perhaps we should talk more about the cis effect than the trans effect. With that I would like to turn it over to Henry and see if he has any comment.

**Henry Holtzclaw:** I would like to turn it over very quickly to the group for discussion. It seems to me that this paper has many interesting aspects. I think perhaps there will be some discussion on trans effect and on the polarization concept *vs.* $\pi$-bonding. I think it would be interesting for us to say something about the structure of the intermediates, in connection with the planar configuration. the tetragonal pyramidal *vs.* the trigonal bipyramidal. I wonder how important may be the idea of an octahedral intermediate with the solvent molecules building up the octahedron, perhaps then resulting in the tetragonal pyramidal or trigonal bipyramidal configuration. Perhaps some discussion may come on this point.

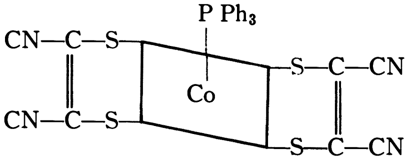
I note that some data in the paper emphasize, for the examples given, that nickel and palladium reactions are considerably faster than the platinum(II) reactions. This, I believe, is true for all the examples cited in the paper. It might be interesting to discuss this point. I would like now to open the topic for discussion from the audience.

**Harry Gray:** First, I want to comment on your point concerning the expansion of the *d*-orbitals to the outer sphere. I don't think there is any appreciable *d*-orbital expansion out this far, certainly not in the $Co(CN)_5H_2O^{-2}$ case.

My second comment concerns the structure of the pentacyanocobalt compound of Prof. Wilmarth, and I have some information there. Carl Ballhausen and I suggested sometime ago that to stabilize a square pyramid, one should try to make a high bond order along the axis involving the *xz*- and *yz*-orbitals—put a ligand in very close so that the potential $\sigma$-orbital which the sixth ligand must use, is consequently of very high energy owing to this bringing in of the ligand in the other pole position. I would agree with Prof. Halpern that the structure of the pentacyanidecobalt if it exists as such without the sixth group, would be a square pyramid. I cite at least two complexes that support this view.

We were gratified to see that the $d^6$-complex, $Ru(P\ Ph_3)_3Cl_2$, now has been shown by Ibers to have a square pyramidal structure with no interaction in the sixth position. The metal-phosphorus distance in the axial position is at least 0.2A. shorter than the ruthenium-phosphorus distance in the plane, thus suggesting this condition for the square pyramid.

The other complex is one that we prepared with this obscure ligand in the cobalt system, also with triphenylphosphine in the pole position.



The spectrum does not change with excess triphenylphosphine and since it is diamagnetic it must be a real square pyramid.

Prof. Basolo wants us to go back to steric effects completely. I feel that we have really never abandoned steric effects, and it is rather inconsistent for one of the coproposers of crystal field stabilization energy to be telling us to go back to steric effects.

I would like to bring up a couple of points here because I think Basolo and Baddley's experiment of blocking the fifth and sixth positions is a very good one. I would like to ask them if they would do the experiment, if they have not done it, in which chloride, bromide, and iodide are replaced as leaving groups to see if the order reverses to give the octahedral halide leaving order, rather than the planar one in which iodide is slower than chloride. This would help firm up this case.

I don't really believe that steric effects are going to dominate the reaction mechanisms to this extent. That is, it seems to me that xenon tetrafluoride, which has a square planar structure, will almost certainly undergo exchange with fluorides by a dissociative mechanism. The first orbital available is at high energy, and I would predict, although the steric factors are favorable for bimolecular reaction, that electronically it is unfavorable. Thus, we can't ignore the fact in planar substitution that a planar $d^8$-complex is unsaturated in the $\sigma$-system as a $p$-orbital is available. You can certainly block it, and it can't react; but the $\sigma$-orbital availability must be an important part of the reasoning.

Also tetracarbonylnickel which isn't sterically hindered but is $d^{10}$, exchanges with radiocarbon monoxide by dissociative mechanism, and I think it could go to the same trigonal bipyramid without much steric difference. I wouldn't want these comments to swing everybody over to steric effects and say that really there is nothing interesting in substitution reactions—all the six-coordinate ones go one way, all the planar ones go the other way, and the electronic structure doesn't matter. This will drive people out of substitution mechanisms into the more interesting field of electron transfer mechanisms where electronic effects must be important.

Next, I would like to speak on the mechanism of planar substitution, which hasn't been brought out too well today.

If my memory serves me correctly, two different mechanisms have been suggested for planar substitution; the first one, by a trigonal bipyramidal intermediate, was suggested in 1954 and 1955 by Chatt and Orgel. In 1958, an alternative mechanism for planar substitution was suggested in which $\pi$-bonding is not very important. With ligands such as diethylenetriamine, the so called dissociative mechanism was suggested.

I would like to take this opportunity in Prof. Pearson's presence, and in his words, to demolish this mechanism.

In 1960 I decided to start on the experiment which would either be for, or strictly against the dissociative mechanism of planar substitution. There is a mechanism, which goes via the trigonal bipyramidal intermediate, the simple one and the nonsticky collision which was suggested as an alternate mechanism in 1958 by Basolo, Pearson and Banerjeu, and amplified in Basolo and Pearson's book (*4*). This nonsticky collision mechanism was suggested because the square pyramidal intermediate which is required supposedly has a more favorable crystal field stabilization energy than the trigonal bipyramid.

I will illustrate these mechanisms with the system that we used to test them. In the diethylenetriamine system, let's say with the bromide as leaving group, diethylenetriamine ties down three positions.

This square pyramidal mechanism or the nonsticky collision says that when a substance like iodine collides with the complex, a square pyramid is formed initially with another solvent which aids the dissociation of the bromide; hence the dissociative mechanism.

This mechanism is rather peculiar because the iodide then just doesn't drop into place, but instead an aquo complex intermediate is formed. That is, the iodide that collides, in order to preserve electronic stabilization, does not go through any peculiar angles, but in fact just collides and helps dissociate the bromide, leading to an aquo complex as the intermediate. This aquo complex is labile, according to the theory, and reacts rapidly with the iodides in solution, by some unspecified mechanism, to give the final product.

The other mechanism leads directly to reaction; the iodide comes in, bromide moves "down" the system, goes through a distorted trigonal bipyramid, and the bromide goes off. It is a sticky collision.

These mechanisms can be easily tested, because Olcott and I, and several other people knew that the reaction of Pt(dien)$Br^+$ with hydroxide is absolutely independent of the hydroxide concentration and is slow but goes to completion.

The reaction of the proposed intermediate in the nonsticky collision mechanism proceeds very rapidly with hydroxide—when it doesn't have to substitute very fast. And in fact, in competition experiments that Olcott and I did with hydroxide and all the other possible reactants in solution, hydroxide was 100% efficient in capturing the aquo complex intermediate.

The stage is therefore set for the competition experiment in which the bromo complex is put in and all the various ligands which react rapidly with this complex at their characteristic second-order rates, and a little hydroxide to see if any aquo complex is generated during the reaction. The results are best demonstrated in the system, Pt(dien)$Br^+$, plus iodide, plus hydroxide. This works nicely because hydroxide is the thermodynamic product; thus hydroxide will finally prevail.

The spectrum of the bromide complex is characteristic with a maximum at 260 mμ and an ε of 250.

The spectrum of the iodide complex has a maximum at 300 mμ and an ε of about 400.

The hydroxide, without this charge transfer feature here, is essentially a blank in the 250–300 m$\mu$ region.

Starting the experiments with a bromide, the iodide product is obtained first, at its characteristic, unchanged $k_2$ rate, and then the slow base hydrolysis of the iodide to the hydroxo product at its characteristic $k_1$ base hydrolysis rate. As far as I am concerned, this is consistent only with the sticky collision mechanism, via the simple trigonal bipyramid and eliminates the dissociative mechanism completely in all the cases tested. Iodide, chloride, and bromide were tested as entering groups. Nitrite has bothered us, as has azide and thiocyanate—these three and the three halides we have tried. It appears that in all the cases studied there is absolutely no catalysis in the formation of the hydroxo product with any good reagent, which eliminates all the mechanisms except, in my opinion, the simplest one, via the trigonal bipyramid.

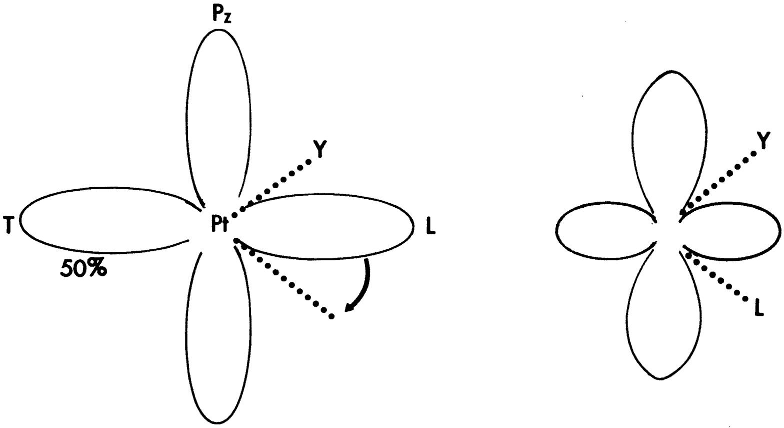
My next comment is on the mechanism of the trans effect.

There are two existing theories: the electrostatic theory of Grinberg, and the $\pi$-bonding theory of Chatt and Orgel. In my opinion, the electrostatic theory of Grinberg should be thrown out completely because it is misleading. The polarization theory, implies that groups which can polarize the platinum strongly would be high in the trans effect series. This isn't exactly what Grinberg says, but this is the trap people fall into. This leads to a reversal just in the ion polarizability term in predicting for the halides. Fluoride is very small and polarizes the platinum. Walter Kautzman pointed out to me, that in his opinion the electrostatic theory was completely misleading and probably wrong. Since he is almost never wrong, I started thinking about the course of the trans effect as far as the $\sigma$-orbitals are concerned. It became clear that if we accept Chatt and Orgel's $\pi$-bonding theory, there is also a suitable quantum mechanical explanation for the $\sigma$-effects that have been observed. That is, both hydride and methide ion are very high in the trans effect series, and that forced us some years ago to bring up the electrostatic theory of Grinberg again.

Briefly, as Prof. Basolo points out in his paper, and Prof. Basolo and Pearson pointed out nicely in a review on the trans effect, the situation in the $\pi$-bonding theory is a stabilization of the trigonal bipyramidal intermediate because there are more orbitals in the trigonal plane available for $\pi$-bonding in the trigonal bipyramid than in the square planar complex. The same is also true in the $\sigma$-system. The trans effect is directional, and in my opinion, it has to be orbital or quantum mechanical.

The $\sigma$-system is certainly directional. That is, there is a $p$-orbital, which is shared between the trans ligand and the leaving group, which I will call L. This is the one-directional $\sigma$- orbital involving L.

The platinum has an empty $p_z$ orbital which is used in the new $\sigma$- structure in the trigonal bipyramid. The Y entering group comes in and L moves down. Whereas only one $p$-orbital in the T—L plane was used in the $\sigma$-structure of the planar complex, two $p$-orbitals are used for three ligands in the trigonal bipyramid. The point is, in Pauling language, the trans ligand has 50% of the important trans $p$-orbital system in the ground state, and $66\frac{2}{3}$% of this $p$-orbital in the transition state. When L moves down, T gets more of the directional $\sigma$- system. Hence, I think that groups such as hydride and methide, which have polarizable or good $\sigma$-donor systems which can use the extra $p$-character to firm up the $\sigma$- structure in the



trigonal bipyramid, will give high $\sigma$- trans effects. Remarkably, the trans effect series, is nearly the same as another series, the nephelauxetic series. Nonpolarizable $\sigma$- and $\pi$- groups are low in trans effect and low in nephelauxetic effect. Groups that can shift by changing the orbital structure in the plane, can delocalize more electrons in one direction or the other in the transition state, and are the ligands that are high in the labilizing series. If one can accept the $\pi$-bonding theory of the trans effect, one should be able to accept the directional $\sigma$- orbital effect as well.

**Dr. Basolo**: Dr. Gray is correct in his statement that the "dissociation" mechanism proposed earlier (*3*) for substitution reactions of Pt(II) complexes has now been largely replaced by a direct displacement process involving the solvent and the reagent. This is the mechanism shown in Figure 2. It has been elegantly demonstrated by competition experiments between $OH^-$ and $Y^-$ for a Pt(II) substrate (*5*). However, the effect of added $HC_2H_3O_2$ or $H_3BO_3$ on the rate of chloride ion exchange with *trans*-$[Pt(py)_2Cl_2]$ shown in Table IV and the recent report (*6*) of evidence for $[Pt(NH_3)_2(NO_2)_2Cl]^-$ in the reaction of *trans*-$[Pt(NH_3)_2NO_2Cl]$ with $NO_2^-$ may possibly suggest a "dissociation" mechanism in these reactions. Dr. Gray may wish to comment on this.

**Dr. Gray**: There is no question that is what he suggests. In fact, I think the point is a good one. What is the energetic course of planar substitution, the de-

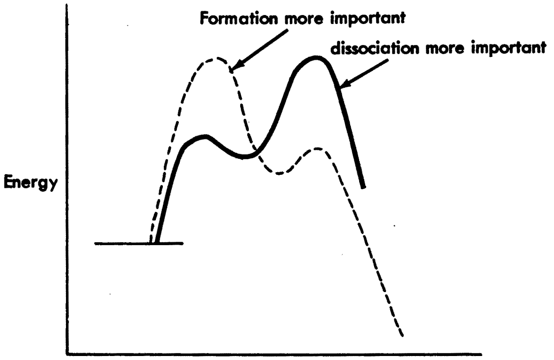


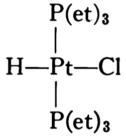
*Figure F. Energy curves for formation and dissociation of trigonal bipyramid* tailed course? If we accept the trigonal bipyramid for the moment, is the formation or dissociation of the trigonal bipyramid more important? In transition state language, is it this type of curve, or the formation and then a bump of this type.

Paul Haake believes that with nitrite he can detect the formation of the tetragonal pyramid, but it is just a bump on the curve leading to the trigonal bipyramid. However there is an early fast rate with nitrite that we have observed, which is misleading. You must know the $k_1$ rate, to be able to correct for this properly. I am not sure Haake corrected for this effect properly in his work. The detailed results haven't been published. Until they are, it would be difficult to assess this information; but as Paul indicated to me, he interprets the rate effect as a bump on the way to the trigonal bipyramid.

I certainly think that the formation of the trigonal bipyramid is the most important step in most cases. If you look at the steric information, when you block fifth or sixth position you do not get a factor of 2 when you block one position; you get a retardation factor such as 30 or 50, indicating that moving the leaving group down into the leaving position is very important.

**Jack Halpern:** I want to report another observation relating to the trans effect, which involves measuring an isotope effect of the trans effect.

Charles Falk in our laboratory has recently measured the effect of substituting deuterium for hydrogen in the complex



$$\begin{array}{c} P(et)_3 \\ | \\ H—Pt—Cl \\ | \\ P(et)_3 \end{array}$$

on the rate of substitution of $Cl^-$ by pyridine, a reaction that Gray, Basolo, Pearson, *et al.*, first reported. These measurements refer to the $k_2$ of their rate law, (–ie. the second order path) and we find no detectable contribution for this particular reaction from the $k_1$ path. The observed isotope effect turns out to be $k_H/k_D = 1.4$ which is large for a secondary isotope effect.

We didn't really have any strong views on what to expect in this experiment. We could think of reasons why the isotope effect might be in either direction. From the point of view that the $\sigma$-trans effect arises from a weakening of the metal—ligand bond by an inductive effect of the trans ligand, a larger trans effect might have been expected for deuterium, in the light of indications that in certain organic reactions deuterium exerts a stronger inductive effect than hydrogen. On the other hand, insofar as the transition state of the square planar substitution reaction presumably involves five strongly bonded ligands compared with four in the ground state, the electron density on the platinum should be increased and the binding of the ligands weakened. This should give rise to a deuterium isotope effect in the observed direction and apparently, on balance, this effect wins out.

**Arthur Adamson:** I object to the phrase "collision." I don't really believe that molecules zip around in solution colliding with each other as they do in a gas phase.

I do believe in the solvent cage effect, and that it takes a while for species to diffuse in and out; so the analog of the gas phase collision is the much less frequent "encounter."

I also have a comment about the trigonal bipyramid *vs.* square pyramid configurations. Little physical motion of atoms is required to go from one to the other. There can be, I think, a tendency to take symmetry arguments too literally as black and white situations. The full symmetry of these complexes is considerably less than the symmetry one derives just from the arrangements of atoms next to the central ion. I do think it is possible to depend too much on exact symmetry designations.

**Michael Anbar:** I would like to comment on the relatively low reactivity of the hydroxide ion, or the fact that the hydroxide is outstanding because of its slow reactivity.

If one considers the hydration of the hydroxide and remembers that the hydroxide once it goes into an activated complex has to peel off its water of hydration, a completely different picture emerges. We looked at the reactivity of the hydroxide in the bimolecular base-catalyzed substitutions both in the case of chloramine and of ethyl iodide (*1*, *8*). Investigating these systems in concentrated hydroxide solutions and calculating the concentration of the so called free hydroxide ions shows that the hydroxide ion is much more reactive than its form in dilute solution. This means, in the kind of sticky mechanisms where you introduce the hydroxide into the complex, it is likely to be much less reactive than one expects from such a strong base.

In terms of reactivity, one should really measure the reactivity of hydroxide ions also in the nonhydrated form. This can be achieved only in concentrated solutions, and even there one must correct for its hydration.

**Dr. Basolo:** We know what the facts are with $OH^-$ but are much less certain why these are the facts. There is no doubt that $OH^-$ is the poorest of all these reagents towards Pt(II). The hydroxide ion does not compete with the solvent water, nor does methoxide ion compete with methyl alcohol, even at concentrations of $0.5M$ anion.

Exactly why this is, we are not certain. One can simply say that $OH^-$ is a hard base, whereas (Pt(II) is a class A metal or soft acid, and this hard-soft combination is unstable. It is also possible to suggest that the repulsive interaction between the filled *d*-orbitals on Pt(II) and the filled *p*-orbitals on $OH^-$ make it a poor reagent. The same is true of $F^-$ which is also a poor reagent. Other halide ions have low energy, vacant *d*-orbitals which can accept electrons and decrease the effect of the filled *p*-orbitals. This makes these halide ions better reagents than $F^-$.

One interesting point here is that $OH^-$ is a poor reagent towards Pt(II) systems which react via bimolecular displacement. However, $OH^-$ is an excellent reagent towards Co(III) ammines containing N—H hydrogen, where $OH^-$ is the only reagent that competes successfully with the solvent water. This argues strongly against a nucleophilic displacement reaction by the attack of $OH^-$ on Co(III), and supports the view that some other mechanism is involved.

Dr. Gray suggests then there may be some danger in stressing steric factors rather than electronic factors in accounting for the properties of metal complexes. He says that this is not necessary because everyone knows that steric factors are important. I might add that everyone is also aware of the importance of electronic factors. The tremendous success of the crystal field theory and molecular orbital theory in explaining the properties of transition metal complexes is now common knowledge. There seems to be ample justification for the statement in the conclusion of this paper, that in certain systems steric factors predominate in affecting the properties of metal complexes.

**Dr. Anbar:** Just one little comment. I was referring to solutions say from 3 to 5 up to 10*M* hydroxide where you can get the hydroxide or the less hydrated than the dehydrated form. So I don't know whether you can investigate your systems under these conditions, but these are the conditions under which we investigated those systems.

**Dr. Basolo:** To the best of my knowledge there is no data on the hydrolysis rates of Pt(II) complexes at $OH^-$ concentrations greater than 0.5*M*. All that is known experimentally is that the solvolysis rates do not depend on $OH^-$ up to 0.5*M* $OH^-$. Thus, under these conditions $OH^-$ is a poor reagent relative to many other nucleophiles.

**Joseph Jordan:** I believe that one point which Dr. Gray has raised can perhaps be resolved on the basis of almost *a priori* considerations, in conjunction with a comment by Dr. Adamson. I think he made a very convincing point that in dilute aqueous solutions it is necessary to form the chemical configuration of the intermediate before its "energy activation" occurs. This would certainly favor the formation of the trigonal bipyramid before decomposition. Generally, one should perhaps revise one's thinking of the transition state theory as far as reactions in dilute solutions are concerned. My impression is that the intermediates referred to by Prof. Taube, which do not have a memory of their history of formation, differ from a genuine activated complex. The latter may "remember" its history because of its very short lifetime. Because of mean free path considerations in liquids it is difficult to think of such "genuine transition states" in dilute solutions.

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## 5

# Bridging Groups in Electron Transfer Reactions

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**A moderately successful classification of carboxylate bridging groups in the reaction of the pentaamminecobalt(III) complexes with $Cr^{+2}$ (aq.) is this; (a) a chelate function is present that can act with the carboxylate function on the Co(III); (b) a remote polar group such as carboxyl or carbonyl is in conjugation with the carboxyl group on Co(III); (c) neither of these special functions is present. Within class (c), adjacent attack occurs, and, but for two exceptions, the rate is remarkably insensitive to wide variations in the carboxylate group. Variations do occur within a factor of about four in rate, and these may result from inductive and/or steric effects. Group (b) as a class shows rates of reaction much higher than Group (c). In some systems of this class remote attack appears to take place.**

By now numerous data have been accumulated on the rate at which $Cr_{aq}^{+2}$ and other reducing agents react with complex ions of the type $Co(NH_3)_5CO_2R^{+2}$. Several structural features of the ligand have been recognized as affecting its efficacy in mediating electron transfer from the reducing agent to the oxidizing agent. One important feature is a conjugated bond system extending from a remote polar group to the carboxyl associated with the Co(III) (*5*, *20*). A ligand with this structure makes electron transfer possible by remote attack, and leads to an increased reaction rate. When the ligand contains groups which lead to stronger association of $Cr_{aq}^{+2}$ with the oxidizing agent, as when a chelate function is built into it, the rate is also increased (*6*).

These effects are not the only significant or interesting ones, but others, though worthy of direct attention, have been considered only in a desultory fashion. It has, therefore, seemed worthwhile to prepare a review of the observations and to pose some of the questions bearing on them which are a current concern. This seems all the more worthwhile because even the two effects which have been explicitly described and discussed are only imperfectly understood. Thus, although the role of electron transfer through a bridging ligand has been documented and although the mechanism of electron transfer through bridging groups has been discussed (*11*, *13*), the relation of the theoretical treatments of the observations has not been established.

Many more questions will be asked than answers supplied. A number of questions will undoubtedly have answers which are obvious to readers of this paper, but it is likely that some at least will challenge their inventiveness. If the problems which are outlined provoke thoughtful discussion and suggest experiments which illuminate the issues, the purpose of this paper will be fully served.

Comparisons of reaction rates provide the basis for many of the questions. However, any explanation which accounts for rate differences, but ignores temperature coefficients is at the very least incomplete and may actually be wrong. Where temperature coefficient data exist, they have been taken into account, but few observations are so well understood that both reaction rates and their variation with temperature are accounted for.

Except for a few ligands, namely certain of those in which attack is at a remote carbonyl group, the organic ligand is transferred to the chromium during reaction of the Co complex with $Cr^{+2}$. Though formation of a Cr(III)–ligand complex does not prove that direct transfer of the ligand takes place, we assume that in every instance we are dealing with a bridged activated complex. In many cases $Cr^{+2}$ is very inefficient in trapping the free ligand present in solution when the reducing agent is oxidized to $Cr^{+3}$ by a Co(III) complex. The assumption that a bridging mechanism operates in the systems we will discuss is liable to criticism in only a few cases.

The oxidizing complexes dealt with are all of the pentaamminecobalt(III) class, and only the reactions with $Cr^{+2}$ are considered systematically.

### *Variations in Rate for Adjacent Attack*

Table I summarizes kinetic parameters for the reaction of $Cr^{+2}$ with carboxylatopentaamminecobalt(III) complexes of ligands which favor neither chelation of the reducing agent nor reaction by remote attack.

Use has been made of the fact that the specific rate values for a series of complexes containing ligands such as those in Table I are nearly constant, and any substantial rate increase has been attributed to some "special effect." But the fact that the specific rates reported in Table I vary so little itself deserves attention. The ligands do differ markedly in properties, and this difference is reflected in a variation in the dissociation constants of between $10^4$ and $10^5$ for the corresponding organic acids. Since $Cr^{+2}$ presumably attacks an oxygen of the carboxyl group, the specific rate should reflect the difference in the availability of the unshared electrons on the oxygens. A rate decrease is indeed noted in the series $CH_3CO_2^-$, $ClCH_2CO_2^-$ and $Cl_2CHCO_2^-$ as the effect of the electron withdrawing power of R increases. But even this decrease is not reliable. For, owing to the way $\Delta F\ddagger$ is resolved into $\Delta H\ddagger$ and $\Delta S\ddagger$, the rate for the complex containing $ClCH_2CO_2^-$ will be even greater at a higher temperature than that for the acetato complex.

The slow rate of reduction of the acetato complex (0.18 $M^{-1}$sec.$^{-1}$) compared, for example, to the aquo complex (0.5 $M^{-1}$sec.$^{-1}$) is noteworthy (*24*). The acetato

**Table I. The Rate of Reaction of $Cr_{aq}^{+2}$ with Selected Pentaamminecobalt (III) Complexes**

(At 25°C. ± 1.0°, $\mu$ = 1.0 except where otherwise indicated)

| *Ligand* | $k$, $M^{-1}sec.^{-1}$ | $\Delta H\ddagger$ | $\Delta S\ddagger$ | *Ref.* |
|---|---|---|---|---|
| $CH_3CO_2$ | 0.18 | 3.0 | −52 | *20* |
| $ClCH_2CO_2$ | 0.10 | 7.9 | −37 | *6* |
| $Cl_2CHCO_2$ | 0.074 | 2.5 | −55 | *6* |
| $F_3CCO_2$ | 0.052 | . . . | . . . | *12* |
| Benzoate | 0.14 | 4.9 | −46 | *6* |
| *o*-Chlorobenzoato | 0.074 | 6.0 | −43 | *6* |
| *p*-Chlorobenzoato | 0.21 | 10.0 | −28 | *6* |
| *p*-Hydroxybenzoato | 0.13 | 9.6 | −30 | *6* |
| Isophthalato | 0.13 | 2.1 | −56 | *20* |
| $HCO_2$ | 7 | . . . | . . . | *2* |
| $^{+}H_3NCH_2CO_2$ | 0.06 | . . . | . . . | *15* |

carries a lower positive charge than the aquo complex and, formally at least, offers an opportunity for "remote" attack at the carbonyl oxygen. (Attack at Co—O—C oxygen would correspond to attack at $H_2O$ in the aquo complex.) It is not known, in the case of carboxyl acting as a bridging group, whether $Cr^{+2}$ attacks the carbonyl or the Co—O—C oxygen. It is possible that in one series of complexes, for example, those of simple carboxyl ions, attack is at one of these positions, but when a chelating function is introduced, the position of attack changes.

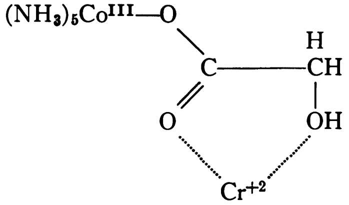
In addition to inductive effects, and the possibility that the position of attack may be different for one complex than for another, steric effects are also undoubtedly a factor. The acid dissociation constants show that $HCO_2^-$ is less basic than $CH_3CO_2^-$, but the rate of reduction of the formato complex is much faster than that of the acetato. Enough effects exist to explain almost any result qualitatively, but they are not well enough understood to sustain even qualitative predictions.

The way $\Delta F\ddagger$ decomposes into $\Delta H\ddagger$ and $\Delta S\ddagger$ is as remarkable as the slow rate of reduction of the acetato complex. Other results as well as those for the activation parameters give rise to questions. What is the origin of the very unfavorable entropy of activation? Why are $\Delta H\ddagger$ and $\Delta S\ddagger$ so strongly affected by substitution at a site well removed from the reaction site (compare entries for benzoate and *p*-chlorobenzoate in Table I) when the effect on the rate is so minor? Why don't the values of $\Delta S\ddagger$ for the first three complexes in Table I change monotonously within the series?

### *The Effect of a Chelate Function in the Bridging Ligand.*

When the bridging ligand is malonate (*22*), the reaction rate is approximately twice that when it is acetate. The reaction product in this system is the chelated malonato complex. This observation is consistent with the view that chelation of the $Cr^{+2}$ by malonate takes place in the activated complex but does not prove this to be the case. Nothing is known about the rate at which a complex such as $(H_2O)_5CrO_2CCH_2CO_2H)^{+2}$, if it were formed, would react to form the chelate although the results which follow suggest a slow rate. With glycolate as the bridging group (*2*), the specific reaction rate at 25° C. and $\mu$ = 1.0 is 3.0. For this system there is evidence indicating a chelated species as the primary reaction product. The extinction coefficient at $\lambda$ = 411 m$\mu$ for the Cr(III) reaction product is 39.3. This changes with a half-life of 22 ± 2 hr. at 25°C. to 30.9. The final value of the extinction coefficient is identical with that measured for the Cr(III)-glycolate complex prepared by direct combination, then separating the species of charge +2 from the residual $Cr(H_2O)_6^{+3}$ with a cation exchange resin. The higher extinction coefficient for the initial product suggests a higher degree of chelation than for the final product, which may be an equilibrium mixture of chelated and non-chelated forms.

Complexes of the α hydroxy acids as a class react more rapidly than those of the parent complexes and in view of the results cited, it seems reasonable to ascribe this rate increase to chelation of $Cr^{+2}$ in the activated complex.



For other ligands such as malonate, which contain a chelating function but have no other obvious property which would facilitate electron transfer, it seems reasonable to ascribe the rate increase to chelation of $Cr^{+2}$. In any event, it is interesting to consider the rate data for these complexes in view of this possibility, and a number of such data are presented in Table II.

The rate increase in the glycolato, lactato, methyllactato series agrees with the view that chelation occurs in the activated complex. The basicity of the OH

**Table II. Effect of Chelation on Rate**

| *Ligand* | at 25°C., $\mu = 1.0$ <br> $k$, $M^{-1}$ *sec.*$^{-1}$ | $\Delta H‡$ | $\Delta S‡$ | *Ref.* |
|---|---|---|---|---|
| Glycolate | 3.1 | 9.0 | −26 | 2 |
| Methoxyacetate | 0.42 | 9.3 | −23 | 2 |
| Lactate | 6.7 | ... | ... | 2[a] |
| Methyllactate | 11.8 | 9.1 | −24 | 2 |
| α Malate[e] | 2.7 | | | 2[b] |
| β Malate[e] | 0.36 | | | 2 |
| Malonate[e] | 0.29 | ... | ... | 2[c] |
| $HO_2CCHC_2H_5CO_2$[e] | 0.22 | 1.7 | −54 | 2 |
| $HO_2CC(CH_3)_2CO_2$ | 0.07 | ... | ... | 2 |
| $HO_2CHC_6H_5CO_2$[e] | 0.65 | ... | ... | 2 |
| $C_2H_5O_2CCH_2CO_2$ | 0.45 | | | 14 |
| $HO_2CCH_2CH_2CO_2$ | 0.17 at 14°C. | | | 20 |
| $CH_3O_2CCH_2CH_2CO_2$ | 0.17 | | | 20 |
| Phthalate | 0.075 | | | 20 |
| Salicylate | 0.15 at $\mu = 3.0$ | | | 12[d] |
| $^{-}O_2CCH_2CO_2$ | $\sim 2.5 \times 10^3$ | | | 22 |
| Phthalate ion | 2.7 | | | 20 |
| Salicylate ion | $\sim 2 \times 10^8$ | | | 22 |

[a] The specific rate reported here does not agree with that reported in (*6*), nor did we find evidence as reported there for the path inverse in $H^+$ even when $(H^+)$ was made as low as $0.02M$.

[b] In agreement with results in (*6*), we find two forms of the malato complex, and we were apparently able to make a rather clean separation of the two forms. Our rate measurements, however, do not agree with those in (*6*).

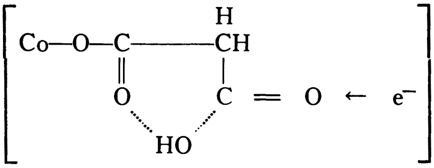
[c] In reference *22*, the specific rate is reported as 0.34. Since the term $k_1$ (complex) $(Cr^{++})$ is small compared to either $k_2$ (complex) $(Cr^{++})/(H^+)$ or $k_3$ (complex) $(Cr^{+2})$ $(H^+)$ it is difficult to get a precise value of $k_1$; further as Svatos and Taube caution, the values of $\Delta H_1‡$ and $\Delta S_1‡$ reported in (*22*) are not reliable.

[d] In (*6*) a value of 0.07 at 17° is reported.

[e] Each of these show paths involving $1/(H^+)$, but since $K_{diss.}$ for the complex acids has not been measured, the specific rates for the reactions of the anion ligand complexes cannot be calculated.

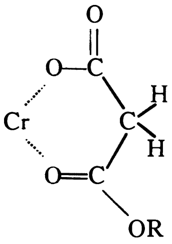
should increase with increased replacement of H by $CH_3$. When the hydrogen of the OH group is replaced by $CH_3$, a steric factor probably comes into play and the benefit from chelation is less than for the glycolate. The higher rate for the $\alpha$ malate presumably means that this is the form which has the OH linked $\alpha$ to the carboxyl on the Co(III); the effect of OH in chelation should diminish as this group becomes further removed from the adjacent carboxyl.

The neutral carboxyl group is not very effective in increasing the reduction rate of the complex. However, when the proton is removed from the carboxyl, the effect can increase and is greatest when the carboxyl ion is in a configuration favorable to chelation. Thus, the inverse ($H^+$) path is not even observable for acid succinate in the same acidity range as that for which this path is important in the acid malonato reaction. The acid dissociation constants are known well enough so that the behavior difference between acid malonato and acid succinato can not be entirely ascribed to different acidities of the complexes. The results obtained with the acid malonate complexes, as reported in Table II, incidentally provide no support for the hypothesis (*22*) that electron transfer takes place by remote attack across hydrogen bonds.



When malonate or phthalate ions are the bridging ligands, an important component of the remote carboxyl effect is undoubtedly its assistance in binding the $Cr^{+2}$, thus, improving the opportunity for electron transfer through the adjacent carboxyl. But for glycolate, this explanation probably does not suffice. The evidence is that the glycolate chelate is no more stable on $Cr^{+3}$ than is the open structure, and it does not seem likely that the chelate will be more stable for $Cr^{+2}$ than is the open structure. Possibly an electronic factor is a component of the total effect. In general terms, the change in symmetry produced by chelation may effect the electron distribution in $Cr^{+2}$ so as to increase the probability for electron transfer.

An interesting phenomenon is ester hydrolysis accompanying the reaction of certain half ester complexes with metal ion reducing agents. Fraser (*7*), reports complete hydrolysis of the ester link in the reaction of the methyl succinato half ester complex with either $V^{+2}$ or $Eu^{+2}$. This observation is all the more remarkable when one realizes that the reduction rate of the half ester complexes is almost identical to that of the acido complexes. The reaction rate of $Cr^{+2}$ with $(NH_3)_5CoO_2CCH_2CO_2C_2H_5^{+2}$ shows only the term which is independent of acid (*14*) (by contrast the acid malonato complex displays in addition (*22*) both a term first order in ($H^+$) and one inverse in ($H^+$)). Spectrophotometric analysis of the solution resulting from the reaction shows that about 60% of the Cr(III) product is the malonate chelate. Experiments using cation exchange resins show that it carries a charge of +1. Thus, we can conclude that at least 60% of the ester is hydrolyzed in the reaction. The effects observed with $Cr^{+2}$ have straightforward though not necessarily correct explanations along the following lines: an inter-

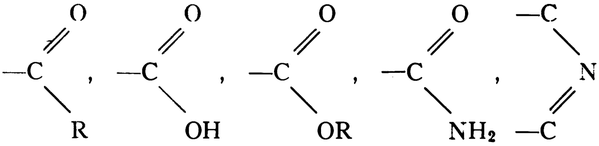


mediate of the type shown above is formed which then ruptures at the Cr—O bond (to form the half ester complex) or ruptures at the C—O bond leading to hydrolysis leaving the chelate ring intact. But this explanation does not account for the effects observed with $V^{+2}$ and $Eu^{+2}$. Both $V^{+3}$ and $Eu^{+3}$ form very labile complexes, and it is unlikely that C—O bond rupture would compete with $M^{+3}$—O bond rupture. Nor does the explanation account for the oxygen tracer result reported by Fraser (*7*), which indicates that at least 40% alkyl-oxygen fission takes place.

The energy parameters for the reaction of complexes containing chelating ligands merit some attention. Those systems studied in detail show higher values of $\Delta H\ddagger$ than most systems for which only the adjacent carboxyls come into play; to compensate for the change in $\Delta H\ddagger$, $\Delta S\ddagger$ is much more favorable for the complexes which present chelating functions to the reducing agent. It is difficult to understand the source of an entropy increase of some 30 units when chelation takes place. Perhaps the mode of attack on the adjacent carboxyl is actually different for the chelating than the ordinary ligands.

### *Ligands Having Conjugated Bond Systems*

In only a few cases is there direct proof that remote attack takes place when complexes containing conjugated bond systems extending from a remote polar group (for example



to the adjacent carboxyl react. For most systems of this kind the evidence supporting remote attack is a reaction rate larger than that for complexes like those in Table I, and the absence of other special effects such as chelation. The conjugated systems usually feature a term first order in $H^+$, which, in some cases can be taken to indicate that remote attack occurs for the path corresponding to this term.

We will be concerned with rate differences of different conjugated systems and with how electron transfer takes place. Specifically, we will try to distinguish the "resonance" mechanisms from "chemical" mechanisms in which electron transfer takes place to the ligand rather than through it.

A relationship between a reaction rate involving electron transfer through a conjugated bond system and the mobile bond (*4*) order has been suggested (*13*) and has been examined by Fraser (*8*) and by Manning, Jarnagin, and Silver (*18*). Many of our comparisons are for similar bond systems, and for these the differences in mobile bond order will not be in question. Some of the comparisons suggest, perhaps demonstrate, the importance of steric factors. Maximum conjugation demands special geometry and some molecules which formally have the bond sequence necessary for conjugation do not lend themselves to the remote attack mechanism because steric effects make it difficult to achieve the required geometry. This is illustrated by comparing terephthalate as a ligand with phthalate (*1*). The rate of reduction of the terephthalate complex is about 36 (17°C.), while for phthalate it is 0.075, namely in the same range as the ligands of Table I. Fraser (*8*) provides another comparison: when 4′-carboxybiphenyl 4-carboxylate is the ligand, the rate of reduction is very rapid, but when iodine is substituted in the 2,2′ positions, the specific rate is 0.12 $M^{-1}$sec.$^{-1}$ at 25°C.

Steric effects are undoubtedly a factor in the reactivity of halogen substituted fumaric acid complexes to Cr$^{+2}$ (*18*). The results of rate measurements for these species are shown in Table III. Specific rates are entered both for the (H$^+$) independent path (path 1, $k_1$) and for the path first order in (H$^+$) (path 2, $k_2$).

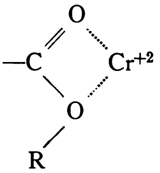
**Table III. Comparison of the Rates of Reduction by Cr$^{+2}$ of Complexes of Substituted Fumaric Acid**

(T = 25°C., $\mu$ = 1.0; all data are from ref. (*18*) except for the first entry which is from (20).)

| *Ligand* | $k_1$ $M^{-1}$ *sec.*$^{-1}$ | $k_2$ $M^{-1}$ *sec.*$^{-1}$ | $\Delta H_1\ddagger$ | $\Delta S_1\ddagger$ |
|---|---|---|---|---|
| Fumarate | 1.3 | 3.5 | 6.7 | −36 |
| Chlorofumarate | 1.3 | 1.2 | . . . | . . . |
| Chlorofumarate | 0.09 | 0.5 | 6.4 | −47 |
| Bromofumarate | 0.70 | . . . | 11.9 | −24 |
| Bromofumarate | 0.10 | . . . | 11.0 | −26 |
| Iodofumarate | 0.89 | . . . | 6.0 | −39 |
| Iodofumarate | 0.10 | . . . | . . . | . . . |
| Dichlorofumarate | 0.19 | 0.9 | 9.1 | −32 |
| Diiodofumarate | 0.10 | . . . | 6.5 | −42 |

Steric interference of the halogen with the carboxyl can be expected. Therefore, the ligand molecule will have difficulty in achieving the coplanar arrangement necessary for optimum conjugation when it is substituted by halogen. But a simple steric factor does not explain why one of the isomeric forms of the monosubstituted molecules reacts rapidly, and the other reacts at a rate characteristic of adjacent attack. Fraser has concluded that the molecule of each isomeric pair which reacts the more rapidly has the hologen remote from the carboxyl on Co(III). The halogen interferes with the coplanarity of the carboxyl to which it is $\beta$ rather than to which it is $\alpha$. If the effects are steric, it indicates that coplanarity is a less stringent requirement for the carboxyl on the Co(III) than for the carboxyl which Cr$^{+2}$ attacks. Does this mean that electron transfer takes place *to* the ligand in these cases?

The rate at which Cr$^{+2}$ reacts with a variety of half-ester complexes of fumaric acid is not very different from the rate at which it reacts with the fumaric complex. Thus, the specific rates for the methylfumarate (*20*), phenylfumarate (*9*), and fumaric acid (*20*) complexes are 1.4, 1.5, and 1.3 respectively. However, when terephthalic acid is esterified, the specific rate drops (*9*) to a value low in the range of those characteristic of adjacent attack. E. S. Gould has independently checked the values reported in (*9*) for the methyl half-ester complex. If it is assumed that the activated complex for remote attack requires the configuration

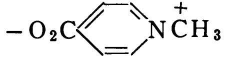


with the R coplanar with the ring, then the small rate for the methyl terephthalate half ester complex can be understood, because steric interference makes the coplanar arrangement difficult even when R = $CH_3$. However, this analysis is not in accord with the result (*9*) that ester hydrolysis is essentially complete when the methyl terephthalate complex reacts even at an acid concentration so low that the path first order in $H^+$ (which the terephthalate complexes do exhibit) cannot be important.

We will now specifically consider electron transport mechanisms in the reactions of cobaltic complexes of organic ligands with $Cr^{+2}$. We will be concerned principally with the distinction between resonance transfer mechanisms and mechanisms in which the organic ligand is first transformed to a radical ion, the electron in due course being passed on to the Co(III) centers. (This point appears to be the principle issue in the discussion which Libby has offered of the data on rates of reduction of Co(III) complexes, stressing the resonance transfer mechanism (*17*). Of course transfer to the ligand is also subject to the restrictions of the Franck-Condon Principle.) In view of the electronic structure of Co(III) it is not unreasonable to expect a finite life time for a radical-ion reducing intermediate associated with it. Sound kinetic evidence for an intermediate of this kind has been reported (*3*) in the oxidation of formatopentaamminecobalt(III) by $MnO_4^-$. EPR spectroscopy may provide direct evidence for radical ion intermediates. Such experiments are now in progress in collaboration with J. P. Hunt and L. Piette.

The difference in reaction rates for the phthalato complex ($k = 0.075$) and for the maleato (*10*) ($k = 200 + 100\ (H^+)$) is large. Since the ligands have a similar geometry, I suggest that the difference arises because maleate, but not phthalate, is readily reduced to a radical ion by $Cr^{+2}$. Consistent with this suggestion is the fact that when $Cr_{aq}^{+2}$ is added to free maleic acid, it is rapidly reduced, but phthalic acid is unaffected in a similar experiment. Maleate is partially isomerized (*9*) to fumarate when the maleato complex is reduced by $V^{+2}$ or $Cr^{+2}$. These results are also consistent with this interpretation since they seem to require that a radical-ion intermediate be formed. Coplanarity of the maleate, if this ligand is to be reduced to a radical ion, is not required as it is for a resonance transfer mechanism.

Invoking the reducibility of the ligand in certain instances helps explain some other comparisons. Thus, it has been a matter of concern that electron transfer by remote attack through an esterified carboxyl group is accompained by such drastic effects as hydrolysis of the ester, while electron transfer through a carbonyl, when this is part of a ketonic or aldehydic function, takes place easily. This occurs even though there are no opportunities here for the kind of chemistry which accompanies electron transfer in the half-ester complexes. Possibly the mechanisms of electron transfer are actually different in the two systems The first may be true resonance transfer, which for reasons that are not yet clear calls for interaction of the reducing agent with both oxygens (as outlined above). In the ketone and aldehyde case a radical ion mechanism may operate. Aldehydes and ketones are more readily converted to radical ion intermediates by reduction than are acids. It may be significant in this context that the specific rate for the reduction of the *o*-benzoylbenzoate complex (*12*) by $Cr^{+2}$ is greater ($k = 5.4$ at 25°) than that of the acid phthalato (0.075) or even that of the phthalato ion (*20*) complex (*2.7*). We can understand the comparison if we consider the rate-determining step to be electron transfer to the organic group.

The rapid rates of reduction of the oxalato (*10*) ($k = 450 + 1{,}000\,(H^+)$) and of the pyruvate (*2*) complexes ($2.1 \times 10^3$ at 25°C. and $(H^+) = 0.1$) can hardly be understood as caused by chelation. Binoxalate does not chelate unless the proton is lost, and the rate law for the reduction of the complex shows that it brings a proton into the activated complex. Pyruvate almost certainly is not chelated in the product. Both groups are rapidly reduced by $Cr_{aq.}^{+2}$ when they are feee from the cobalt center. (The reduction of $H_2C_2O_4$ by $Cr_{aq.}^{+2}$ was explored by R. Milburn and the present author (*29*). The observations on pyruvate were made by R. Butler (*2*)). The complexes of pyridine-2-carboxylate and pyridine-4-carboxylate are rapidly reduced by $Cr^{+2}$ at least in the forms which present the nitrogen without associated protons. Radical ion intermediates for these structures are not unreasonable. In fact, a stable free radical derived from *N*-ethyl-4-carbethoxypyridinyl has been reported (*16*). Although attack by the reducing agent, when  is the ligand, is probably limited to the adjacent carboxyl, the reduction rate of this complex is at least 5 fold greater than for any of the complexes (except formate) in Table I. It has been suggested that in contrast to the usual case of adjacent attack (in which the electron is transferred to the Co(III) center) here we may have electron transfer from the adjacent carboxyl to the organic group (*12*).

The large rate increase alone for acid oxalate or pyruvate compared to glycolate suggests that some specific effect is operating. It has been argued that this cannot be solely chelation, and this seems to be true particularly for the pyruvate. No large rate increase for remote attack can be expected from the decrease in Co(III)—Cr(III) repulsions. Note the small effect (last entry in Table I) of increasing the positive charge on the ligand. Perhaps electron transfer through the adjacent carboxyl is inherently inefficient. The benefit from remote attack (i. e. involving the ketonic carbonyl) then arises because a different route to Co(III) is provided. This seems even more likely in the pyruvate case because the rate-determining step may be the formation of the radical ion intermediate, the electron in due course passing on to Co(III). Some explanations for the slow rate via adjacent carboxyls are: attack on CoO oxygen is inefficient for steric reasons; on the carbonyl oxygen it is inefficient because this requires resonance transfer and this is inherently inefficient because of poor overlap of the $\pi$ system with the cobalt acceptor orbital.

Finally, in support of the hypothesis that in some cases electron transfer to the organic ligand takes place, we may note that slight deviations from the stoichiometry one $Cr^{+2}$ to one Co(III), have been observed in a number of reactions (*12*) of Co(III) complexes with $Cr^{+2}$. That some reduction of the organic ligands takes place does not prove that a radical ion intermediate is involved in the reduction of Co(III), but it is strongly suggestive. Unless the reaction leading to the reduction of the organic ligand is actually second order in $Cr^{+2}$, a radical ion intermediate must be formed. Net reduction of the ligand by a second $Cr^{+2}$ may then compete with reduction by the radical ion of Co(III).

The suggestion that radical ion intermediates are involved can be directly tested in some cases. The EPR spectroscopy test has already been mentioned. Another test compares the reduction rates of complexes having two different metal ion centers, but the same charge. Another test uses a variety of reducing agents of differing strengths. The results of this test are difficult to interpret because ligand reducibility may be a factor also in the resonance transfer process that involves superexchange. The facility of electron transfer by this mechanism depends on the energy difference between unoccupied orbitals and the ground state. This is a factor also in the chemical mechanism. In principle, a reducing agent which is not powerful enough for net transfer of an electron to one of the unoccupied orbitals could still use the orbital if electron transfer takes place by superexchange.

It is not certain at the present stage that radical ion intermediates are involved in any of the reactions we have been discussing. But even if such intermediates are involved, the generalization to other metal ion centers must be made cautiously. The electron accepted by Co(III) is one of $d\gamma$ symmetry and it enters an antibonding orbital. When the electron accepted is in a $d\epsilon$ orbital, in our cases non-bonding, the reactivity pattern may be entirely different. Overlap of the acceptor orbital with the $\pi$ bond system of a ligand containing bonds in conjugation will be efficient. For this reason resonance transfer should take place more readily and radical ion intermediates are expected less frequently. When $d\epsilon$ oxidizing complexes react, direct transfer from a reducing agent such as $V(dip)_3^{+2}$ to a conjugated system may take place without intervention of a polar group. In an extensive search (*1*) we have found no evidence for this kind of process in reactions of pentaammine Co(III) complexes with $V(dip)_3^{+2}$. Work on the reduction of pentaammine ruthenium(III) ($d\epsilon^5$) complexes is in progress (*21*) and the results will be especially interesting compared with those for Co(III) complexes.

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# Discussion

**Henry Taube:** I want to outline and amplify some points that are made in the paper; but first, I want to make a general observation not touched on in the paper, namely that the subject under discussion has unfortunately continued to be highly parochial. Many results that I shall discuss have been generated by people who have been or who now are closely associated with me, and it has distressed me that not many others have become interested in the subject. There are signs that this situation is beginning to change—Jack Halpern for example, and Dr. Jarnagin have recently published contributions to this area—and it is a welcome change. In this subject, as in others in science, a more vigorous and healthy growth takes place if the results are checked by different laboratories and if there is a cross-fertilization of ideas.

This subject should not be left without noting that some aspects of the work are very arduous. Though it is often easy to design experiments which if performed would demonstrate one point or another, the work which they entail can be very difficult because the substances required are difficult to prepare. New synthetic procedures are needed badly. One now being developed by A. Sargeson, which depends on the removal of coordinated azide by $NO^+$ in the presence of a nucleophile, promises to be useful for a number of preparations.

Turning to the paper itself, I want to point out that considerable variation has been built into the ligands which are featured in Table I. The possible influence of steric effects and of differences in inductive effects of the organic radical bearing the carboxyl have been commented on in the paper. It is worth pointing out in addition, that the entries suggest that $Cr_{aq.}^{+2}$ as a reducing agent cannot take advantage of a conjugated bond system for electron transfer unless a suitable polar group is part of the system. Thus benzoato complex is not reduced more rapidly than the acetato complex for example. Earlier work showed that the crotonato complex also is reduced at an approximately normal rate. In work done by L. Bennett we have found no evidence of mediation by the conjugated bond systems when $V(bip)_3^{+2}$ is the reducing agent. This is true whether or not the conjugated bond system includes a polar group.

The entry for the glycinato complex, which in the acidic solution bears a proton, provides a measure of the effects produced by a positive charge close to the scene of reaction. The effect is not large, at least in the solutions of high ionic strength which are being used in the experiments.

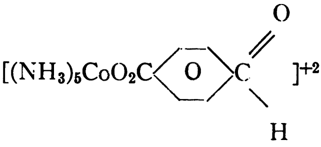
In considering attack by $Cr^{+2}$ at the carboxyl coordinated to Co(III), it is important to learn at which of the two oxygens attack occurs. But before considering how this might be done, we should settle the question as to whether or not the two oxygens are distinguishable. R. T. M. Fraser has recently interpreted infrared evidence as showing that the carboxyl is symmetrically bound, at least for certain cases, in the solid state. Work on the exchange of oxygen between carboxylatopentaamminecobalt(III) complexes and solvent done by R. B. Jordan and C. Andrade shows unambiguously that the oxygens are distinguishable in solution when the ligands are formate, trifluoracetate, or oxalate. With formate as the ligand, a single exchange half life is observed at high acidity; but when the concentration of $H^+$ decreases, there is marked curvature in the McKay plot consistent with the view that the two oxygens exchange at different rates. The data suggest further that a single oxygen is responsible for the exchange of the carboxyl oxygen with the solvent, and the other oxygen equilibrates by an interchange mechanism.

Though evidence for the dissimilarity of the two oxygens of a bound carboxyl has been obtained in each of the systems studied, important aspects of the observations are not reproducible. Thus, although all the data obtained with formate as ligand show that at low acidity one oxygen exchanges less rapidly than the other, the exchange half times for the slower oxygen differ a great deal between experiments. The interchange process is apparently subject to some kind of catalysis, but we have not yet discovered the nature of the catalyst.

A system which is very instructive in considering the factors that may affect the rate of reaction by adjacent attack is $Cr_{aq}^{+2}$ reacting with $[(NH_3)_5$-  $CoO_2C\langle O \rangle N^+CH_3]^{+3}$. As shown by E. S. Gould, and by Dr. Fraser and Peters, the rate of reaction is perhaps five to six times more rapid than it is in the normal cases. Yet attack at the terminal N seems very unlikely. We may be dealing here with an example in which electron transfer takes place to the ligand forming a radical ion. Since electron transfer is not to the Co(III) center, the process is not governed by the rates which apply in the case of acetate or trifluoracetate as ligand. The experiment suggests very strongly that even when we are dealing with adjacent attack, the radical attached to the carboxyl group can profoundly affect the rate of electron transfer. It shows that one must be very cautious in drawing conclusions about the position of attack from rate comparisons.

I have nothing further to add to the discussion of the effects arising when a chelating function is built into the bridging ligand except to report that D. Huchital, who is investigating the reaction of the malonate half ester complexes with the pentaamminecobalt(III) center with reducing agent, finds no evidence for ester hydrolysis when $V^{+2}$ or $Eu^{+2}$ is used. This contrasts with Dr. Fraser's report for the succinate half ester complexes reacting with the same reducing agents.

The third part of the paper is concerned with complexes containing ligands which have conjugated bond systems connecting two polar groups. An important question here is whether the reducing agent attacks at an adjacent, or remote carboxyl group. As I mentioned earlier, one must be cautious in basing conclusions solely on rate arguments. Experiments in which the reaction products are investigated can, in certain cases, provide direct evidence on the point at issue. One type of experiment of this kind involves the search for ester hydrolysis. Evidence for remote attack based on this kind of experiment was reported by Dr. Fraser and myself in 1959 and subsequently, other systems have been described by Dr. Fraser. We are having trouble with the subject now. James Hurst has been trying to build on the earlier work and has repeated some of the experiments with the methylfumarato complex but has not observed ester hydrolysis.

The case for remote attack, however, does not rest solely on these experiments, and I will outline some others which suggest that remote attack does take place in certain systems. D. LaFollette has re-examined the chemistry of the reaction of Cr$^{+2}$ with  , and has confirmed and stated quantitatively the result reported earlier (4), that in this case the ligand is not bound to Cr$^{+3}$. He finds that the ligand can be recovered completely by solvent extraction and has shown furthermore, that when the ligand is actually entrapped by Cr$^{+3}$, the rate of dissociation is small. These results mean that Cr$^{+2}$ does not attack the adjacent carboxyl, and it is reasonable to suppose that the position of attack is at the carbonyl. A carbonyl function coordinated to Cr$^{+3}$ is expected to be lost rapidly by aquation. It is interesting that when the carbonyl is meta to the carboxyl, about 50% of the ligand is again formed free in solution, and the remainder is bound. Thus, it appears that electron transfer can take place between meta positions although the rate is much less than when the carbonyl is para to the carboxyl. The total specific rate for the reduction of the meta formyl benzoato complex is only 0.15 $M^{-1}$ sec.$^{-1}$

The effect of H$^+$ on the rate of reduction of complexes of the class under present discussion needs further consideration. The suggestion has been made that the path first-order in (H$^+$) indicates remote attack. This suggestion was based on what seemed to be the only reasonable interpretation of the fact that H$^+$ is involved in these systems, but not in those in which simple carboxylates act as ligands, namely that the proton associates with H$^+$ on the adjacent carbonyl, thus redistributing the double bond and improving conjugation between the two polar groups. But it is also possible that the proton is situated on the remote carboxyl, or elsewhere apart from the adjacent, and by virtue of its positive charge facilitates electron transfer to the ligand by adjacent attack.

Finally—and I think the subject is becoming ripe for development on this level—let us turn to the question of the mechanisms by which electron transfer takes place. One important distinction is whether the electron transfers by a resonance mechanism or by a chemical one. Different observations can be made depending on this difference in mechanism. Perhaps one of the most significant is based on the fact that if there is resonance transfer, preparation for receiving the electron will be made at the Co(III) center, but if the electron transfers to the ligand, this kind of preparation at the metal ion center is not required. An experimental approach to distinguish between the two cases may be this: when Co(III) receives the electron directly, there may be a strong discrimination between the isotopes of oxygen in a bond such as Co—O—, but when rate-determining electron transfer takes place to the ligand, the isotopic discrimination may be much less.

**Jack Halpern:** I want to emphasize that the evidence obtained about the mechanisms of these processes is really of two kinds. There are the direct experiments that yield chemical evidence such as transfer of ligands or ester hydrolysis and so on, and the implications of these is often unequivocal. The other kind of evidence has to do with drawing inferences from the dependence of reaction rate on variation of ligands, and here we are on much less solid ground although I think potentially this approach is a powerful one. The problem is that there just is not a sufficient background of experience and data to assist us in interpreting these trends. Furthermore, the theory that we might use as a guide is also poorly developed and is a difficult subject to make progress on.

Until now most of the data we have had on systematic variation of ligands, or the effect of these variations on rate, have been with carboxylatopentaammine complexes. One reason for this is that these are among the slower reactions and have been more readily susceptible to kinetic studies.

More extensive data in other systems concerning the dependence of rate on ligand is being accumulated, and as yet we are far from understanding these, particularly in the bridged reactions. The subject of outer sphere reactions and the factors affecting the rate are in a somewhat better state.

One of the points that becomes clear as one probes further into this subject is that the way in which the rate of these reactions varies with ligand variation is specific not only to the class of ligands under investigation but also to the particular reaction. This is brought out clearly if one examines the various electron transfer reactions that have now been studied involving halides as bridging ligands. These data, normalized in each case with respect to the fluoro complex of the series are depicted in Figure A.

Confining ourselves for the moment to reactions known to go via inner sphere bridging mechanisms, namely those involving $Cr^{+2}$ and $Co(CN)_5^{-3}$ as reductants, the trend in each case is for the rate to increase along the series F < Cl < Br < I, the largest increase occurring in each case in going from F to Cl.

For most of the other reactions the mechanism is uncertain. Among these, the reduction of $Co(NH_3)_5X$ by $Fe^{+2}$ and $Eu^{+2}$ exhibit the reverse trend (—i.e., Br < Cl < F). We think, but are not certain, that these are inner sphere reactions.

On the other hand, the reductions by $V^{+2}$, for which the mechanism is uncertain, and the reduction by $Cr(dipy)_3^{+2}$, which presumably is outer sphere, follow the same trends as the inner sphere reductions by $Cr^{+2}$.

I think that we are a long way from understanding the effects of ligand on the rate well enough to interpret this picture in detail, or to predict it with any confidence without knowing the answers; but I do think this kind of data will move us toward a better understanding of what such trends imply.

I don't really have much to add on the subject of the mechanism of electron transfer through these conjugated systems. It is disappointing that this subject has not developed to a greater extent since L. E. Orgel and I attempted very inadequately to treat its theory. But both the theoretical and experimental aspects—finding the right systems that will give information about those parameters which can be used to test the theory—are very difficult and I think we will have to keep trying.

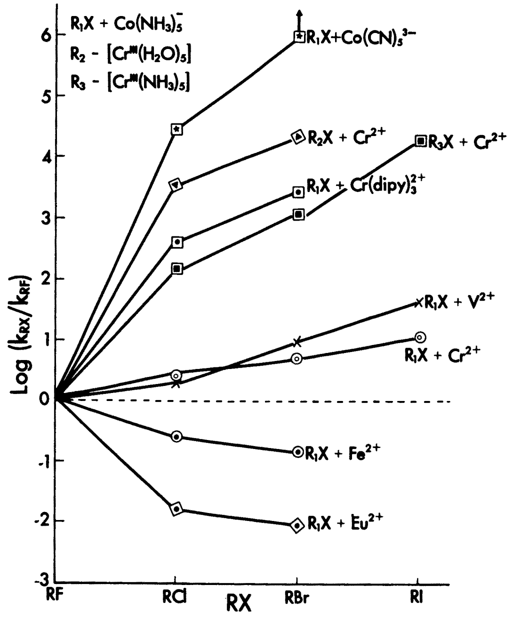
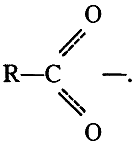


*Figure A. Plot of Log* ($k_{RX}/k_{RF}$) *vs. RX*

**R. T. M. Fraser:** The nature of the oxygens in the carboxylato group is interesting, and perhaps we should review the infrared evidence. In an ester or an organic acid, a frequency can be assigned to the C=O absorption and one to the —C—O—. J. V. Quagliano (*1*) has shown that the shift in these frequencies which occurs when the acid is complexed with a metal can be related to the changing nature of the bond: in the trisoxalatocobalt(III) complex, the Co—O— bond can be regarded as 50% ionic. When the acid is not chelated, the two frequencies coincide with those observed for the simple salt;



$$R-C\begin{matrix}/\!\!/O\\ \backslash\!\!\backslash O\end{matrix}\ -.$$

Our recent work shows that steric effects are important in electron transfer via bridging groups. For example, in the reduction of the carboxylatopentaammine-cobalt(III) complexes by Cr(II), the rate constants decrease as follows:

| *Ligand* | *k, $M^{-1}$ sec.$^{-1}$* |
|---|---|
| formato | 7 |
| acetato | 0.14–0.32 |
| butyrato | 0.08 |
| cyclopropanecarboxylato | 0.125 |
| cyclobutanecarboxylato | 0.05 |
| cyclopentanecarboxylato | 0.072 |
| cyclohexanecarboxylato | 0.04 |

*Figure B. Rate constants for the reduction of the carboxylatopentamminecobalt(III) complexes by Cr(II)*

(The two values reported for the acetato are interesting: the smaller is the literature value, the larger is the value that my Kansas colleagues have determined more recently.) We have not found any examples of lower rates for adjacent attack, and this limits the possibility of discovering remote attack by paths which are not very good electron conductors. If the remote attack is slower than the slowest adjacent attack, we will not be able to separate the two paths with any degree of certainty. To overcome this, we have replaced the carboxyl group with a nitrogen. The parent compound for the series thus becomes hexamminecobalt(III), with a rate constant of $9 \times 10^{-5}\ M^{-1}\ \text{sec.}^{-1}$ for the Cr(II) reduction. Now it is possible to study ligands where the constant for remote attack lies below 0.04, and results so far have been very exciting (*3*). For example, with reference to electron transfer between meta positions, the rate constant at 25°C. for the Cr(II) reduction of the ethyl nicotinate-*N*-pentaamminecobalt(III) ion is $1.5 \times 10^{-2}\ M^{-1}\ \text{sec.}^{-1}$ which yields a rate constant of $6.7 \times 10^{-6} < k < 3 \times 10^{-4}\ M^{-1}\ \text{sec.}^{-1}$ for remote attack in the nicotinatopentaamminecobalt(III) system.

**D. E. Peters:** Dr. Taube and Dr. Gould have presented evidence for electron transfer at a nitrogen site (*5*). Using pentaamminecobalt(III) complexes of various pyridine carboxylic acids these workers found two paths in the rate expression which they call the acidic and basic paths. For the alkylpyridinium complexes, namely the *N*-methyl derivatives, only one term in the rate was found.

At the 145th ACS meeting in New York, September 1963, Dr. Fraser and coworkers reported observing an increase in rate with increasing pH for the *N*-methyl derivative as well as for the pyridine-4-carboxylato complex as shown in Figure C. We recently have found similar behavior for the pyridine-2-carboxylato complex and its *N*-methyl derivative. In view of the acid dependency found for the *N*-alkyl pyridinium derivatives of these complexes, it does not seem likely that the acid dependency of the reaction can be explained merely by acidic and basic forms of the complex since the *N*-alkyl pyridinium derivatives do not possess such a basic form.

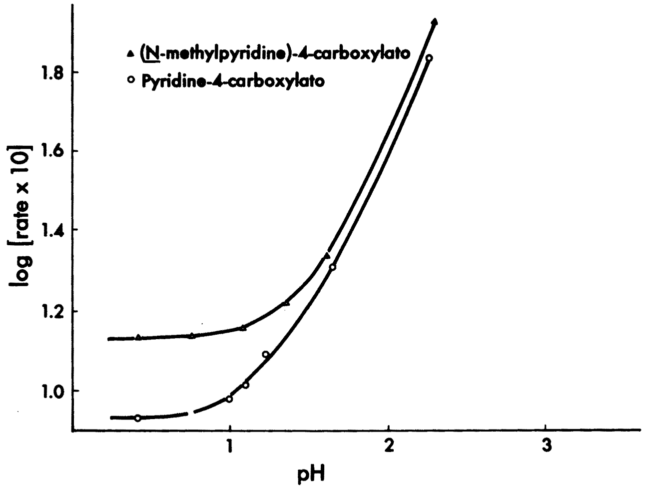


*Figure C. Log of rate constant vs. pH*

**James H. Espenson:** I would like to comment about some of the rates that Prof. Halpern referred to.

We have recently studied iron(II) ion as a reducing agent with some cobalt(III) complexes, as have some other investigators. Our rates are in at least qualitative agreement with those obtained by others. In the series of reactions of halopentaamminecobalt(III) ions with iron(II), the highest rate occurs with the fluoride; this is the same trend cited by Dr. Halpern.

Another interesting point is the relative rates of the reactions of the azido and thiocyanatopentaammines. The relative rates of these two reactants with iron(II) ion are similar to those with chromium(II), that is, the azido is four to five powers of ten more rapid than is the thiocyanato. I am suggesting that this might be a criterion for inner sphere activated complex as opposed to an outer sphere complex. With trisdipyridylchromium(II) ion, which must react via an outer sphere process, the azido and thiocyanato rates are relatively comparable, and the same also for vanadium(II) ion which also probably procedes via an outer sphere activated complex.

I would appreciate Dr. Halpern's comments on whether he thinks this provided a valid criterion for inner sphere reactions in those cases.

**Dr. Halpern:** This criterion cannot be completely valid since I can cite one example, namely the reductions of $Co(NH_3)_5NCS^{+2}$ and $Co(NH_3)_5N_3^{+2}$ by $Co(CN)_5^{-3}$, which involves inner sphere electron transfer accompanied by ligand transfer. In this case both complexes react at approximately the same rate.

I think this points to one of the factors involved in determining the rates of inner sphere electron transfer, and perhaps I should have commented on this in connection with the data I cited earlier. In an electron transfer reaction accompanied by the transfer of a ligand X from cobalt(III) to chromium(II), we are breaking a bond between the ligand and cobalt and forming a bond between the ligand and the chromium. The thermodynamic trend is certainly among the factors influencing the rate of electron transfer.

I think this would provide at least a partial explanation of some of these different trends. For example, the large rate increase with $Co(CN)_5^{-3}$ as reductant in going from $Co(NH_3)_5F^{+2}$ through to $Co(NH_3)_5Br^{+2}$ is in line with the favored thermodynamic trend with respect to the stability of both the bond being broken and that being formed.

On the other hand, the reverse trends exhibited by $Eu^{+2}$ and $Fe^{+2}$ as reductants imply in part that we are gaining more from the increasing stability of the bond being formed as we go from Br to F than we are losing from the stability of the bond being broken. I think this is also pertinent to the question of comparison of azido and thiocyanato complexes. With $Co(CN)_5^{-3}$ as reductant, the stable form of the product complex is sulfur-bonded, so that the orientation of the ligand in the oxidant is favorable for remote attack on the sulfur end, whereas the situation is unfavorable for $Cr^{+2}$ and $Fe^{+2}$ as reductants.

This points to one of the great weaknesses in our understanding of this subject, namely our lack of knowledge of the thermodynamics of many of these processes. This is difficult to come by because many of these redox steps are not reversible; hence we cannot obtain thermodynamic data in the usual way from equilibrium studies and must instead resort to thermochemical measurements of which we need more.

**Robert G. Linck:** I would like to point out a correlation that I have found by considering some of the data reported in the literature.

If one looks at models of these carboxylatopentamminecobalt(III) complexes—we are concerned with just the simple acetates at the moment—and puts a pentaquochromium(II) ion onto the carbonyl oxygen, there is very little difference in steric hindrance in the various complexes as the carboxylic acid is varied. This suggests that the differences in rate constants are determined principally by electronic effects.

Unfortunately, there are only five rate constants for simple acetato complexes reported (*2*, *8*). However, a plot of the log of these rate constants *vs.* R. W. Taft's $\sigma$-parameter (*7*), which is a measure of electronic effects only, gives an extremely good correlation (Figure D).

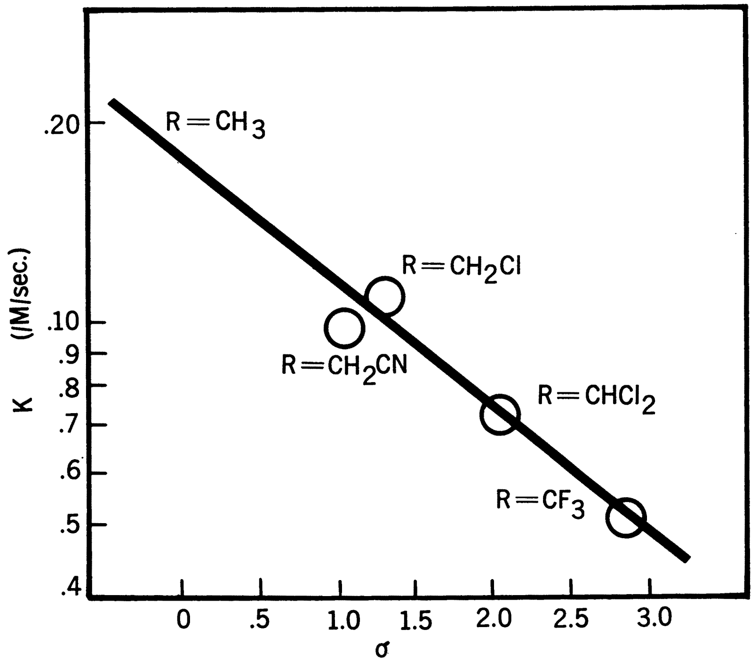
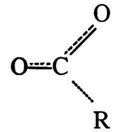


*Figure D. k vs.* $\sigma$ *for* $(NH_3)_5Co{-}OOCR^{+2}$

I propose that possibly steric effects are unimportant in these reactions but that electron density on the two oxygens is important. If one does a simple Hückel treatment of the system



and varies the $\alpha_0$ in accordance with the $\sigma$-parameter, a qualitative agreement is found between the data and the theory of Dr. Halpern and Dr. Orgel (*6*). This agreement may be fortuitous considering the crude calculations, but I think it is worth extending the investigation of acetato complexes, chosen to include a wider range of $\sigma$-values, in order to determine whether or not the correlation does hold.

**Harry Gray:** Two points in Prof. Taube's paper quoted as experiments in progress haven't been mentioned. Both are concerned with the mechanism of electron transfer, because the transmission in the ligand, wherever the attack is, is through the $\pi$-system, and in cobalt(III) in the $\sigma$-system. This is probably the reason that Prof. Taube has suggested there may be a detectable radical ion intermediate, because of the improbability of resonance transfer from $\pi$ to $\sigma$. The experiment to test this, of course, is the electron resonance experiment in which one tries the reduction by chromous and looks for the ESR signal of the radical ion.

The other point is that if one is going to see resonance transfer as Libby suggested, one would investigate the $\pi$-to-$\pi$-system, the first case being $d^5$ low spin which has a hole in the $\pi$-orbital level. There probably wouldn't be any hold up in resonance transfer mechanism in ruthenium(III) complexes.

**Dr. Taube:** We have been held up in the work on ruthenium(III) because we have had difficulty with the rapid flow apparatus.

**John P. Hunt:** So far we have not seen any organic free radicals in these experiments. We have looked mainly at the maleatopentammine Co(III) system's reacting with chromium(II) and vandium(II). In the chromium system this problem is complicated by a large chromium(III) ESR signal. In the case of vanadium, we sometimes see small traces of vandium(IV) form which we don't completely understand.

We have also tried to look directly at the reduction of some organic substances such as *p*-nitroaniline which can be reduced electrolytically to a very stable free radical, and with either vanadium(II) or chromium(II) we cannot see this free radical.

We think, however, that this certainly doesn't mean that there aren't any free radicals; it means that the detection of these free radicals is going to be very difficult in these metal ion systems. We have to use flow techniques, oxygen-free solutions, and things of this sort in order to do it, and it's rather difficult.

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## 6

# Oxidation or Reduction of Ligands by Metal Ions in Unstable States of Oxidation

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**Oxidation and reduction of ligands owing to an interaction with their central atom have been reviewed. These reactions were divided into two major groups: (a) Reactions in which the interaction between a ligand and a central atom results in the formation of an unstable complex which undergoes a monomolecular change in the oxidation state of the central atom, yielding a modified ligand. (b) Cases in which a stable metal-ligand system undergoes a change in the oxidation state of the metal atom on interaction with another reagent. This is followed by an interaction between the metal atom and its ligand. As a result of this process the metal ion may be recovered either in its initial or in a different stable state of oxidation.**

The electronic interaction between cations and ligands is well known to affect the reactivity of the former in redox reactions with other reagents, including the solvent and ligands themselves (*17*, *28*, *43*, *80*). The formation of $\sigma$-bonds with the ligand stabilizes higher states of oxidation of the central atom, whereas $\pi$-orbital interactions may increase the stability of lower states of oxidation (*74*, *79*, *80*). If the electron affinity of the ligand bound to a central atom at its higher state of oxidation is not large enough, it will eventually be oxidized; alternatively, if its electron affinity is substantially higher than that of the central atom, the oxidation of the latter may take place.

The definition of stability of an oxidation state of a given atom is meaningless without referring to its immediate environment. Any ligated metal atom which undergoes a redox process with its ligands at a measurable rate is here defined as being in an unstable state of oxidation. This is somewhat broader than the conventional thermodynamic definition which uses water, both solvent and ligand, as its point of reference.

This paper will review cases in which the stability of the oxidation state of the ligated central atom is limited by the redox instability of the ligand. The stability of the central-atom–ligand system will be referred to in terms of reaction kinetics, rather than from the standpoint of a change in free energy. In other words, the stability of a system, as defined here is limited by the mechanism of its redox reaction. This may determine its lifetime from infinity down to the microsecond region where the existence of the unstable ligated system may be inferred only by indirect evidence. It should be noted however, that any unstable system referred to is a metal-ligand complex which includes all partition functions and is in equilibrium with its precursors, and it should be distinguished from an activated complex of any kind. Metal-ligand systems which undergo reversible redox reactions while at equilibrium, are still defined as being in unstable states of oxidation.

It should be emphasized here that the existence of a stable complex between a metal ion at a given state of oxidation and a ligand is not necessarily a prerequisite for the two species to form a complex in the transition state. Moreover, it is very likely that the activated complex of the transition state substantially differs in its configuration from the stable metal-ligand complex. It is obvious that a metal–ligand complex may, in many cases, have a higher probability of undergoing the appropriate changes to an activated complex. On the other hand, in some cases the formation of a metal-ligand complex will inhibit the interaction of the two species to give the configuration of the activated complex. In such cases one may consider the two processes of forming the stable and activated complexes as two independent competing processes, rather than two consecutive reactions.

In general, ligands do have to undergo a two equivalent change in their state of oxidation before reaching a stable state, whereas metal ions, in most cases, may change their state of oxidation in single equivalent steps without forming intermediates of extremely high reactivity. This difference in the redox behavior between central atoms and ligands results in the great complexity of redox interactions between the two species. Polyatomic ligands may also undergo redox reactions which involve bond cleavage in the ligand group, and which are not electron transfer processes in the narrow sense.

A given central atom-ligand system may be formed in four different ways: first, by substitution of another ligand of the central atom (1); second, by a change in the coordination number of the central atom, owing to its conversion to a different state of oxidation (2); third, by a chemical change in a bound ligand which is converted to a different chemical species without cleavage of the metal-ligand bond (3); and finally, by a change in the oxidation state of the central atom (4).

$$\mathrm{MX + L \rightarrow ML + X} \tag{1}$$

$$\mathrm{MX_n + L \rightarrow MX_nL} \tag{2}$$

$$\mathrm{ML + X \rightarrow ML' + Z} \tag{3}$$

$$\mathrm{M^{+a}L + X \rightarrow M^{+b}L + Z} \tag{4}$$

In our notation only the ligand, L, which takes part in the redox process will be included, whereas other ligands of the same central atom will not be denoted.

There are two major routes of formation of an unstable metal-ligand system: (a) The metal ion in its given state of oxidation interacts with the ligand to give an unstable system (via Mechanisms 1 or 2). (b) The metal-ligand system is stable to begin with, and only by reacting with a third reactant undergoes a change in its oxidation state which converts it to an unstable system. The change in the oxidation state may occur either in the central atom (Mechanism 4), or primarily in the ligand (Mechanism 3).

If the metal-ligand unstable system formed by the third reactant breaks down instantaneously, resulting in a change in the oxidation state of the central atom, one encounters the well known ligand-catalyzed redox reactions (*48*, *86*). Since this paper is concerned with changes in the oxidation state of ligands, the ligand-bridged redox reactions are not within its scope.

Unstable systems formed in aqueous solutions by both routes will be discussed in this review. However, special reference will be made to systems formed by the last two mechanisms, including some recent results from the author's laboratory. We do not intend to include all the cases reported on oxidation or reduction of ligands, but rather to systematize the different reaction mechanisms.

### *Unstable Systems Formed by the Interaction of Ligands with Metal Ions in "Stable" States of Oxidation.*

As stated above, we will refer here to reactions of the type

$$MX_{(stable)}^{+a} + L \rightarrow X + ML_{(unstable)}^{+a} \rightarrow M^{+b} + P \qquad (5)$$

where X may be any ligand, including water, L, a ligand liable to undergo a redox process by $M^{+a}$, and P, the product of L after reaction. $MX^{+a}$ may eventually also undergo a redox reaction to form $M^{+b} + Z$. However, as long as this reaction is much slower than the rate of formation of $ML^{+a}$, $MX^{+a}$, in the presence of L, may still be referred to as a "stable" system. This statement is true of the aquo complexes of transition metal ions in their higher or lower states of oxidation—e.g., Co (III), Mn(III) or Cr(II), V(II), Ti(III), respectively.

**Oxidation of Ligands.** Reactions of the type

$$M^{+a} + L \rightleftharpoons ML^{+a} \rightarrow M^{+(a-1)} + P \qquad (6)$$

will proceed from left to right if the rate of the reverse reaction R' $= k'(M^{+(a-1)})$ (P) is smaller than the forward reaction, R $= k(ML^{+a})$. In other cases $ML^{+a}$ may be considered as a thermodynamically stable species. The removal of P by a third reagent will obviously shift the equilibrium of Reaction 6 to the right, making R the rate-determining step. Taking, for example, water as a ligand, one encounters equilibrium reactions of the type

$$M(H_2O)_n^{+a} \rightleftharpoons M(H_2O)_{n-1}^{+(a-1)} + H^+ + OH$$

or

$$M(H_2O)_n(OH)^{+a} \rightarrow M(H_2O)_n^{+a} + OH$$

which may be shifted to the right by reagents which react with OH in preference to $M(H_2O)_{n-1}^{+a-1}$. This mechanism has been suggested for the reduction of Ce(IV) by thallous ions (*48*).

In most cases the equilibrium of Reaction 6 lies either far to the left or far to the right. In the special case of balanced equilibrium, Reaction 5 may be shifted to the right even by small changes in the environment of the given system, such as a change in ionic strength, which was shown to affect the equilibrium (*36*),

$$IrBr_6^{-2} \rightleftharpoons IrBr_5^{-2} + Br$$

Water and $OH^-$ ions have been shown to be oxidized to form oxygen following Mechanism 6. This mechanism has been postulated in the case of Co(III) (*19*), and of Cu(III) ions (*4*). In the latter case it was shown by competition kinetics that OH radicals are the primary products of decomposition of $H_2O$ by tervalent copper in acid solution (*4*).

Oxidation reactions by ferric ions have been shown, with very few exceptions (*20*), to proceed by a mechanism involving the formation of a complex with the oxidized ligand,

$$Fe(III) + L \rightarrow Fe(III)L \rightarrow Fe(II) + P$$

This includes the oxidation of sulfite (*56*) and of hydrogen peroxide (*45*, *65*), as well as the oxidation of organic ligands like acetylacetonate (*16*, *72*). The reaction of chromic ions with hydrogen peroxide has been also claimed to proceed via Mechanism 5 (*93*). Analogous to the behavior of ferric ions (*56*), the reduction of $Cu^{+2}$ by sulfite ions (*89*) very likely proceeds by

$$Cu(II)SO_3 \rightarrow Cu(I) + SO_3^-$$

Another oxidation reaction of the same type is that of bromide ions by Ce(IV) which was shown to proceed via $Ce(SO_4)_2Br^-$ and $Ce(SO_4)_2Br_2^{-2}$ as intermediates (*59*).

The mechanism of oxidation of organic ligands is rather similar to that of inorganic ligands. The oxidation of various organic compounds by transition metal ions was shown, with only few exceptions (*6*, *50*), to involve the participation of the organic substrate as a ligand.

A classical case in the field of oxidation of organic ligands is the decomposition of the manganic oxalate complexes (*31*, *84*, *85*)

$$Mn^{+3} + C_2O_4^{-2} \rightleftharpoons MnC_2O_4^+ \rightarrow Mn^{+2} + C_2O_4^-$$

$$Mn(C_2O_4)_2^- \rightarrow Mn(C_2O_4) + C_2O_4^-$$

Similar mechanisms were postulated for the oxidation of glycols by periodate (*32*) and Ce(IV) (*33*, *34*), and for the oxidation of glycerol by Ce(IV) (*44*). In these cases the existence of intermediate complexes was demonstrated. The oxidation of formaldehyde by Ce(IV) was also claimed to involve a pre-equilibrium of a Ce(IV)–formaldehyde complex (*51*). A similar complex was postulated in the formaldehyde-$MnO_4^-$ reaction (*49*, *87*). The oxidation of isopropyl alcohol by chromate ions follows a similar mechanism, and a chromate ester was formed as intermediate (*94*).

The oxidation of aniline by $Cu^{+2}$ (*60*), which was claimed to proceed completely analogous to Reaction 5, is an example of Cu(II) as the oxidant.

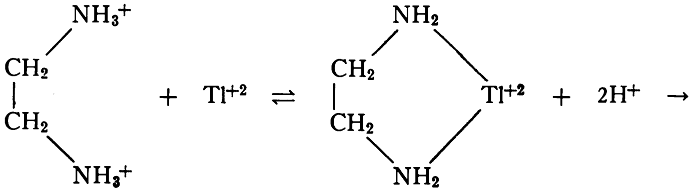
$$PhNH_2 + Cu^{+2} \rightleftharpoons PhNHCu^+ \rightarrow Cu^+ + PhNH \rightarrow PhNH{=}HNPh$$

Similar mechanisms were postulated for the $Cu^{+2}$—catalyzed oxidations of methyl benzoin, ascorbic acid, (*7*) and various other reducing ligands (*39*).

Finally we will refer to oxidation reactions by $Tl^{+2}$ ions. These ions are formed under radiolytic conditions from thallous ions

$$Tl^{+} + OH \rightarrow Tl^{+2} + OH^{-}$$

Tl(II) ions were shown to oxidize selectively ethylenediamine (*10*) and glycine (*7*), rather than undergo disproportionation.



$$\rightarrow Tl^{+} + NH_2CH_2CH_2{}^{+}NH_2 \rightarrow NH_2CH_2CHNH_2 + H^{+}$$

This reaction is analogous to the $Mn^{+3}$ oxalate reaction (*84*), except that the $Tl^{+2}$–ethylenediamine complex is less stable, and the metal-catalyzed reaction is completely inhibited in acid solutions, and by the addition of competing ions like $Zn^{+2}$.

A special group of reactions which may be classified in this section is represented by the general formula

$$ML^{+a} + Y \rightarrow MLY^{+a} \rightarrow M^{+(a-1)} + LY^{+} \qquad (7)$$

In many cases of this type $ML^{+a}$ would decompose spontaneously, but at a much slower rate. The function of Y is to stabilize the free radical formed from the ligand following a single electron transfer to the central atom. It is assumed here that a L—Y bond is formed in the rate-determining step, and it is the interaction of Y with the ligand, and not with the central atom, which characterizes this group of reactions.

The oxidation of iodide by Fe(III) (*41*) follows the pattern of Mechanism 7

$$FeI^{+2} + I^{-} \rightarrow Fe^{+2} + I_2^{-}$$

and so does oxidation of iodide by $Co(NH_3)_5I^{+2}$ (*95*). The analogous oxidation of thiocyanate by Fe(III) (*21*), and the reaction of ferric azide with azide radicals (*30*), are other examples. The reduction of $Co(NH_3)_5I^{+2}$ by iodine atoms, methyl, and hydroxy radicals to form Co(II) + $I_2$, MeI, and IOH, respectively (*46*), also follow the same mechanism. The fact that Y reacts directly with L is suggested by the formation of MeI, rather than MeOH, which would be formed by the reaction of Me· with the cobalt complex as a whole. Further evidence for direct reactions between oxidants and bound ligands may be inferred from the products of the reaction between $Co(NH_3)_5I^{+2}$ and hydrogen peroxide (*47*).

In the oxidation of bromide by thallic ions a double electron transfer from the central atom to two separate ligands was postulated (*27*)

$$TlBr_2^{+} \rightleftharpoons Tl^{+} + Br_2.$$

The same results may be interpreted by a double electron transfer to a single ligand, which seems more plausible from the kinetic standpoint

$$TlBr^{+2} + Br^- \rightleftharpoons Tl^+ + Br_2$$

Similarly, the $TlBr_3$ term in the same study (*27*), may be interpreted as

$$TlBr_2^+ + Br^- \rightleftharpoons TlBr + Br_2 \rightleftharpoons Tl^+ + Br^- + Br_2.$$

**Reduction of Ligands.** In contrast to the many systems where the oxidation of a ligand by the central atom could be demonstrated, there are relatively few examples of unstable metal-ligand systems that result in the reduction of the ligand

$$M^{+a} + L \rightarrow ML^{+a} \rightarrow M^{+(a+1)} + L^{-1} \qquad (8)$$

As examples, one can cite the autoxidation of Fe(II) to Fe(III) in aquo and complexed forms (*42*, *49*),

$$Fe(II)X + O_2 \rightleftharpoons Fe(II)XO_2 \rightarrow Fe(III)X + O_2^-.$$

The Co(II)-catalyzed autoxidation of cystein, where a $CoXO_2$ complex was claimed to be formed as intermediate (*69*), is another example.

Fission of the ligand molecule may take place during the redox process of the metal-ligand system. This is generally true of systems in which the ligands are bound to the metal through an oxygen atom.

$$M^{+a} + YO \rightarrow M^{+a}OY \rightarrow MO^{+a} + Y \qquad (9)$$

$$\text{or} \qquad MO^{+(a-1)} + Y^+$$

This mechanism can be illustrated by the reaction of ferrous ions with hydrogen peroxide (*42*), the reduction of organic peroxides by cuprous ions (*63*), as well as by the reduction of perchlorate ions by Ti(III) (*35*), V(II) (*58*), Eu(II) (*71*). The oxidation of chromous ions by bromate and nitrate ions may also be classified in this category. In the latter cases, an oxygen transfer from the ligand to the metal ion has been demonstrated (*8*). As analogous cases one may cite the oxidation of $Cr(H_2O)_6^{+2}$ by azide ions (*15*) (where it has been demonstrated that the Cr—N bond is partially retained after oxidation), and the oxidation of $Cr(H_2O)_6^{+2}$ by *o*-iodobenzoic acid (*6*, *8*), where an iodine transfer was shown to take place.

### *Unstable Systems Formed by the Interaction of Stable Metal Ligand Systems with Oxidants or Reductants.*

The interaction of a stable system with an oxidant or a reductant may produce an unstable system. Considering unstable systems in which only the central atom undergoes a redox change, the comprehesive reviews of Taube (*86*), Halpern (*48*) and Sutin (*83*), may be consulted. Our discussion is limited to unstable systems, the *ligands* of which are undergoing a redox reaction. The reactions discussed here will be classified according to the inducing reactants, namely oxidants and reductants. Another criterion of classification will be whether the central atom undergoes a redox change simultaneously with the ligand.

**Oxidation of Stable Systems not Involving a Permanent Change in the Oxidation State of the Central Atom.** The two possible overall mechanisms for this type of oxidation reaction may be formulated as follows:

$$ML^{+a} + X^{+b} \rightarrow ML^{+(a+1)} + X^{+(b-1)};\ ML^{+(a+1)} \rightarrow M^{+a} + L^{+} \qquad (10)$$

$$ML^{+a} + X \rightarrow MLX^{+a} \rightarrow M^{+a} + XL \qquad (11)$$

(X is not a metal ion).

The intermediate of Reaction 10 may be considered as being in a formal higher state of oxidation. In Reaction 11 a kind of bridged complex via the oxidized ligand is formed, and one may consider this mechanism as a direct oxidation of the ligand by the oxidizing agent. The rate of the latter oxidation may be different from that of oxidizing a free ligand, just as the rate of redox reactions of the central atom are affected by ligands (*86*).

Starting with examples of Mechanism 10 in inorganic chemistry, one may cite the oxidation of cuprous thiosulfate by ferric, vanadate, molybdate, and chromate ions (*38*).

$$CuS_2O_3^- + M^{+a} \rightarrow M^{+(a-1)} + CuS_2O_3 \rightarrow Cu^+ + S_2O_3^- \rightarrow S_2O_6^{-2}$$

Mechanism 10 has been demonstrated in the oxidation of $Co(NH_3)_5I^{+2}$ by Ce(IV), Co(III), and eventually Fe(IV) (*46*).

$$Co(NH_3)_5I^{+2} + Ce(IV) \rightarrow Ce(III) + Co(NH_3)_5I^{+3} \rightarrow Co(NH_3)_5^{+3} + I\cdot$$

The oxidation of $Co(NH_3)_5I^{+2}$ by double electron transfer oxidants, like $H_2O_2$, proceeds according to Mechanism 11 where the formation of IOH at an intermediate stage has been demonstrated (47).

In the field of organic ligands the oxidation of oxalic acid ligated to different central atoms provides us with almost any pattern of behavior of oxidized ligands. The oxidation of oxalate by permanganate in the presence of manganous ions (*1*, *68*) proceeds according to Mechanism 10

$$Mn^{+2} + C_2O_4^{-2} \rightleftharpoons MnC_2O_4$$

$$MnC_2O_4 + MnO_4^- \rightleftharpoons MnC_2O_4^+ + MnO_4^{-2}$$

$$MnC_2O_4^+ \rightarrow Mn^{+2} + C_2O_4^-$$

This contrasts with the behavior of $Cl_2$ as oxidant in the same system (*84*), where $Mn^{+3}$ was shown to be first formed, and only subsequently forming the $MnC_2O_4^+$ and $Mn(C_2O_4)_2^-$ complexes.

Since the oxidation of oxalic acid involves the transfer of two electrons before forming a stable product, the oxidized intermediate may either break down to give a $C_2O_4^-$ radical, or it may be long lived enough to undergo a second reaction with the oxidant. The latter mechanism has been demonstrated in the oxidation of chromic oxalate by ceric ions (*88*).

$$Cr(C_2O_4)_2^- + Ce(IV) \rightarrow Cr(C_2O_4)_2^{\circ} + Ce(III)$$

$$Cr(C_2O_4)_2^{\circ} + Ce(IV) \rightarrow Cr(C_2O_4)_2^+ + Ce(III)$$

$$Cr(C_2O_4)_2^+ \rightarrow Cr(C_2O_4)^+ + 2CO_2$$

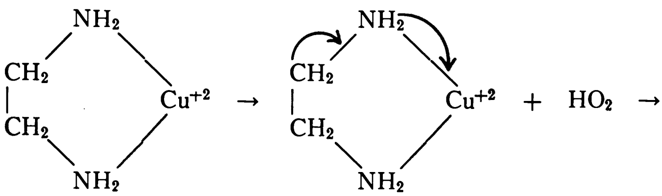
If the oxidant is a double equivalent reactant like $H_2O_2$ or $Cl_2$, the oxidation of oxalate takes place without the formation of any long lived intermediate. This has been demonstrated in the oxidation of $Co(NH_3)_5(C_2O_4)^+$ by $H_2O_2$, where $CO_2$ and

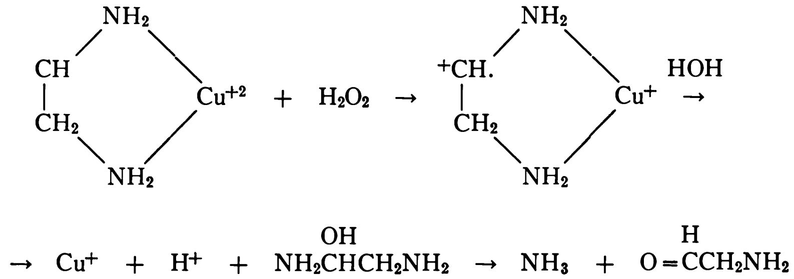
$Co(NH_3)_5H_2O^{+3}$ are produced (*81*). The formation of an intermediate of the type $Co(NH_3)_5(C_2O_4)^{+2}$ would result in the fast reduction of the Co(III) (*81*). If this oxidation proceeds by two fast, consecutive steps, it is hard to decide between a Co(IV) as central atom of the short lived intermediate and a partially oxidized oxalate radical ligated to Co(III). An analogous behavior has been observed in the oxidation of *p*-aldehydobenzoate ligated to cobalt, by double electron transfer reactants (*40*).

Special consideration will be given to the interaction of Cu(II) complexes with oxidizing agents yielding oxidized ligands. Since part of the available information has not yet appeared in print, the experimental findings will be described in more detail.

It was found that copper ions sensitize the radiolytic oxidative deamination of diamines (*10*, *12*), and glycine (*7*). This effect was shown as caused by the interaction of $HO_2$ radicals with the amine–copper complex. The implications of these findings to radiobiology have been discussed elsewhere (*3*). It was further found that copper ions catalyze the oxidative deamination of ethylenediamine and glycine by $H_2O_2$ in alkaline solutions (*7*). Similar results were obtained for histidine and glutamic acid (II). The addition of isopropyl alcohol, in amounts equivalent to those of the ethylenediamine, does not affect the extent of deamination. In the presence of ferrous ions an extensive deamination is also observed, but it is completely suppressed by the addition of isopropyl alcohol (*7*). This indicates that the latter deamination is caused by the action of OH radicals (*10*). Ferric ions, in the presence of $Cu^{+2}$, enhanced the deamination extensively, but this effect was not suppressed by isopropyl alcohol. The $Fe^{+3}$–$H_2O_2$ reaction results in the formation of $HO_2$ radicals, which induce the copper-catalyzed reaction. $Co^{+2}$ ions were found to have a catalytic effect similar to that of $Cu^{+2}$ on the oxidative deamination. Other ions examined including $Mn^{+2}$, $Cd^{+2}$, $Zn^{+2}$, $Au^{+3}$, and $Ag^{+}$ did not show any catalytic effect on the oxidation reaction. When the latter ions were present together with $Cu^{+2}$, they inhibited the catalytic reaction as they competed for the ligand (*7*). Reducing agents including iodide, sulfite, and ferrocyanide did not induce any deamination in the presence of $Cu^{+2}$. It was further found that $Cu^{+2}$ also catalyzes the oxidative deamination by chloroiridate (IV) and by hypochlorite (*7*).

The $Cu^{+2}$–catalyzed oxidation by $HO_2$ radicals could be interpreted by assuming that the chelating ligand tends to undergo hydrogen abstraction by a free radical faster than the free ligand. This would be caused by a partial withdrawal of electrons from the ligand, followed by a weakening of the C–H bonds. The hydrogen abstraction would then be followed by a reduction of the Cu(II) to Cu(I) and the formation of glycinealdehyde.



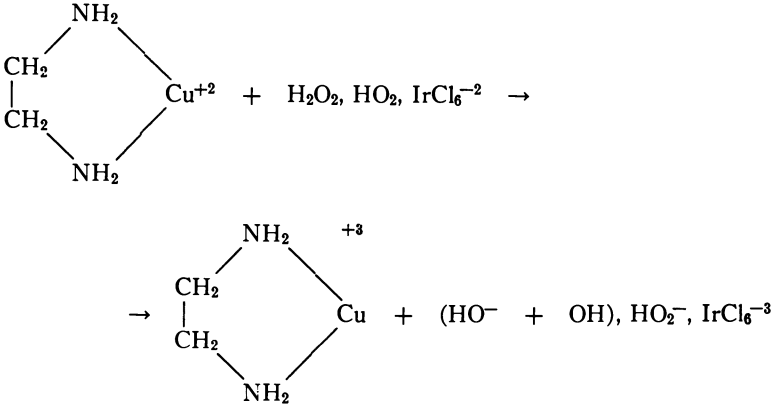


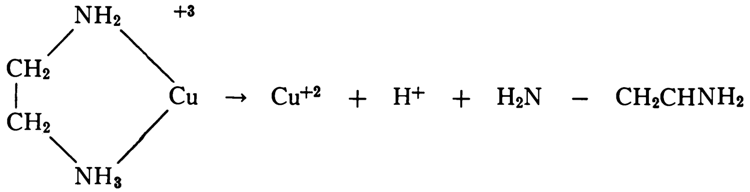
This mechanism is inconsistent with the following facts: First, no effect is observed when $Cu^{+2}$ is replaced by $Zn^{+2}$ or $Cd^{+2}$, which should have the same inductive effect on the electrons of the ligand. Second, in view of the extremely low redox stability of Cu(I) bound to the same ligands (*52*, *57*), it is not likely that Cu(II) should undergo partial reduction by the ligand–i.e., that the electron withdrawal by Cu(II) should exceed that induced by $H^+$ or other cations. Finally, no increased reactivity of the copper bound ligand towards OH or H radicals has been observed (*10*). These radicals are known to react with aliphatic compounds via hydrogen abstraction.

The deamination by $HO_2$ or $H_2O_2$ cannot be the result of a reduction of Cu(II) as the corresponding Cu(I) complexes of ethylenediamine or glycine, which are unstable (57), undergo disproportionation to Cu° and Cu(II) without affecting the ligand (*52*); moreover, reagents which do reduce $Cu^{+2}$ to $Cu^+$ did not induce deamination.

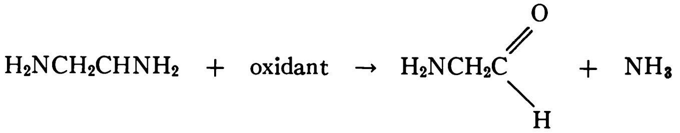
A hydride transfer from the methylene group to the copper ion followed by the oxidation of the latter by the oxidizing agent is also unlikely, in view of the fact that the deamination reaction is not affected by the addition of nucleophiles like chloride ions, which would be expected to interfere with a pre-equilibrium involving hydride ions.

A mechanism which is consistent with the experimental findings implies the oxidation of the Cu(II) complex, followed by a subsequent decomposition of the ligand to produce ammonia and glycinaldehyde.





$$\mathrm{Cu^{+2} + H^+ + H_2N - CH_2CHNH_2}$$



$$\mathrm{H_2NCH_2CHNH_2 + oxidant \rightarrow H_2NCH_2CHO + NH_3}$$

The abstraction of an α-hydrogen is essential for the deamination process. This can be implied from the fact that tetramethylethylenediamine and α-amino isobutyric acid do not undergo deamination under the same conditions (*11*).

Since the reactivity of the complex seems to depend primarily on the copper atom, the latter may be regarded as the temporary center for the positive charge; in other words, tervalent copper is formally produced as an intermediate.

The proposed mechanism agrees completely with that suggested by Allen for the copper-catalyzed oxidation of oxalate by peroxydisulfate (*2*).

$$\mathrm{Cu(C_2O_4)_2^{-2} + S_2O_8^{-2} \rightarrow Cu(III)(C_2O_4)_2^- + SO_4^- + SO_4^{-2}}$$

$$\mathrm{Cu(III)(C_2O_4)^- \rightarrow Cu(I)(C_2O_4)^- + 2CO_2}$$

alternatively $\mathrm{Cu(III)(C_2O_4)_2^- \rightarrow Cu(C_2O_4) + C_2O_4^-}$ (*68*, *84*).

The copper-catalyzed oxidation of diethylamine by peroxydisulfate in alkaline solution (*29*) was also suggested as proceeding via Cu(III), and so was the catalytic decomposition of $S_2O_8^{-2}$ (*18*). Further, the formation of Cu(III) as intermediate may account for the Cu-catalyzed oxidation of $Mn^{+2}$ to $MnO_4^-$ by $OBr^-$ (*38*).

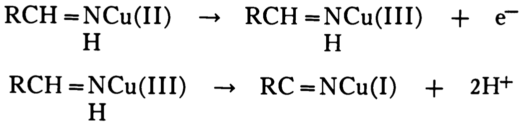
The formation of Cu(III) in complexed form as an intermediate is not surprising, as copper has been reported to exist in the tervalent state in fluoro (*62*), hydroxy (nonaqueous) (*90*), periodato and tellurato complexes (*54*, *67*), as well as in an $Al_2O_3$ lattice (*22*). Sodium cuprate (III) has been prepared in concentrated sodium hydroxide solutions by the action of ozone, hypochlorite, or persulfate on sodium cuprite(II). Cu(III) is stabilized in these environments by coordination and eventually by lattice energy. It is suggested that chelation by the diamines or amino acids decreases the oxidation potential of Cu(III) low enough to allow its formation by relatively mild oxidants. This is analogous to the effect of organic complexing agents on the oxidation potentials of Ag(II) and Ag(III) (*70*). Moreover, it has been predicted that planar complexes of Cu(II) will tend to lose another electron and be converted to Cu(III) (*43*). The chelating agent may eventually undergo oxidation by elimination of a $H^+$ resulting in a decomposition of the oxidized complexes; this behavior is in analogy to the "classical" oxidation of alcohols by chromate (*94*).

Several analogous systems which have been previously studied, may be reexamined in view of the mechanism suggested for the copper-catalyzed oxidative deamination. It was reported by Nyilasi that copper and cobalt ions catalyze the autoxidative deamination of diamines in alkaline solutions at 100°C. (*75*). This effect is specific for the 1, 2 and 1, 3 diamines (*12*), obviously owing to the formation of complexes with these metal ions. Similar observations were reported by the same author on the autoxidative behavior of amino acids (*77*, *78*). The induction period observed in these reactions strongly suggests that the build-up of peroxides is a prerequisite for the catalytic reaction. In view of the specific catalytic effect on the oxidative deamination of chelating diamines it seems improbable that the observed effect is due to the formation of RO' and ROO· radicals from the peroxides (*91*), by the reactions $ROOH + Cu^+ \rightarrow Cu^{+2} + RO\cdot + OH^-$ and $ROOH + Cu^{+2} \rightarrow Cu^+ + H^+ + ROO\cdot$, because these radicals, if formed, are nondiscriminating oxidants. Shortening the induction period in the presence of reducing agents like glycolic, ascorbic, and tartaric acids, which was observed by Nyilasi, is most probably caused by the ease of the uncatalyzed autoxidation of these reactants yielding ROOH, which is then available for the metal-catalyzed reaction. Here we suggest that the observed behavior may be fully explained by our findings on the copper-diamine–$H_2O_2$ system in dilute solutions at room temperature. In other words, the selective autoxidation of chelating diamines and amino acids is attributed to the oxidation of the chelated Cu, resulting in the oxidation of the ligand.

The autoxidation of phenylenediamine, catalyzed by $Cu^{+2}$ (*37*), is another reaction which may follow our proposed mechanism, although an alternative route cannot be excluded (*73*).

In view of our discussion on the behavior of the Cu(II)–Cu(III) system it is very likely that the catalytic effect of cobalt ions, both in the diamine–$H_2O_2$ system (*7*) and in the studies of Nyilasi (*75*, *76*, *77*), is due to the formation of Co(IV). It is further suggested that autoxidation of *N*-hydroxyethylenediamine, catalyzed by cobalt ions (*53*), is also due to the formation of Co(IV). The mechanism proposed by the authors for the latter reaction involves a rather unlikely nucleophilic substitution of an alcoholic hydroxyl or an amino group by an $OO^-$ group. The oxidation of the Co(III) complex to the Co(IV) state, followed by the rejection of an $\alpha$-hydrogen as $H^+$, seems much more likely. The elimination of an $\alpha$-hydrogen has a comparable chance for any $\alpha$-hydrogen on the given molecule, yielding the variety of products observed in this autoxidation.

Another reaction which may be re-interpreted in view of our hypothesis, is the autoxidative conversion of aldimines to nitriles, catalyzed by $Cu^{+2}$ (*23*). The authors suggest a mechanism in which the aldimine RCH=NH is oxidized by $Cu(II)(NH_3)_4OMe^+$ to a RC=NH radical, which does not react with Cu(II) but is oxidized by $O_2$ to RC≡N. This scheme does not seem very convincing, as RC=NH should be a better reducing agent than the aldimine; further, if $O_2$ reacted with the radical, one would expect $RC(O_2)$=NH to be formed, resulting most probably in RCOOH (*91*). Next, it was claimed that the oxidizing power of $Cu(NH_3)_4OH^+$ is far lower than that of the methoxy analog. This is surprising in view of the relatively weak bond of the $OH^-$ or the $OR^-$ in the copper tetramine complex (*43*). A more plausible interpretation of the results could be offered if one assumed that the copper is bound to the aldimine, and that this complex is oxidized to Cu(III) by $O_2$, ROOH or perhaps even by disproportionation (2RCH=NHCu(II) → RCH=NHCu(I) + RCH=NHCu(III)). Subsequently the RCH=NHCu(III) complex undergoes a two-electron transition to Cu(I), owing to stabilization of the product by π-bonding.

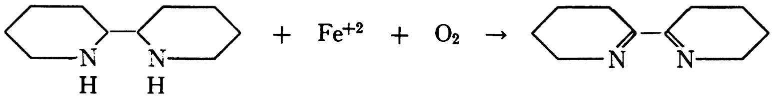


$$\mathrm{RCH{=}\underset{H}{N}Cu(II)} \rightarrow \mathrm{RCH{=}\underset{H}{N}Cu(III)} + e^-$$

$$\mathrm{RCH{=}\underset{H}{N}Cu(III)} \rightarrow \mathrm{RC{=}NCu(I)} + 2H^+$$

If RC═NHCu$^{+2}$ is formed as intermediate, it is probably too short-lived to interact with oxygen. The inhibitory effect of water observed in this reaction may be explained by the hydration of the aldimine, which in the hydrated form, is less likely to stabilize Cu(I) and facilitate the transition from Cu(III) to Cu(I).

The last work to be considered from our standpoint on the metal-catalyzed autoxidation of organic ligands, is the autoxidation of α, α -dipiperidyl to α, α′-bis Δ$^4$-piperidine in alkaline solutions (*66*), which is most probably catalyzed by Fe$^{+2}$ ions.



This is analogous to the RCH═NH → RC═N (*23*) reaction, as well as to the α-hydrogen abstraction in the catalytic oxidation of ethylenediamine (*7*). As Fe$^{+3}$ does not oxidize the substrate, it is suggested that a Fe(II) complex of dipiperidyl is oxidized by ROOH to the Fe(IV) state (*25*). Owing to the stabilization of Fe(II) by the π-electrons of the final product, a double electron transfer takes place without formation of a free radical. A free radical, formed by a single electron transfer, would interact with oxygen under the given conditions, resulting in ring fission.

Another copper-induced reaction which may be reinterpreted in view of our mechanism is the copper-induced chlorination of ketones (*64*). It seems reasonable to suggest that Cu(II) bound to the ketone is oxidized to Cu(III) by $CuCl_2$, which, in the given medium, is less stable than Cu(I). Subsequently, Cu(III) oxidizes its chlorine ligand in a double electron transfer to Cl$^+$, followed by the latter's addition to the enolic double bond.

It should be stated here that the suggestion of Cu(III) as the oxidation state in different oxidation and autoxidation reactions does not exclude the participation of Cu(II)–Cu(I) couple in other reactions, where Cu(II) is easily reduced by the substrate-e.g., iodide or sulfite ions (*4*). Likewise, the Co(II)–Co(III) couple was shown to operate in the oxidation of cystein (*69*), which was shown to proceed according to

$$\mathrm{Co(II)\ (Scy)} + O_2 \rightarrow \mathrm{Co(II)\ (Scy)}O_2 \rightarrow O_2^- + \mathrm{Co(III)\ (Scy)}^+ \rightarrow \mathrm{Co}^{+2} + \mathrm{Scy}$$

(HScy = Cystein).

In the last three examples it is evident that the substrates are oxidized by Cu$^{+2}$ and Co$^{+3}$, respectively, and in the absence of oxygen; this distinguishes the last systems from those discussed above.

**Oxidation of Stable Systems Resulting in a Permanent Change of the Oxidation State of the Central Atom.** In the majority of oxidation reactions of stable systems the central atom will be oxidized, whereas the ligands do not undergo any apparent chemical change. In many of these redox reactions the ligand may undergo a reversible redox transformation leaving it at the end in its initial chemical state (*86*). In other specific cases where the central atom is in a highly oxidized state and the ligand requires a double electron transfer before reaching a new stable form, oxidation of the system may result in the simultaneous reduction of the central atom.

$$ML^{+a} + X^{+b} \rightarrow X^{+(b-1)} + ML^{+(a+1)} \rightarrow M^{+(a-1)} + L^{+2} \qquad (12)$$

It is hard to estimate the lifetime of $ML^{+(a+1)}$, but it is short enough to avoid an interaction with another molecule of the oxidant. This distinguishes the given intermediate from those discussed previously, which either broke down spontanously to yield a free radical, or were stable enough to interact a second time with the oxidant.

The oxidation of cobaltioxalate by ceric and cobaltic ions which results in the quantitative reduction of the Co(III) to Co(II), simultaneously with the oxidation of the oxalate to $CO_2$ (*81*), is an outstanding example of this type of reaction. Other analogous cases are the oxidations of cobalti-*p*-aldehydo-benzoate by Co(III), $MnO_4^-$ and $S_2O_8^{-2}-Ag^+$ (*40*), and of $(NH_3)_5Co(III)(HCOO)^{+2}$ by $MnO_4^-$ yielding partially Co(III) (*26*). The last case is an example of an intermediate which is long lived enough to react with the oxidant if the latter is present in an appreciable excess.

Another interesting case is the oxidation of a system resulting in the simultaneous oxidation of the central atom and the ligand. Reference is made here to the oxidation of certain aquated transition metal ions, at their low states of oxidation by the action of $H_3O^+$. The oxidation of $Mn^+$ by $H_3O^+$, which was shown to involve a hydride transfer from the ligand (*9*), follows this type of behavior. The oxidation of Cr(II) by $H_2O$ proceeds by an analogous mechanism (14).

**Reduction of a Stable System Resulting in Reduction of a Ligand.** Ligands, as a group, are far better electron donors than acceptors. Thus, electron transfer reductions of ligands should be rather unlikely, and in fact, no such case has hitherto been reported.

This type of reaction may be formulated by

$$ML^{+a} + Y \rightarrow ML^{+(a-1)} + Y^+ \qquad (13)$$

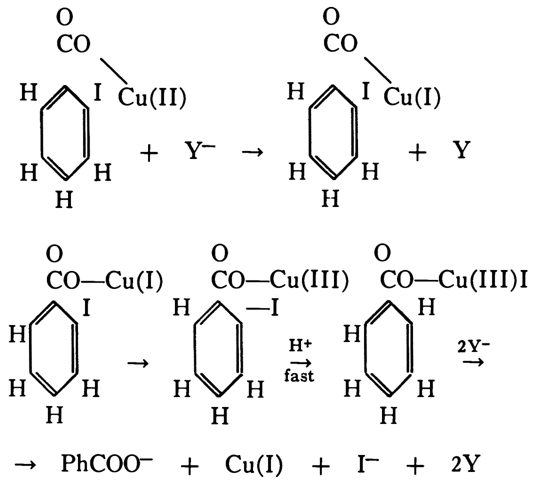
$$ML^{+(a-1)} \rightarrow M^{+a} + L^-$$

It is hard to envisage a ligand, which generally requires a double equivalent transformation, being reduced in preference to the central atom. Even if $L^-$ is formed as intermediate by direct interaction with Y, it is likely to act as a reductant, and the equilibrium $M^{+a} + L^- \rightleftharpoons M^{+a-1} + L$ will be shifted to the right. This is in fact the mechanism of ligand-bridged redox reactions as demonstrated in the case of Co(III)L–Cr(II) reactions (*86*).

Another possibility is an atom transfer from the ligand to the central atom (a double equivalent transformation), which has been discussed above. In that case, $M^{+a}$, in a low state of oxidation, is ligated to a ligand L, which is capable of oxidative atom transfer. This mechanism does not require, however, any interaction between a reducing agent, Y, and the system, $ML^{+a}$.

We have only one example of a reaction in which a stable oxidized system $ML^{+a}$ is reduced by a reducing reagent, Y. This reduction induces an oxidative atom transfer to the central atom. In the de-iodination of *o*-iodobenzoic acid (*5*, *6*) the system $ML^{+(a-1)}$, formed from $M^{+(a-1)}$ and L, is also a *stable* system, so that the reduced system is not equivalent to $ML^{+(a-1)}$. *o*-Iodobenzoic acid forms, in neutral aqueous solutions, a 1:1 complex with cupric ions which is chemically stable. The same acid also forms a stable complex with cuprous ions. However, when the cupric complex interacts with reducing agents–e.g., azide, iodide, or sulfite ions, as well as ascorbic acid or formaldoxime, a fast de-iodination occurs, forming benzoic acid and iodide ions as final products. No copper-catalyzed isotopic exchange between *o*-iodobenzoic acid and iodide ions takes place under the given conditions. The meta and para isomers as well as the esters of *o*-iodobenzoic acid do not undergo de-iodination. Other metal ions including $Hg^{+2}$, $Zn^{+2}$, and $Cd^{+2}$, in the presence of the same reducing agents, do not induce any de-iodination in the substrate. The reaction is first-order in each of the reactants—the substrate, copper ions, and the reducing agent. The rate of de-iodination was found to be independent of pH in the neutral region. No general acid catalysis was observed, nor could any isotope effect be demonstrated by changing the solvent from $H_2O$ to $D_2O$.

From the given experimental results it is inferred that the reduction of the iodobenzoate–cupric complex produces a system of unstable configuration, which decomposes by atom transfer before it has a chance to readjust to the stable iodobenzoate–cuprous complex



The action of *o*-iodobenzoic acid as oxidant has also been observed in the oxidation of chromous ions, where an atom transfer has also been demonstrated (*6*, *8*). The double equivalent redox reaction is inferred from the formation of benzoic acid as the product of de-iodination.

The decomposition of the reduced complex is facilitated, most probably, by an electrophilic substitution of $I^+$ by $H^+$. This is a relatively fast step, as no acid catalysis or H–D isotope effect could be demonstrated. The presence of Cu(I) in a favorable position close to the iodine atom facilitates the reduction of the ligand.

This case is related to the acid-catalyzed de-iodination of aromatic compounds which proceeds via its conjugate acid,

$$PhI + H^+ \rightleftharpoons PhIH^+ \rightleftharpoons PhH + I^+$$

where the rate determining step is the decomposition of $PhIH^+$ (*82*). The latter process is however, much slower ($>10^6$) than the copper-catalyzed reaction (*13*).

The specific phenomenon in this copper-induced reaction is the configuration of the reduced complex which facilitates the oxidation of Cu(I) to Cu(III). The effect of configuration on the redox behavior of a ligand may be important in interpreting metal-induced enzymatic redox reactions.

## *Conclusion*

It has been shown that many redox reactions in anions and similar species may be induced by ligation to transition metal ions. One may consider metal ions as bridging between the oxidant and the oxidized ligand somewhat in an analogous manner to a ligand bridge in a metal-metal redox reaction.

The great number of metal-induced redox reactions of ligands justifies the effort in classifying them according to their mechanisms by the following criteria:
(1) Spontaneous decomposition of metal-ligand complexes resulting in oxidized or reduced ligands.
(2) The interaction of stable metal-ligand systems with oxidizing or reducing reactants, resulting in a redox change in the ligand.

The formation of ligated transition metal ions at unstable high states of oxidation, its implications in the mechanisms of metal-catalyzed autoxidation, and the effect of configuration of a metal-ligand system on its redox stability have been pointed out. These considerations may be helpful in interpreting more complex metal-ligand systems including metal-enzyme reactions.

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# Discussion

**Michael Anbar:** For two years I have been interested in the redox changes in ligands owing to the oxidation of metal ions. Since I could not find a review of the developments in this field, I decided to systematize the available material on this type of reaction myself.

It is difficult to start at the beginning and do a complete job. Hence, my review is not comprehensive.

One factor that hinders the advancement of science is that people who enter a new field rely on reviews perhaps more than on the original papers. Since a review is much more subjective than an original paper, the reported material and developments are apt to be biased. My systematization is rather arbitrary, but on the other hand I tried to collect representative examples of the different types of reactions involved.

When I wrote this review, I was not aware of the Yalman Exclusion Principle—i.e., that no two reactions can proceed by the same mechanism. Therefore, I tried to systematize various reactions into groups according to certain criteria. Possibly I may have over-systematized in some cases.

Since the review has been written, more results have come up in our laboratory. I would like to report on them and complete some of the information presented in our paper.

First, I will comment on the existence of copper(III) in complex form. I have mentioned that a hydroxy complex or oxy complex has been produced in solid state by Klemm. We have succeeded recently in preparing the same compound, sodium cuprate, in aqueous solution, by oxidizing copper in a highly concentrated sodium hydroxide solution. Copper is dissolved in saturated sodium hydroxide (50% w/w) and yields a 0.2*M* homogenous solution. This system may be oxidized by the means of persulfate, hypochlorite, or ozone. We have used three oxidants. In each case, a precipitate of an insoluble sodium cuprate is formed. When this salt is dissolved in a more dilute sodium hydroxide solution, even as concentrated as 3*M*, the copper(III) will decompose water to give oxygen. This precipitate does not contain any chloride or hypochlorite. The composition of the ozone-produced cuprate is the same as that formed by hypochlorite oxidation. The product of persulfate oxidation is less pure because of sulfate occlusion in the precipitate, and I would not recommend it as a preparative method.

My second comment is on the reaction of Cu(III) with water. My review mentions some results, but I want to add that we were able to show that hydrogen peroxide is formed as an intermediate in the reaction of Cu(III) with water. This was achieved by using carrier $H_2O_2^{1616}$ in $H_2O^{18}$. After the final decomposition of the Cu(III) the residual hydrogen peroxide was decomposed and found to contain $H_2O_2^{1818}$. Next, we were able to show that no ozone or oxygen atoms are formed as intermediates in this decomposition. When this reaction of Cu(III) in normal water under a pressure of $O_2^{1818}$ is carried out no scrambling occurs—i.e., no $O_2^{1618}$ is formed, but only a mixture of $O_2^{1818}$ and $O_2^{1616}$. If ozone were formed, it should have induced some $O_2^{1618}$—$O_2^{1616}$ exchange in water and we would have found that this exchange is a sensitive test for checking the presence of ozone or oxygen atoms. Thus, the decomposition of water by Cu(III) involves the formation of hydrogen peroxide as intermediate, but not of oxygen atoms.

Next I would like to comment on reactants which induce oxidative deamination of ethylenediamine. In the paper I have referred to $HO_2$, hydrogen peroxide, and fluoroiridate as oxidants. Lately, we have added hypochlorite ions to this list. I would further like to comment on the mechanism of the copper-induced oxidation of ethylenediamine. In the paper I have postulated a single electron transfer and the formation of a free radical as intermediate. We have no evidence, however, that such a free radical is formed. When I discussed this reaction with John Edwards, he mentioned some of his old results on the copper-catalyzed oxidation of glycols by persulfate. In this reaction he was able to show, by the lack of polymerization, that no free radicals were formed as intermediates. Our postulation of a free radical intermediate was based on the fact, that under radiolytic conditions the same product is obtained in the presence as in the absence of copper. This again is not unambiguous proof. It is possible that there is a consecutive oxidation of the amine by a two-electron transfer, without formation of any free radical as intermediate. One could suggest using ESR to settle this point. Detecting a free radical is significant. If, on the other hand, no free radical is found, nothing is proved because it may still be there at a very low concentration. In view of the broadening of lines in the ESR in the presence of copper ions, this is not a very promising experiment.

In another part of my review, I referred to the reduction of different oxyanions, including perchlorate, bromate, and nitrate by metal ions like chromous or vanadous. I suggested that an oxygen transfer may occur in these eactions. At present, we have evidence, at least in two cases, that oxygen transfer actually takes place. In the case of the oxidation of chromous by $O^{18}$ labelled bromate and nitrate ions, we have found on the chromium(III) formed, a substantial amount—50% or more—of $O^{18}$ originating from the bromate or the nitrate.

I would like to suggest another possible interpretation of our results on the oxidation of manganese(I) by water. In the paper I suggested a mechanism by which a hydride transfer takes place from the ligand water to $H_3O^+$ to form $H_2$; this is consistent with the experimental results. We could, however, explain the same results by an interaction of hydrogen atoms with the water ligands that surround the manganese. Abstraction of a hydrogen atom from the first coordination shell would result in the oxidation of Mn(I) to Mn(II). The latter mechanism is believed to account for the oxidation of ferrous ions, and it is relevent to our discussion in the review because water in solution is not likely to undergo hydrogen abstraction by hydrogen atoms; but water ligated to ferrous ions may undergo this reaction with the formation of hydrogen gas.

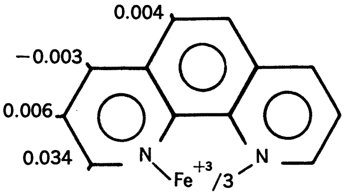
In the case of chromous ions, we again looked for the composition of the hydrogen evolved from chromous solutions, again in the presence of isopropyl alcohol. This was the analytical technique used to detect hydrogen atoms. Again we were not able to produce any H—D but $H_2$ only. This suggests a hydride transfer mechanism in the reducing of water by Cr(II).

My last comment concerns the thallic bromide system. I suggested a different mechanism for this exchange reaction than that postulated by Dr. Dodson and his colleagues, and suggested in the paper that these two mechanisms may be distinguished by examining salt effects. I have to withdraw this suggestion because salt effects will influence the pre-equilibria very similarly to the rate-determining step. Thus, salt effects will hardly distinguish these two mechanisms, and some other experiment will be necessary.

**Robert Plane:** I think Dr. Anbar has provided excellent documentation for the general feeling that more ligands are reducing agents than are oxidizing agents. The reason for this, of course, is that an oxidizing agent will be electron deficient, and hence will be a poor ligand. Although there are many examples of ligands which are reducing agents, the very fact that these ligands coordinate to a metal ion makes them poorer reducing agents, both thermodynamically and at least in a naive kinetic sense. However, Dr. Anbar points out nicely that there are examples where catalysis does occur, and he accounts for this in terms of a mismatch in stoichiometry between the reducing agent and the oxidizing agent. Ligands very often are oxidized by two electron jumps, and if one picks a so called one-electron oxidizing agent, there will be a mismatch which can be helped by reducing the metal of the complex. This however, raises the question of oxidizing part of a molecule while reducing part of the same molecule which, in turn, has to do with the distribution of electrons within molecules.

**Arthur Wahl:** Martin Dietrich, David Larsen and I have studied tris(1,10-phenanthroline)iron(II) and iron(III) systems and have looked at the proton NMR spectrum of the two oxidation states and mixtures of the two oxidation states (*2, 11*).

From spectra comparison of the two pure species contact shifts are obtained from which one can calculate spin densities in the phenanthroline ring. For the paramagnetic species the spin density on the 2—9 carbons is 0.034; on the 3—8, 0.006; on the 4—7, —0.0003; and on the 5—6, 0.004.



If one sums these values over all the equivalent hydrogens and all three rings, about one quarter of the spin density is in the ligands, which indicates that the ionic charge is distributed between the ligands and the iron. We have no information, of course, about the spin densities on the other four carbons, or on the nitrogens.

For mixtures of the two oxidation states, the contact shifts depend directly on the relative mole fractions of the two states, indicating that the system is in the limit of rapid exchange. From this and the concentrations of the two species, one can calculate that the second-order rate constant involving the electron transfer must be greater than $10^5$ $M^{-1}$ sec.$^{-1}$ at 25°C. This limit applies not only to the phenanthroline iron(II)—(III) system but also the iron(II)—(III) complexes with the following methyl derivatives of phenanthroline:

4,7-dimethylphenanthroline
5,6-dimethylphenanthroline
3,4,7,8-tetramethylphenanthroline
3,5,6,8-tetramethylphenanthroline

These results are consistent with the very fast net electron transfer which Norman Sutin and others have observed for similar systems.

**Jack Halpern:** I wish to comment on two points that arise directly from Dr. Anbar's remarks. The first concerns the oxidation of ethylenediamine by copper. It seems to me that in the oxidation of organic ligands by copper(II) one mechanism that ought to be considered seriously is that involving transfer of a hydride ion to the metal. We have shown unequivocally that in the reactions of $H_2$, catalyzed by copper(II), a relatively stable species, $CuH^+$, is formed by transfer of a hydride from molecular hydrogen to cupric—i.e.,

$$Cu^{+2} + H_2 \rightarrow CuH^+ + H^+.$$

The activation energy of this process is only 26 kcal., which implies considerable stability for CuH relative to Cu and a hydrogen atom. Thus, it seems that the same species may form in other systems that can transfer hydride ions, and there is indeed evidence in related systems for the formation of analogous hydrido complexes by such hydride transfer—e.g.,

$$PtCl_2(PEt_3)_2 + CH_3CH_2O^- \rightarrow HPtCl(PEt_3) + Cl^- + CH_3CHO.$$

It seems that similar mechanisms could accommodate the oxidation of ethylenediamine by cupric ion—i.e.,

$$Cu^{+2} + NH_2CH_2CH_2NH_2 \rightarrow CuH^+ + NH_2CH_2CH{=}NH + H^+$$

to form an intermediate which may be further stabilized by coordination. I think such a possibility should be considered very seriously.

The second point relates to this as well as to your observation that the abstraction of hydrogen from water molecules is assisted by coordination of the water, particularly with $Fe^{+2}$. The mechanism of ferrous oxidation by hydrogen atom has been a controversial question, and several mechanisms have been proposed. Among them are one suggested by Jortner, Czapski, Stein, and myself involving the addition of hydrogen atoms to the ferrous ion to form a hydrido iron complex analagous to $CuH^+$—i.e.,

$$Fe^{+2} + H \rightleftharpoons FeH^+, \quad FeH^+ + H^+ \rightarrow Fe^{+3} + H_2.$$

I believe that since then Stein's group in Jerusalem has accumulated evidence which suggests that at least under some conditions this is the main reaction path of ferrous ions with hydrogen atoms. In view of this, I wonder specifically what evidence you had bearing on this point. This is important, not only in relation to this class of mechanisms, but also to the more general problem of how the interaction involved in the relatively ionic coordination of a ligand such as water to a metal ion would reflect in weakening a covalent P—H bond.

**Dr. Anbar:** First, concerning hydride transfer, our information shows that with longer chained diamines, say 1,3-propylenediamine and certainly, 1,4-butylenediamine, the catalytic effect of copper disappears. With a longer chain the coordination is essential for the reaction. Then, an internal hydride transfer has to be assumed, that is an intramolecular and not extramolecular process.

The question is, what does the oxidant do in this case? One would say that it reoxidizes the copper.

**Dr. Halpern:** This is right.

**Dr. Anbar:** Good. Now, why do you suppose that a chelated copper ion is more likely to form the hydride than a nonchelated hydride?

**Dr. Halpern:** Conceivably to stabilize the intermediate. I wrote the reaction out that way (–i.e., omitting coordination of the amine to the copper) to call attention to the specific point of hydride transfer. Conceivably, such transfer could occur intramolecularly.

**Dr. Anbar:** In the case where you examined the reaction of copper with hydrogen, what was the effect of chelation on this process?

**Dr. Halpern:** This is a somewhat complicated matter. Complexing $Cu^{+2}$ with different ligands affects its reactivity toward $H_2$ as follows: in general, ligands that come off easily—i.e., that are not strongly bound and that are basic, (e.g., acetate) assist this reaction because they participate in the process apparently by stabilizing the proton which is released.

On the other hand, ligands that are very strongly held, (e.g., ethylenediamine) exert a blocking effect and reduce the reactivity. The order of reactivity of different copper(II) complexes was found to be: acetate > sulfate > chloride > aquo > glycinate > ethylenediamine.

Clearly, this is a different system in detail, and the only feature that I want to carry over is the possibility of hydride transfer to the copper, which we know to be a strong hydride acceptor. One could, of course, accommodate this feature of the mechanism by a variety of detailed schemes, including one involving chelation.

**Dr. Anbar:** In this case one should examine the acid effects of HD exchange on the methylene. Further, in the equilibrium

$$—CH_2—NH_2—Cu^{+2} \rightleftharpoons CH^+\text{-} NH_2—CuH^+$$

oxidation would be shifted to the right by a nucleophile, say chloride ion; this however could not be demonstrated. Referring to the reaction of hydrogen atoms with with manganous ions, we do not know yet whether such a reaction actually occurs. When you irradiate a neutral solution containing isopropyl alcohol labelled with deuterium in the $\alpha$-position, you get a certain yield of HD. If manganous ions are introduced, HD drops considerably, whereas the total yield of hydrogen does not. From this, we postulated the mechanism of hydride transfer. This implies reduction of the manganese by the precursor of the hydrogen atom, and subsequent oxidation of the manganese by the water.

**Dr. Halpern:** But any mechanism of capture is consistent with this; it needn't be abstraction.

**Dr. Anbar:** You have to capture it and come up with essentially the same amount of hydrogen. This hydrogen, however, has to come off from the water as can be seen from its composition. This means that no more hydrogen atoms can be formed; otherwise, they would abstract hydrogen from the isopropyl alcohol.

**Dr. Halpern:** But all that is necessary to explain your observation is that this intermediate be fairly long lived and then that two of these ultimately combine. There is some evidence for a similar phenomenon in the case of free radicals. J. K. Kochi and F. F. Rust (*9*) have shown that transition metal ions, among them Fe(II), catalyze the recombination of free radicals by what appears to be substantially this kind of mechanism—i.e., the transition metal stabilizes the radical against abstraction presumably by forming a complex with it, which then lives long enough to combine with another one.

**Dr. Anbar:** This is a possibility, at least for ferrum and for copper. In the case of manganese, I am quite skeptical.

**Gilbert Gordon:** We have been studying the reduction of various halogenates, such as chlorate, chlorine dioxide, chlorite, hypochlorite, and chlorine by metal ions. In contrast to the comments of Richard Yalman, there does appear to be some order.

We find in general that the following mechanism

$$M^{+\nu} + ClO_2 = M^{+\nu+2} + OCl^- \quad \text{(rate determining)}$$

$$OCl^- + ClO_2^- = ClO_3^- + Cl^-$$

is consistent with the experimental results. For example, with uranium(IV) and chlorite, the first step corresponds to oxygen atom transfer to form uranium(VI) plus hypochlorite (*6*). The hypochlorite is not reduced by the uranium(IV) but reacts directly with the chlorite to form chlorate. As the reaction proceeds and more chloride is formed, the chloride and hypochlorite react to form chlorine, which also can oxidize the chlorite to form more of the product, chlorate (*7*).

In 1949, Henry Taube and H. Dodgen (*2*) reported, that in the reaction of hypochlorite or chlorine with chlorite, the principal product in concentrated solution is indeed chlorine dioxide and not chlorate. They also report that there is another reaction which produces some chlorate. We now have detailed rate studies which show that in dilute solution the initial reaction appears to be

$$ClO_2^- + Cl(I) = (Cl - ClO_2)$$

followed by autodecomposition into chlorate and chloride directly. In more concentrated solutions, this intermediate disproportionates in a bimolecular reaction to form chlorine dioxide and chloride. This appears to be consistent with Dr. Taube's results.

In the case of vanadium(II), iron(II), and chromium(II), chlorate is also formed as an intermediate. In the case of chromium(II), there is apparently some reaction with hypochlorite. But even in this case, there appears to be an additional step corresponding to the reaction between chlorate and chromium(II).

In all four cases, we have strong experimental evidence for two distinct reactions with chlorite. One of these reactions corresponds to the oxidation of the metal ion by chlorite, followed by the rapid formation of chlorate. Another interesting point is that the relative order of rate of metal ion plus halogenate is found to be:

$$ClO_2^- > ClO_2 > OCl^- > Cl_2 > ClO_3^-.$$

In all cases, the rate of the chlorite metal reaction is faster than the other halogenate reaction by a factor of between 5 and 50, depending on the temperature and the hydrogen ion concentration. Unfortunately, there are some complicated hydrogen ion effects on these reactions, and some of these comparisons cannot be made directly.

One last point. In the reaction of uranium(IV) where it is convenient to do a tracer experiment because there is only one metal ion product, we have actually determined the number of oxygens transferred to the uranyl ion product from the chlorite, and this number corresponds to 1.3 oxygen per chlorite transferred to the uranium. This is consistent with the results we reported some years ago (*5*) on the oxidation of uranium(IV) with $PbO_2$ and $MnO_2$, where indeed more than one oxygen is transferred. In conclusion, we feel that we have some direct evidence for two-electron transfer in these reactions and the formation of a chlorine(I) intermediate followed by the formation of chlorate.

**Dr. Plane:** I would like to comment briefly on this topic of oxygen-atom transfer to metal ions. In the case of chromous, we have oxidized Cr(II) both with $O_2$ (*10*) and also with $H_2O_2$ (*1*). In both cases, there is complete oxygen-atom transfer from the oxidizing agent to the chromium, even more than is necessary to satisfy the stoichiometry. Furthermore, it is interesting that in the case of the oxygen molecule on chromous, it is postulated that the chromous gets oxidized to chromium(IV), which one firmly believes exchanges oxygen rapidly with water. Indeed, with T. B. Joyner and Wayne Wilmarth's results in the Cr(II)—$NH_3$ system, there is a significant amount of oxygen transfer to the water (*8*). This does not happen in the absence of ammonia, at least in our particular system, and one wonders if indeed chromium(IV) is formed at all.

**G. A. Rechnitz:** I would like to contribute some unpublished information which I think has some bearing on the systems discussed by Dr. Anbar. One of these is very puzzling, and I would be very grateful for any suggestions.

We have tried to study the decomposition of ruthenium(II) in aqueous media containing high concentrations of chloride, according to

$$RuCl_4^{-2} + H_2O \rightarrow Ru(III) + H_2$$

The oxidation product is ruthenium(III), without question, and gas chromatography has shown that the other primary product is hydrogen gas.

The reaction was carried out in approximately $2.5M$ potassium chloride medium, slightly acidic to prevent hydrolysis. The rate is both pH and chloride independent. This surprised us because we first expected this to be reduction of hydrogen ion.

We repeated the experiments in $D_2O$. Ruthenium(II) was prepared by electrolysis at constant potential from ruthenium(III) or (IV), so there were no other chemical species introduced into this system. This entire experiment can be carried out in $D_2O$. We found no primary kinetic isotope effect which also surprised us.

I am not able to offer an entirely convincing explanation here. We are tempted to propose the hydrated electron suggested by Dorfman to account for the lack of kinetic isotope effect.

Secondly, we studied the oxidation of oxalate by cerium(IV) in sulfuric acid. This reaction is analagous to the classical manganese(III) oxalate reaction studied by H. Taube and also by F. Duke. Indeed, it proceeds through an intermediate containing one or more oxalates per cerium. This decomposes to give cerium(III) and other products. The point I want to raise is that we have been able to detect free radicals in this reaction, using EPR experiments and a flow system. So far, it has not been possible to say whether the radical is the oxalate or $CO_2$ radical, both of which have been proposed in other studies.

Finally, in connection with the comments of Dr. Gordon, we have looked at the reduction of chlorate by hexachloroiridate. The final products, of course, are hexachloroiridate and chloride. The reaction is stoichiometric. So far, no tracer experiments have been done to try to identify any of the unstable intermediates; but both of the iridium species are well known to be substitution inert, and the reaction surely involves a one-electron reduction of chlorate.

**Dr. Halpern:** I don't know whether this is relevant to the first reaction or not, but we have also been struggling with the study of various reactions of ruthenium chlorides including ruthenium(II) chloride for a long time. Among the reactions studied is the formation of olefin and carbonyl complexes of ruthenium(II). These form readily in aqueous solution and are fairly stable. James and Kemp, working on these systems in my laboratory have studied in some detail the kinetics of the reactions:

$$\mathrm{Ru(II)} + C_2H_4 \rightarrow \mathrm{Ru(II)}\,(C_2H_4)$$

$$\mathrm{Ru(II)} + \mathrm{HCOOH} \rightarrow \mathrm{Ru(II)}\,(\mathrm{CO}) + H_2O$$

In both of these cases, the kinetics are approximately consistent with a dissociative mechanism of the type

$$\mathrm{Ru(II)Cl}_n \rightarrow \mathrm{Ru(II)Cl}_{n-1} + \mathrm{Cl}$$

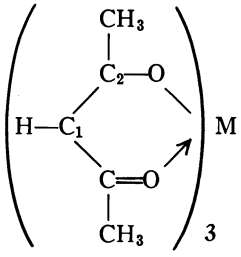
$$\mathrm{Ru(II)Cl}_{n-1} + C_2H_4 \rightarrow \mathrm{Ru(II)Cl}_{n-1}(C_2H_4)$$

The kinetic dependence on $Cl^-$ is a little uncertain, presumably because we are working in a region where varying $Cl^-$ also varies the composition of the species present. But the dependence on the ethylene concentration and on the formic acid agrees precisely with this mechanism, and I think it unequivocally demonstrates that there is a dissociative step involved. Thus, at high concentrations of reactants ($C_2H_4$ or HCOOH) the rate of formation of the complex becomes independent of the concentration of the entering group. I wonder if a similar mechanism applies to the oxidation of Ru(II) by water; the rate of the process is determined perhaps by the same dissociative step which in this case is permitting entry of a water molecule into the coordination shell of the ruthenium, followed by a subsequent redox process.

**Dr. Rechnitz:** These comments are very helpful. I think I neglected to mention that there is no chloride dependence on the rate, nor is there any effect owing to Ru(III).

**Dr. Halpern:** If the entry of water following the dissociation is rapid enough, this would be the case; but one implication of this, of course, is that the limiting rate in all these cases ought to be the same. This is at least approximately true for the two reactions which have been studied. It would be interesting to compare your limiting rates with ours.

**D. R. Eaton:** Prof. Taube and Dr. Anbar have mentioned a number of metal ligand systems where the interaction of the metal *d*-electrons with the ligand $\pi$-system may be important. I think it may be important to distinguish two cases here, namely, whether the *d*-electrons are going to interact principally with a ligand-bonding orbital or with a ligand-antibonding orbital. This question can sometimes be answered by NMR contact shift studies of the type reported by Prof. Wahl. We have evidence that both kinds of interaction can occur. Their relative importance can be different for the same ligand coordinated to different metals, or for the same metal complexed with different ligands. For example, in the trivalent acetylacetonate series it seems that the predominant interaction in the compounds from titanium(III) through to iron(III) is with the bottom antibonding ligand orbital. This is relatively unambiguous because the spin density distributions in the bonding orbital and the antibonding orbital are quite different. In particular for the top bonding orbital, a positive spin density is predicted at position 1; for the bottom antibonding orbital a negative spin density is predicted. Throughout this series, it appears that delocalization of positive spin to the antibonding orbital is predominant, but the extent of the charge transfer decreases with increasing atomic number. On the other hand, for the spin-paired ruthenium(III) compound, the opposite is true, and it seems that interaction with the top bonding orbital, leading to ligand—metal charge transfer, occurs. This is perhaps consistent with a naive picture in which the bonding and the antibonding ligand orbitals fall below and above the metal *d*-orbitals, and the latter gradually fall in energy on passing along the series.



I will mention one other case in which the metal is kept constant but the ligand is changed. In the aminotroponeimineate chelates (*3*) with 4-coordinate tetrahedral nickel, the interaction is definitely with the top bonding ligand orbital; whereas in Ni(II) pyrromethene complexes (*4*) the interaction appears to be with the bottom antibonding ligand orbital. This seems consistent with molecular orbital calculations since in the pyrromethene case a low antibonding orbital is predicted, and in the aminotroponeimineate case there is a relatively high bonding orbital.

It is also interesting that the molecular orbital calculations indicate a state for square planar porphyrin complexes quite similar to the pyrromethenes, so that delocalization to the antibonding orbital may again be important. Apparently the relative positions of bonding and antibonding ligand orbitals is going to determine the direction of the possible electron transfer. In one case it is a question of transfer from the ligand to the metal; in the other case, it is a question of transfer from the metal to the ligand.

**Gordon Harris:** Dr. Plane has asked for general and specific comments on catalysis, but so far these have all been specific. I would like to mention a general type of complex oxalate reaction which has been a mystery to me for a long time, and ask Dr. Anbar whether he might comment on it.

One type of reaction which has been studied a great deal is

$$2\ \mathrm{Co(III)L}\ C_2O_4^{-n} \rightarrow 2\ \mathrm{Co(II)} + CO_2 + C_2O_4^{-2} + 4\ \mathrm{L}$$

$$(\mathrm{L}{=}C_2O_4^{-2} \text{ or diamine chelate})$$

In this reaction, oxalate ion may be oxidized intramolecularly by cobalt(III) ion, but it is interesting to compare the three different systems in which there are three, two, or one oxalate ions with the cobalt(III) cation. The last one can be boiled in $1.0M$ acid for an hour and nothing happens. In the first one, decomposition will occur very readily in aqueous solution at 50°C., so that oxalate exchange can't be measured, for instance. The middle one has not been studied in any detail yet, as far as I know, but there is oxidation-reduction in this too, though much slower than in the first. I wonder if this inhibiting effect of the nonreacting ligand, the diamine, on the oxidation has any simple explanation.

**Dr. Anbar:** I did not encounter many cases which demonstrated a secondary ligand effect of some kind. I think this is more along Dr. Harris' line than mine. I will answer Dr. Halpern's question concerning the hydride transfer.

We don't observe oxidative deamination in the absence of oxidants. We may boil ethylenediamine with copper indefinitely without any chemical changes taking place. This observation is in addition to the lack of chloride-induced deamination, which conflicts with the hydride transfer mechanism. Moreover, if this mechanism did occur, it would imply a copper-induced exchange of hydrogen between the methylene group and water.

**Dr. Halpern:** I think one would have to invoke special reasons why you wouldn't observe it.

**Dr. Anbar:** In fact, the mechanism you suggested for the formation of hydrogen via the ferrum hydride should evolve hydrogen from this system just as well, with a consequent oxidation of the substrate.

**Dr. Halpern:** Unless it is reversible—i.e., unless the hydride transfers back for some reason.

**Dr. Anbar:** Well, if it is reversible, one has to get an exchange. This is what you imply.

**Dr. Halpern:** But it doesn't invoke the oxidizing agent in that step, so you are quite right.

**Dr. Anbar:** In other words, in the absence of an oxidizing agent, you would expect an induced exchange between the methylene group and water—an exchange with a half-life of less than a minute, since it has to proceed faster than the deamination.

**Dr. Halpern:** Yes, as a first approximation, subject to the question of whether the hydride also exchanges with the solvent.

**Dr. Anbar:** No, it is either yes or no. There is only one way. Although we never checked on it, such an exchange is extremely unlikely.

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# 7

# Kinetic Patterns of Ligand Reactivity

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**In many cases, the rate behavior of ligand reactions is governed by the same gross mechanistic features as those for the free ligands. When the electrophilic attack of an aromatic species, *L*, is examined, the order of the rate constants for the reactions is: the free ligand > metal complex > protonated ligand. An electrostatic model of such reactions is developed to estimate the relative rate constants of the complex and the parent ligand. For other systems, such as redox reactions of aliphatic ligands, coordination may result in a masking which simply stops the reaction for steric reasons. In all cases the kinetic behavior is described in terms of the stability constants of the complexes concerned and the rate constant characteristic of each such substrate species which is present.**

One of the unsolved problems of modern coordination chemistry is the prediction of changes in ligand reactivity which arise on coordination. Ideally, this prediction should be in terms of both the kinetic and thermodynamic behavior of the ligand reaction. While there are undoubtedly reactions of coordinated ligands which are not found for the free species, it is more profitable at present to examine systems where the changes in reactivity are more regular. It is assumed that the reactivity patterns of the ligand are merely modified (or masked) by coordination, rather than completely altered. With this starting point, we can examine some typical ligand reactions which can also be studied either in the presence of various amounts of metal ions or in a stable complex. We can then divide such known reactions into three general classes:

1. Reactions of the ligand which are so retarded by coordination that the rate constants are very different for the free and the complexed species. Diazo coupling of aromatic phenolates falls into this class.

2. Reactions of the ligand which are very slow in the absence of an electron pair acceptor or metallic coordination center. Basic hydrolysis of amino acid esters is an example of such a reaction.
3. Reactions whose rate is not greatly affected by coordination. Here the reactive site of the ligand is usually quite distant from the coordination center, though a very active attacking reagent can lead to much the same result if it is sufficiently unselective.

Coordination may change the character of a reaction by affecting either thermodynamic or kinetic factors, or both. Only kinetic factors will be considered here. Kinetic effects may be produced by changes in $\Delta H\ddagger$, $\Delta S\ddagger$, or both, and it is almost impossible to preclude small thermodynamic changes in such reactions. The latter are often less important and will be tentatively ignored.

Since coordination can alter the behavior of a reacting system in many ways, (*18*), we will limit our consideration to relatively simple systems—those in which a ligand forms a $\sigma$-type coordinate bond with an acceptor species. While many mixed complexes are catalytically important, we will assume that their kinetic behavior is the same as simple complexes to a first approximation.

**Ligand Polarization.** Polarization is the most important immediate consequence of ligand coordination. The fact that ligand polarization can assist some of the ligand reactions was first expounded in detail and used by Meerwein (*14*, *24*). Meerwein also provided (but never published) the first interpretation of the way in which coordination may affect the path of the activated complex along the reaction coordinate. Fairly comprehensive reviews of this type of reaction are available (*14*, *18*). However, the kinetic aspects have rarely been discussed in detail (except for biochemical cases (*23*, 8)), because comparative experimental data are meager. Therefore, the examples cited below fall into several loosely related groups.

**Metal Ions and Protons.** Because of the similarities of the reactions of protons and metal ions with Lewis bases, there is much to recommend a comparison of the two processes to furnish a guide to the behavior of metal complexes. This comparison shows the enormously greater effect of the proton due to its greater polarizing power. Although metal ions have been called "super-acid" catalysts by Westheimer (*38*), they are normally much less effective than the proton on a mole–for–mole basis. However, they do permit essentially acid catalyzed reactions in neutral or basic media. Two fundamental reasons for the greater effect of the proton are: (a) the proton-donor atom distance is usually much shorter than the metal-ion-donor atom internuclear distance in comparable compounds (the electric field intensity falls off as $q/r^2$) and (b) the effect of the charge of the metal ion is usually shared by four to six donor atoms; so for any one atom, its full effect is partially reduced by the interaction with these other ligands. The full charge of the proton is usually embedded in the electronic charge cloud of a single donor atom. Back bonding will reduce the effect of such ionic charge on the metal even further and must be important in differentiating the effect of transition and non-transition element coordination centers.

A critical problem related to this is predicting the relative charge displacements which arise on coordination to a series of metal ions or of one metal ion in a series of different coordination environments. In this latter case there is a guide given by Nyholm (*26*) which is a corollary of Pauling's principle of electroneutrality.

Nyholm states that the displacement of charge toward the central ion decreases as the number of ligands increases. Thus, the ligands should exhibit chemical behavior similar to that of the free ligand, as the coordination number of the central ion increases. Since most metal ions tend to attain a constant coordination number by interaction with the solvent when required, this guide must be used with circumspection when a polar solvent is used. Replacing the other ligands by more polarizable ones also decreases the polarization of a given ligand. A related problem which is more difficult to formulate in specific terms is the relative electronegativity of various ligands. Part of this problem is to relate the electronegativity of the ligand to the orbitals from which the shared electrons will come. Another part is to assign some quantitative measure to the various electronegativities which a ligand may exhibit (*15*, *41*).

**Kinetic-Thermodynamic Correlations.** The ligand reaction rate can vary greatly as the metal ion is changed, especially for redox reactions or those with very specific stereochemical demands. In cases where only the acidity of the metal ion is important one might expect more regularity. For very regular systems a "Brönsted Catalysis Law" for metal ions should be valid. Thus,

$$k_M = G_M K_M^{\gamma}$$

where $k_M$ is the rate constant for metal ion catalysis by the ion $M$, $K_M$ is the stability constant of the complex involved, and $G_M$ and $\gamma$ are constants characteristic of the reaction, solvent, and temperature. There are relatively few reactions for which both rate and equilibrium constants are available for the simple reason that stability constants are difficult to measure accurately with a system undergoing reaction rapidly enough to allow good rate data to be obtained. In some cases where data are available such a relationship does not hold, e.g. the metal-ion catalyzed hydrolysis of ATP at pH 9 (*36*). In closely related reactions, such as the same reaction at pH 5, the qualitative data available indicate that it might hold. In the range of pH 7–8, many of the metal ions must be present as partially or completely hydrolyzed species if free, so the catalytically effective species are probably never the simple metal ions, where transition metal ions are involved. Another reaction where a regular trend would be expected is the metal-ion catalyzed hydrolysis of an amino acid ester. For this reaction the effectiveness of the first row transition metal ions follows the order of the stability constants as predicted by the Irving-Williams order (*16*).

**Generalized Rate Equations.** This last reaction is typical of a large class of reactions which may proceed simultaneously by several parallel paths. The rate can be expressed as the sum of several contributions from the uncatalyzed and catalyzed paths. The overall rate for the hydrolysis of an amino acid ester in the presence of a metal salt may be expressed as

$$Rate = \sum_{i=1}^{N} k_i[ML_i][\mathrm{OH}^-] + k_{\mathrm{H}}[\mathrm{H}^+][L] + k_{\mathrm{OH}}[\mathrm{OH}^-][L] + \sum_{h=1}^{N} k_h[ML_h][\mathrm{H_2O}]$$

Here both acid and base catalyzed reactions must be considered. Such reactions exhibit a complicated temperature dependence. Each of the individual rate constants will be governed by a different Arrhenius expression, and the equilibrium constants governing the concentrations of the various $ML_i$ are also temperature dependent. This can be stated explicitly by using stability constant, $\beta$.

$$\beta_i = [ML_i]/[M][L]^i \text{ or } [ML_i] = \beta_i[M][L]^i,$$

so one may write

$$\text{Rate} = \sum_{i=1}^{N} k_i\beta_i[M][L]^i[\mathrm{OH}^-] + k_\mathrm{H}[\mathrm{H}^+][L] + k_\mathrm{OH}[\mathrm{OH}^-][L] + \sum_{h=1}^{N} k_h\beta_h[M][L]^h[\mathrm{H_2O}]$$

The temperature dependence of $\beta_i$ allows it to be expressed as $\exp(-\Delta G_i^\circ/RT)$. The fraction of the metal tied up as $ML_m$ is related to the total concentration of metal, $C_M$, by the expression $[ML_m] = \alpha_m C_M$, and $\alpha_m$ can be expressed as

$$\alpha_m = \frac{\beta_m}{\sum\limits_{i=0}^{i=N} \beta_i[L]^{i-m}}\text{; here } \beta_0 = 1, \textit{ so}[ML_m] = C_M \frac{\beta_m}{\sum\limits_{i=0}^{i=N} \beta_i[L]^{i-m}}$$

This can be combined with the rate expression and the temperature dependence of the $\beta_i$'s to give (where the attack of water on the complexes is ignored, i.e. $k_h = 0$ for all $h$),

$$\text{Rate} = \sum_{j=1}^{j=N} k_j^\circ e^{-\Delta E_j^\ddagger/RT}[\mathrm{OH}^-]C_M \frac{e^{-\Delta G_j^\circ/RT}}{\sum\limits_{i=0}^{i=j} e^{-\Delta G_j^\circ/RT}[L]^{i-j}} + k_\mathrm{H}[\mathrm{H}^+][L] + k_\mathrm{OH}[\mathrm{OH}^-][L]$$

This will give the rate of a base catalyzed reaction involving simple complexes. Obviously if hydroxy complexes are involved, they must be used in the rate expression in addition to, or in place of, the simple complexes. If the attack of the complexes by water is important, the terms in $k_h$ can be included to obtain a term analogous in form to that resulting from the attack of hydroxide ion. One result of the temperature dependence is that gross rates of such reactions may be expected to exhibit temperature extrema. Both $k_\mathrm{H}$ and $k_\mathrm{OH}$ also show an exponential temperature dependence.

### *Aromatic Systems*

**Electrophilic Reactions.** There is sufficient information available on electrophilic substitution of aromatic ligands to examine the utility of the general equation in the limit of one complex. The rate of the diazo coupling reaction of 8-hydroxyquinoline-5-sulfonic acid and its zinc chelate has been determined in an acetate buffer system at pH 5 (*22*). The diazonium salt used was that derived from sulfanilic acid. This attacks the 7-position of the quinoline ring. In a system containing this ligand and zinc ion, there are four possible substrates for this reaction: the phenolate ion, the free phenol, the 1:1 zinc complex and the 2:1 complex. The phenol does not undergo the diazo coupling reaction in simple systems since this is a reaction of the phenolate ion exclusively under such conditions. If the rate of formation of the diazo-coupled product is determined in a system where varying amounts of zinc are added, one obtains very interesting results. If only the initial rates are considered, the pseudo first-order rate constants obtained for the coupling reaction are as follows:

| $\mathrm{Zn}^{+2}$/ligand | 0.00 | 1:2 | 1:1 | 5:1 | 10:1 | 50:1 | 100:1 |
|---|---|---|---|---|---|---|---|
| $k_1 \times 10^3$/min. | 39.3 | 32.9 | 25.6 | 12.9 | 10.3 | 7.89 | 7.87 |

The initial decrease in the pseudo first-order rate constant as the mole ratio (zinc/ligand) increases indicates that the complexes formed are less readily attacked than the phenolate originally present in solution. The final levelling off of the rate at high ratios shows that these solutions ultimately contain all of the ligand in the same form and that the complex is also subject to the diazo coupling reaction. If the stability constants of all the relevant complexes were known with some degree of precision, it would be possible to determine the rate constant for each separate complex. In this particular system the aromatic ligand must compete with the acetate of the buffer to form complexes. Therefore, the constants determined for use here must be for mixed complexes. From the reported equilibrium constants for this system in the absence of acetate it can be estimated that the ratio of the concentration of $Zn(OR)_2$ to that of $Zn(OR)$ is about $10^{-4}$. The rate in terms of the principal reacting species is:

$$\text{Rate} = [RN_2^+]\{k_{21}[RO^-] + k_{22}[ROZn] + k_{23}[Zn(OR)_2]\}$$

Because of the small concentration of the 2:1 complex the last term can be ignored. From the extreme rate values in the absence of zinc and with an excess of zinc, $k_{21}$ and $k_{22}$ are determined as $2.4 \times 10^4$ min.$^{-1}$ and 1.57 min.$^{-1}$ respectively. These values can be combined with the trend in the rate constants to give the stability constant of the reactive complex, presumably Zn(OR)(OAc), as $3 \times 10^7$. For the simple zinc complex in water the literature values of the stability constant for the 1:1 complex vary from $2.5 \times 10^8$ to $6.3 \times 10^8$. The diazo coupling reaction of the complex indicates the smaller effect of coordination *vis a vis* protonation since this reaction is very sensitive to such effects and does not proceed with phenols. Unfortunately the choice of cations for such a reaction is restricted since the cation should not interfere with the analytical methods used to obtain the kinetic data; nor should it introduce additional reactions such as occur with transition metal cations which can catalyze the decomposition of the diazonium salt via a redox process.

Another electrophilic substitution reaction which has been examined for both a free ligand and its metal complexes is mercuration. The rate of mercuration of aromatic compounds can generally be given by a second order expression of the type:

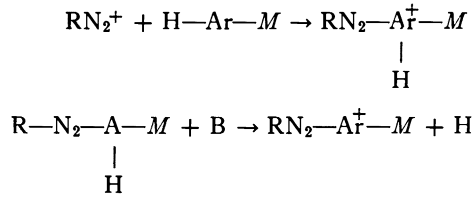
$$\text{Rate} = k_2[\text{Aromatic}][Hg(OAc)_2]$$

The same kind of a rate law has been found for the mercuration of copper oxinate in glacial acetic acid. Here the rate of formation of the mercurated complex is given by the expression:

$$\text{Rate} = k_2 \cdot 2[Cu(8 - HQ)_2][Hg(OAc)_2]$$

where $Cu(8 - HQ)_2$ is copper oxinate and the factor two arises from the fact that each molecule of the copper complex contains two reactive aromatic systems. In the example studied it was found that the copper complex undergoes mercuration much more rapidly than the free phenol in the same environment (*5*). The activation energy for the mercuration of the complex was found to be 19 kcal. and the frequency factor had the unusually high value of $9.6 \times 10^{12}$. This can be compared with the frequency factor reported by D. H. Busch and his co-workers for the alkylation of thiol complexes of nickel (II) (*3*). These workers found a frequency factor in the range 5 × $10^6$ to 2 × $10^8$ as expected for a reaction occurring at localized portions of a large molecule. In the mercuration reaction the attacking reagent may undergo some variation in structure with temperature.

In the electrophilic substitution reactions of coordinated aromatic ligands for which rate data are presently available, there is every indication that the mechanism of the reaction is unchanged in its essentials. Following the lead of the physical organic chemists the course of the reaction of the complex and the diazonium ion can be depicted as:



$$\mathrm{RN_2^+ + H{-}Ar{-}}M \rightarrow \mathrm{RN_2{-}}\underset{\substack{|\\ \mathrm{H}}}{\overset{+}{\mathrm{Ar}}}{-}M \qquad \text{step 1}$$

$$\mathrm{R{-}N_2{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{A}}{-}M + \mathrm{B} \rightarrow \mathrm{RN_2{-}}\overset{+}{\mathrm{Ar}}{-}M + \mathrm{HB^+} \qquad \text{step 2}$$

There is every reason to believe that the first step is rate determining in the coupling reaction of both the free and coordinated species. The overall reaction is thus $S_E2$ in both cases. The diazo coupling studies show how different the results of coordination to a proton and to a metal ion may be.

Without supporting rate data, it is not possible to exclude a mechanism change of a given reaction when attacking agents are changed. Thus, the benzoylation of copper oxinate can be easily effected when aluminum chloride is used as a catalyst. The acetylation of this same complex has not yet been successfully carried out even under forcing conditions (*5*). It seems possible that coordination can seriously disrupt the normal path of a reaction when that path involves $\pi$ complex formation.

**General Order of Rate Constants.** The rate constants of electrophilic reactions of aromatic ligands and their metal complexes fall in the order $k_L > k_{ML} > k_{HL}$. The difference between these rate constants becomes greater as the activity of the attacking reagent decreases. When $L$ is a phenolate, $HL$ is the phenol; when $L$ is an amine, $HL$ is the corresponding ammonium derivative. The possible synthetic applications of this sequence can be appreciated from the fact that 8-hydroxyquinoline is usually sulfonated with 15 to 30% oleum, while its copper (II) complex can be readily sulfonated in 70% sulfuric acid (*5*).

Since electrophilic substitutions of $ML$ are slower than those of $L$ the reverse should be the case for nucleophilic reactions. At present there is no evidence concerning homogeneous systems with metal ions on this point, although the heterogeneous systems consisting of pyridine or its derivatives and a copper salt indicate that this may be true. An unusual kind of coordinate bond is found in *N*-oxides. The behavior of pyridine-*N*-oxide and its derivatives has been studied in detail and provides information concerning the reactivity of systems containing this kind of bond. The pyridine ring of pyridine-*N*-oxide shows all the signs one expects from the formation of an electron withdrawing coordinate bond. Thus, electrophilic substitution is rendered more difficult and the relative reactivity of the ring positions may be altered. Correspondingly, nucleophilic substitutions are generally facilitated. The oxygen atom behaves as a more electronegative species than the metals which form complexes with pyridine. Thus, the orientation of nitration in pyridine-*N*-oxide is to the 4-position while in pyridine itself and the ruthenium complex, $RuPy_3Cl_3$, the orientation is to the 3-position (*34*). The electron withdrawing power of the oxygen is also greater than that of typical Lewis acids such as aluminum chloride since pyridine complexes of these species exhibit the same orientation for halogenation as the free ligand (*28*).

**Some Related Examples.** A closely related problem is the rate behavior of aromatic donors in Friedel-Crafts acylation and analogous reactions. Here coordination plays a dual role. The initial Lewis acid which is added is taken up by the best donor species, frequently the substrate. Once this reaction is at equilibrium, additional amounts of Lewis acid can react with the other species present to generate the effective electrophile. The kinetic behavior of such systems was first delineated by Olivier in 1914. He studied the reactions:

$$BrC_6H_4SO_2Cl + AlCl_3 = BrC_6H_4SO_2Cl \cdot AlCl_3$$

$$BrC_6H_4SO_2Cl \cdot AlCl_3 + C_6H_6 = BrC_6H_4SO_2C_6H_5 \cdot AlCl_3 + HCl$$

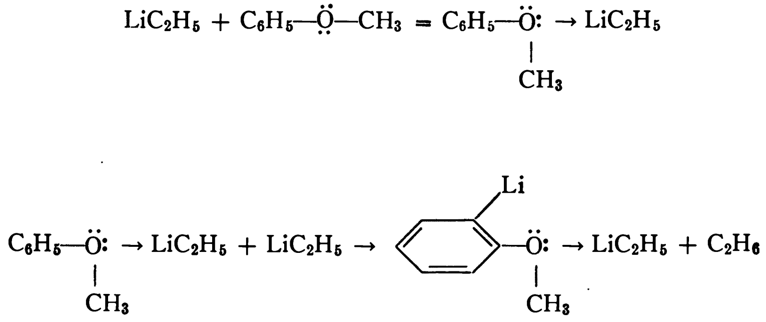
The rate of the second reaction is quite low as long as there is enough free sulfonyl chloride to react with additional amounts of aluminum chloride. Once this is no longer true, further additions of catalyst enormously increase the reaction rate (*27*). The recently discovered swamping catalyst effect in the halogenation of aromatic donor species (*35*) probably exhibits analogous kinetic behavior. The basic rate expression found by Olivier consisted of only one term for reaction when a relatively small amount of aluminum chloride was present:

$$dx/dt = k[Z \cdot AlCl_3] = kK_1[AlCl_3][Z]$$

where $K_1$ is the dissociation constant of the aluminum chloride complex and the sulfonyl chloride, Z. When enough aluminum chloride was present in the reaction mixture so that a fair amount was free, the reaction was accelerated considerably, with the apparent rate constant increasing by a factor of ten. This rate increase is greater than that projected by the above rate expression for variations in $[AlCl_3]$, that Olivier felt that under the conditions used by him, only the complex $Z \cdot AlCl_3$ entered into the reaction. Further interaction of benzene and aluminum chloride is possible.

The reaction of benzoyl chloride and benzene is catalyzed by aluminum chloride and also proceeds via a complex, $C_6H_5COCl \cdot AlCl_3$ (*37*). The reaction of the complex itself with benzene is very slow. When additional aluminum chloride is added to the complex and benzene mixture, the rate is increased enormously. Action of the additional aluminum chloride may follow at least two separate routes. The first involves an activation of one or the other benzene ring by forming a $\pi$ complex. The second involves formation of a much more reactive complex in which two aluminum chloride molecules are coordinated to the benzoyl chloride, one through the chlorine and the other through the oxygen. This would then facilitate the formation of the reactive $C_6H_5CO^+$ ion or its equivalent. However, the literature contains no evidence for a complex, $C_6H_5COCl \cdot 2AlCl_3$. The reaction most probably proceeds via an activation which does not involve the formation of a second $\sigma$ type coordinate bond.

When the substrate forms a complex with the attacking species (but in a way not conducive to further reaction) the net result may be merely to increase the amount of attacking species required for a given degree of reaction. This situation is apparently found in some metalation reactions involving alkyllithium (*32*). A kinetic investigation of the reaction of ethyllithium and anisole showed it to be second order in ethyllithium and apparently first order in anisole (*12*). This is consistent with the reaction scheme:



$$LiC_2H_5 + C_6H_5\text{—}\ddot{\underset{..}{O}}\text{—}CH_3 = C_6H_5\text{—}\underset{\displaystyle CH_3}{\underset{|}{\ddot{O}}}\!:\rightarrow LiC_2H_5$$

The rate of ethane formation was used to obtain kinetic data on this reaction. The effect of coordination on the reaction is primarily to vary the substrate and perhaps retard the reaction somewhat by a slight depletion of electron density from the ortho position.

**Electrostatic Models.** For polar reactions it is possible to develop an electrostatic model. This is necessarily an oversimplification, though it does allow the gross features of such systems to be delineated. Thus, when a complex and the free ligand both react with the same gross mechanism, it is possible to estimate the electrostatic contribution to the change in entropy of activation when the reaction is polar or ionic. Following Laidler (*21*) we can estimate the electrostatic contribution to the entropy of activation as:

$$\Delta S\ddagger_{e.s.} = -10Z_AZ_B \text{ (for water)}$$

If $Z_A$ is the charge on the attacking reagent, $Z_{B1}$ that on the ligand and $Z_{B2}$ is the charge on the metal ion prior to coordination, then

$$\Delta S\ddagger_{e.s.},\ \textit{ligand} \approx -10Z_AZ_{B1}$$

$$\Delta S\ddagger_{e.s.},\ \textit{complex} \approx -10Z_A(Z_{B1} + Z_{B2})$$

and the change in going to the complex is then

$$\Delta\Delta S\ddagger_{e.s.} \approx -10Z_AZ_{B2}$$

An alternative expression based on the single sphere activated complex can also be developed, but its use requires a knowledge of the radii of the activated complex as well as the reactants. The change in the entropy of activation predicted depends on the solvent and the charge on the species attacking the substrate. If the solvent is water and the attacking species is positively charged, coordination will make the entropy values more negative and make the attainment of the transition state more difficult. If the attacking species is negatively charged, the opposite is true.

The same models may be used to obtain the ratio of the rate constants for the ligand and the complex. For the simple two-sphere model the result may be given as:

$$\ln \frac{k_C}{k_F} = -\frac{Z_M Z_B e^2}{\epsilon d_{AB} k T}$$

where $k_C$ is the rate of the reaction for the complex, $k_F$ that of the free ligand, $Z_M$ is the charge on the metal, $Z_B$ is the charge on the attacking species, $\epsilon$ is the dielectric constant of the reaction medium, $d_{AB}$ is the separation distance of the substrate and attacking species in the activated complex (assumed to be the same in the reaction of both the complex and free ligand), $k$ is Boltzmann's constant, and $T$ is the absolute temperature. An analogous equation can be derived for an ion dipole reaction.

These equations show the general theoretical basis for the empirical order of rate constants given earlier; for electrophilic attack on an aromatic ligand $L$, its metal complex $ML$, and its protonated form H$L$, one finds $k_L > k_{ML} > k_{HL}$. Conflicting reports in the literature state that coordination can both accelerate electrophilic aromatic substitution (*30*) and slow it down enormously (*2*). In the first case the rates of nitration of the diprotonated form of *o*-phenanthroline and its Co(III) and Fe(III) complexes were compared. Here coordination prevents protonation in the mixed acid medium used for nitration and $k_{ML} > k_{H_2L}$. In the second case the phenolate form of 8-hydroxyquinoline-5-sulfonic acid and its metal chelates were compared. The complexes underwent iodination much more slowly, if at all, and $k_L > k_{ML}$.

### Aliphatic Systems

The information available on aliphatic systems is much more diversified than that on aromatic systems though the effects of ligand polarization are similar. In general, metal ions allow us to generate the ligand polarization which assists nucleophilic attack. For suitable ligands this can be effected in a basic environment where protons cannot furnish the same general effect.

**Amino Acid Ester Hydrolyses.** The metal-ion catalyzed hydrolysis of amino acid esters was first discovered by Kroll (*20*) and later studied by other investigators (*39*, *1*, *6*). The mechanism has been the subject of some dispute, but it is now obvious that there are at least two reactions in such systems. The first is found at pH 2–8, high metal to ester ratios and corresponds to a second order reaction in which the hydroxide ion or water attacks the chelated 1:1 complex. This reaction must be examined under conditions which do not precipitate the metal. The second reaction in these systems is a second order reaction where the hydroxide ion attacks a 2:1 or higher complex in which the amino acid ester function is not necessarily chelated. This reaction is much slower because the polarizing power of the metal cation is spread over two or more ligands. The reaction is found in solutions at high pH which have high ligand to metal ratios. The relative contributions these two reactions make to a given system may be separated since their rates differ widely; the concentrations of the complexes may be adjusted in the reaction mixtures. However, this has not been done completely for any such system. Bender and Turnquest (*1*) carried out a study in a buffer system composed of glycine and its hydrochloride. They postulated that the reaction proceeds through a mixed complex containing both ester and glycine. Under comparable circumstances the mixed complex involving glycine was a much more effective catalyst than that with the buffer used by Kroll (tris(hydroxymethyl)aminomethane). Bender and Turnquest present evidence supporting a mechanism in which the ester first coordinates to the copper through its amino group. It then undergoes a transient interaction with copper via its carbonyl group which then adds on water and undergoes a proton shift to give: glycine:Cu:$NH_2$—$CH_2$—$C(OH)_2(OCH_3)$. It then splits off water to give an exchange reaction, or methanol to give glycine in a hydrolytic reaction. The participation of the buffer system in this reaction makes the mechanisms of such reactions somewhat different from the same system when no buffer is present.

**Bromination of Beta Keto Esters.** The work of K. A. Pedersen on the bromination of beta keto esters in the presence of copper(II) and other divalent metal ions provides several examples of reactions proceeding via complexes (*29*). The complexes provide an alternative and much more rapid route for the bromination reaction. These reactions are accelerated by bases which take up a proton from the beta keto esters. For such substrates, e.g. ethyl acetoacetate, the general expression for the pseudo first order rate constant in the presence of copper has the form:

$$k = k_0 + k_0'[\mathrm{Cu(II)}] + k_B C_B + k_B'[\mathrm{Cu(II)}]C_B$$

where $k$ is the pseudo first-order rate constant and both the normal and the base catalyzed reactions are subject to metal ion acceleration. When copper(II) is the metal ion present, with ethyl acetoacetate present as substrate and acetate ion as base, the rate constant has the explicit form:

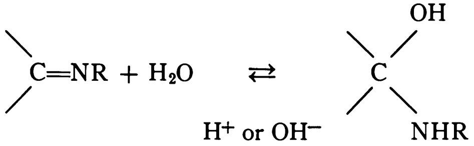
$$k^* = 0.4343k = 0.01855 + 2.69[\mathrm{Cu(II)}] + 8.21[\mathrm{Ac^-}] + 1143[\mathrm{Cu(II)}][\mathrm{Ac^-}].$$

The rate determining step in this reaction is the transfer of a proton from the free or coordinated ethyl acetoacetate to a base which may be water ($k_0$ and $k_0'$ terms) or another base ($k_B$ and $k_B'$ terms). Coordination makes this process easier to effect through the general acid strengthening character of the process for ligands. The mechanism of this reaction is apparently the same for both the complex and the free ligand. Pedersen also carried out studies on the bromination of 2-carbethoxycyclopentanone in the presence of several different metal ions. In this case coordination also has a distinct accelerating effect. The rate constant at 18°C. as before, can be expressed as

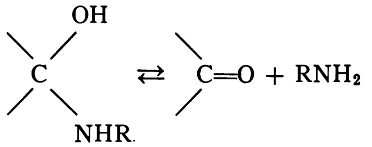
$$k^* = 0.0350 + \sum k_I^* C_I$$

where $C_I$ is the concentration of the metal ion $I$, and $k_I^*$ is the rate constant for the reaction due to this added ion. For the ions examined $k_I^*$ values were: Cu(II), 3.17; Ni(II), 2.15; Zn(II), 0.55; Pb(II), 0.28; and Mn(II), 0.17. Here the order seems to be the same as that of the stability constants, so a Brφnsted type relation may hold.

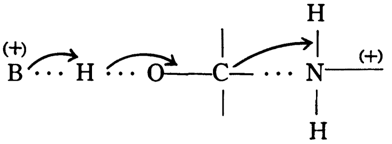
**Hydrolyses of Schiff Bases.** The behavior of Schiff bases and their complexes has been sufficiently studied so that the similarities of the kinetic paths of their hydrolyses can be clearly delineated. The reaction is interpreted in terms of a change in the rate determining step as the pH is changed. In neutral solutions the rate determining step is considered (*7*) the hydration step:



Under acidic conditions the rate determining step is the subsequent splitting:



The transition state for the hydrolysis is given by Cordes and Jencks (*7*) as:



The coordination of the nitrogen atom should assist the electronic shifts postulated here.

Eichhorn and his co-workers have thoroughly studied the kinetics of the formation and hydrolysis of polydentate Schiff bases in the presence of various cations (*9*, *10*, *25*). The reactions are complicated by a factor not found in the absence of metal ions, *i.e.*, the formation of metal chelate complexes stabilizes the Schiff bases thermodynamically but this factor is determined by, and varies with, the central metal ion involved. In the case of bis(2-thiophenyl)-ethylenediamine, both copper (II) and nickel(II) catalyze the hydrolytic decomposition via complex formation. The nickel(II) is the more effective catalyst from the viewpoint of the actual rate constants. However, it requires an activation energy of 12.5 kcal., while the corresponding reaction in the copper(II) case requires only 11.3 kcal. The values for the entropies of activation were found to be $-30.0$ e.u. for the nickel(II) system and $-34.7$ e.u. for the copper(II) system. Studies of the rate of formation of the Schiff bases and their metal complexes (*25*) showed that prior coordination of one of the reactants slowed down the rate of formation of the Schiff base when the other reactant was added. Although copper (more than nickel) favored the production of the Schiff bases from the viewpoint of the thermodynamics of the overall reaction, the formation reactions were slower with copper than with nickel. The rate of hydrolysis of Schiff bases with *ortho*-aminophenols is so fast that the corresponding metal complexes cannot be isolated from solutions containing water (*4*).

The Schiff base formed between 2-pyridinealdehyde and ethylenediamine forms copper complexes in boiling methanol or ethanol, in which one molecule of alcohol has added across one of the C=N double bonds (*13*). This reaction is analogous to the one postulated by Cordes and Jencks as the rate determining step in neutral solutions for the hydrolysis of the free Schiff bases. In this case the alkoxy group goes on the carbon and the hydrogen goes on the nitrogen. Donor groups in the chelate remain coordinated to the copper and this appears to stabilize this intermediate which might otherwise react further. A hindrance to further reaction to give the amine and the aldehyde by solvolysis is the difficulty of transferring the alkyl group from the oxygen to the nitrogen. The analogous complex formed from 1,3-propanediamine and 2-pyridinealdehyde does not tend to add alcohol, presumably because the complex which forms is less strained. These complexes are of the type [Cu(Schiff base)*X*]*X*, where *X* is a univalent anion.

The kinetic parameters above are very similar to those for the hydrolysis of a simple Schiff base, benzalaniline, having an activation energy of 13.2 kcal. and an entropy of activation of about −37 e.u. (*40*). It appears that the rate determining step for hydrolyses of the complexes is the second step, the splitting off of the aldehyde. Under suitable conditions, the intermediates in such hydrolyses for bis complexes (of Schiff bases derived from ethylenediamine) have been isolated. Only one of the ligands is hydrolyzed, and the nitrogen which had been present in the Schiff base is still coordinated to the central metal (*17*).

**Masking.** It is interesting to determine whether coordination masks a ligand completely toward reaction with a given reagent, or only slows down the reaction rate by a large factor. When sufficient data are available on the complexes present in solution, it is possible to determine whether a limiting reaction rate is due to the complex or to the small amount of ligand which is dissociated from it. The question which must be answered is whether or not the limiting rate is equal to the rate of release of ligand from the complex. The periodate oxidation of glycerol and glycerol-telluric acid complexes provides an example. Here the rate drops as the molar ratio of telluric acid to glycerol is increased. The rates of formation and dissociation of the glycerol-telluric acid complex have been determined previously (*11*). The rates of the periodate oxidation of glycerol and glycerol in the presence of telluric acid were determined at pH 8 and are as follows (*19*):

| $[H_6TeO_6]$ | $k_2$ ($M^{-1}$ sec.$^{-1}$) |
|---|---|
| 0 | $22.0 \times 10^{-2}$ |
| 0.00625 | $5.15 \times 10^{-2}$ |
| 0.01250 | $3.14 \times 10^{-2}$ |
| 0.0250 | $1.39 \times 10^{-2}$ |
| 0.0375 | $9.40 \times 10^{-3}$ |

If complexed and free glycol both react with periodate, the rate expression at constant pH will have the form:

$$\text{Rate} = k_2^{\circ}[H_5IO_6][\text{glycerol}] + k_2'[H_5IO_6][\text{complex}]$$

If only the free glycerol is attacked, the second term vanishes. The equilibrium constant governing the complexation is

$$K = [\text{complex}]/[\text{glycerol}][H_5TeO_6^-]$$

If the reaction of the complex can be ignored, the rate equation can then be written as:

$$\text{Rate} = k_2^{\circ}\,\frac{[\text{complex}]}{[H_5TeO_6^-]}\cdot\frac{1}{K}\,[H_5IO_6] = k_2''[H_5IO_6]$$

where $k_2''$ is the measured apparent rate constant; then $k_2''$ is a composite of the terms preceeding the concentration term for periodate. Since $H_6TeO_6$ is a weak acid, its ionization constant can be written as

$$K_i = (H_5TeO_6^-)(H^+)/(H_6TeO_6)$$

rearranging terms gives

$$k_2'' = \frac{k_2^\circ[\text{complex}][H^+]}{K[H_6TeO_6]K_i}$$

When the reaction is carried out at constant pH and when the ratio of telluric acid to glycerol is large, then

$$d \log k_2''/d \log[H_6TeO_6] = -1$$

Data which allow this equation to be tested must be on solutions which have a high ratio of telluric acid to glycerol. In the table below this is satisfied as the concentration of glycerol in all the solutions is $4.13 \times 10^{-3}M$. The pH of the reaction medium is 8.0.

| $[H_6TeO_6]$ | $k_2''$ | $\log k_2''$ | $\log[H_6TeO_6]$ | $\frac{\Delta \log k_2''}{\Delta \log[H_6TeO_6]}$ |
|---|---|---|---|---|
| .0125 | .0314 | −1.5351 | −1.9031 | |
| .0250 | .0139 | −1.8570 | −1.5935 | −1.04 |
| .0375 | .0094 | −2.0269 | −1.4260 | −1.02 |

These data indicate that the complexed telluric acid is undergoing no apparent reaction. If any such reaction occurs, its rate constant is very, very small.

Such effective masking may be traced to two factors; (*a*) the inertness of the telluric acid complexes and (*b*) the near identity of the demands of oxidant and tellurate on the coordinating properties of the ligand. The decrease in reaction rate here is consistent with a very slow release of ligand from the tellurate complex as established by Edwards and his co-workers (*11*).

**Stereospecific Ligand Reactions.** One would expect the reaction of a coordinated asymmetric species with another asymmetric species to be stereospecific. While ligand replacement reactions of this sort are well established, other kinds of reactions have been investigated only rarely, so little data are available. Richtmeyer and Hudson (*31*) found that the reducing power of D-altrose was only about 56% of that of L-altrose towards the alkaline copper tartrate reagent of Schaffer and Hartmann (*33*). The "relative reducing power" was found by determining the amount of the alkaline copper tartrate consumed in 15 minutes while the samples were held at 20°C. The relative reducing powers are especially interesting.

**Relative Reducing Power**

| *Sugar* | *D-tartrate reagent* | *L-tartrate reagent* |
|---|---|---|
| D-Glucose | 100 | 100 |
| D-Altrose | 53.2 | 87.5 |
| L-Altrose | 86.0 | 53.4 |
| D-Arabinose | 73.1 | 84.8 |
| L-Arabinose | 83.1 | 72.9 |

These values indicate that the rate of reaction of D-altrose with D-tartrate is the same as that of L-altrose with L-tartrate and that other rates pair up similarly. Similar data were obtained for some other pairs of enantiomers. Unfortunately no kinetic data are available on these systems.

## *Conclusion*

A large number of ligand reactions exist where both the kinetic patterns and the general mechanistic features are modified, rather than destroyed, by coordination. These reactions can furnish much information on the way coordination *per se* will affect the kinetic and thermodynamic aspects of a reaction. Generally, these will be reactions where specific redox properties of the central ion are not involved. In many of these cases coordination can provide a rational basis for the modification of synthetic procedures.

## *Acknowledgements*

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# Discussion

**Mark M. Jones:** There is one change that I could make in the paper. About ten years ago Daryle Busch and John Bailar (*1*) reported an intermediate type described under hydrolyses of Schiff bases, and I want to apologize for omitting it in the literature.

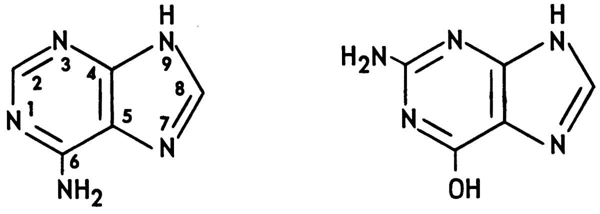
This entire area of study is highly controversial, and the views that I have presented in this paper are certainly not to be taken as a consensus. They are quite strongly partisan. Other viewpoints are quite varied, and I have been privileged to present mine. Other investigators have not been so privileged, and I think one purpose of the discussion is to allow these people to present their views.

**Gunther Eichhorn:** I should like to discuss an example of metal catalysis that does not fit the picture presented in Dr. Jones' paper. It is a process mediated by either metal ions or protons, with the latter functioning more efficiently. We have become interested in reactions of metal ions with polynucleotides, in the hope of using these coordination reactions to determine the sequence of bases along a polynucleotide chain.

The four bases whose sequence determines the hereditary information in ribonucleic acid (RNA), the naturally occurring polynucleotide, are adenine, cytosine, guanine, and uracil. These structures are as shown in Figure A.

In RNA these bases are attached to the ribose phosphate chain as shown in Figure B. Synthetic polynucleotides can be produced that are like RNA in every respect except that they contain only one of the four bases; they are called Poly A, Poly C, and Poly U. Poly G unfortunately cannot be prepared in high molecular weight form; hence Poly I (in which the guanine amino groups have been removed) is prepared instead.

We have been looking at reactions which degrade these molecules by splitting phosphate bonds. This problem is important for sequential analysis since agents are required that split phosphate bonds attached to one nucleotide base preferentially to phosphate bonds attached to other bases. It appears that the cleavage by zinc (II) is indeed such a specific reaction.



**Adenine** **Guanine**

**Cytosine** **Uracil**

*Figure A. Structures for adenine, guanine, cytosine and uracil*

Metal ions can attach themselves at two different types of sites on a polynucleotide—i.e., the phosphate and the donor groups on the bases. Some of the metal ions do indeed bind at one site, and some metal ions at the other. Those binding to the phosphate will promote the cleavage of the phosphate bond, whereas metal ions binding on the base will inhibit such cleavage in a manner that illustrates one of Dr. Jones' points very well.

The attachment of zinc to the phosphate groups and the subsequent cleavage of the phosphate bonds demonstrate the case opposite to Dr. Jones', in that metal ions are much more effective than protons in this cleavage reaction. Evidently this is caused by stabilization of the intermediate by chelation of the metal to the hydroxyl group as well as to the phosphate. In fact, deoxyribonucleic acid (DNA), which is like RNA except that it lacks the 2′-hydroxyl group, cannot be cleaved by metal ions.

RNA and the synthetic polynucleotides can be cleaved in the absence of divalent metal ions by basic hydrolysis as shown in Figure C, in which the formation of small oligonucleotides from highly polymeric nucleotide chains is followed. In the absence of divalent metal, the reaction rates are approximately the same for RNA, Poly I, and Poly A.

On the other hand, in the presence of zinc ions (Figure D) the RNA, Poly A, and Poly U all have a much higher reaction rate than Poly I. Apparently the reac-

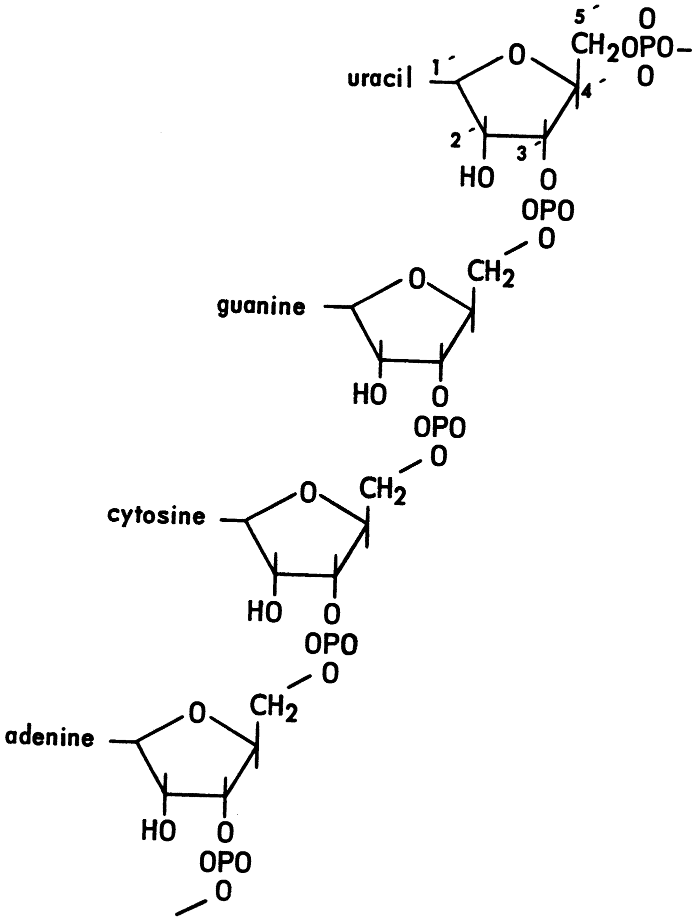


*Figure B. Attachment of the four bases to the ribose phosphate chain*

tion with zinc does involve some specificity in its discrimination between the phosphate bonds attached to different bases in a polynucleotide chain.

Just as zinc reacts with the phosphates, silver(I) reacts with the bases. Figure E shows some titration curves for 1:1 mixtures of silver ion and polynucleotides. Below alkaline pH, silver ions do not compete with any protons on Poly A and Poly C (A and B); on the other hand, Poly I and Poly U (C and D) compete rather effectively. This conclusion is borne out in a comparison of the ultraviolet spectra of the silver complexes of Poly I and Poly A with the spectra of the uncomplexed polynucleotides (Figures F and G).

Figure H shows experiments in which metals bind to phosphates and bases simultaneously—i.e., degradation (at pH 7) of the polynucleotides by zinc in the presence of silver ion. Silver inhibits the degradation of Poly A and Poly C, which do not readily react strongly with silver.

We have thus illustrated two ways in which metal ions can produce specific reactions on a polynucleotide chain. Attachment to the phosphate can result in

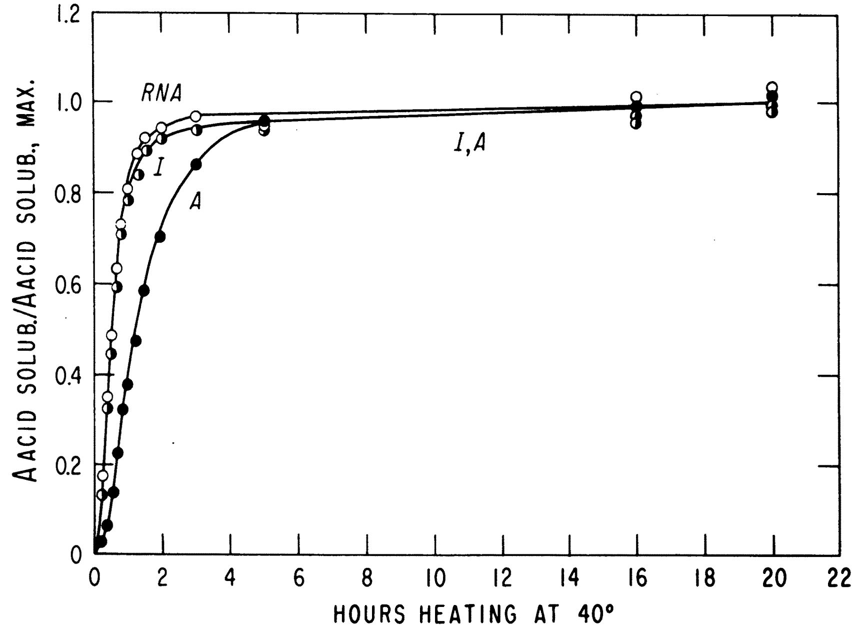


*Figure C. Cleaving of RNA and the synthetic polynucleotides in the absence of divalent metal ions by basic hydrolysis*

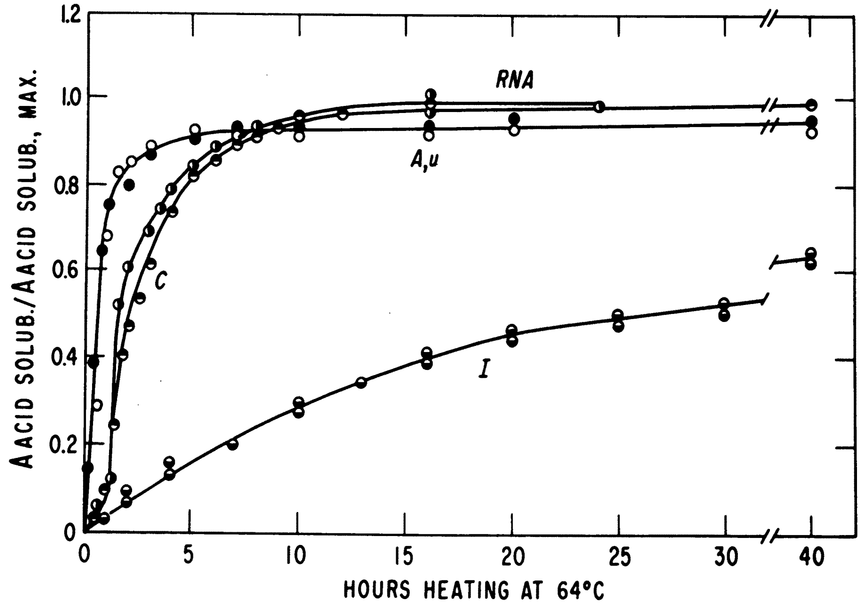
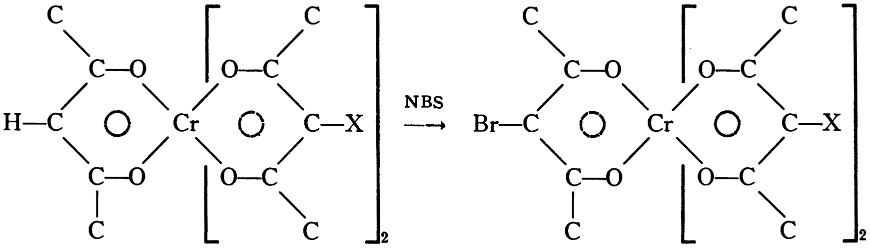


*Figure D. Cleaving of RNA and synthetic polynucleotides in the presence of zinc ions.*

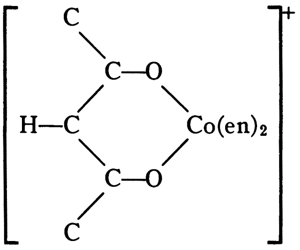
the preferential cleavage of some phosphate bonds, and attachments to the bases can result in inhibiting such cleavages in a specific fashion.

**James Collman:** We have been working with reactions of coordinate ligands. Although most of our work has been of a qualitative nature, we have observed certain reactions which illustrate changes in the reactivity of a ligand brought about by altering the metal complex. I thought it might be appropriate to comment on a few of these because they are different from the general theme that Dr. Jones has expressed.

In the first example, we studied the competitive bromination of two disubstituted trisacetylacetonates of chromium. The dichloro compound (X = Cl) reacts with *N*-bromosuccinimide much more rapidly than the dinitro compound (X = $NO_2$). The reaction is thought to involve electrophilic substitution. This substantial influence of substituents on the reaction rate is undoubtedly an electronic rather than a steric effect.



The effect of the overall charge of the complex on ligand reactivity is illustrated by bis(ethylenediamine)-acetylacetonatocobalt(III). The acetylacetonate ring in this charged complex fails to react with *N*-bromosuccinimide—even under forcing conditions. By contrast, neutral chelates such as tris(acetylacetonate)cobalt react rapidly with NBS. This enormous difference in ligand reactivity must be ascribed to the charge on the complex. The cationic complex does undergo slow deuteration in strongly acidified $D_2O$. This reaction can be followed by nuclear magnetic resonance.



Finally, I would like to comment briefly on the effect of the metal on ligand reactivity. In a number of instances chelate rings in the trisacetylacetonates of rhodium(III), cobalt(III), and chromium(III) undergo electrophilic substitutions at different rates. The relative reactivity of these complexes is chromium > cobalt ≫ rhodium. Thus far our data are only qualitative.

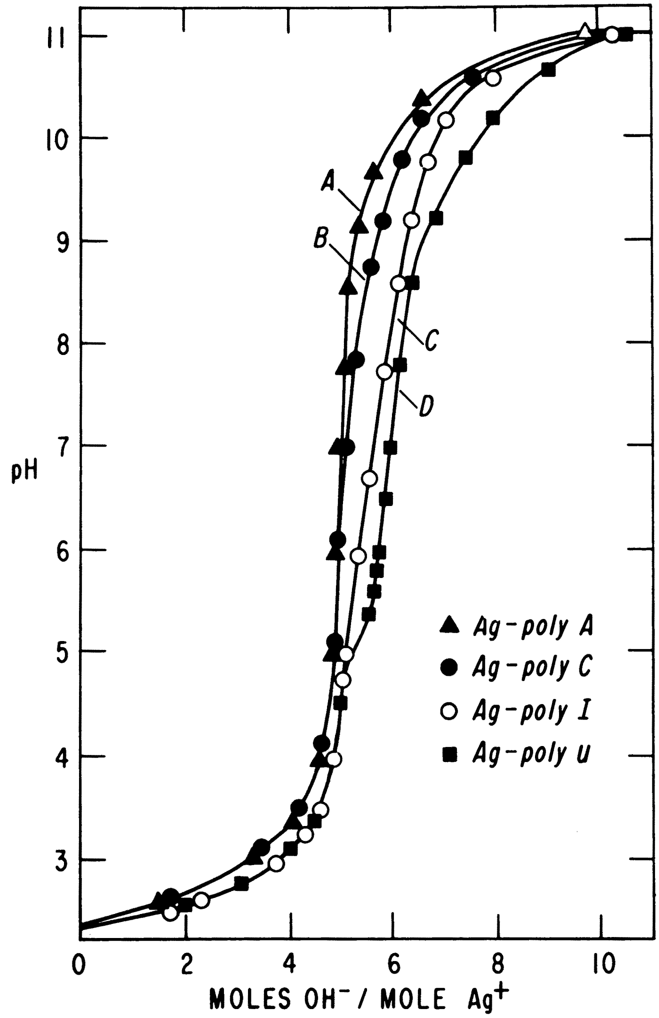
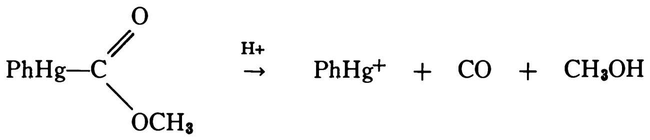


*Figure E. Titration curves for 1:1 mixtures of silver ion and polynucleotides*

**Raymond Dessy:** We have been led to observations which I would like to sketch briefly.

These involve, not the transition metals which have been stressed here but rather nontransition metals, which could be described as $d_{10}$, $d_0$, and no-$d$ cases.

The first observation was that substances containing mercury bonded to the unusual carbomethoxyl group,



$$PhHg{-}C(=O)OCH_3 \xrightarrow{H+} PhHg^+ + CO + CH_3OH$$

in dimethylsulfoxide solvent (a poor coordinator for anions) undergo cleavage by acetic acid to liberate methyl alcohol, carbon monoxide, and a phenylmercury anion compound. In the absence of halide ion, the reaction goes at an unobservable rate. As a matter of fact we generate this particular compound in the presence of acetic acid. Only when halide ion is present does this reaction proceed. With the rate constants we have observed, the ratio $k^{x^-}/k^0$ is greater than $10^4$. The sequence of catalytic activity observed is: iodide ion > bromide ion > chloride ion. Strangely enough this same sort of effect can be seen in a $d_0$ case, the decomposition of tributyltin hydride, again in dimethylsulfoxide solvent; acetic acid provides a proton source which will discharge against the incipient hydride ion to give hydrogen gas. When halide ion is added the reaction is truly catalytic in halide ion. From the rate data and kinetics it is possible now to obtain an exact expression for the ratio, $k^{Cl^-}/k^0$. This is the rate at which this reaction proceeds in the presence of stoichiometric amounts of chloride ion to the rate of the reaction when chloride ion is absent. Again, it is about $10^4$.

The halide sequence is completely reversed: chloride ion > bromide ion > iodide ion. This has caused us some problem, but as yet we have no explanation for it. In both cases there is enough evidence from other kinetic investigations and deuterium labelling to realize that the metal with the attached organic group R

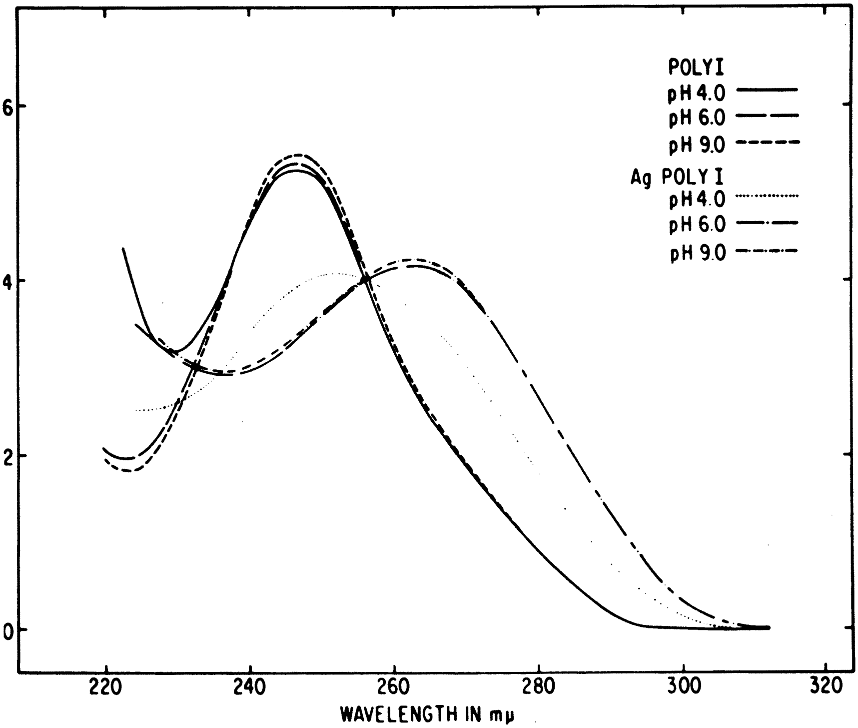
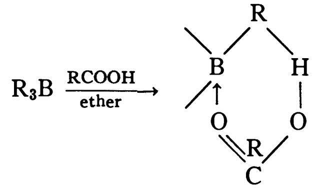


*Figure F. Ultraviolet spectra of silver complexes of Poly I and Poly A compared with the spectra of the uncomplexed polynucleotides* becomes coordinated with halide ion, and that this coordination step affects the reactivity of R.

This would indicate that at least in these two cases, $d_{10}$ and $d_0$, the reactivity of a ligand, an alkyl group, or a hydrogen attached to a metal can be affected by placing another ligand on the metal.

We have also looked at a no-*d* case where we have cleaved $R_3B$ compounds, triethylboron, with carboxylic acids in an ethereal environment. Once again we have the possibility of coordinating a substance like a carboxylic acid with our boron compound in a six-membered ring,



When the boron compound coordinates with the carboxylic acid in this way, two things result. First it labilizes the potential carbanion. One can prove this by infrared observations where, in going from $BH_3$ to $BH_4$, such coordination weakens the BH linkage. At the same time, this should increase the acidity of the

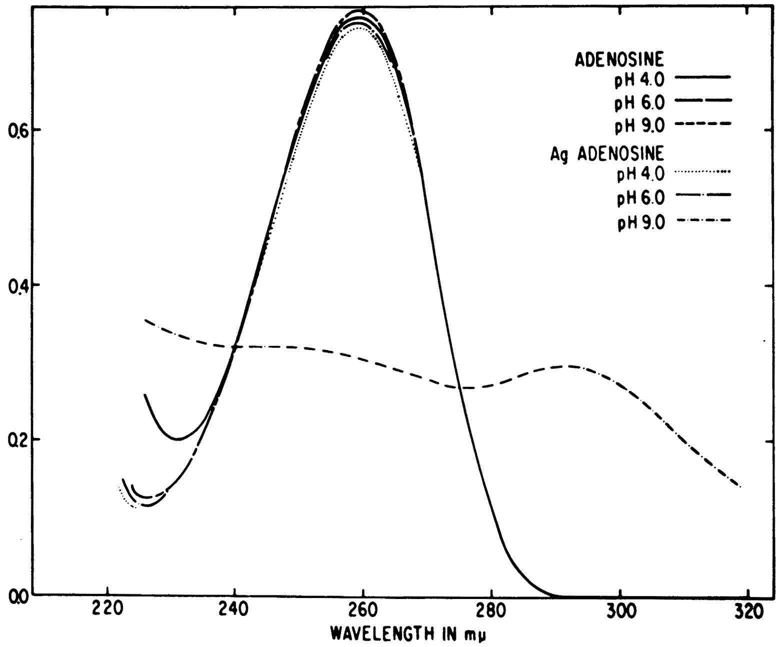


*Figure G. Ultraviolet spectra of silver complexes of Poly I and Poly A compared with the spectra of the uncomplexed polynucleotides*

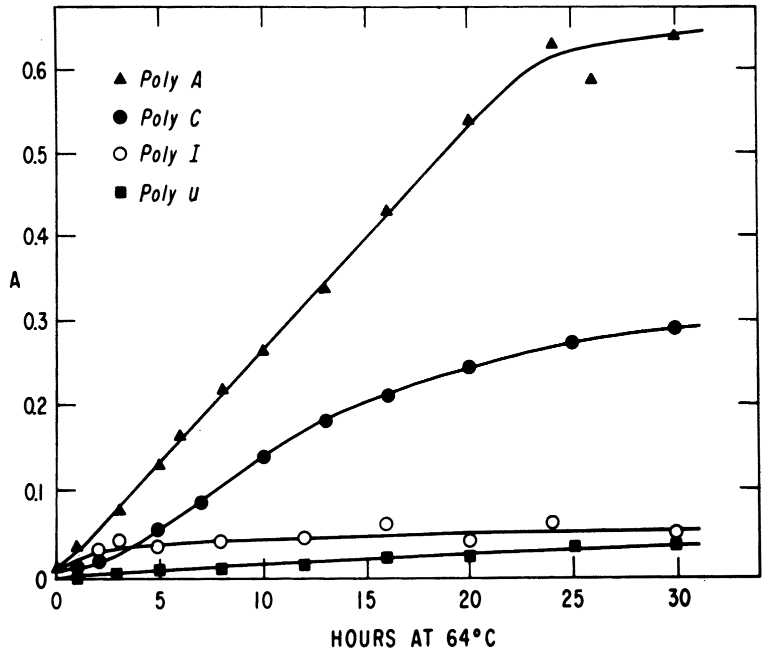
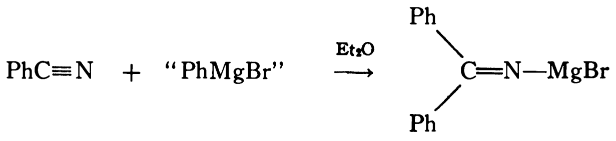


*Figure H. Degradation of the polynucleotides by zinc in the presence of silver ion*

proton and lead, as we can observe very nicely, to the production of RH and $R_2BO_2CR$. Interestingly the kinetic observations that result from varying the acid strength are just what might be expected from such a process. A plot of the log of the second-order rate constant for this reaction *vs.* the pKa's of the acids used, gives a correlation—as a matter of fact (Figure I) a linear one (but I think that is more coincidence than anything else)—and the slope is not what you might expect from electrophilic attack on the carbon of the $R_3B$ compound by proton. The stronger the acid, the slower the reaction. The only explanation I can think of is that the nucleophilic character of the oxygen is the important factor.

These three systems then indicate that attaching ligands to simple organometallic compounds can change their reactivity markedly. It is not necessary to look at this type of direct coordination; even changes in the environment can obviously modify organometallic reaction rates, and apparently the coordination chemist is much more familiar with this. But this type of knowledge has not been transferred over very well to organometallic chemistry. One case we have observed is reactions of nitriles with Grignard reagents. This leads to an addition across the —C≡N.



$$PhC{\equiv}N + \text{“}PhMgBr\text{”} \xrightarrow{Et_2O} (Ph)_2C{=}N{-}MgBr$$

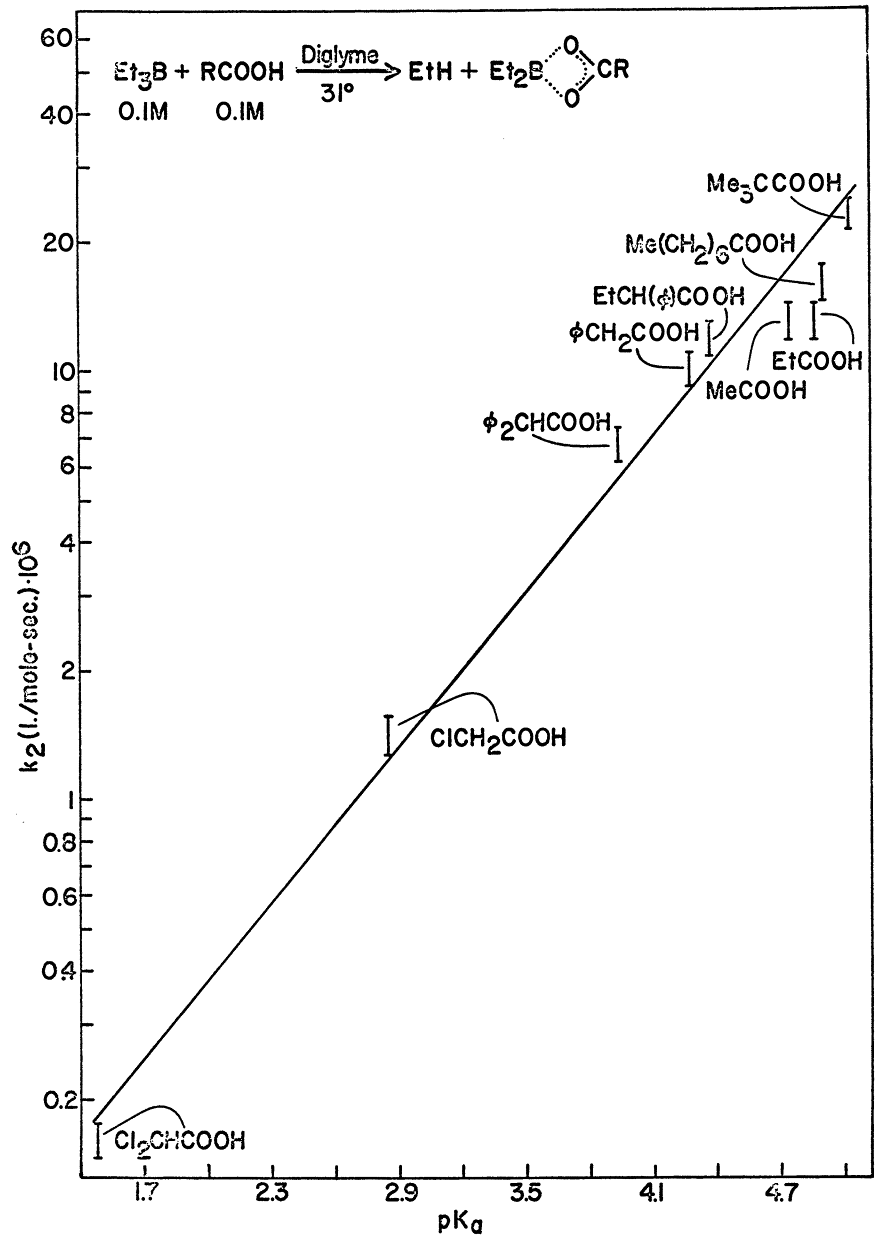


*Figure 1. Log of second-order rate constant vs. $pK_a$*

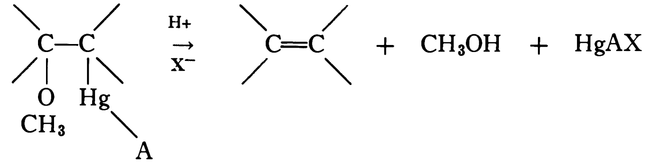
In ether solvents this reaction is very slow. As a matter of fact, it may take 24 to 30 hours to accomplish at reasonable concentration. But adding materials like lithium perchlorate accelerates the reaction by a factor of about 100, and it is over in 15 minutes. Presumably, some type of ion quadrapole association is occurring, let's say, between the Grignard reagent and the lithium perchlorate. Now we are able to affect the reactivity of an organometallic compound not only by direct coordination but by changing its solvent environment.

**Leonard Katzin**: I can't comment on all these examples that Dr. Dessy has presented, but certainly these can be viewed as anion replacement reactions of a conventional inorganic type, with inversion of the order of the anions. I am not sure if it is typical of the hydrides or if it is typical of the quadrivalent metals, because the one example I am thinking of is a thorium compound, inorganic. This is solid material prepared by treating thorium metal with hydrochloric acid, with which it reacts violently leaving large amounts of solid ThH(OH)O. It is decomposed by adding a little fluoride, which is the continuation of the series here. Two things are duplicated. One is the fact you have the hydride, but also you have a tetravalent metal. At this point I wouldn't say which is the determining factor in how this series runs, but certainly that is the same sort of thing; and here it would depend on the actual structure of this complex. But if the ether is coordinated to the magnesium, it is possible that even though perchlorate is generally a poor donor, it might be better than ether and displace the ether at this time.

**Jack Halpern**: I want to ask Dr. Dessy two questions. Sometime ago we looked at substantially the same reaction (i.e., decomposition of methoxycarbonyl mercuric acetate) in aqueous solution, and we found also that this decomposition is catalyzed by hydrogen ion and by chloride ion. The rate is first-order in ($H^+$), but we found that in addition to a path first-order in ($Cl^-$) there were also appreciable contributions from higher order paths, certainly second-order and possibly also third. This implies that the process is further aided by coordination of more than one halide to the metal. I wondered whether there were any corresponding indications in these solvent systems.

The other point concerns the persistent controversy about the detailed mechanisms of general reactions of this type—i.e., the deoxymercuration reactions, not only of methoxycarbonyl compounds but also of the corresponding olefin adducts. These are clearly concerted processes that are aided in some way by coordination of $X^-$ on the mercury and coordination of $H^+$ on the oxygen. There has been controversy, in which Wright and others have participated, as to whether the detailed mechanism involves a cyclic intermediate, in other words whether undissociated HX participates in the reaction or whether the assistance at the metal and oxygen centers are independent processes. Have you any comments on this?

**Dr. Dessy**: First, I think Maurice Kreevoy feels that the deoxymercuration reaction



(i)

can involve proton participation, often with some type of halide assistance. Dr. Kreevoy has stated—and I agree with him—that in the decomposition we looked at we may have chosen reactant concentrations which would not reveal, from the kinetic data, higher orders in halide ion. As a matter of fact, in the deoxymercuration reaction that he studied, where the anion is iodide ion, the kinetics indicate that the reaction is first-order in substrate, and may be zero- or first-order in proton, and zero-, first-, or second-order in iodide ion. Unless we went back and looked better at this system, which I have no intention of doing, I would say it is possible that more than one halide ion could be there. I have always felt that the odd order in halide, 1.6, that you had—

**Dr. Halpern**: That was actually a composite order.

**Dr. Dessy**: Yes, and it indicates why you had such a difficult time with the kinetics. The solvent system that was used had hydrogen bonding possibilities with the halide ion. Henry Kuivila has decomposed tributyltin hydride in alcohol solvents with carboxylic acids, and there is no effect of halide ion. Apparently the tin under those conditions cannot compete with the solvent for the halide ion. Halide ion is all hydrogen bonded.

With respect to the Wright controversy, I would rather not comment.

**John Bailar**: We have observed a case or two in which Schiff's base is formed directly from ligands in solution. I don't think it is always necessary to have the free aldehyde and the free amine. If they are insoluble, that is another matter.

Yesterday I attributed to Prof. Dwyer a very nice piece of work on the rearrangement of the dichlorotriethylenetetramine complex. I have discovered since that this work was done by Dr. Sargeson, and I want to give him credit for it.

You might be interested in some ligand reaction work we are doing. Someone remarked yesterday that the discussion doesn't seem to be relevant to the papers presented except that they are on the same general topic, I have taken that as justification to comment on a reaction we are studying which is biological and thus ties in with Gunther Eichhorn's paper, though the work is vastly different.

This goes back to the time when Pasteur discovered three methods of resolving organic compounds. One can pick the enantiomorphs out with tweezers, or form diastereoisomers, or let bacteria eat them. People have used the first two methods to resolve inorganic complexes, but they haven't used the third. It occurred to me some time ago that perhaps bacteria would eat some of these complexes and maybe they would be stereospecific about it. I have some preliminary results which may interest you.

John Gildard has resolved the complex tris(ethylenediamine)cobalt(III) into the D and L form, and by forming diastereoisomers he has treated these separately with pseudonoma bacterium. The results have been very, interesting indeed.

These bacteria will eat the D-form of this compound, or at least they consume the nitrogen of the ethylenediamine. They can't get at the carbon, apparently; we have to add some other source of carbon or they won't grow, and of course, the bacteria need enzymes and small amounts of mineral matter.

When the bacteria are exposed to the L-complex, a very interesting picture appears. Not only will they not eat the L-isomer, but it inhibits their growth; so obviously this bacterial method cannot be used to resolve the trisethylenediamine complex. There are, of course, thousands of bacteria and hundreds of complexes which we can study.

I believed that when the bacteria ate away an ethylenediamine molecule that nitrogen and carbon dioxide would escape and that would be that. But the bacteria are much more complex, and they convert the ethylenediamine into an amino acid or something of that sort. This complexes again, and a rather complicated picture is built up. However, I am highly encouraged, because the bacteria do behave differently toward these two stereoisomers, and whether we resolve the complex or not, which was the original goal, doesn't really matter.

**Gilbert Haight:** For many years, I have been studying molybdate-catalyzed reductions of such weak complexing agents as perchlorates and nitrates, using the Bray technique of studying rate laws and stoichiometry and deducing the rest.

In order to interpret these studies we had to postulate a complex between the inert nitrate or perchlorate and the molybdate. I would like to show you some analagous studies we have done in order to justify these complexes and some of the reactions we have obtained with chromate.

We have found that $HCrO_4^-$ in dilute solutions will undergo condensation with hydrogen phosphate, bisulfate, and even hydrochloric acid in water to form these mixed anhydrides like $CrSO_7^{-2}$. We have been able to measure equilibrium constants, and I wondered if this wouldn't prove fruitful in studying such reactions as the oxidation of sulfite with chromate. Sulfite is oxidized to a mixture of dithionate and sulfate.

There has been a great deal of work showing synergistic effects when chromates are reduced. The very active intermediates—chromium(V) and chromium(IV)—seem to oxidize reducing agents the chromate itself will not. I think most of you are familiar with the oxidation of manganese(II) to manganese dioxide in the presence of reducing agents when chromate is used.

In sulfite we have, apparently, a reducing agent which can function both as an oxygen acceptor and an electron acceptor and can serve as its own trap for these active Cr(IV) and Cr(V) intermediates. We have carried out the kinetics of this reaction at pH 5 in an acetate buffer, where, according to the literature, the species present in solution are $HCrO_4^-$ for the chromate and $HSO_3^-$ for the bisulfite. The kinetics follow the stoichiometry

$$\mathrm{Cr(VI)} + 2\,HSO_3^- \rightarrow \mathrm{Cr(III)} + \tfrac{1}{2}S_2O_6^{-2} + SO_4^{-2}$$

since the rate law is first-order in chromate and second-order in sulfite. The reaction is also first-order in hydrogen ion. This leads to a mechanism involving the preformation of $CrSO_6^{-2}$. We think this is a pre-equilibrium because some fast reaction work done in Gil Gordon's laboratory at Maryland recently has shown that the reaction is initially slower during the first few milliseconds than in the eventual steady state.

When a second sulfite or $SO_2$, if you like, or $H_2SO_3$ attacks $O_3CrOSO_2^{-2}$, it goes all in one fell-swoop to chromic ion, to which sulfate is attached at the end of the reaction, and an $SO_3\cdot^-$ radical. One can't precipitate sulfate with barium immediately after the reaction. Coordination of the chromium(III) stabilizes the radical until it can react with another as was mentioned by Dr. Halpern. This mechanism accounts for both the stoichiometry and kinetics.

A point that seems to have been coming out of all of our work is that in interactions, especially oxidation-reduction reactions involving oxygenated species, we have to consider such condensations as this. I shouldn't be surprised if they were involved in a lot of the reactions involving simple metal ions which are hydrated. A recent article (*2*) states that bichromate also condenses with an aquo complex of cobalt with a much higher formation constant than that for $CrSO_7^{-2}$ and with the elimination of a proton, which should make that more difficult than the formation of $CrSO_7^{-2}$. I think we are going to see more of this sort of anhydride occuring in redox reactions.

I don't know if this is the influence of the central atom sulfur on the ligand chromate, or the central atom chromium on the ligand sulfate.

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(2) Sullivan, J. C., French, J. E., *Inorg. Chem.* **3,** 832 (1964).

# 8

# Insertion Reactions of Metal Complexes

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**The insertion reaction is encountered with surprising frequency in organometallic chemistry. Many types of unsaturated molecules undergo the reaction with many different metal compounds. For example, compounds containing metal-hydrogen, metal-carbon, metal-oxygen, metal-nitrogen, metal-halogen, and metal-metal bonds have reacted with one or more of the following unsaturated compounds: carbon monoxide, olefins, dienes, acetylenes, carbonyl compounds, and cyanides. There are still many gaps in our knowledge of the insertion reaction, but already it has been applied in numerous unusual and useful chemical syntheses.**

The reaction mechanism of the various metal complexes clearly have much in common. The recently recognized insertion reaction appears to be a particularly good example of a reaction which is general among the metal compounds. In the following discussion I intend to point out the generality of the insertion reaction with examples from the literature and from our own work. The most complete series of substantiated insertion reactions involves the organocobalt carbonyl complexes, and these reactions will form the nucleus of the discussion.

The insertion reaction is the addition of a covalent metal compound, M–X, to a neutral unsaturated molecule, :Y, forming a new complex where the unsaturated molecule has inserted itself between the metal and the atom which was initially bonded to the metal.

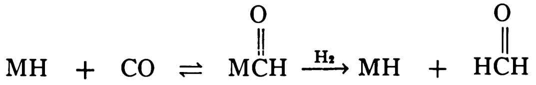
$$\text{M–Z} + \text{:Y} \rightarrow \text{M–Y–Z} \qquad (1)$$

The unsaturated molecule :Y may be carbon monoxide, an olefin, a conjugated diene, an acetylene, a carbonyl compound, various unsaturated carbon-nitrogen compounds, or probably any of several other unsaturated materials. The reactive part of the covalent metal compound is usually a metal-hydrogen, metal-carbon, metal-oxygen, metal-halogen, metal-nitrogen, or metal-metal group. This reaction is actually a special case of an addition reaction in which the molecule that is adding is a covalent metal compound. Since the covalent metal compound is completely added in one step, a cis addition is expected.

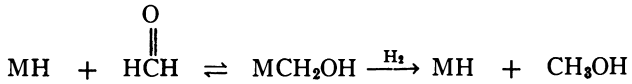
The insertion reaction is usually more complicated than equation (1) would indicate. The evidence now available suggests that M–X must be coordinately unsaturated in order to react with :Y. Therefore, before the insertion reaction can occur, a preliminary step is often required to form M–Z from a coordinately saturated species. Furthermore, the insertion reaction may not go to completion or may not even go at all, unless there is another ligand molecule present to form a stable, coordinately saturated compound from M–Y–Z as the final product.

### *Carbon Monoxide Insertion Reaction*

**Metal Hydrides.** The simplest reactions in this group are the various catalytic reduction reactions of carbon monoxide. Methane or higher hydrocarbons, methanol or higher alcohols, and a variety of other oxygenated organic compounds may be formed, depending upon the catalyst and reaction conditions (*23*). There is little evidence about the mechanism of these reactions, but the initial step in every example is probably a carbon monoxide insertion into a metal hydride, followed by reduction reactions.



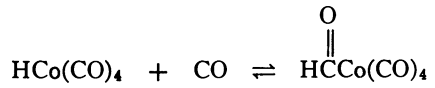
$$MH + CO \rightleftharpoons M\overset{\overset{O}{\|}}{C}H \xrightarrow{H_2} MH + H\overset{\overset{O}{\|}}{C}H \qquad (2)$$



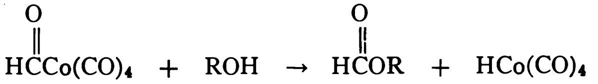
$$MH + H\overset{\overset{O}{\|}}{C}H \rightleftharpoons MCH_2OH \xrightarrow{H_2} MH + CH_3OH \qquad (3)$$

The hydride involved is probably on the surface of the catalyst.

A similar mechanism may explain the formation of formate esters in the hydroformylation reaction (*90*, *64*).

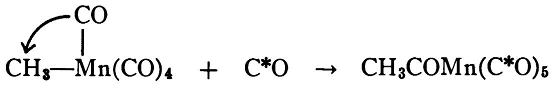


$$HCo(CO)_4 + CO \rightleftharpoons H\overset{\overset{O}{\|}}{C}Co(CO)_4 \qquad (4)$$



$$H\overset{\overset{O}{\|}}{C}Co(CO)_4 + ROH \rightarrow H\overset{\overset{O}{\|}}{C}OR + HCo(CO)_4 \qquad (5)$$

**Metal-Carbon Compounds.** The existence of the insertion reaction and, in fact, the first convincing example of it, was reported by Coffield and co-workers in 1957. They showed that alkylmanganese pentacarbonyls would absorb carbon monoxide, sometimes reversibly, to form acylmanganese pentacarbonyls (*16*). They further showed in 1959 (*17*), by means of $C^{14}$ labeled CO, that with methylmanganese pentacarbonyl, a coordinated carbon monoxide inserted rather than the incoming carbon monoxide.



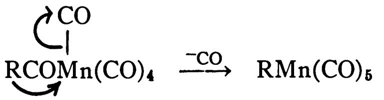
$$CH_3{-}\overset{\overset{CO}{|}}{Mn}(CO)_4 + C^*O \rightarrow CH_3COMn(C^*O)_5 \qquad (6)$$

These reaction rates have been measured, but the data do not distinguish between two likely mechanisms (*14*). An important question, therefore, is unanswered: does the coordinated carbonyl group insert before the new CO is added or does the incoming CO push the coordinated carbonyl into the acyl position?

The mechanism of the reverse reaction, the elimination of CO from an acylmetal carbonyl to form an alkylmetal carbonyl, is also not clear. Two possibilities exist: the acylmetal carbonyl may simply dissociate into a coordinately unsaturated acylmetal complex and CO and then rearrange to the alkylmetal carbonyl:

$$RCOMn(CO)_5 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} RCOMn(CO)_4 \rightarrow RMn(CO)_5 \qquad (7)$$

or, the acyl carbonyl may become a coordinated carbonyl as another carbonyl group departs.



$$\overset{CO}{RCOMn(CO)_4} \xrightarrow{-CO} RMn(CO)_5 \qquad (8)$$

The alkylcobalt tetracarbonyls react completely analogously with carbon monoxide, forming acylcobalt tetracarbonyls (*43*).

$$RCo(CO)_4 + CO \rightleftharpoons RCOCo(CO)_4 \qquad (9)$$

The reaction is reversible (*33*). The cobalt derivatives are considerably more reactive than the corresponding manganese compounds. Acetylcobalt tetracarbonyl dissociates about 2250 times more rapidly than the corresponding acetylmanganese pentacarbonyl does (*33*).

The generality of the carbon monoxide insertion reaction is clear from reports that methylcyclopentadienyliron dicarbonyl (*16*), ethylcyclopentadienylmolylbdenum tricarbonyl (*66*), alkylrhenium pentacarbonyls (*50*), alkylrhodium dihalo carbonyl bisphosphines (*34*), allylnickel dicarbonyl halides (*35*), and mono-and di-alkyl derivatives of the nickel, palladium, and platinum bisphosphine halides (*9*), also undergo the reaction. The reaction of Grignard reagents (*24*), and of boron alkyls (*51*) with carbon monoxide probably takes place by the same mechanism.

Whether coordination of the carbon monoxide is required before insertion can take place in all these examples is not clear. But since it is required in the alkylmanganese pentacarbonyl reaction, it is not unreasonable to expect the same to be true in the other cases.

As expected, coordinating molecules other than CO can react and result in the shift of a coordinated CO to an acyl CO. Cyclohexylamine, for example, reacts with alkylmanganese pentacarbonyls to produce acylmanganese tetracarbonyl cyclohexylamine complexes (*59*).

$$RMn(CO)_5 + C_6H_{11}NH_2 \rightarrow RCOMn(CO)_4(C_6H_{11}NH_2) \qquad (10)$$

Similarly, alkylcobalt tetracarbonyls react with triphenylphosphine (*44*, *45*) or with phosphites (*36*) to give high yields of acylcobalt tricarbonyl triphenylphosphines or phosphites.

$$RCo(CO)_4 + PR_3 \rightarrow RCOCo(CO)_3PR_3 \qquad (11)$$

**Metal-Oxygen Compounds.** A few examples of the insertion of carbon monoxide into metal-oxygen groups have been reported. The best known is the reaction of mecuric acetate in methanol solution with carbon monoxide, forming methoxycarbonylmercuric acetate (*83*) which probably involves the following steps (*32*):

$$CH_3COOHgOCOCH_3 + CH_3OH \rightleftharpoons CH_3COOHgOCH_3 + HOCOCH_3 \quad (12)$$

$$CH_3COOHgOCH_3 + CO \rightarrow CH_3COOHgCOOCH_3 \quad (13)$$

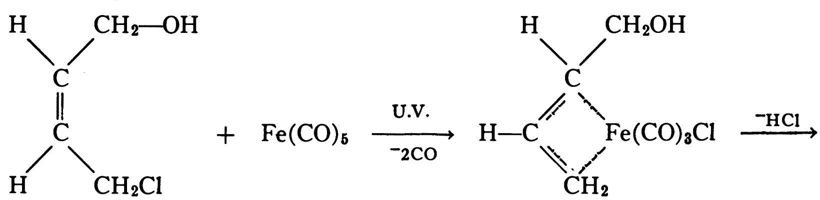
The formation of formate esters in the hydroformylation reaction (*90, 64*) may be explained by a CO–alkoxide insertion reaction as well as by the CO–hydride insertion mechanism mentioned above. Aldehydes formed in the hydroformylation reaction can be reduced by cobalt hydrocarbonyl (*27*) presumably by way of an addition of the hydride to the carbonyl group (*90, 2*). If the intermediate in the reduction is an alkoxycobalt carbonyl, carbon monoxide insertion followed by hydrogenation would give formate esters (*90, 64*).

$$\begin{array}{l} RCHO + HCo(CO)_4 \rightleftharpoons RCH_2OCo(CO)_4 \xrightarrow{H_2} RCH_2OH + HCo(CO)_4 \\ \qquad\qquad\qquad\qquad\qquad\qquad \Updownarrow CO \\ RCH_2OCHO + HCo(CO)_4 \xleftarrow{H_2} RCH_2OCOCo(CO)_4 \end{array} \quad (14)$$

Additional support for the carbon monoxide–alkoxycobalt insertion reaction is found in the reaction of *tert*-butyl hypochlorite with sodium cobalt carbonyl. This reaction, if carried out at −80°C. in ether solution under nitrogen or carbon monoxide, leads to about a 10% yield of *tert*-butoxycarbonylcobalt tetracarbonyl which has been isolated as the monotriphenylphosphine derivative. The major product seems to be cobalt octacarbonyl, possibly formed by decomposition of an intermediate *tert*-butoxycobalt tetracarbonyl (34). This reaction appears to be a true insertion reaction although a direct attack of a coordinated carbonyl group upon oxygen cannot be ruled out.

$$\begin{array}{l} (CH_3)_3COCl + NaCo(CO)_4 \rightarrow (CH_3)_3COCo(CO)_4 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow CO \\ (CH_3)_3COCOCo(CO)_3P(C_6H_5)_3 + CO \xleftarrow{P(C_6H_5)_3} (CH_3)_3COCOCo(CO)_4 \end{array} \quad (15)$$

Another probable example of a CO insertion into a metal-oxygen group is the reaction of *cis*-4-chloro-2-buten-1-ol with iron carbonyl under ultraviolet light (*34*). By analogy with the reaction of simple allylic halides under the same conditions (*34*), the first intermediate in the chlorobutenol reaction is probably 1-hydroxymethyl-π-allyliron tricarbonyl chloride (I). The alcohol group, presumably in the endo position (*54*), then can displace chloride from the iron atom, giving the bicyclic ether II. An insertion reaction by CO between the iron atom and the oxygen group will yield the observed product, III.



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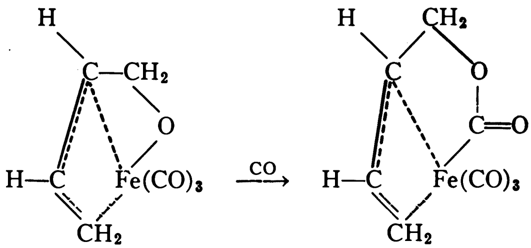


II III

**Metal-Nitrogen Compounds** The cobalt catalyzed reaction of primary and secondary amines with carbon monoxide leads to the formation of formamide derivatives. Dimethylamine, for example, gives *N*,*N*-dimethylformamide in 60% yield (*90*, *91*). Very likely cobalt-nitrogen compounds are intermediates which undergo a CO insertion and then reduction. The following mechanism has been suggested for the reaction (*90*).

$$(CH_3)_2NH + Co_2(CO)_8 \rightarrow (CH_3)_2NCo(CO)_4 + HCo(CO)_4 \quad (17)$$

$$(CH_3)_2NCo(CO)_4 + CO \rightarrow (CH_3)_2NCOCo(CO)_4 \quad (18)$$

$$(CH_3)_2NCOCo(CO)_4 + HCo(CO)_4 \rightarrow (CH_3)_2NCHO + Co_2(CO)_8 \quad (19)$$

Other metal carbonyls also catalyze the formylation of amines (*90*).

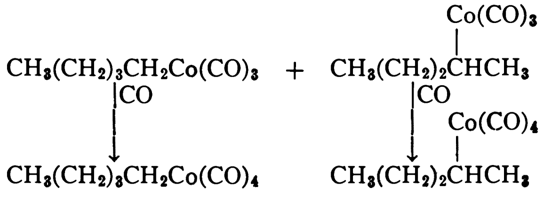
## *Olefin Insertion Reactions*

**Metal Hydrides.** Adding metal hydrides to olefins has been known many years. Some of these appear to be insertion reactions, i.e., olefin additions with aluminum hydrides (*112*), certain tin hydrides (*98*), certain germanium hydrides (*77*) mangesium hydride (*76*), boron hydride (*11*), and various transition metal hydrides.

The addition of cobalt hydrocarbonyl to olefins has been investigated and information on the detailed mechanism of the reaction obtained. The reaction of 1-pentene with cobalt hydrocarbonyl to produce a mixture of 1- and 2-pentylcobalt tetracarbonyls was shown to be inhibited by carbon monoxide (*46*). The inhibition very likely arises because the reactive species is cobalt hydrotricarbonyl rather than the tetracarbonyl. The carbon monoxide, by a mass action effect, reduces the concentration of the reactive species.

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \quad (20)$$

$$HCo(CO)_3 + CH_3(CH_2)_2CH{=}CH_2 \rightleftharpoons$$



$$\begin{array}{ccc} & & Co(CO)_3 \\ & & | \\ CH_3(CH_2)_3CH_2Co(CO)_3 & + & CH_3(CH_2)_2CHCH_3 \\ \downarrow CO & & \downarrow CO \qquad Co(CO)_4 \\ & & \qquad\quad | \\ CH_3(CH_2)_3CH_2Co(CO)_4 & & CH_3(CH_2)_2CHCH_3 \end{array} \quad (21)$$

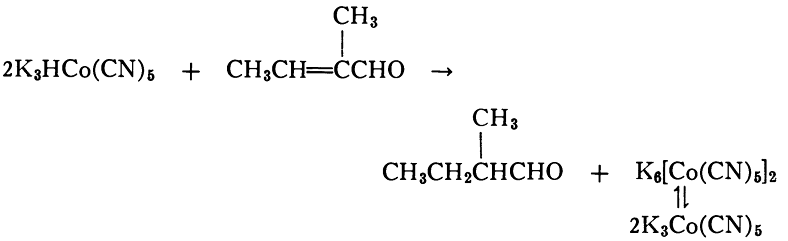
Whether the coordinately unsaturated hydride is required so that the olefin can coordinate with the cobalt before insertion, or the hydrotricarbonyl is just more reactive towards the olefin, is not clear. The former explanation appears more probable in view of the carbonyl work mentioned above (*46*).

Cobalt hydrocarbonyl is a very reactive compound. It reacts extremely rapidly with triphenylphosphine, probably by a first-order dissociation mechanism, producing cobalt hydrotricarbonyl triphenylphosphine (*44*). This demonstrates the very ready replacement of one ligand by another. Cobalt hydrocarbonyl also catalyzes the isomerization of olefins. Under conditions of the hydroformylation reaction, olefin isomerization is observed. But there is controversy as to whether or not rearranged aldehydes (aldehydes which cannot be produced by simple addition to the starting olefin) are produced mainly by rearrangement of an intermediate in the reaction (*28*, *75*, *55*) or by reaction of isomerized olefins (*55*).

$\alpha$, $\beta$-Unsaturated aldehydes and ketones are rapidly reduced by cobalt hydrocarbonyl to the saturated carbonyl compounds and cobalt octacarbonyl (*27*). Very probably an insertion reaction forms an $\alpha$- or $\beta$-cobalt carbonyl derivative which reacts very rapidly with more hydrocarbonyl.

$$CH_2{=}CHCHO + 2HCo(CO)_4 \rightarrow CH_3CH_2CHO + Co_2(CO)_8 \qquad (22)$$

$\alpha$, $\beta$-Unsaturated carbonyl compounds are also reduced by potassium pentacyanocobalt hydride (*61*). A similar mechanism involving a metal hydride addition seems likely.



$$2K_3HCo(CN)_5 + CH_3CH{=}\overset{\overset{CH_3}{|}}{C}CHO \rightarrow CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCHO + \begin{array}{c}K_6[Co(CN)_5]_2\\ \upharpoonleft\downharpoonright\\ 2K_3Co(CN)_5\end{array} \qquad (23)$$

A hydride of vitamin $B_{12}$ coenzyme has been prepared and found to add to activated olefins (acrylic acid) and acetylene (*56*).

Manganese hydrocarbonyl, though much less reactive than cobalt hydrocarbonyl, does add to some activated olefins. Tetrafluoroethylene for example reacted to give tetrafluoroethylmanganese pentacarbonyl (*95*).

$$HMn(CO)_5 + CF_2{=}CF_2 \rightarrow HCF_2CF_2Mn(CO)_5 \qquad (24)$$

Catalytic reduction of olefins by heavy metal catalysts probably involves metal hydride addition reactions also. If this is correct, the observed inhibition of the reduction by carbon monoxide, phosphines, sulfur compounds, and other materials with unshared electrons is exactly what would be expected if a vacant orbital on the hydride is required before addition can take place.

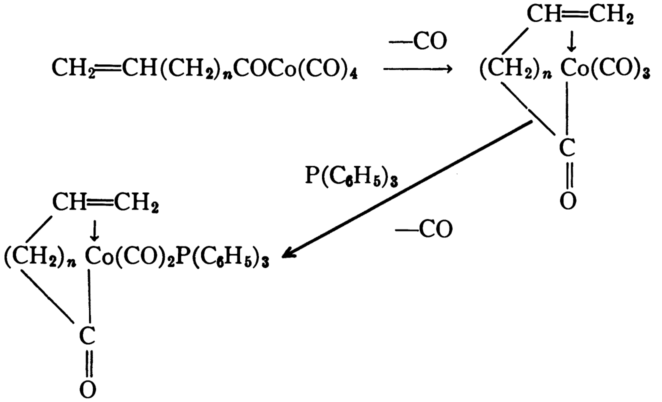
**Metal-Carbon Compounds.** Clear examples of olefin insertions into transition metal-carbon groups are rare. The obvious reaction of olefins with alkyl- or acyl-cobalt tetracarbonyls are slow, complicated, and incomplete under the usual laboratory conditions. Under high pressure at elevated temperatures, in the presence of a hydrogen donor and carbon monoxide, insertion reactions apparently take place rapidly and more cleanly, producing ketones. Ethylene, for example, gives high yields of diethyl ketone under the proper conditions (*88*). Presumably this synthesis involves three separate insertion reactions: ethylene first reacts with cobalt hydrocarbonyl, forming ethylcobalt carbonyl (ethylene insertion into a cobalt hydrogen group) (*46*); then carbon monoxide insertion occurs, forming propionylcobalt tetracarbonyl; and finally, ethylene is inserted between the propionyl group and the cobalt atom, forming 2-propionylethylcobalt carbonyl. This compound is then reduced to ketone either by cobalt hydrocarbonyl or by hydrogen from the hydrogen donor present. Again, each insertion reaction probably requires a reactive, coordinately unsaturated species, which, for simplicity, has not been shown in the following equations.

$$CH_2{=}CH_2 + HCo(CO)_4 + CO \rightleftharpoons CH_3CH_2COCo(CO)_4 \qquad (25)$$

$$CH_3CH_2COCo(CO)_4 + CH_2{=}CH_2 \rightleftharpoons CH_3CH_2COCH_2CH_2Co(CO)_4 \qquad (26)$$

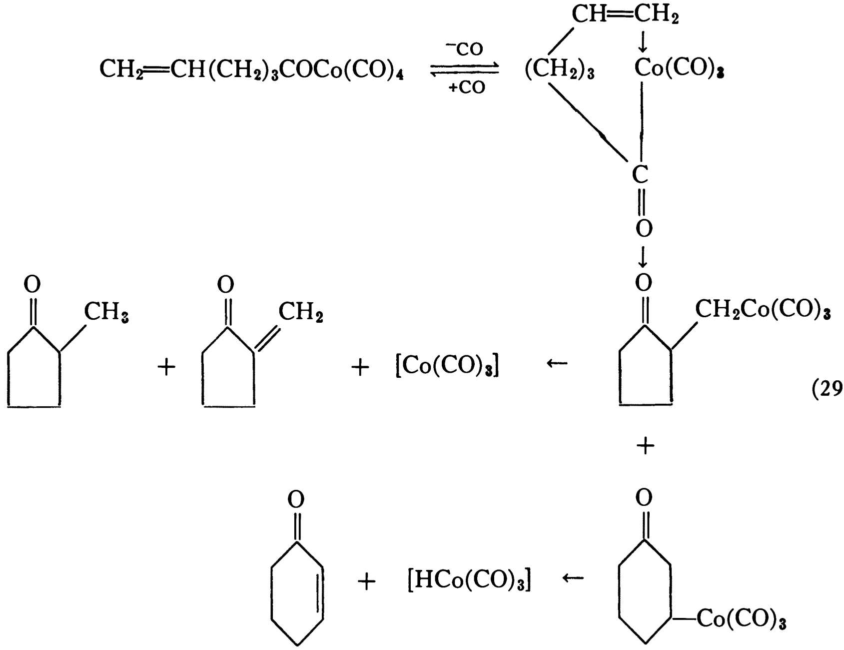
$$CH_3CH_2COCH_2CH_2Co(CO)_4 + 2[H] \rightarrow CH_3CH_2COCH_2CH_3 + HCo(CO)_4 \qquad (27)$$

Evidence for the insertion of an olefin group between an acyl group and a cobalt atom has been obtained more directly by analyzing the decomposition products of ω-unsaturated acylcobalt tetracarbonyls ($CH_2{=}CH(CH_2)_nCOCo(CO)_4$). The products of thermal decomposition of these complexes depend upon the value of $n$. When $n = 0$ or 2 the compounds form relatively stable cyclic olefin π-complexes which may be isolated as monotriphenylphosphine derivatives (*47*). The π-acrylylcobalt tricarbonyl ($n = 0$) gives an amorphous polymer on heating (*37*), whereas the



(28)

π-4-pentenoylcobalt tricarbonyl ($n = 2$) yields carbon monoxide and 1-methyl-π-allylcobalt tricarbonyl on heating (*47*). When $n = 1$, thermal decomposition of the complex leads exclusively to π-allylcobalt tricarbonyl (*47*). The complex with six carbons in the side chain, 5-hexenoylcobalt tetracarbonyl ($n = 3$), which exists only as the linear tetracarbonyl, however, decomposes into cyclic ketones at 25°C. The reaction products consist of 16% 2-methyl-2-cyclopentenone, 54% 2-methylcyclopentanone, and 8% cyclohexenone. No other organic products were found. Presumably, the missing material (22%) was derived from unsaturated ketones (probably polymer) if the amount of hydrogen in the starting complex and products is to be the same. The cobalt was found as cobalt octacarbonyl (*37*). This reaction appears to be a clear example of the insertion of an olefin between an acyl group and a cobalt atom. Since the complex with $n = 2$ formed a cyclic $\pi$-complex (but did not cyclize, either because loss of CO to form the more stable $\pi$-allyl complex was a more favorable reaction or because of steric problems) it is reasonable to expect that the complex with $n = 3$ also formed a $\pi$-olefin complex prior to forming cyclic ketone. A consistent mechanism is shown below.



(29)

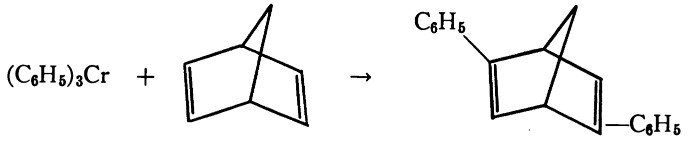
The 2-methylenecyclopentanone initially formed presumably rearranges into 2-methyl-2-cyclopentenone under the reaction conditions. The final step of the mechanism, elimination of the cobalt carbonyl group, is not well understood; but the same kind of elimination and reduction reactions occur with known 3-ketocobalt complexes. As mentioned above, crotonaldehyde, acrolein (*27*), and glycidaldehyde (*38*) react rapidly with cobalt hydrocarbonyl under similar conditions to give reduction products, rather than forming stable alkyl- or acyl-cobalt tetracarbonyl derivatives.

Recently Stone has reported the addition of methyl- and phenylmanganese pentacarbonyl to highly fluorinated ethylene derivatives. For example, tetrafluoroethylene reacted readily with methylmanganese pentacarbonyl at 90°C., or under ultraviolet light at room temperature, to produce 1,1,2,2-tetrafluoropropylmanganese pentacarbonyl in high yield (*103*).

$$CH_3Mn(CO)_5 + CF_2{=}CF_2 \rightarrow CH_3CF_2CF_2Mn(CO)_5 \qquad (30)$$

The high temperature or ultraviolet light very likely is required to produce a coordinately unsaturated species by CO dissociation from the methylmanganese compound.

Similarly, activated olefins react with triphenylchromium. Bicyclo [2.2.1] hepta-25-diene reacts to produce 2,5-diphenylbicyclo [2.2.1] hept-2-ene. The mechanism of this reaction is not clear, but an initial addition of phenylchromium to the unsaturated system is probably involved (*67*).



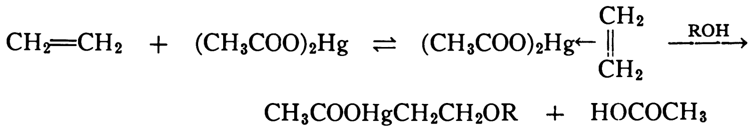
(31)

The Ziegler polymerizations of olefins (*92*, *5*) and the aluminum (*108*), gallium, beryllium, and indium (*111*) alkyl growth reactions also seem to be examples of olefin insertion reactions of metal-carbon compounds. Despite great effort concerning the mechanism of the polymerization reactions, relatively little has been learned about the actual catalytic species involved.

The report of Bestian & Clauss that methyltitanium trichloride will undergo a slow growth reaction with ethylene in polar inert solvents at low temperatures (*6*) is considerably important because of its relation to the Ziegler polymerization reaction.

Lithium (*4*, *110*), magnesium (*76*), and potassium (*109*, *110*) alkyls can also be added to olefins under the appropriate conditions.

**Metal-Oxygen Compounds.** The addition of metal-oxygen compounds to olefins is exemplified by the addition of mercuric acetate to olefins in hydroxylic solvents (*83*). Both cis and trans adducts may be obtained depending upon the structure of the olefin. Where trans addition is hindered by substitutents, cis addition appears to occur (*3*, *94*). Ward and Henry have obtained kinetic evidence that the addition of mercuric acetate to ethylene in aqueous solution involves the prior formation of a π-ethylene complex. Presumably, trans addition results from attack by external solvent or ion, and cis addition results from ligand addition (*101*).



$$CH_2{=}CH_2 + (CH_3COO)_2Hg \rightleftharpoons (CH_3COO)_2Hg{\leftarrow}\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \xrightarrow{ROH} \qquad (32)$$

$$CH_3COOHgCH_2CH_2OR + HOCOCH_3$$

The oxidation of olefins to carbonyl compounds by palladium (II) ion can be regarded as an addition of a palladium hydroxide group to the olefin followed by a hydrogen shift. Kinetic evidence suggests the following mechanism for the oxidation of ethylene by palladium chloride in aqueous solution containing excess chloride ion (*21*, *49*, *99*).

$$PdCl_4^{-2} + CH_2{=}CH_2 \rightleftharpoons [PdCl_3CH_2{=}CH_2]^- + Cl^- \qquad (33)$$

$$[PdCl_3CH_2{=}CH_2]^- + H_2O \rightleftharpoons [PdCl_2(H_2O)CH_2{=}CH_2] + Cl^- \qquad (34)$$

$$[PdCl_2(H_2O)CH_2{=}CH_2] + H_2O \rightleftharpoons$$

$$[PdCl_2(OH)(CH_2{=}CH_2)]^- + H_3O^+ \qquad (35)$$

$$[PdCl_2(OH)CH_2{=}CH_2]^- \rightleftharpoons [PdCl_2CH_2CH_2OH]^- \qquad (36)$$

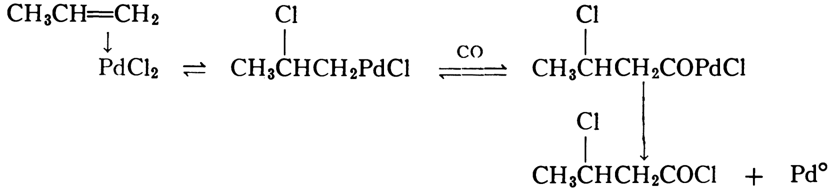
$$[PdCl_2CH_2CH_2OH]^- \rightarrow Pd^\circ + Cl^- + HCl + CH_3CHO \qquad (37)$$

Thallium acetate adds to olefins (*58*) also, but the stereochemistry of the addition has not been determined.

**Metal-Halogen Counpounds.** One of the few examples of an olefin insertion into a metal-halogen compound has been reported by Tsuji. The reaction, which also supports the idea that sigma-bonded metal-carbon compounds are intermediates in the palladium chloride–olefin oxidation reaction, was the addition of carbon monoxide to the ethylene palladium chloride $\pi$-complex in nonaqueous solvents to produce a moderate yield of 3-chloropropionyl chloride (*96*).

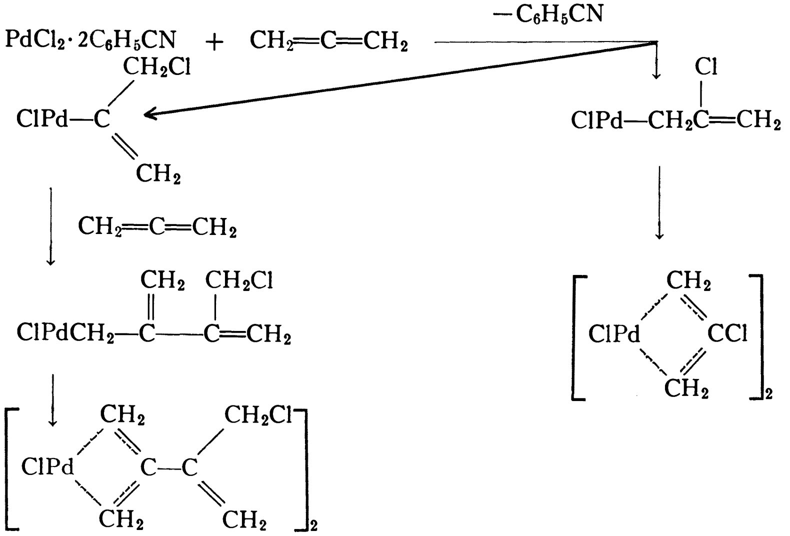
$$CH_2{=}CH_2 \cdot PdCl_2 + CO \rightarrow Pd^\circ + ClCH_2CH_2COCl \qquad (38)$$

Contrary to the ionic mechanism suggested by Tsuji, an insertion mechanism explains the facts much better. An external attack of carbon monoxide at the most positive carbon atom of propylene in a palladium chloride complex, as Tsuji proposed, would be expected to produce 3-chloro-2-methylpropionyl chloride rather than the observed product, 3-chlorobutyryl chloride. Since oxidation of propylene by Pd (II) ion gives acetone rather than propionalydehyde, a CO insertion reaction and elimination should produce the observed compound, 3-chlorobutyryl chloride



$$\underset{PdCl_2}{\underset{\downarrow}{CH_3CH{=}CH_2}} \rightleftharpoons CH_3\overset{\overset{Cl}{|}}{C}HCH_2PdCl \xrightleftharpoons{CO} CH_3\overset{\overset{Cl}{|}}{C}HCH_2COPdCl \longrightarrow CH_3\overset{\overset{Cl}{|}}{C}HCH_2COCl + Pd^\circ \qquad (39)$$

Palladium chloride bis(benzonitrile) reacts with allene probably by an insertion mechanism to produce $\pi$-2-chloroallylpalladium chloride dimer and products containing two allene units per palladium atom (*84*). It would appear that the palladium chloride addition to allene occurs both possible ways to one of the double bonds. Addition of the palladium to the terminal position would give a $\pi$-allyl



(40)

compound, while addition of the palladium to the middle carbon atom would produce an isopropenylpalladium chloride. This then could react with a second allene molecule, again by insertion, to give the other observed products, the 2-chloroisopropenyl-π-allylpalladium chloride dimers.

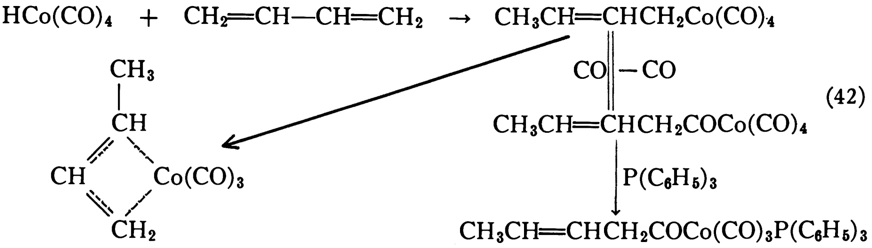
**Compounds with Metal-Metal Bonds.** There is one clear example of the addition of a compound with a metal-metal bond to an olefin. Cobalt octacarbonyl reacts with tetrafluoroethylene to form a symmetrical adduct (*102*).

$$Co_2(CO)_8 + CF_2{=}CF_2 \rightarrow (CO)_4CoCF_2CF_2Co(CO)_4 \qquad (41)$$

### *Insertion Reactions of Conjugated Dienes*

**Metal Hydrides.** The metal hydrides appear to be considerably more reactive towards conjugated dienes than towards olefins.

Cobalt hydrocarbonyl reacts rapidly with conjugated dienes, initially forming 2-butenylcobalt tetracarbonyl derivatives. These compounds lose carbon monoxide at 0°C. or above, forming derivatives of the relatively stable 1-methyl-π-allylcobalt tricarbonyl. As with "normal" alkylcobalt tetracarbonyls, the 2-butenyl derivatives will absorb carbon monoxide, forming the acyl compounds; but these acyl compounds also slowly lose carbon monoxide at 0°C. or above, forming π-allyl complexes. The acyl compounds can be isolated as the monotriphenylphosphine derivatives (*47*).



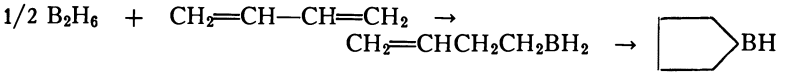
(42)

Again, cobalt hydrotricarbonyl probably adds initially. The addition could be either a 1,4-addition or a 1,2-addition in which cobalt initially adds to the second carbon atom of the diene, and then undergoes an allylic rearrangement. The 3-pentenoylcobalt tricarbonyl triphenylphosphine prepared in this manner contains considerably more of the cis isomer than the same compound prepared from trans crotyl bromide and sodium cobalt tetracarbonyl. This, indicates that the hydrocarbonyl prefers cis addition (*47*).

Manganese hydrocarbonyl reacts analogously with conjugated dienes. The 2-butenylmanganese pentacarbonyls are stable enough to be isolated readily. The products are mixtures of cis and trans isomers. Heating converts them into 1-methyl-π-allyl-manganese tetracarbonyl derivatives (*65*).

Potassium pentacyanocobalt hydride reduces conjugated dienes to mono-olefins (*61*). The reaction mechanism probably involves an addition of the hydride to the diene followed by reduction with a second molecule of hydride (*61*).

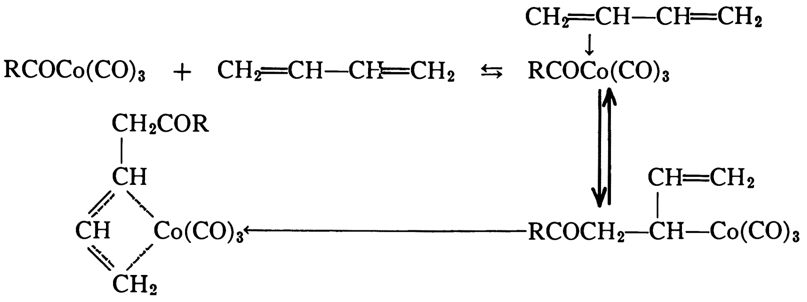
Boron hydrides add to conjugated dienes, giving linear (12) and cyclic compounds (*60*). The cyclic products are the result of two 1,2-additions (*60*).



(43)

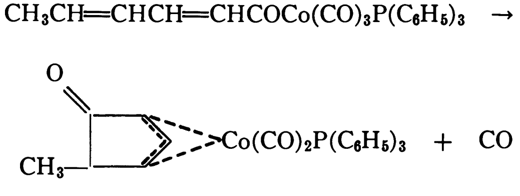
Trimethyltin hydride adds mainly 1,2 to piperylene, but a variety of other organotin compounds are also formed. This suggests that the reaction may be a radical addition (*18*).

**Metal-Carbon Compounds.** The diene insertion reaction with metal-carbon compounds is clearly shown by the organocobalt tetracarbonyls. Solutions of alkyl- or acyl-cobalt tetracarbonyls react readily with a variety of conjugated dienes, forming high yields of 1-acylmethyl derivatives of π-allylcobalt tricarbonyl. Presumably, an acylcobalt tricarbonyl is reacting. One double bond of the diene system inserts between the acyl group and the cobalt atom, probably by first forming a π-complex; then the other double bond coordinates with the cobalt, producing the relatively stable π-allyl system (*39*, *40*).



(44)

If the conjugated diene group is in the acyl chain of the acylcobalt carbonyl, then cyclization is possible. Thus, sorbylcobalt tricarbonyl triphenylphosphine on heating to 80°C., cyclizes to 2-methyl-π-cyclopentenonylcobalt dicarbonyl triphenylphosphine (*41*).

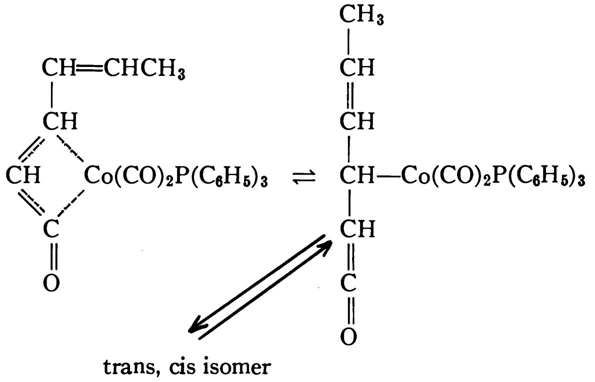


(45)

This reaction is particularly interesting because the starting compound has the trans, trans structure and the product must arise from a cis intermediate in order to form the ring. A possible isomerization mechanism involves a ketene intermediate.

$$CH_3CH{=}CHCH{=}CHCOCo(CO)_3P(C_6H_5)_3 \underset{CO}{\overset{-CO}{\rightleftharpoons}}$$

trans, trans isomer

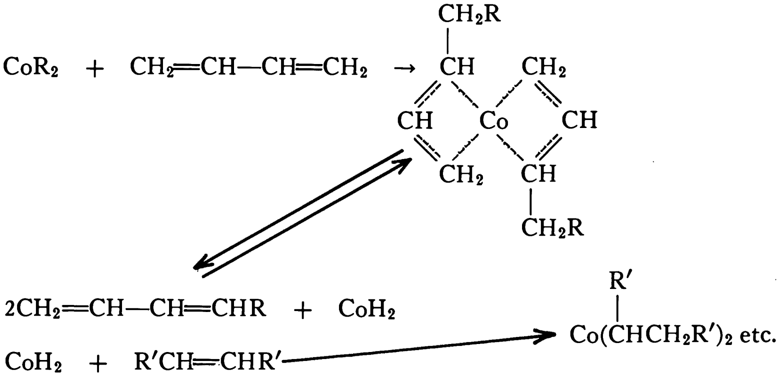


(46)

The diene polymerizations catalyzed by organometallic compounds are probably further examples of diene insertion reactions of metal alkyls (*25*). But there is little evidence on the detailed mechanisms of these polymerizations.

As recently reported, cobalt-catalyzed addition of olefins to butadiene is probably an example of the addition of cobalt alkyls to butadiene (*106*). The catalyst was the type prepared by reaction of cobalt chloride with an aluminum alkyl in the presence of a diene. A bis-π-allylcobalt derivative is probably formed. The unstable π-allylcobalt compounds probably decompose (reversibly) into cobalt hydride. The hydride would add to the olefin present to form a dialkyl, which could then add again to the diene.

$$CoCl_2 + AlR_3 \rightarrow AlCl_2R + CoR_2 \qquad (47)$$



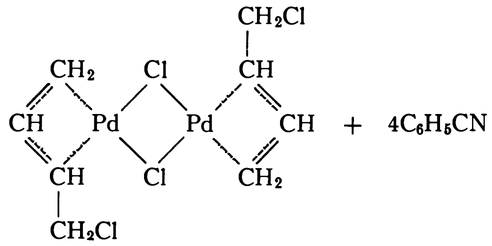
(48)

$$CoH_2 + R'CH{=}CHR' \longrightarrow Co(\overset{R'}{\overset{|}{C}}HCH_2R')_2 \text{ etc.} \qquad (49)$$

**Metal-Oxygen Compounds and Metal-Metal Compounds.** Clear examples of diene insertions with metal-oxygen or metal-metal groups are not known.

**Metal-Halogen Compounds.** An unusual example of the addition of a metal halide to a conjugated diene has been reported. The complex formed from palladium chloride and butadiene has been shown to be a dimer of 1-chloromethyl-π-allylpalladium chloride, (*85*). Whether this is a true insertion reaction or some type of ionic reaction has not been determined, but its close analogy with the olefin–palladium chloride insertion reaction mentioned above would suggest an insertion mechanism for the diene reaction also.

$$2\ PdCl_2 \cdot 2C_6H_5CN\ +\ 2\ CH_2{=}CH{-}CH{=}CH_2\ \rightarrow$$



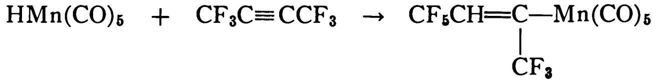
(50)

This reaction is quite general and a variety of $\pi$-allylpalladium complexes have been prepared by it (*86*).

### *Acetylene Insertion Reactions*

**Metal Hydrides.** Metal hydrides generally react readily with acetylenes, often by an insertion mechanism. Cobalt hydrocarbonyl gives complicated mixtures of compounds with acetylenes. The only products which have been identified so far are dicobalt hexacarbonyl acetylene complexes (*34*). Greenfield reports that, under conditions of the hydroformylation reaction, acetylenes give only small yields of saturated monoaldehydes (*30*), probably formed by first hydrogenating the acetylene and then reacting with the olefin. Other workers have identified a variety of products from acetylene, carbon monoxide, and an alcohol with a cobalt catalyst, probably cobalt hydrocarbonyl. The major products observed were succinate esters (*74*, *19*) and succinate half ester acetals (*19*).

Manganese hydrocarbonyl, in one example, has given the expected adduct with an acetylene. Hexafluoro-2-butyne reacted to give the adduct IV (*95*).



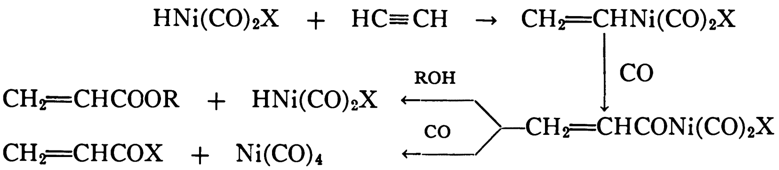
$$HMn(CO)_5\ +\ CF_3C{\equiv}CCF_3\ \rightarrow\ CF_5CH{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}Mn(CO)_5 \qquad (51)$$

IV

Probably the nickel carbonyl-catalyzed synthesis of acrylates from CO, acetylene, and hydroxylic solvent (*78*) involves an acetylene–hydride insertion reaction, followed by a CO insertion, and hydrolysis or acyl halide elimination. The actual catalyst in the acrylate synthesis is probably a hydride formed by the reversible addition of an acid to nickel carbonyl.

$$Ni(CO)_4\ +\ HX\ \rightleftharpoons\ HNi(CO)_2X\ +\ 2CO \qquad (52)$$

This hydride then may add an acetylene molecule to form the vinyl derivative. A carbon monoxide insertion will produce the acrylyl nickel compound which can yield acrylate esters by either of two routes. Direct alcoholysis of the acylnickel group may take place, as occurs with acylcobalt compounds (*42*); or, an acyl halide (or other acyl derivative, e.g., acyl alkanoate) may be eliminated. Alcoholysis of the acyl halide would then complete the catalytic cycle (*35*).

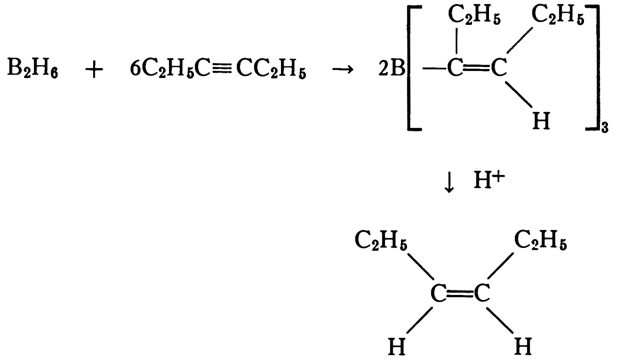


(53)

$$CH_2{=}CHCOX + ROH \rightarrow CH_2{=}CHCOOR + HX \qquad (54)$$

It has been very difficult to obtain direct evidence on the mechanism of the acrylate synthesis because the intermediate compounds are extremely reactive.

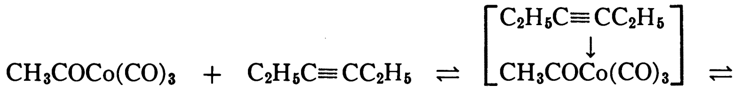
Boron (*13*) and aluminum hydrides (*104*) add cis to acetylenes, forming substituted vinylmetal compounds. Hydrolysis of these compounds provides a route to cis-olefins.



(55)

**Metal-Carbon Compounds.** Metal-carbon compounds add to acetylenes also. Alkyl- or acyl-cobalt carbonyls undergo insertion reactions readily with a large variety of acetylenes. Disubstituted acetylenes and highly branched monoacetylenes give mainly a single type of product, π-butenolactonylcobalt tricarbonyl derivatives (*34*). For example, acetylcobalt tetracarbonyl and 3-hexyne react in a few hours at room temperature to give a good yield of 2,3-diethyl-π-(2, 4)-penteno-4-lactonyl cobalt tricarbonyl, IX. The reaction seems to involve the insertion of the acetylene between the acetyl and cobalt tricarbonyl groups, perhaps by way of an intermediate π-complex (V), to give complex VI. This complex can then undergo a CO insertion reaction, forming VII which probably exists as the π-acrylyl type complex (VIII). The latter compound can then cyclize by a third insertion reaction; this time the terminal acyl carbonyl inserts between the other acyl group and the cobalt tricarbonyl group, producing the observed product, IX.

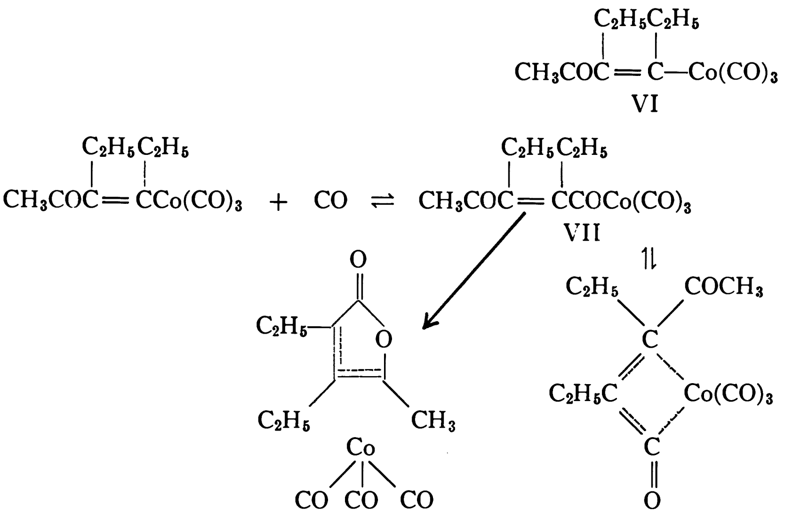
$$CH_3COCo(CO)_4 \rightleftharpoons CH_3COCo(CO)_3 + CO \qquad (56)$$



$$CH_3COCo(CO)_3 + C_2H_5C{\equiv}CC_2H_5 \rightleftharpoons \left[\begin{matrix} C_2H_5C{\equiv}CC_2H_5 \\ \downarrow \\ CH_3COCo(CO)_3 \end{matrix}\right] \rightleftharpoons$$

V

(57)



VI

VII

IX

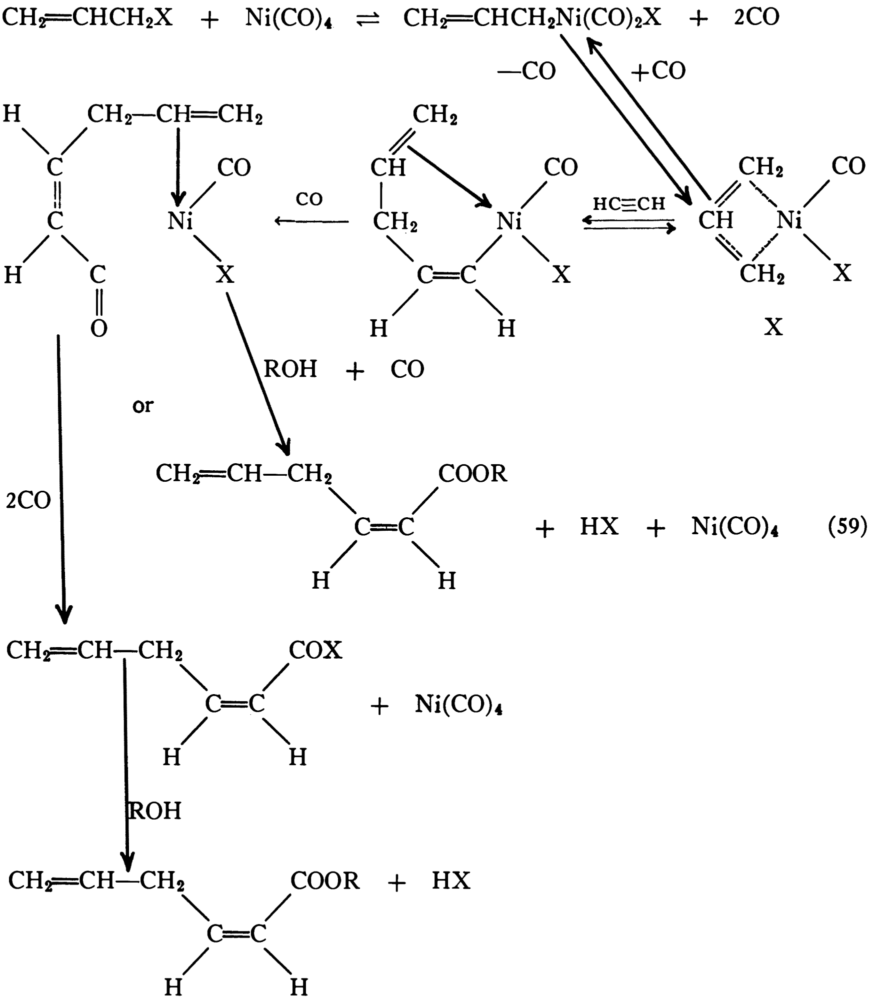
VIII

(58)

The final product can be isolated easily as the triphenylphosphine complex. This reaction is also general as far as the acylcobalt carbonyl is concerned, but the yields vary widely depending upon which acetylene is used (*34*). Presumably, the presence of substituents on the acetylene favors the cyclization step rather than the formation of linear products. The larger the substituents the more favorable the cyclization becomes. If cyclization does not take place relatively rapidly, linear compounds and polymers of acetylene, or of acetylene and CO are probably formed. Thus, these reactions demonstrate the insertion reaction of both acetylenes and ketonic carbonyl groups.

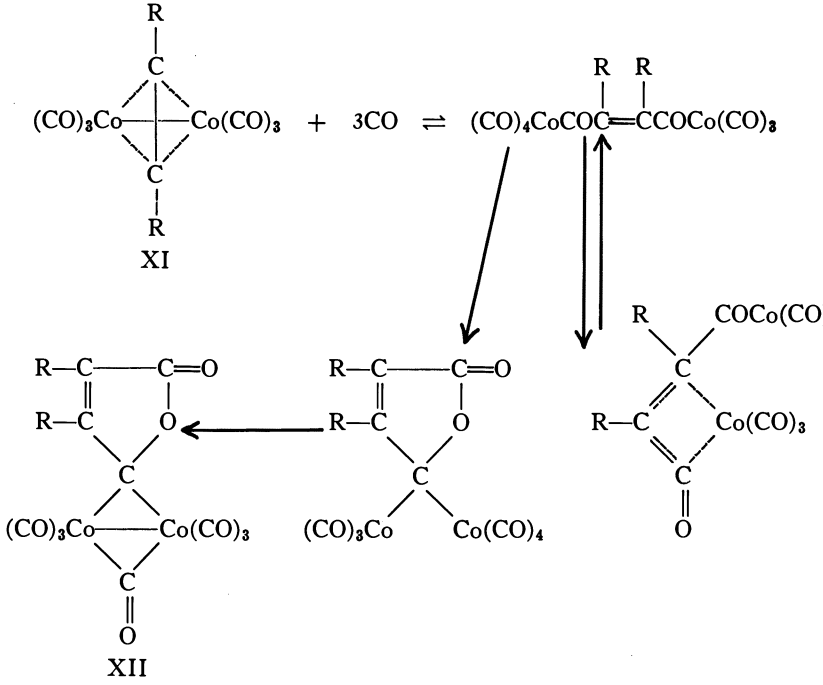
Another clear example of an acetylene insertion reaction was reported by Chiusoli (*15*). He observed that allylic halides react catalytically with nickel carbonyl in alcoholic solution, in the presence of CO and acetylene, to form esters of cis-2,5-hexadienoic acid. The intermediate in this reaction is very probably a $\pi$-allylnickel carbonyl halide, X, which then undergoes acetylene insertion followed by CO insertion and alcoholysis or acyl halide elimination (*35*). Acetylene is obviously a considerably better inserting group than CO in this reaction since with acetylene and CO, the hexadienoate is the only product, whereas, with only CO, the 3-butenoate ester is formed (*15*). [See Reaction 59].

Reaction 59 differs from the cobalt-acetylene insertion mentioned above because the cobalt prefers to insert CO before the acetylene, and the nickel the reverse. Whether or not this difference results from specific effectsof the $\pi$-allylnickel system is not known; but it is a good possibility since the allylic double bond is probably coordinated to the nickel throughout the reaction.


CH2=CHCH2X + Ni(CO)4 ⇌ CH2=CHCH2Ni(CO)2X + 2CO
—CO
+CO
CO
HC≡CH
ROH + CO
or
2CO
ROH
+ HX + Ni(CO)4
+ Ni(CO)4
COOR + HX
COX

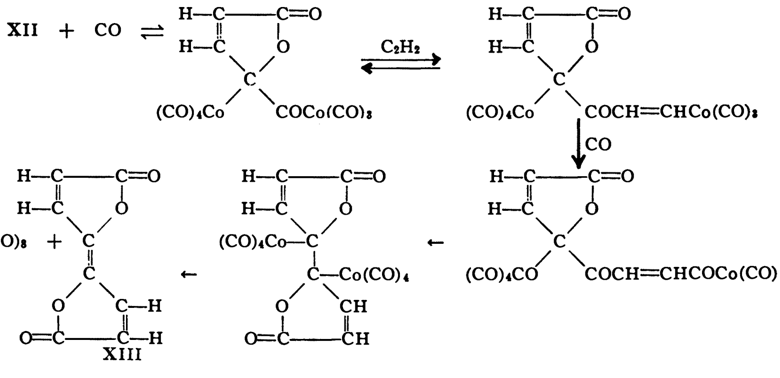
(59)

The formation of the butenolactone complex, XII, by the action of carbon monoxide on acetylene dicobalt hexacarbonyl complexes, XI, (*89*) seems to be a closely related reaction. It probably involves the following steps:



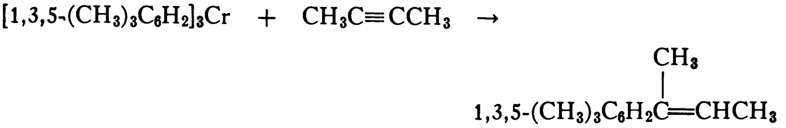
(60)

Under more vigorous conditions, complex XII can apparently add more acetylene and carbon monoxide, forming a bifurandione, XIII (*1*, *79*, *82*). A reasonable mechanism for the dione formation would be a CO insertion, then an acetylene insertion, and another CO insertion, followed by cyclization by ketone insertion, and finally a $Co_2(CO)_8$ elimination.



(61)

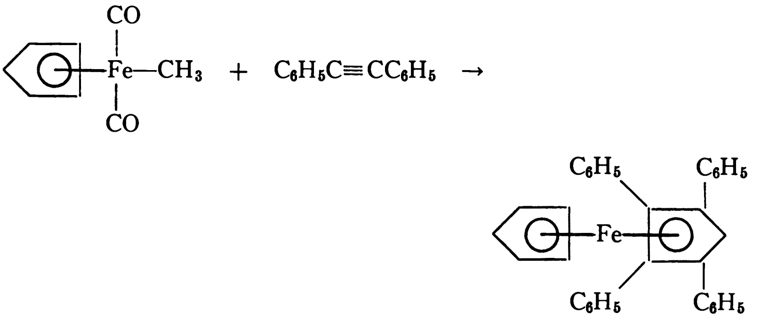
Triarylchromium complexes also react with acetylenes producing arylolefins (*68*). An insertion mechanism appears likely, but the intermediate adducts have not been detected.



$$[1,3,5\text{-}(CH_3)_3C_6H_2]_3Cr + CH_3C{\equiv}CCH_3 \rightarrow 1,3,5\text{-}(CH_3)_3C_6H_2C(CH_3){=}CHCH_3 \qquad (62)$$

Trimethylchromium reacts with diphenylacetylene to give hexaphenylbenzene and tetraphenylcyclopentadiene. The latter compound may have been formed by insertions and a cyclization reaction (*97*).

Several cyclopentadienyl(alkyl)metal carbonyl derivatives have reacted with acetylenes. In some examples, insertion reactions may also be involved, although the mechanisms have not been investigated. Cyclopentadienyl(methyl)iron dicarbonyl with diphenylacetylene gave a 10% yield of cyclopentadienyltetraphenylcyclopentadienyliron (*71*).



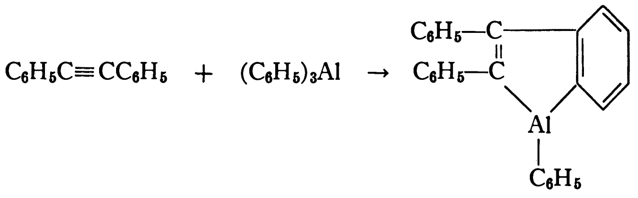
(63)

Similarly, acetylene itself gave ferrocene. Cyclopentadienyl(methyl)molybdenum tricarbonyl reacted with diphenylacetylene to produce some tetraphenylcyclopentadiene. The corresponding ethylmolybdenum derivative gave some tetraphenylmethylcyclopentadiene. The cyclizations involved in these reactions and the trimethylchromium reaction above are quite unusual and certainly deserve further study.

Wilke has shown that aluminum alkyls add readily to acetylenes, giving the expected adducts (*105*).

$$(C_2H_5)_3Al + HC{\equiv}CH \rightarrow (C_2H_5)_2AlCH{=}CHCH_2CH_3 \qquad (64)$$

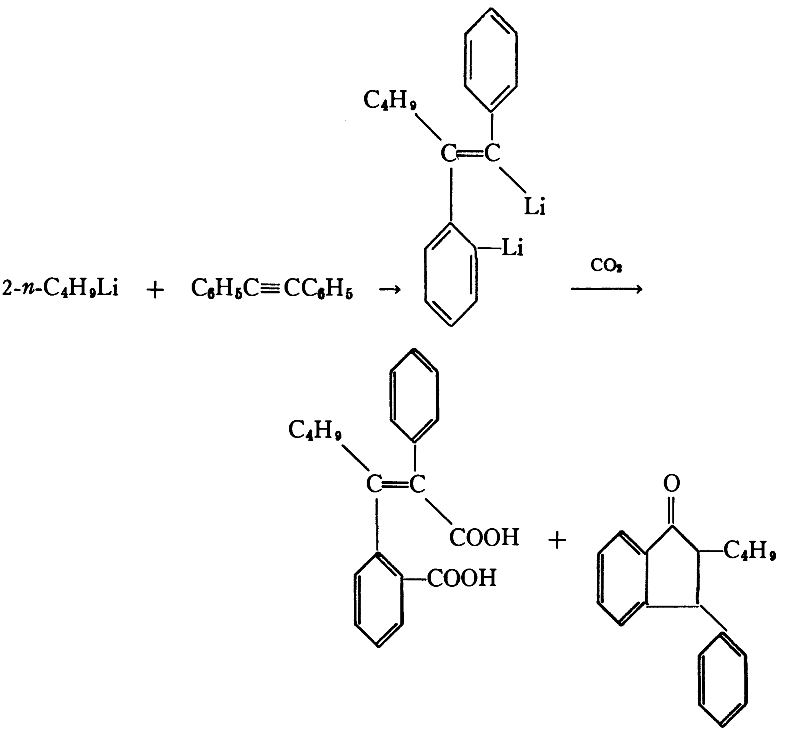
The reported addition of triphenylaluminum to diphenylacetylene to form 1, 2, 3-triphenylbenzaluminole (*22*) is another clear example of an acetylene insertion, this one being followed by a cyclization reaction.



(65)

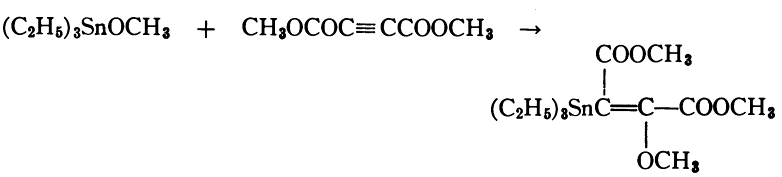
The polymerization of acetylene by Ziegler catalysts very likely involves metal alkyl–acetylene insertion reactions also (*26*).

*n*-Butyllithium has been added to diphenylacetylene, but the reaction is complicated by metalation of the aromatic system (*69*).



(66)

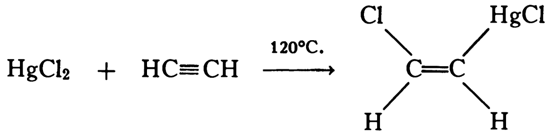
**Metal-Oxygen Compounds.** Clear examples of the addition of transition metal alkoxides to acetylenes are not known; however, the addition of trialkyltin alkoxides has been reported. Triethyltin methoxide, for example, reacts with dimethyl acetylenedicarboxylate to give the vinyltin derivative XVI (*63*).



$$(C_2H_5)_3SnOCH_3 + CH_3OCOC{\equiv}CCOOCH_3 \rightarrow (C_2H_5)_3Sn\overset{\overset{\displaystyle COOCH_3}{|}}{C}{=}\underset{\underset{\displaystyle OCH_3}{|}}{C}{-}COOCH_3$$

XIV (67)

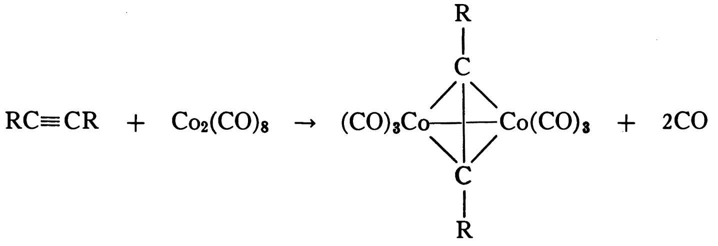
**Metal-Halogen Compounds.** Mercuric salts react readily with acetylenes, forming various products, depending upon the salt and reaction conditions. Mercuric chloride appears to undergo a clean insertion reaction with acetylene, giving *cis*-2-chlorovinylmercuric chloride in the vapor phase (*72*, *73*).



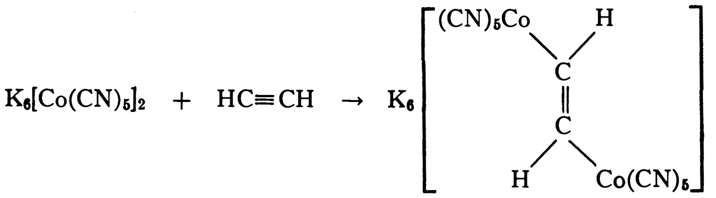
(68)

In solution, the trans isomer is produced, presumably because external chloride ion is adding to the acetylene-mercuric chloride π-complex (*72*, *73*).

**Compounds with Metal—Metal Bonds.** Additions of compounds with metal-metal bonds to acetylenes are rare. Perhaps the addition of acetylenes to cobalt octacarbonyl (*29*) should be considered an insertion reaction even though the metal-metal bond is not broken since the acetylene finally is bonded to both metal atoms.


(69)

Similar acetylene addition reactions take place with bis-cyclopentadienylnickel carbonyl dimer (*93*). Changing from carbonyl to cyanide ligands seems to allow the formation of a true vinyl derivative. Thus, potassium pentacyanocobaltate, which may react as a dimer with a cobalt-cobalt bond (*20*), reacts with acetylene to give the adduct XV (*31*). The product was thought to be the trans isomer, but the data were not conclusive.

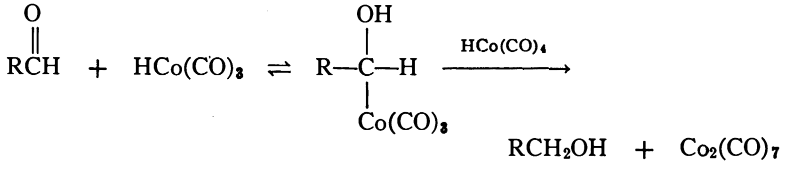

XV

(70)

If it is the trans isomer, the product may be formed by a radical rather than insertion reaction.

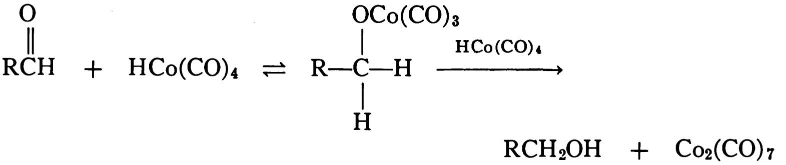
## *Insertion Reactions of Carbonyl Compounds.*

**Metal Hydrides.** It is likely that the reduction of aldehydes to alcohols by cobalt hydrocarbonyl (*27*) is an example of a carbonyl insertion reaction with a metal hydride. It is not clear which way the hydrocarbonyl adds to the carbonyl groups —whether it forms a cobalt-carbon bond (*2*), or a cobalt-oxygen bond (*90*).



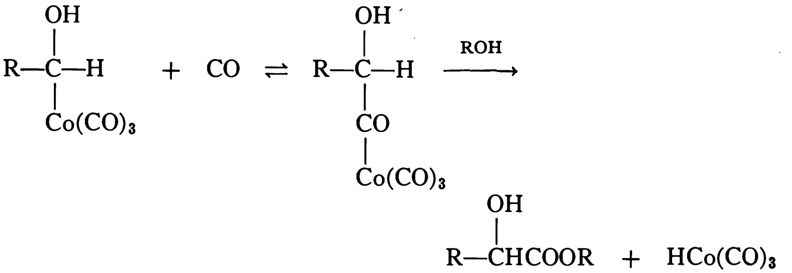
$$RC(=O)H + HCo(CO)_3 \rightleftharpoons R{-}C(OH)(H){-}Co(CO)_3 \xrightarrow{HCo(CO)_4} RCH_2OH + Co_2(CO)_7 \quad (71)$$

or



$$\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{RCH}}} + \mathrm{HCo(CO)_4} \rightleftharpoons \mathrm{R{-}\underset{H}{\overset{OCo(CO)_3}{C}}{-}H} \xrightarrow{\mathrm{HCo(CO)_4}} \mathrm{RCH_2OH} + \mathrm{Co_2(CO)_7} \qquad (72)$$

A known reaction of cobalt hydrocarbonyl suggests that the cobalt-carbon bond may be preferred. It has been reported that, under rather vigorous conditions, acetaldehyde or formaldehyde react with CO and a cobalt catalyst to give $\alpha$-hydroxy acids or esters in alcohol solution (*7*). The intermediate with the carbon-cobalt bond probably is undergoing a CO insertion reaction, folllwed by a hydrolysis or alcoholysis reaction.

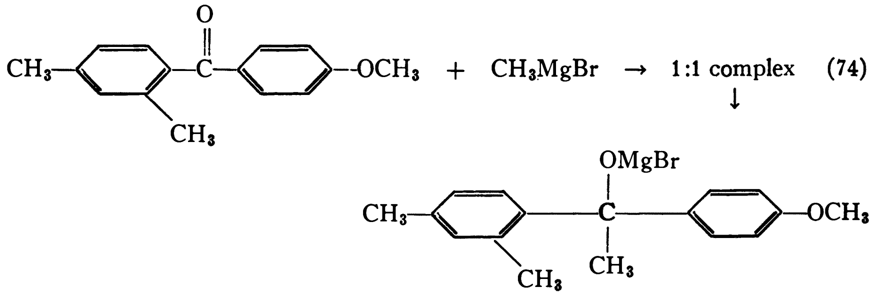


$$\mathrm{R{-}\underset{Co(CO)_3}{\overset{OH}{C}}{-}H} + \mathrm{CO} \rightleftharpoons \mathrm{R{-}\underset{\underset{Co(CO)_3}{CO}}{\overset{OH}{C}}{-}H} \xrightarrow{\mathrm{ROH}} \mathrm{R{-}\overset{OH}{C}HCOOR} + \mathrm{HCo(CO)_3} \qquad (73)$$

If the formation of formate esters under hydroformylation conditions involves the carbonylation of an alkoxycobalt carbonyl as suggested previously (*90*), this would be evidence that cobalt hydrocarbonyl adds the reverse way to acyl groups. Since the formation of formate esters can be explained as well by a CO insertion into a cobalt-hydrogen group followed by alcoholysis, however, the data would be explained best if a cobalt-carbon bond was formed in the hydride reduction of acyl compounds.

Of course, many other nontransition metal hydrides which reduce carbonyl compounds are known; but there is little conclusive evidence on the mechanism of these reactions.

**Metal-Carbon Compounds.** Well-known examples of the insertion reaction of acyl carbonyl groups between metal and alkyl groups include the Grignard reaction and alkyllithium reactions. There is evidence that the carbonyl compound and the Grignard reagent can form a 1:1 complex before reacting. Thus, 4-methoxy-2′, 4′-dimethylbenzophenone formed a 1:1 complex with methylmagnesium bromide which was observed spectroscopically. The rate of disappearance of the complex was equal to the rate of appearance of Grignard reaction product (*87*),

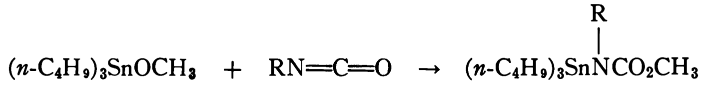


(74)

A structure for the intermediate has not been proposed, but a carbonyl π-complex is a good possibility.

Two examples of the addition of cobalt-carbon compounds to carbonyl groups were given above under acetylene reactions, suggesting this reaction is also generally important.

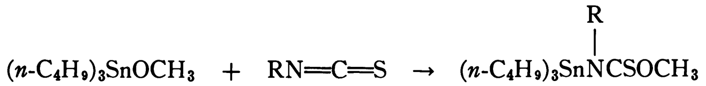
**Metal-Oxygen Compounds.** Trialkyltin alkoxides are remarkable for the variety of addition reactions they undergo with carbonyl and thiocarbonyl compounds. Bloodworth and Davies have reported reactions of tri-*n*-butyltin alkoxides with isocyanates, carbon dioxide, sulfur dioxide, isothiocyanates, carbon bisulfide, chloral, and ketene. The reactions observed were as follows:



$$(n\text{-}C_4H_9)_3SnOCH_3 + RN{=}C{=}O \rightarrow (n\text{-}C_4H_9)_3Sn\overset{R}{\overset{|}{N}}CO_2CH_3 \tag{75}$$

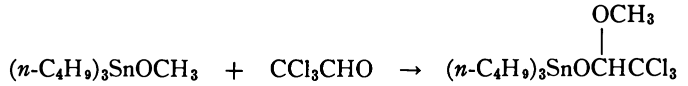
$$(n\text{-}C_4H_9)_3SnOCH_3 + CO_2 \rightarrow (n\text{-}C_4H_9)_3SnOCO_2CH_3 \tag{76}$$

$$(n\text{-}C_4H_9)_3SnOCH_3 + SO_2 \rightarrow (n\text{-}C_4H_9)_3SnOSO_2CH_3 \tag{77}$$



$$(n\text{-}C_4H_9)_3SnOCH_3 + RN{=}C{=}S \rightarrow (n\text{-}C_4H_9)_3Sn\overset{R}{\overset{|}{N}}CSOCH_3 \tag{78}$$

$$(n\text{-}C_4H_9)_3SnOCH_3 + CS_2 \rightarrow (n\text{-}C_4H_9)_3SnSCSOCH_3 \tag{79}$$



$$(n\text{-}C_4H_9)_3SnOCH_3 + CCl_3CHO \rightarrow (n\text{-}C_4H_9)_3SnO\overset{OCH_3}{\overset{|}{C}}HCCl_3 \tag{80}$$

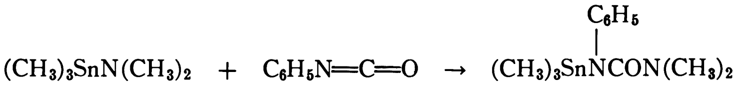
$$(n\text{-}C_4H_9)_3SnOC_2H_5 + CH_2{=}C{=}O \rightarrow (n\text{-}C_4H_9)_3SnCH_2CO_2C_2H_5 \tag{81}$$

Since these reactions take place in nonpolar solvents under mild conditions, insertion mechanisms may be operating (*8*).

**Metal-Nitrogen Compounds.** Very little work has been done on addition reactions of metal-nitrogen compounds. The trimethyltin dimethylamide apparently does undergo reactions analogous to those of the trialkyltin alkoxides just discussed. For example, the following reactions were observed with carbon dioxide, carbon disulfide, and phenylisocyanate (*57*):

$$(CH_3)_3SnN(CH_3)_2 + CO_2 \rightarrow (CH_3)_3SnOCON(CH_3)_2 \tag{82}$$

$$(CH_3)_3SnN(CH_3)_2 + CS_2 \rightarrow (CH_3)_3SnSCSN(CH_3)_2 \tag{83}$$



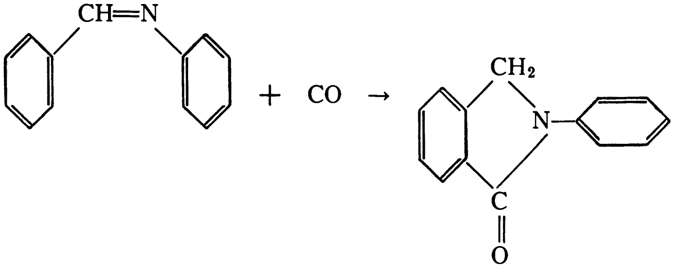
$$(CH_3)_3SnN(CH_3)_2 + C_6H_5N{=}C{=}O \rightarrow (CH_3)_3Sn\overset{C_6H_5}{\overset{|}{N}}CON(CH_3)_2 \tag{84}$$

Similar reactions have been reported for the related silicon compounds, the dialkylaminotrimethylsilicones (*10*). Since these reactions are catalyzed by amines, they are probably ionic.

### *Insertion Reactions of Carbon-Nitrogen Groups*

**Metal Hydrides and Metal-Carbon Compounds.** Numerous examples of reductions and additions of metal hydrides or alkyls to unsaturated carbon-nitrogen compounds are known. I shall mention only two examples pertinent to this discussion.

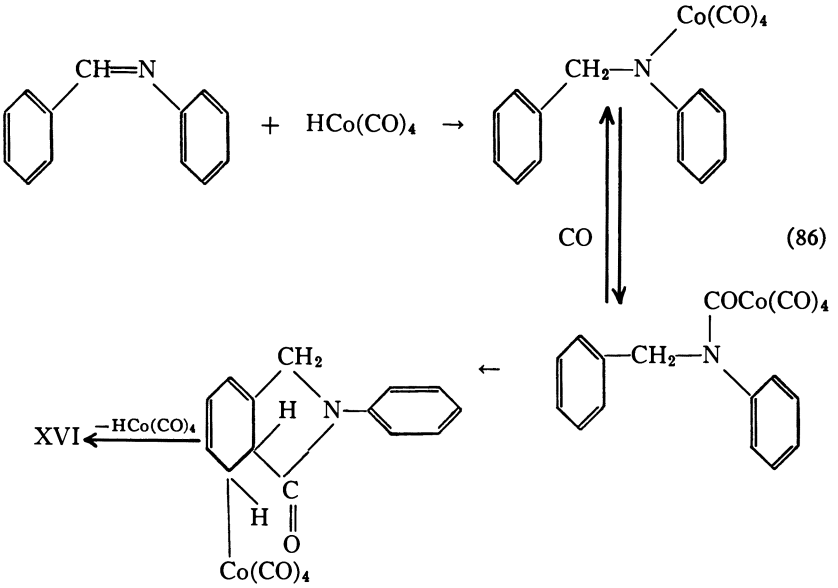
The Schiff bases from substituted benzaldehydes and anilines will carbonylate in the presence of cobalt carbonyl, as catalyst at 225°C. producing phthalimidine derivatives, XVI, in good yield (*70*, *52*). This reaction may be explained as an



XVI

(85)

addition of cobalt hydrocarbonyl, formed by dehydrogenation reactions, to the carbon-nitrogen double bond to give a cobalt-nitrogen bond which then undergoes CO insertion. The carbonyl cobalt derivative then may add to the aromatic system and eliminate cobalt hydrocarbonyl, giving the observed product, XVI. A related



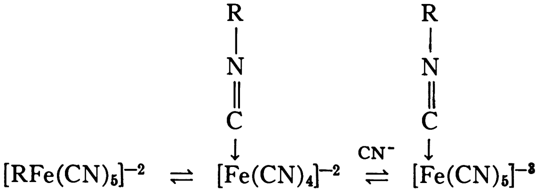
(86)

mechanism involving the addition of cobalt octacarbonyl to the carbon-nitrogen double bond as the initial step has been proposed by Sternberg and Wender (*90*).

Similar reactions are probably involved in the carbonylation reactions of oximes (*80*), oxime ethers (*53*), nitriles (*81*), and of diazo compounds (*53*).

The well-known alkylation of ferrocyanide ion to form isocyanide iron complexes (*48*) can be explained by an insertion mechanism if the metal is alkylated initially, and then metal alkyl adds across a cyanide group. This mechanism also explains how external radioactive cyanide ion can enter the isocyanide ligands (*48*).

$$[Fe(CN_6]^{-4} + RX \rightarrow [RFe(CN)_5]^{-2} + X^- + CN^-$$



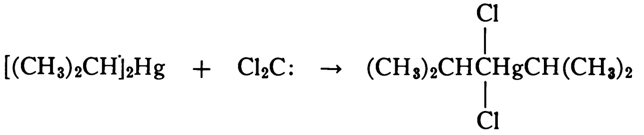
$$[RFe(CN)_5]^{-2} \rightleftharpoons \overset{\begin{array}{c}R\\|\\N\\\|\\C\\\downarrow\end{array}}{[Fe(CN)_4]^{-2}} \overset{CN^-}{\rightleftharpoons} \overset{\begin{array}{c}R\\|\\N\\\|\\C\\\downarrow\end{array}}{[Fe(CN)_5]^{-3}} \qquad (87)$$

## *Carbene Insertion Reactions*

Diazomethane is known to react with a large variety of metal halide derivatives, to produce halomethylmetal compounds (*107*). These reactions may well be methylene insertion reactions.

$$MX_n + nCH_2N_2 \rightarrow M(CH_2X)_n + nN_2 \qquad (88)$$

More recently, dichlorocarbene has been added to diisopropylmercury to give an insertion product, 1,1-dichloro-2-methyl-l-propyl(isopropyl)mercury (*62*).



$$[(CH_3)_2CH]_2Hg + Cl_2C: \rightarrow (CH_3)_2CH\overset{\begin{array}{c}Cl\\|\end{array}}{\underset{\begin{array}{c}|\\Cl\end{array}}{C}}HgCH(CH_3)_2 \qquad (90)$$

## *Conclusion*

The list of groups or molecules for which some evidence exists that insertion reactions can take place, includes carbon monoxide, olefins, dienes, acetylenes, acyl groups, certain carbon-nitrogen groups, and carbenes. Perhaps the list should be extended to include molecular oxygen since several metal alkyls are known to form peroxides with oxygen. Recently oxygen has even been shown to form a coordination compound with a transition metal, iridium (*100*). The examples discussed strongly suggest that the insertion reaction is very generally important among transition metals as well as nontransition metal compounds. Obviously, much work remains to substantiate the generality of the reaction. But the real value of this classification is that it suggests new chemistry to investigate. One can imagine the eventual development of synthetic methods, based upon the insertion mechanism, for combining carbon monoxide, olefins, dienes, acetylenes, ketones, etc., in a variety of linear and cyclic combinations. Clearly, the reaction offers the possibility of discovering many new catalytic syntheses of organic compounds as well as new methods for the preparation of organometallic complexes.

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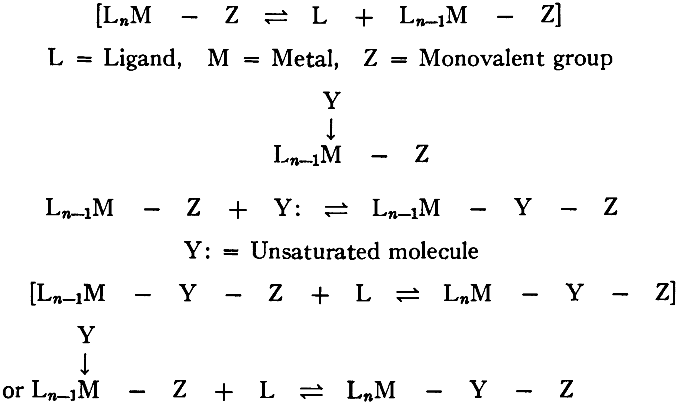
# Discussion

**Richard F. Heck:** The purpose of my paper has been to point out a reaction which appears more widely in the periodic table than most people realize. This general reaction is the insertion reaction and it might be used more widely to make some organometallic compounds which are not available now.

The mechanism of this reaction is not well understood. It is a kind of three- or four-center addition. Some variations of this mechanism are:



$$[L_nM - Z \rightleftharpoons L + L_{n-1}M - Z]$$

L = Ligand, M = Metal, Z = Monovalent group

$$\overset{\overset{Y}{\downarrow}}{L_{n-1}M} - Z$$

$$L_{n-1}M - Z + Y: \rightleftharpoons L_{n-1}M - Y - Z$$

Y: = Unsaturated molecule

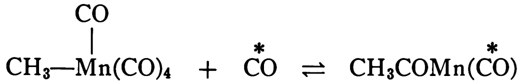
$$[L_{n-1}M - Y - Z + L \rightleftharpoons L_nM - Y - Z]$$

$$\text{or } \overset{\overset{Y}{\downarrow}}{L_{n-1}M} - Z + L \rightleftharpoons L_nM - Y - Z$$

*Figure A. The insertion reaction*

There is considerable evidence that at least many of these reactions require coordinately unsaturated compounds to proceed. In those cases, a dissociation step may be the first part of the reaction. Then these coordinately unsaturated compounds react with an unsaturated molecule—it can be most anything as long as it has an available pair of electrons—and this inserting molecule goes in between the metal atom and one of the groups initially bonded to the metal. If the starting material is coordinately unsaturated, so is the product. A final step must be the formation of a coordinately saturated product by some final reaction, either with another ligand or by decomposition of this insertion product.

There is considerable controversy as to whether or not this reaction involves a $\pi$-complex as a true intermediate. There seems to be no real proof that $\pi$-complexes are true intermediates although it seems clear that they are present in these reaction mixtures. If these $\pi$-complexes are really intermediates, the mechanism is more complicated. It is possible that these can be formed directly from coordinately saturated compounds by a displacement of one of the original ligands by this Y molecule. It is also possible that insertion will not take place unless another ligand is present to move this Y group into the insertion position. There is only one case that I know of in the literature where it has been shown conclusively that a coordinated ligand is the one that inserts. This is the well known manganese carbonyl carbonylation,



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle CO}{|}}{Mn}(CO)_4} + \overset{*}{\mathrm{CO}} \rightleftharpoons \mathrm{CH_3COMn(\overset{*}{C}O)_5}$$

*Figure B. The manganese carbonyl carbonylation (5)*

This is well known data but unfortunately it has never been published. It was given at the London Coordination Conference. The reaction involved the addition of radioactive carbon monoxide to methylmanganese pentacarbonyl. The carbon monoxide entering did not go in the acyl position but went exclusively in a coordination position. It seems that at least in this one example it is a coordinated ligand that is inserting.

I am inclined to think that this same kind of mechanism is operating in many other cases, that is, that the inserting molecule must be coordinated and then it can insert. But I know of no evidence for this in any other cases.

In the figures I have summarized some of the insertion reactions from the literature which we studied.

| *H—M* | *R—M* | | *RO—M* | *$R_2N$—M* |
|---|---|---|---|---|
| $HCo(CO)_4$(?) | $RMo(CO)_3Cp$ | $[\pi{-}C_3H_5NiX]_2$ | $ROCo(CO)_4$ | $[R_2N{-}Co(CO)_4]$ |
| | $RMn(CO)_5$ | $RPdX(PR'_3)_2$ | $\{[\pi{-}C_3H_4CH_2O]Fe(CO)_3\}$ | Fe |
| | $RRe(CO)_5$ | $RPtX(PR'_3)_2$ | | Cu |
| | $RFe(CO)_2Cp$ | RLi | | |
| | $RCo(CO)_4$ | RMgX | | |
| | $RRhX_2(CO)(PR'_3)_2$ | $R_3B$ | | |

*Figure C. Carbon monoxide insertion reactions*

Figure C shows carbon monoxide insertion reactions. There are a number of reduction reactions of carbon monoxide catalyzed by transition metals, and these, I believe, all involve an insertion of carbon monoxide into a metal hydride as an initial step. Cobalt hydrocarbonyl reacts with carbon monoxide to give formate derivatives. This is probably an insertion reaction also.

Many transition metal alkyls react with carbon monoxide to give acyl compounds. In all these cases the acyl derivatives can be detected at least by infrared methods and in most cases isolated. Molybdenum, manganese, rhenium, iron, cobalt, rhodium, nickel, palladium, and platinum alkyls, Grignard reagents, and boranes, all react with carbon monoxide, and one can explain the products from these on the basis of carbon monoxide inserting into the metal alkyl.

Two alkoxide derivatives also seem to insert carbon monoxide. The products obtained when these alkoxides are formed in the presence of carbon monoxide have CO inserted between the oxygen and the metal. These two products can also be explained on the basis of the alkoxide attacking a coordinated carbon monoxide. Hence, these cases certainly are not clear.

There are a number of amine-catalyzed carbonylation reactions which are catalyzed by cobalt carbonyl and iron carbonyl. It seems to me that these are insertion reactions of metal amides, where carbon monoxide is inserted and then some kind of a reduction or subsequent reaction gives the observed products, urea derivatives or carbamates in alcohols. We do not know the structure of the iron compound; it is probably similar to the cobalt species shown.

Copper salts, cupric or cuprous also will catalyze the carbonylation of amines. Piperidine, for example, gives a urea derivative with carbon monoxide, and it, too, is probably a metal amide—carbon monoxide insertion reaction.

| *H—M* | *R—M* | *RO—M* | *X—M* | *M—M* |
|---|---|---|---|---|
| $HMn(CO)_5$ | $RTiCl_3$ | $Pd^{+2}$ | $X_2Pd$ | $Co_2(CO)_8$ |
| $HCo(CO)_4$ | $R_3Cr$ | $Tl^{+3}$ | $X_2Hg$ | |
| $H_2Mg$ | $RMn(CO)_5$ | $(RCOO)_2Hg$ | | |
| $H_6B_2$ | $RCOCo(CO)_4$ | | | |
| $HAlR_2$ | $RLi$ | | | |
| $HGeR_3$(?) | $RK$ | | | |
| $HSnR_3$(?) | $R_2Mg$ | | | |
| | $R_3Al$ | | | |

*Figure D. Olefin insertion reactions*

Figure D shows some olefin insertion reactions. Hydride additions to olefins have been known for a long while. Among these many examples, manganese hydrocarbonyl, and cobalt hydrocarbonyl, magnesium hydride, diborane, alkylaluminum hydrides, germanium and tin hydrides all add quite readily to olefins. These last two cases are questionable because the mechanism is not clear. Some of these additions occur without a catalyst; some are speeded up by ultraviolet light; some are catalyzed by Group VIII metals. So it is not clear whether all these reactions are the same or whether there are several different mechanisms.

A number of metal alkyls add readily to double bonds. These include the titanium alkyls, chromium aryls and alkyls, the alkylmanganese carbonyls, acylcobalt carbonyls, alkali metal alkyls, the magnesium alkyls, and aluminum alkyls.

Among some metal oxygen compounds which add, palladium and thallium ion both oxidize olefins and apparently the initial step is the addition of a metal hydroxide across the olefin double bond. The intermediates have not been isolated because they go on to other products; but kinetic and other evidence indicates that the addition of the hydroxide is the initial step. In the well known mercury acetate addition to olefins in alcohol solution one can isolate the $\beta$-hydroxy or alkoxy ethylmercury derivatives.

Two metal halides have been found to react with olefins by what appears to be insertion reaction. Palladium chloride and mercury chloride both will add to olefins. The palladium alkyls canot be isolated, but they go on to products which can be accounted for by an initial addition.

One complex with a metal—metal bond that has been added to an olefin is cobalt octacarbonyl. It reacts with tetrafluoroethylene and it seems reasonable that this is an insertion reaction; but again it has not been proved.

Figure E shows some conjugated diene insertion reactions. As expected, these compounds react similarly to the olefins—the same reagents add. Manganese

| *H—M* | *R—M* | *RO—M* | *X—M* |
|---|---|---|---|
| $HMn(CO)_5$ | $RCOCo(CO)_4$ | $(RCOO)_2Hg$ | $X_2Pd$ |
| $HCo(CO)_4$ | $[R_2Co]$ | | |
| $HCo(CN)_4^{-3}$ | | | |
| $H_6B_2$ | | | |
| $HSnR_3$(?) | | | |

*Figure E. Conjugated diene insertion reactions*

hydrocarbonyl, cobalt hydrocarbonyl, the cobaltpentacyanide hydride, diborane, and, again, the aluminum and tin hydrides add. The mechanism in the last two examples is still uncertain. Two alkyl- or acyl-cobalt compounds have been added. The acylcobalt tetracarbonyls add to give $\pi$-allylcobalt derivatives. Dialkylcobalt compounds, which have not been isolated but probably are present in the reaction mixture, add to dienes in a similar way, probably giving $\pi$-allyl intermediates.

Mercury acetate adds to dienes just as it does to olefins, and so does palladium chloride. Here again a $\pi$-allyl derivative is obtained. The formation of the $\pi$-allyl derivative, I think, occurs after the initial addition and probably has nothing to do with the first insertion step.

| *H—M* | *R—M* | *RO—M* | *X—M* | *M—M* |
|---|---|---|---|---|
| $HMn(CO)_5$ | $RMo(CO)_3Cp$ | $ROSnR'_3$ | $X_2Hg$ | $Co_2(CO)_8$ |
| $HCo(CO)_4$ | $R_3Cr$ | | | $K_6[Co(CN)_5]_2$(?) |
| $[HNi(CO)_2X]$ | $RFe(CO)_2Cp$ | | | |
| $H_6B_2$ | $RCOCo(CO)_4$ | | | |
| $HAlR_2$ | $[\pi—C_3H_5NiX]_2$ | | | |
| | $RLi$ | | | |
| | $R_3Al$ | | | |

*Figure F. Acetylene insertion reactions*

Figure F shows some acetylene insertion reactions. These, too, are similar to the olefin insertion reactions. The manganese and cobalt hydrocarbonyls again add. Chloronickelcarbonyl hydride, which I believe is an intermediate in many of the nickel carbonyl-catalyzed reactions, adds to olefins. Diborane and the aluminum hydrides also add.

Again several alkyls add—molybdenum, chromium, iron, cobalt, nickel, the alkali metal alkyls and aluminum alkyls react. A tin alkoxide has recently been studied by Russian workers and found to add to acetylenes. Mercury chloride, of course, adds and two cobalt—cobalt bonded compounds add to acetylene. The second is questionable because it dissociates in solution and the reaction may be a radical reaction, one cobalt adding to each end of the triple bond.

| *H—M* | *R—M* | *RO—M* | *$R_2N$—M* |
|---|---|---|---|
| $HCo(CO)_4$ | $RLi$ | $ROSnR'_3$ | $R_2N—SnR'_3$ |
| $H_6B_2$ | $RMgX$ | | $(R_2N)_3$ As |
| $HAlR_2$ | $R_3Al$ | | |

*Figure G. Carbonyl insertion reactions;*
*$RCHO$, $R_2C=O$, $R—N=C=O$, $CO_2$, $CH_2=C=O$*

Figure G shows some insertion reactions of carbonyl compounds. In the isocyanate and ketene cases, the addition takes place, not to the carbonyl double bond, but to the carbon—nitrogen or the carbon—carbon double bond.

Cobalt hydrocarbonyl, diborane, and aluminum hydrides add, I think, to all of these carbonyl compounds. Of course, there is the well known Grignard reagent and the alkyllithium additions to carbonyl compounds. Aluminum alkyls add, and we could have listed all the other alkali metal alkyls. Recent work has shown that the tin alkoxides add readily to all these derivatives, and similarly, a tin amide adds to most of these carbonyl compounds.

Recently an arsenic amide derivative has reacted with an isocyanate, adding across the carbon—nitrogen double bond. I think this is the first example of a group V element which seems to be undergoing an insertion reaction.

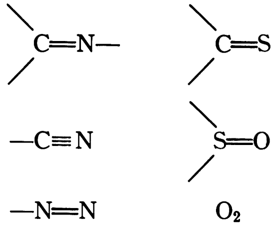


*Figure H. Miscellaneous insertion reactions*

Finally, in Figure H are some additional unsaturated groups for which some evidence exists that they undergo insertion reactions also: the carbon—nitrogen double bond, the nitrile group, the azo group, the carbon—sulfur double bond, the sulfur oxide group, and the oxygen molecule. I think it is clear from these examples that this is a general reaction. Perhaps the mechanisms don't all involve insertion reactions, but they are similar enough to look as if they belong in the same group. This reaction holds promise for making many new, unusual, and useful compounds, and I think it will be used considerably in the future.

**Raymond Dessy**: I would like to focus on three problems. Dr. Heck has already mentioned one, the importance of complexing these carbonyl metal hydride compounds with olefins, or for that matter, the importance of complexing any olefin with these transition metal catalysts in leading to final product. Does a four-center transition state of some type occur directly, or is another mechanism involved? I also hope that somebody would comment on what Dr. Heck has called coordinative unsaturation. His view, I think, is that the first step in many of the carbonyl reactions with cobalt involves loss of enough CO to give a coordinatively unsaturated cobalt. Finally, I would like to consider some data from a paper that Dr. Heck published in 1961 (*6*) concerning the reactions of isobutylene with the cobalt hydrocarbonyl under two types of conditions. One condition, the so called oxo condition which is about 120°C. under a fairly high pressure of hydrogen, gave products which he quoted directly from the literature. This leads to aldehyde material. The aldehyde group introduced occupies what might be called a primary carbon. In his own work at 0°C., where the isolation took place by reaction with triphenylphosphine, then methyl alcohol and iodine, the product is, of course, not an aldehyde but an acid ester. The skeletal arrangement would indicate that the tertiary carbon atom is used for the attachment site of the cobalt. Overall yields were about 20%. This is to be compared with the reaction of the corresponding epoxide with hydrocarbonyl or carbonyl anion that he recently reported (*7*). This gives a product derived from opening the epoxide ring in a way which uses the primary carbon again as the point of attachment for the cobalt. There is one other reaction in this vein, which leads to the question that I would like to ask. The reactions of acrylic esters under oxo conditions gives a skeletal arrangement in the product, which puts the aldehyde group on the terminal carbon atom of the acrylic ester; while under conditions of 0°C., followed by isolation of a product by triphenylphosphine/methyl alcohol/iodine reaction, the skeletal arrangement in the product indicates that the cobalt attaches itself to carbon atom-2. Although 20% of the other product is there, this is the main product.

I would like to read from two of Dr. Heck's papers:

"The high electron density of the double bond in isobutylene results in an acid type addition, while the low electron density in methyl acrylate leads predominantly to a hydridic addition. The change in the direction of addition of cobalt hydrotetracarbonyl with temperature is probably a reflection of the relative stability of the adducts. Thus, if the addition is reversible, the products at elevated temperatures could reflect the relative stabilities of the adducts rather than their initial concentrations" (*6*).

Apparently the explanation for these two different results, in terms of the carbon skeleton of a product, was ascribed to the stabilities of the intermediates at these two temperatures; the difference in direction of addition between the methyl acrylates and the isobutylene was caused by the electron density at the double bond.

Finally, from a paper in 1963 on the epoxide work we have a quotation:

"The mechanism most consistent with all the data is an ionic acid opening of the epoxide"—apparently where the hydrocarbonyl is used as an acid to attack the epoxide—"which is more sensitive to steric effects than to electronic factors. This conclusion may at first appear to be inconsistent with our previous finding that isobutylene reacted with cobalt hydrocarbonyl to give exclusively addition of the cobalt to the tertiary position. The inhibitory effect of carbon monoxide on that reaction, however, indicated that it was probably cobalt hydrotricarbonyl that was actually adding to the olefin and steric effects would be expected to be much less important with the tricarbonyl than with the tetracarbonyl" (*7*).

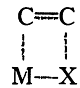
Apparently he feels now that the former reactions really involve the tricarbonyl, loss of CO being important to get the reaction running; whereas epoxide attack perhaps involves a tetracarbonyl, steric factors are more important here.

The problem I would like to focus on perhaps can best be expressed by an analogy with some of Prof. Pearson's comments.

The analogy comes from someone who was impressed by the soft acid—soft base work. As a matter of fact, he felt that acids and bases react to give salts, and soap is a salt, and so we have soft soap.

Since words sometimes hide meaning, we have to be careful that we don't substitute words which don't mean much for ideas. I am very troubled at the moment over what Dr. Heck meant by acid base, how electron density in the olefin could lead to the orientation he mentions. I would like to ask whether or not he can explain this. Finally, if this proves difficult, has he thought about radical processes in this type of thing?

**Jack Halpern**: Perhaps I have more reason than anyone else to be disposed to the view that π-complexing is an important step of the insertion reaction, because I think that possibly we have the only reasonably clear cut case of an olefin insertion reaction where a complex is clearly implicated. This is the ruthenium chloride-catalyzed hydrogenation of certain olefins, which almost certainly involves the insertion of the olefin into a ruthenium hydrogen bond and where certainly a ruthenium olefin complex is involved as an observable reactant. Nevertheless, I am not at all sure to what extent this is a general or necessary feature of such insertion reactions. The important question is whether one or two coordination positions on the metal ion are involved in the transition state of the insertion reaction. For example, if one considers the insertion of an olefin, say into an M—X bond, then the transition state may look something like:



$$\begin{array}{ccc} C & = & C \\ \vdots & & \vdots \\ M & - & X \end{array}$$

There is partial bonding between the metal and the olefin (or perhaps one carbon of the olefin) and between the metal and X, and this uses two coordination positions of the metal. Otherwise only one coordination position is involved, and the transition state is not appreciably stabilized by bonding between the metal and X. If this is the case, then there is less reason to postulate the olefin as initially involved, say as a π-bonded ligand. Perhaps it just comes in from the outside.

In many of these systems, the postulated olefin complex intermediate would be labile. Therefore, its role as a pre-equilibrium intermediate is not terribly relevant to the kinetic problem. I think the relevant feature is whether the favorable paths in these insertion reactions involve the first or second type of transition state. This perhaps de-emphasizes the question of whether or not a π-bonded intermediate is involved but certainly does focus attention on the question of whether a coordinately unsaturated species is involved as a reactant. This is because the first type of transition state will require two coordination positions and hence involve the elimination of some other ligand before it can form, whereas the second will not. I don't know the answer to this question but this is how I would formulate the problem.

We are currently trying to answer specifically the question of whether π-bonded complexes do occur in certain cases where insertion reactions are observed. I think they do because I believe that the same factors which favor stabilization of this type of transition state will also tend to favor formation of π-bonded olefin complexes, which are only slightly removed from this. At the moment Bern Tinker is examining the insertion of olefins in mercuric complexes to see whether there is any indication of π-bonded intermediates. In his paper, Dr. Heck referred to some unpublished work relevant to this theme. I would certainly be interested in anything more he can tell us about that.

**Dr. Dessy**: Many workers have felt that such π-complexing, because of dπ–pπ-back-bonding into the π* of the olefin, can activate the olefin for the subsequent attack. What reality does that have?

**Dr. Halpern**: I think the description can be formulated in a somewhat different way emphasizing the point that you raise; namely, that formation of a metal olefin complex, by virtue of the back-bonding process, puts metal electrons into anti-bonding orbitals of the olefin. This reduces the bond order of the olefin, and in this sense could lead to a view that the olefin is activated. If you prefer, a valence bond representation, a perfectly satisfactory description of a $\pi$-olefin complex would be one in which there is substantial opening of the double bond and formation of partial bonds between the carbons and the metal. I think most people would tend to view this type of species as probably having higher reactivity towards addition than the uncomplexed olefin.

**Dr. Heck:** I believe this can best be described as a compromise between the electronic effects and steric effects.

**R. J. Mawby:** Discussing the insertion reactions of methylmanganese pentacarbonyl, Dr. Heck writes, "An important question, therefore, is unanswered. Does the coordinated carbonyl group insert before the new CO is added or does the incoming CO push the coordinated carbonyl into the acyl position?"

I have been investigating this problem at Northwestern University, under Profs. Basolo and Pearson (*8*). F. Calderazzo and F. A. Cotton (*1*) had previously showed that Reaction 1:

$$CH_3Mn(CO)_5 + CO \rightarrow CH_3COMn(CO)_5 \qquad (1)$$

was first-order in both $CH_3Mn(CO)_5$ and CO over the range of carbon monoxide concentrations used. However, this range was severely limited by the low solubility of CO in the solvents which they employed.

By studying reactions of type (2):

$$CH_3Mn(CO)_5 + L \rightarrow CH_3COMn(CO)_4L \qquad (2)$$

where L is some ligand other than CO, we could work with considerably greater ligand concentrations. The first reaction we studied was $CH_3Mn(CO)_5$ with cyclohexylamine in tetrahydrofuran. We found that the reaction rate was independent of amine concentration over the concentration range studied—from $2.5 \times 10^{-2}M$ to $5 \times 10^{-1}M$. This ruled out the mechanism suggested by Drs. Calderazzo and Cotton for Reactions 1 and 2, which involved an attack by the ligand CO or L, simultaneous with an intromolecular rearrangement to form the acetyl group.

We then studied the reactions of $CH_3Mn(CO)_5$ with triphenylphosphine and triphenylphosphite, using the same solvent, tetrahydrofuran. In these cases the observed rate constant rose with ligand concentration towards a limiting value, which was close to the rate constant obtained using cyclohexylamine (Figure I).

To explain these observations, we postulated a two-step mechanism:

$$CH_3Mn(CO)_5 \rightleftharpoons CH_3COMn(CO)_4 \underset{-L}{\overset{+L}{\rightleftharpoons}} CH_3COMn(CO)_4L \qquad (3)$$

The first step involves an intramolecular rearrangement to form the acetyl group; the second is the reaction of the intermediate with the ligand to give the final product. It is possible that a molecule of solvent is coordinated to the intermediate shown in Equation 3. Since it would have no effect on the form of the rate expression for the reaction, we cannot say conclusively whether or not this is so.

Equation 3 can be conveniently abbreviated as follows:

$$M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MS \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML \qquad (4)$$

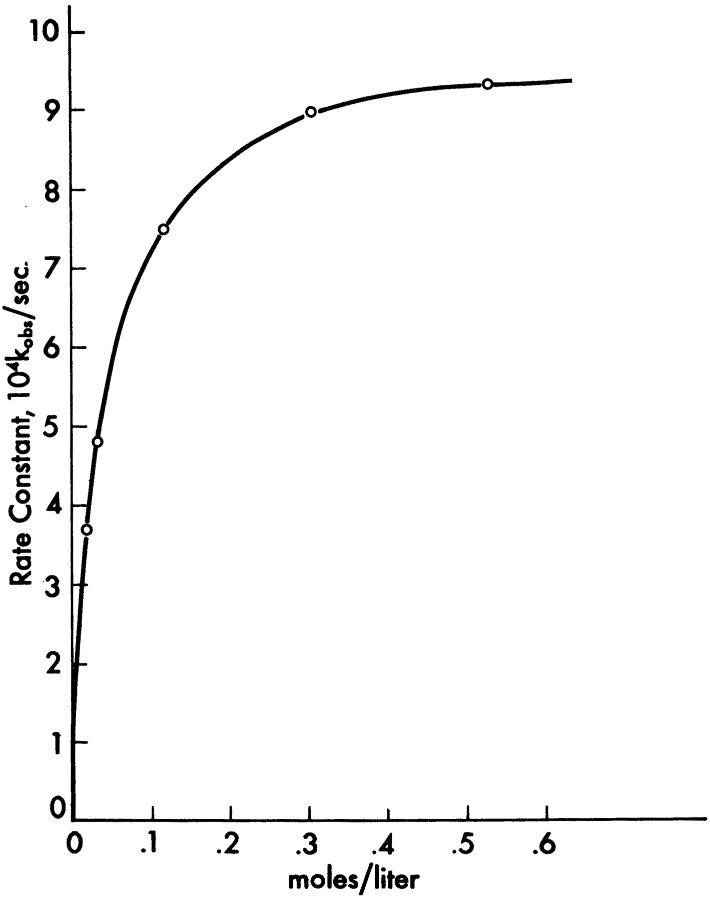


*Figure 1. Reaction of $CH_3Mn(CO)_5$ with triphenylphosphite in tetrahydrofuran; plot of observed rate constant against triphenylphosphite concentration.*

where M represents the starting material, MS the intermediate, and ML the final product. In discussing the kinetics of these reactions I shall ignore $k_{-2}$ because all the reactions mentioned here went to completion.

If the first step of this reaction were rate controlling, the reaction rate would be completely independent of ligand concentration, and evidently this is the case for cyclohexylamine in tetrahydrofuran. The rate expression for this reaction then becomes:

$$\frac{d[\mathrm{ML}]}{dt} = k_1[\mathrm{M}] \qquad (5)$$

However, if the first step is not completely rate controlling, there will be competition for the intermediate, MS, between the second forward step to give the final product, and the reverse of the first step, which leads back to the starting material.

We believe this is the case for the reactions of $CH_3Mn(CO)_5$ with triphenylphosphine and triphenylphosphite in tetrahydrofuran.

Under these conditions, assuming the steady state approximation for the concentration of the intermediate, the rate expression becomes:

$$\frac{d[\mathrm{ML}]}{dt} = \frac{k_1 k_2[\mathrm{M}][\mathrm{L}]}{k_{-1} + k_2[\mathrm{L}]} \tag{6}$$

From this one can obtain an expression relating the observed rate constant to the ligand concentration:

$$\frac{1}{k_{\mathrm{obs}}} = \frac{k_{-1}}{k_1 k_2}\frac{1}{[\mathrm{L}]} + \frac{1}{k_1} \tag{7}$$

If the mechanism is correct, Equation 7 shows that a plot of the reciprocal of the observed rate constant against the reciprocal of the ligand concentration should be linear for the reactions of $CH_3Mn(CO)_5$ with triphenylphosphine and triphenylphosphite. This was found to be the case for both reactions (Figure J), and provides good evidence that the postulated mechanism is indeed correct.

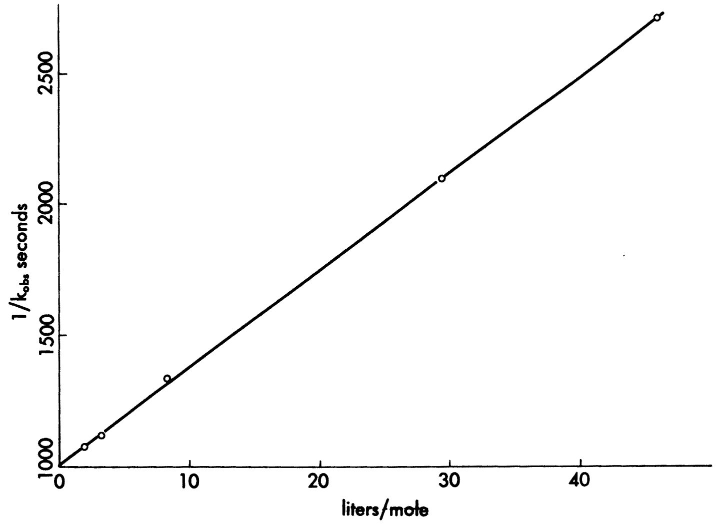


*Figure J. Reaction of $CH_3Mn(CO)_5$ with triphenylphosphite in tetrahydrofuran. Plot of reciprocals.*

In addition, Equation 7 predicts that by extrapolating to a reciprocal concentration of zero, one should obtain a value for $k_1$, the rate of formation of the intermediate from $CH_3Mn(CO)_5$. This should be independent of the ligand used, depending only on the solvent. Figure K shows the values for $k_1$ obtained for the reactions of $CH_3Mn(CO)_5$ with three different ligands in tetrahydrofuran, which are in reasonable agreement with one another.

The observations of Drs. Calderazzo and Cotton (*1*) can also be explained on the basis of this mechanism. In the very low ligand concentrations to which these

| *Ligand* | $k_1$(*sec.*—1) |
|---|---|
| cyclohexylamine | $9.6 \times 10^{-4}$ |
| triphenylphosphine | $9.0 \times 10^{-4}$ |
| triphenylphosphite | $9.9 \times 10^{-4}$ |

*Figure K. Values of $k_1$ for the reaction of $CH_3Mn(CO)_5$ with various ligands in tetrahydrofuran*

authors were restricted by the poor solubility of CO in the solvents used, the second step of the reaction (the reaction of the intermediate with CO) would become rate controlling, leading to the rate expression:

$$\frac{d[\mathrm{ML}]}{dt} = \frac{k_1k_2}{k_{-1}}[\mathrm{M}][\mathrm{L}] \tag{8}$$

which agrees with the observed first-order dependence on both $CH_3Mn(CO)_5$ and CO.

I would like to ask Dr. Heck if he believes that the insertion reactions of $CH_3Co(CO)_4$ proceed by a similar two-step mechanism, or by a concerted mechanism?

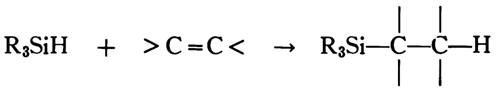
**Dr. Heck:** We have proposed many times that the acyl group is formed before the ligand comes in, but the rates in the cobalt series are too fast to measure. I think cobalt and manganese react similarly.

Have you measured this rate in a hydrocarbon solvent by any chance—one that wouldn't coordinate?

**Dr. Mawby:** In *n*-hexane, the reaction of $CH_3Mn(CO)_5$ with cyclohexylamine was first-order in both reactants, suggesting that a concerted mechanism, involving simultaneous attack by the amine and rearrangement to form the acetyl group, is operating. In mesitylene, which has a slightly higher dielectric constant, we observed a more complicated state of affairs. Both mechanisms appeared to operate side by side, and we obtained rate constants for both the two-step and the concerted mechanisms. Certainly a nonpolar solvent appears to favor the concerted mechanism.

**Alan J. Chalk:** I should like to comment on the point raised by Dr. Dessy on coordinately unsaturated catalysts and on some points in the paper.

John Harrod and I have been looking at the silicon hydride addition to olefins catalyzed by Pt(II)



$$R_3SiH + {>}C{=}C{<} \rightarrow R_3Si\text{—}\overset{|}{\underset{|}{C}}\text{—}\overset{|}{\underset{|}{C}}\text{—}H$$

We discussed this catalysis recently (141st National Meeting of the American Chemical Society, March 1962) in terms of an olefin insertion reaction involving a Pt(II) olefin complex (*3*). We found that catalysis was only accomplished by platinum compounds capable of coordinating olefins. For example, substitution by tertiary phosphines blocks coordination by olefins and greatly reduces the catalytic activity of Pt(II). The substitution by phosphines does not affect the ability of the complexes to cleave the Si—H bond, however. The hindering of a catalytic reaction by blocking coordination sites is a common occurrence and is, I think, a persuasive argument favoring the necessity for a coordinately unsaturated or coordinately labile catalyst.

Concerning Dr. Heck's expectation of a cis addition for the insertion reaction, we have found that the reverse reaction, an elimination, also results in a cis product. Thus, the isomerization of terminal olefins, catalyzed by metal ions which form $\pi$-complexes, produces the cis-2 olefin first (*4*). Subsequently, the trans-2 olefin is formed, however, which requires explanation. Possibly the hydride is, in this case, pulled off the alkyl group by another coordinated olefin rather than by the metal itself.

My last comment concerns the reaction of palladium olefin complexes with carbon monoxide discovered by Tsuji. I agree that this is most likely to proceed by an insertion rather than an ionic mechanism. Chloride attack on coordinated olefin is rare however. Chloride ion is an inhibitor, for example in the palladous chloride catalyzed hydration of ethylene (*9*). I, therefore, wondered whether carbon monoxide was affecting the ease with which chloride attacks olefin. One can postulate that carbon monoxide participates in this insertion either as a gas phase reactant or by first forming a carbonyl olefin complex. Such complexes of the noble metals were unknown, but examining the reaction between carbon monoxide and the halogen bridged olefin complexes of platinum revealed that they are formed very readily (*2*). An attempt was also made to produce $\beta$-iodo acyl iodides by the reaction of iodine, carbon monoxide and olefins in the presence of palladium or platinum chloride. This is, in effect, an attempt to make Dr. Tsuji's reaction catalytic rather than stoichiometric. No carbonyl insertion occurred at 1 atm. of carbon monoxide. However, it was found that iodination of the olefin was catalyzed by platinum olefin complexes and that an additional increase in catalytic activity accompanied the presence of carbon monoxide. There has been much speculation at this conference concerning the possibility of affecting catalytic activity by changing the ligands in the coordination sphere of the catalyst. This would appear to be such a case.

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# 9

# Acid-Base Reactions in Fused Salts

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**An oxide ion acceptor or acid will react with certain oxyanions in fused salts to produce a new acid. The equilibria involved with pyrosulfate and dichromate have been studied quantitatively in fused nitrates and, since nitronium ion is a very strong acid, other oxyions such as bromate and iodate may be studied in fused nitrate solutions. The self-dissociation of nitrate occurs to a slight extent and has been studied quantitatively using an oxygen-oxide ion electrode. By making potentiometric measurements on both the basic and acidic nitrate solutions, one can calculate the self-dissociation constant. Strongly basic oxyanions, such as carbonate, can then be studied directly in regard to the oxide ion in equilibrium with the oxyanion in fused nitrates.**

A fused salt consisting, generally, of an alkali cation and an oxyanion is able to self-ionize the anion to oxide ion and an acidic substance. For example, sulfate may dissociate slightly to form $SO_3$ and $O^{-2}$, nitrate to form $NO_2^+$ and $O^{-2}$, and phosphate to form $PO_3^-$ and $O^{-2}$. Nitrate is the only oxyanion studied to any extent thus far, owing principally to the convenient melting points of its alkali salts and the large temperature range of liquid stability.

The acid-base properties of fused alkali nitrates were first noted when dichromate was added to fused sodium-potassium nitrate eutectic (*1*). Gaseous nitrogen dioxide and oxygen were slowly given off with the conversion of the dichromate to chromate. It was postulated that $NO_2^+$ was formed as intermediate:

$$CrO_7^{-2} + NO_3^- \rightleftarrows NO_2^+ + 2CrO_4^{-2}$$

The effect (upon the overall rate of conversion of dichromate to chromate) of changing the chromate ion concentration was studied. The rate was inversely proportional to the square of the chromate concentration, as well as proportional to the dichromate concentration. Since oxygen and nitrogen dioxide had no effect on the rate, the nitryl ion, $NO_2^+$ was postulated as intermediate. However, the equilibrium constant for the reaction could not be determined because too little $NO_2^+$ was formed.

When pyrosulfate was substituted for the dichromate, the equilibrium reaction became (*3*):

$$S_2O_7^{-2} + NO_3^- \leftrightarrows NO_2^+ + 2SO_4^{-2}$$

Pyrosulfate is a sufficiently strong acid so that a reasonable percentage of the acidity appears in the form of $NO_2^+$, and the overall reaction rate is no longer inversely proportional to the square of the sulfate ion concentration. It was assumed that in both the dichromate and pyrosulfate reactions, the final reaction to produce nitrogen dioxide and oxygen was:

$$NO_2^+ + NO_3^- \rightarrow 2NO_2 + O$$

The oxygen atoms, in solvated or other form, rapidly combine to form molecular oxygen.

The method used for following the conversion of dichromate to chromate or pyrosulfate to sulfate involved measuring the total acidity, $A_T$, as a function of time. In the pyrosulfate case,

$$A_T = [NO_2^+] + [S_2O_7^{-2}], \text{ and } \frac{-dA_T}{dt} = K[NO_2^+].$$

The equilibrium equation, $K = \frac{[NO_2^+][SO_4^{-2}]^2}{[S_2O_7]}$, was combined with the two above equations to give (*3*):

$$\frac{-dA_T}{dt} = \frac{kKA_T}{(K + [SO_4^{-2}])}$$

Since sulfate was always in large excess of $A_T$, the expression, $\frac{kK}{K + [SO_4^{-2}]^2}$, occupies the position of a first order rate constant in any given run and is determined as a first order constant. Thus, numerical values were obtained for $k'$, the pseudo constant, where $k' = \frac{kK}{K + [SO_4^{-2}]^2}$, as a function of $[SO_4^{-2}]$. Plots of $\frac{1}{k'}$ *vs.* $[SO_4^{-2}]^2$ gave an ordinate intercept of $\frac{1}{k}$ and an abscissa intercept of $-K$. Thus, the equilibrium constant for the reaction between pyrosulfate and nitrate was determined. Apparently, the same rate determining step is involved in the dichromate reaction, and the equilibrium constant can be calculated for the dichromate case also. The equilibrium constant for the pyrosulfate reaction is $50.8 \times 10^{-3}$ at 300°C., and $21.8 \times 10^{-3}$ at 275°C. (*5*). The constant for the dichromate reaction is $8.5 \times 10^{-14}$ at 250°C. and $3.8 \times 10^{-12}$ at 300°C.

The existence of the nitryl ion in the presence of acidic substances suggested that nitrate ion in fused alkali nitrates might dissociate into $NO_2^+$ and $O^{-2}$ ions (*5*). To determine the extent of the dissociation, it was necessary to develop an electrode potentiometrically responsive to either $NO_2^+$ or $O^{-2}$. The only possibility for a reversible $NO_2^+$ electrode that came to mind was nitrogen dioxide gas bubbling over platinum. This electrode did respond to $NO_2^+$ in acidic solutions, but as expected, the following non–electrochemical reaction occurred in the presence of oxide ion:

$$NO_2 + O^{-2} \rightarrow NO_2^- + NO_3^-$$

Thus, the utility of the oxygen electrode was explored.

The potential of oxygen over platinum responded nicely to changes in oxygen pressure according to the Nernst expression (*5*). The reference electrode was silver immersed in 0 1*M* silver nitrate in the fused alkali nitrates, the mixture being contained in a thin glass envelope. To test the effect of changes in oxide ion concentration on the potential, a source of pure alkali oxide was needed. It is also ultimately necessary to know $E°$ for the cell $O_2, Pt; \left.\begin{matrix}KNO_3\\NaNO_3\end{matrix}\right\} O^{-2} \Big\| \text{(glass)} \begin{matrix}KNO_3\\NaNO_3\end{matrix} Ag^+,$ 0.1 *M*; Ag, in order to calculate the self-dissociation constants. Since alkali oxides are extremely difficult to prepare in the pure state and to handle, it was decided to produce the oxide ion coulometrically. Consequently, a known current of approximately 8 microamp. was run through the cell, the oxygen electrode acting as the cathode. The current was drawn from an electronically controlled constant current device and timed so that the number of equivalents of charge passing could be calculated. This was assumed to be the number of oxide ions produced. The variation in potential with oxide ion followed the Nernst expression very precisely.

To determine the potential of the electrode on the acid side, pyrosulfate of known concentration was placed in the fused salt. Knowing the equilibrium constant to produce $NO_2^+$, it was possible to calculate the $NO_2^+$ concentration corresponding to the potential measured. Then the self-dissociation constant was calculated as follows:

$$E = E° - \frac{RT}{2F} \ln \frac{P_{O_2}{}^{1/2}}{[O^{-2}]}$$

including the reference electrode potential in the $E°$.

On the acid side, since $K_D = [NO_2^+][O^{-2}]$, the equation becomes

$$E = E° - \frac{RT}{2F} \ln \frac{P_{O_2}{}^{1/2}[NO_2^+]}{K_D}$$

Thus, $K_D$ may be calculated as described above. $K_D$ was found to be $2.74 \pm 0.27 \times 10^{-26}$ at 250° C. and $5.66 \pm 0.1 \times 10^{-24}$ at 300° C. The enthalpy of dissociation is 64 kcal. per mole.

The basicities of $BrO_3^-$, $ClO_3^-$ and $IO_3^-$ (*6*) were studied next. It was first determined that $BrO_3^-$ and $IO_3^-$ were considerably more basic than nitrate ion. Thus, these halates were studied in fused alkali nitrate solutions. The reactions studied were:

$$2Ba^{+2} + XO_3^- + Cr_2O_7^{-2} \rightleftarrows XO_2^+ + 2BaCrO_4$$

The chromate concentration was controlled through the solubility product of $BaCrO_4$ and the barium ion concentration. The equilibrium was followed by the reactions:

$$BrO_2^+ \rightarrow \text{Products } (Br_2, O_2)$$

$$ClO_2^+ + Cl^- \rightarrow \text{Products } (Cl_2 + ClO_2 + O_2)$$

$$IO_2^+ + Br^- \rightarrow \text{Products } (Br_2, IBr)$$

The bromyl ion decomposes spontaneously. Chloryl and iodyl ions were studied through their attack on chloride and bromide ions respectively. By determining the rate of disappearance of dichromate and using an analysis similar to the pyrosulfate-nitrate case, the following equilibrium constants were found for the dichromate-halate reactions which produce halyl and chromate ions (not calculated as $BaCrO_4$, but as $[CrO_4^{-2}]$ in solution) (*2*).

$$K_{BrO_3^-} = 3.5 \times 10^{-8}\ M^{-1}$$

$$K_{ClO_3^-} = 4.0 \times 10^{-11}\ M^{-1}$$

$$K_{IO_3^-} = 2.2 \times 10^{-9}\ M^{-1}$$

$$K_{NO_3^-} = 4.5 \times 10^{-11}\ M^{-1}$$

Nitrate is included for comparison. The chlorate was run with chlorate as solvent since $ClO_2^+$ has about the same acidity as $NO_2^+$. Also, note that $BrO_3^-$ is the strongest base of the three ions.

Kust (*4*) has potentiometrically determined the equilibrium constant for carbonate dissociation in fused sodium-potassium nitrate eutectic:

$$CO_3^{-2} \rightleftarrows CO_2(g) + O^{-2}$$

A mixture of carbon dioxide and oxygen was allowed to bubble over platinum, thus maintaining both gas pressures at known values. This electrode indicated the oxide ion concentration:

$$\frac{1}{2}O_2 + 2e \rightarrow O^{-2}$$

The reference electrode was that used in determining the degree of dissociation of nitrate (*5*).

The values determined are as follows:

| *T °K* | $K \times 10^5$ |
|---|---|
| 523 | 0.40 ± 0.05 |
| 553 | 1.5 ± 0.1 |
| 590 | 9.1 ± 0.5 |

$\Delta H^\circ$ was found to be 27 kcal. and $\Delta S$ was 27 e.u. The large size of the constant compared with the known dissociation of pure sodium carbonate to sodium oxide and carbon dioxide suggests that $NO_4^{-3}$, or orthonitrate is probably formed when oxide ion is placed into fused nitrates. It may well be that the dissociation reaction for pure nitrate should be written:

$$2NO_3^- \rightarrow NO_2^+ + NO_4^{-3}$$

This point needs further investigation.

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# Discussion

**Frederick Duke:** Ten or so years ago I was extensively involved in oxidation-reduction reaction kinetics, and little work had been done at that time on the anions—the oxy anions and the way in which they react. John Edwards and others have done quite a lot with them since and even before. One thing that made it difficult to study these oxy anions as oxidizing agents was the fact that when they were used in aqueous solution the reaction would not proceed unless the acid present was hydrogen ion. There may be some exceptions to that. But in general, hydrogen ion was necessary to make the oxy anions into oxidizing agents. No weaker acid would do anything. A stronger acid in water turns into hydrogen ion and one can't learn very much. We decided to look for some other solvents in which one could get a variety of acidic strengths, all of which would cause these oxy anions to act as oxidants. For example, consider bromate. The question is, when the two hydrogen ions are added does the reaction go to $H_2BrO_3^+$, or to $H_2O$ plus $BrO_2^+$? Just what is the oxidant in these situations? Actually, in aqueous solution it is probably trivial to discuss the difference between these two. At any rate we thought about trying some nonaqueous solvents, and it appeared that the fused alkali nitrates might be very interesting. We didn't expect nitrate ion to be very acidic or basic. We thought we could dissolve almost anything in this solvent and know what it was in the way of an acid. Rather than studying any acid-base properties of the solvent, we began by adding dichromate and thought a good reaction study would be the dichromate-bromide reaction. This reaction is very slow in aqueous solution and it is necessary to add sulfuric acid and heat to make it go. With these solvents we could use temperatures around 250°C., and we thought this would give the right rate for a good kinetic study. Whenever a halide ion is oxidized, the reaction usually is second-order, or at least involves two halide ions because the intermediate, such as $Br_2^-$, is more stable than the atom. Many halogen oxidations involve one-electron transfers. We wanted to find out whether $Br_2^-$ was still stable at 250°C. and whether chromium(V) or (IV) were still important at these high temperatures.

None of these things happened when we tried this reaction. What did happen—and it took some puzzling to figure it out—was that it reacted with a nitrate ion as the solvent to give two chromate ions plus nitryl ion, and the nitryl ion made nitryl bromide which decomposes to bromine and $NO_2$. Incidentally, we found that only one bromide is needed in this reaction, and apparently the $Br_2^-$—the free radical ion—is unstable at 250°C.

There is another reaction that the $NO_2^+$ undergoes that is easier to study than the oxidation of bromide, and that turns out to be simply a combination of nitrate ion probably to form an intermediate $N_2O_5$. These fused salts are very good ionizing solvents, and the stability of $NO_2^+$ in the fused nitrate is caused probably by the fact that $N_2O_5$ is very highly dissociated into $NO_2^+$ and $NO_3^-$. There is some evidence that some of this does exist in solution as molecular $N_2O_5$, and then decomposes to $2NO_2$ and oxygen. It is first-order in $NO_2^+$, giving an oxygen atom at the end, probably $NO_3$, or oxygen solvated with the nitrate ion or something else. At any rate it ends up as oxygen molecules eventually. We decided to study this reaction anyway. It turns out that, even in the presence of a good precipitant for the chromate ion, the reaction will not go from left to right sufficiently to separate the rate constant from the equilibrium constant.

We thought of using nitryl perchlorate in fused nitrates and measuring the absolute rate at which $NO_2^+$ did decompose in combination with nitrate ion. But there are too many problems connected with the using nitryl perchlorate—e.g. getting and keeping it dry. We decided it would be easier and more convenient simply to add a stronger acid at this point to displace the equilibrium far enough to separate the equilibrium constant from the rate constant. The equilibrium goes only slightly from left to right. By then the subsequent reaction is always strictly inverse second-order in chromate. If this occurs appreciably toward the middle, say 10 or 20% of the total acid appearing in the form of $NO_2^+$, then the inverse order in this ion begins to decrease, and can go as far as zero order if the equilibrium goes far enough from left to right. From that decrease in an inverse order it is possible—just like Michaelis and Menton did with enzymes—to separate the rate and equilibrium constants. We did this simply by substituting sulfur for chromium, and rather than adding a precipitant for the salt we had to add excess sulfate on the right to keep the reaction from going too far to the right and the decomposition of the nitryl ion from going too fast.

It is interesting that in both the dichromate and the pyrosulfate case the decomposition of the nitryl ion is independent of the acid added to create it. Therefore, having the product of the rate and equilibrium constants in the case of the dichromate and the rate constants separated out from the pyrosulfate work, the rate constant was divided into the product to give the equilibrium constant for the dichromate. This can be done for a whole series of acids regardless of their strengths, whether they are strong enough so that it can be done independently or not.

There is a group of acids which are metal ions—zinc ion plus nitrate ion, for example. This goes to insoluble zinc oxide plus $NO_2^+$. One reason that I didn't mention these acids is that we are not sure that it is the decomposition of $NO_2^+$ that leads to $NO_2$ and oxygen. It could be a direct decomposition of the zinc nitrate complex ion, and we found that this was the case with bromate. If bromate is added to fused nitrates along with zinc ion, it is not an equilibrium involving zinc oxide and $BrO_2^+$ which occurs, but $ZnBrO_3^+$ is formed. This decomposes directly to the products, one of which is zinc oxide. Hence we really don't know whether these belong to the same category as dichromate in the detailed way that one has to assume to get the equilibrium constant separated from the rate constant.

This consideration led us to determine the equilibrium constant for this reaction

$$NO_3^- \rightleftharpoons NO_2^+ + O^{-2}$$

which is a self-dissociation of nitrate ion and looks very much like the self-dissociation of water. In order to determine this one needs a sensitive method to measure either $NO_2^+$ or $O^{-2}$. Analagous to the way it was done in aqueous solution we looked for an electrode that would respond to either $NO_2^+$ ions or oxide ions. One can get a good electrode for $NO_2^+$ simply by bubbling $NO_2$ over platinum, but it can't be used in the presence of oxide ion because there is a direct reaction of $NO_2$ with oxide ion to make nitrate and nitrite. That excluded this method. We used it only as a point of interest to see if it would work on the acid side, and it does.

Next we considered the oxide ion electrode, and we were a little fearful of this one. There had been some work done in sulfates, and several hundred degrees warmer than this, in which there was some question as to whether or not the oxygen electrode was really acting reversibly on platinum. Furthermore, studies by Yeager and others have shown that whenever one uses oxygen in aqueous solution at electrodes there is a tendency to equilibrate with peroxide rather than with oxide or hydroxide. We were afraid that we might end up with some one-electron transfer reactions and get peroxide ions and the like; but we had to try it because the other electrode just wouldn't work. As it turned out, it worked very nicely.

We had to determine $E^\circ$ for these cells in order to switch to the acid side and involve the equilibrium constant in such a way that it could be determined. This meant adding a carefully known concentration of oxide ion which is by no means simple when working with sodium or potassium. It is possible to make pure sodium oxide. It may be possible to make pure potassium oxide. But one always looks for easier ways to do things because these are difficult things to handle; and we were working with very low-concentrations of oxide ion. One does not like to measure pH up around 14 or 15, but rather around 8, 9, or 10, and we wanted to measure an oxide ion electrochemically. It was rather small in molar concentration—on the order of $10^{-6}M$. First we showed that as we changed the pressure of oxygen over a buffered solution (buffered at an unknown oxide ion value by putting in orthosilicate, sodium orthosilicate) we did indeed get the Nernst slope. Then we coulometrically added the oxide ion from the oxygen electrode with a constant current generator and easily put in small concentrations of oxide ion.

This work has been criticized rather severely by saying that we are just dumping electrons into the reaction, and there had been a lot of pressure on us to make sodium oxide and see if it really gives the same answer. I do think it would be a very nice thing to have done, but I really don't want to do it. I have lost my enthusiasm for that portion of the problem.

The other problem connected with this equilibrium is the fact that $NO_2^+$ does not remain as such in the reaction mixture while one makes measurements; it decomposes fairly rapidly. Hence, it was necessary to know the equilibrium constant for the pyrosulfate precisely and the rate at which it decomposed precisely in order to know, at any particular time after we add pyrosulfate to the fused nitrate, exactly how much $NO_2^+$ was there. It turns out that one can electrochemically follow the rate of decomposition of $NO_2^+$ potentiometrically since this equilibrium persists. As the $NO_2^+$ disappears one can follow it and obtain much better data than we were able to get with chemical analyses. Therefore, the whole job of determining this equilibrium constant is an internal one. We redetermined the equilibrium and rate constants for this reaction simultaneously.

The equilibrium constant is about $2.74 \times 10^{-26}$ at 250°C. and about $5.66 \times 10^{-24}$ at 300°C. with a large $\Delta H$. Titrations with oxide ion with strong acids in this solvent give a large potential change, some 26 pH units. Since we were working at a higher temperature, $RT/2F$ becomes a little larger. In some work done in Egypt, peroxide rather than oxide ion has been used to do the titrations, and it is reported that the peroxide ion, as it hits the acid, decomposes into oxide ion and oxygen. We have looked at this a little and are not sure that one does get complete decomposition of the peroxide ion. Some decomposition occurs, certainly.

Having determined the equilibrium constant one should be able to dissolve any possible source of oxide ion—bromate, chlorate, silicate, phosphate, zinc oxide—make measurements, and tell how basic or acidic the solution is. For example, we believe that transfer of oxide ion from bromate occurs in the same way as nitrate and one gets $BrO_2^+$. This $BrO_2^+$, if indeed that is what we do get, is an excellent oxidant. It reacts with iodide, bromide and anything that bromate normally oxidizes in acid solution. It makes us believe that it is ultimately the oxidant in such a case as bromate. Using $H_2BrO_3^+$, one has to displace water from it with a reducing agent, for example bromide, for the reaction to proceed.

The organic chemists have been claiming for years that they have excellent proof that $NO_2^+$ is indeed the electrophilic displacement agent that causes nitration, particularly on aromatic compounds. To test this we added pyrosulfate to fused nitrate and bubbled some benzene vapors through it on nitrogen or argon. Nothing but benzene came out, in spite of the fact that the reaction mixture was hot, 250°C., and contained $NO_2^+$ ions. Now the organic chemists are going to say that we never did have any $NO_2^+$ there. To forestall that argument we then added water to the benzene and bubbled the nitrogen through both the water and the benzene as it went into the fused salt containing the $NO_2^+$. A lot of nitrobenzene came over. I don't know whether this means that the nitrating agent is really $H_2NO^{3+}$ or whether one needs as good a proton acceptor as water in order to displace the hydrogen—whether it is catalytic, or stoichiometric, or just what. We decided to find out using a homogenous mixture rather than a two-phase (or more) system. We took some sodium benzenesulfonate, which is a good salt and dissolves in fused nitrates, and added it to fused nitrates. We were about to add some pyrosulfate to generate the acid, the $NO_2^+$, when a metathetical reaction occurred, call it an acid-base interchange, to give nitrobenzene and sulfate ions. This appears to be a reversible reaction. We have studied the kinetics of this reaction and know the order and some activation energies. We don't know how valid our figures are since we have never been able to get more than a 50% yield in nitrobenzene; and we think that either the nitrobenzene oxidizes the unreacted sulfonic acid or itself. This seems to react a little faster than just adding nitrobenzene to the fused nitrate—it starts turning black after a while. Since we used a colorometric method for following the reactions, we are skeptical of the data. We tried large amounts to see if we could make a pound of nitrobenzene this way, but the yields decrease greatly when we try to make the sulfonic acid more concentrated. But the more dilute we make it, the better the yield of nitrobenzene. Perhaps this would be a good way to put nitro groups on the heterocycles. But, that is a little too organic for most of us.

We have done a few oxidation-reduction reactions in fused salts, but they aren't terribly interesting. The only reaction that might be interesting is adding iodide ion to chlorate in a neutral to alkaline solution of fused nitrates to give iodate plus chloride. This reaction is not unusual; it has been used for years in aqueous solution to make iodate. But we did some interesting things with this reaction. We made the hypoiodite and chloride intermediates that would occur if one transferred one or two oxygens at a time and not all three. These intermediates react with nitrate ion to give products that are readily identifiable. We didn't get any of these products; so we feel that a Walden inversion operates here. The iodide comes up and all the oxygens switch over to the iodine at the same time from the chloride. We don't have real proof of this, because there are other ways to explain the observations. These intermediates may be far more reactive with the reagents than with the nitrate, but at least there is a little evidence that all three oxygens transfer at once.

**Dieter Gruen:** Prof. Duke has given an admirable discussion of acid-base properties in molten nitrates. I would like to suggest a model for the transition state complex in the reaction

$$Y_2O_7^{-2} + XO_3^- \rightleftharpoons XO_2^+ + 2YO_4^{-2}$$

studied by Prof. Duke in molten alkali metal nitrates. Here $XO_3^- = NO_3^-$, $ClO_3^-$, $BrO_3^-$ or $IO_3^-$; $Y_2O_7^{-2} = Cr_2O_7^{-2}$ or $S_2O_7^{-2}$.

The $Y_2O_7^{-2}$ ions can be represented by two oxygen tetrahedra sharing a corner with the chromium or sulfur atoms at the centers of the tetrahedra. The activated complex $[Y_2O_7ZXO_3]^{-2}$ then consists of an alkali metal ion, Z, in the center of an octahedron of oxygens: three from the $Y_2O_7^{-2}$ group and three from the $XO_3^-$ group.

This model was suggested by spectroscopic studies of dipositive *3d* ions in molten aluminum chloride (*7*). The absorption spectra of dipositive Ti, V, Cr, Mn, Fe, Co, Ni and Cu in molten $AlCl_3$ can be interpreted on the basis of octahedral configurations of chlorides about the central transition metal ions. An explanation of this fact is made plausible by the following considerations.

In the liquid state, x-ray diffraction measurements (*3*) have shown aluminum chloride to consist of $Al_2Cl_6$ dimers. There is considerable evidence that addition of $Cl^-$ to $Al_2Cl_6$ is a stepwise process characterized by the two equilibria

$$Al_2Cl_6 + Cl^- = Al_2Cl_7^-$$

$$Al_2Cl_7^- + Cl^- = 2AlCl_4^-$$

It is likely therefore that the *3d* metal dichlorides dissolve in molten $Al_2Cl_6$ according to the equation

$$MCl_2 + 2Al_2Cl_6 = M(Al_2Cl_7)_2$$

A model for this complex is shown in Figure A. In this model, the $M^{+2}$ ion is octahedrally surrounded by six chlorides belonging to two $Al_2Cl_7^-$ groups, the $Al_2Cl_7^-$ group in turn having a structure composed of two $AlCl_4$ groups sharing a corner.

The analogy of the $M(Al_2Cl_7)_2$ complex with the proposed $[Y_2O_7ZXO_3]^{-2}$ activated state complex resides in the fact that both complexes provide an octahedral site for the metal ion. Spectroscopic data on *3d* metal ions in molten nitrates

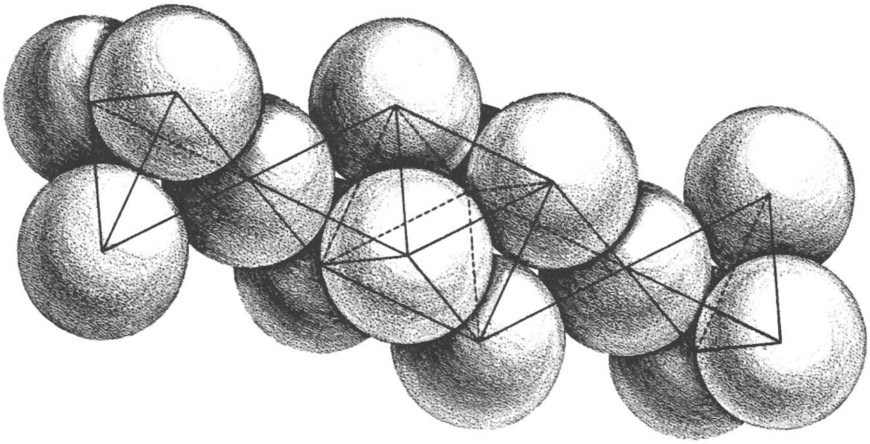

*Figure A. Model of $M(Al_2Cl_7)_2$ complex*

can be most easily interpreted in terms of octahedral coordination by oxygens. Although such measurements cannot be performed on alkali metal ions since they do not possess unpaired *d*-electrons, it is not unreasonable to postulate six fold oxygen coordination for these ions as well. An attractive feature of the $[Y_2O_7ZXO_3]^{-2}$ complex is that it brings the two reactants into close proximity without requiring an excessive accumulation of negative charge at the reaction site.

**Joseph J. Jordan**: Prof. Duke said that one of his motivations for exploring oxidation-reduction in molten salts was his desire to study separately the electron transfer process proper, which in aqueous solutions is invariably complicated and encumbered by overlapping proton transfer.

To me, the most interesting feature of the Lux-Flood acid-base chemistry in molten nitrate solvents is the fact that one does encounter the same type of interplay between acid-base and oxidation-reduction chemistry. However, in this instance the acid-base reaction happens to be, not a proton transfer, but an oxide transfer. I should hope, as Prof. Duke said, that more people would become active in the field of acid-base and electron transfer chemistry in molten salts. This is still an area where it might be possible to draw conclusions from relatively simple, almost qualitative, observations. If one reviews in retrospect the ingenious and sophisticated material presented here, the impression is that almost any conclusion that remains to be drawn in aqueous inorganic mechanisms chemistry has to be based on rather complicated quantitative arguments. Because of the many approximations that must be relied on in these situations, one cannot help feeling that he might lose contact with the tangible reality of the chemistry involved. One of the virtues of molten salts is that a great deal of straightforward chemistry remains to be elucidated, perhaps because this field is still many decades behind the present development of aqueous inorganic chemistry.

Lux-Flood base dissociation equilibria can be divided into two broad categories:

(a) Those in which the conjugate acid is not an electron acceptor;

(b) Those which yield an oxidizing agent as conjugate acid.

Carbonate ion in an appropriate molten salt solvent is an example of (a), the con-

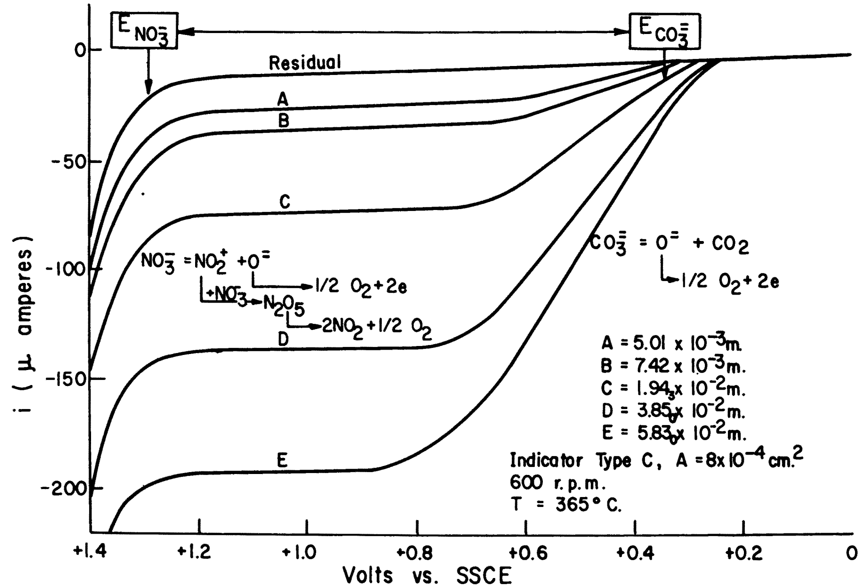

*Figure B. Current-voltage curves of $K_2CO_3$ in $KNO_3$*

jugate acid's being $CO_2$, which is not an electron acceptor. Prof. Duke focused on (b), a typical example of which is the nitrate ion whose conjugate acid, the nitronium ion $NO_2^+$, is a strong oxidizing agent. I should like to present some tangible evidence that oxide dissociation is indeed a phenomenon which is analogous with the dissociation of hydrogen ions from Brønsted acids in conventional solvents. Relevant experimental data are presented in Figure B, which is based on the work of Karl Romberger (*8*) and represents a family of polarograms obtained at a rotated platinum disk electrode in an alkali nitrate solvent melt. In the residual current curve (the top curve, obtained in the pure solvent) as the potential is made more anodic, one notices a current which reflects the oxidation of oxide ion resulting from the dissociation of nitrate. The other plots in B were obtained by dissolving, in the massive nitrate melt, various small concentrations of the Lux-Flood base $CO_3^{-2}$. Carbonate is a stronger Lux-Flood base than nitrate. Curves A, B, C, D, and E correspond to the electro-oxidation of the oxide ions dissociated from the carbonate. They eventually level off in a limiting current domain, because the process is mass transfer controlled (by diffusion and forced convection) in the corresponding range of potentials. The difference in potentials at which $O^{-2}$ is electro-oxidized in the presence of carbonate is striking compared to what happens in the pure nitrate melt. Neglecting irreversibility, this difference results from the fact that carbonate is a much more strongly dissociated oxide donor than nitrate; the equilibrium concentration of oxide ion in the presence of carbonate is about 20 orders of magnitude larger than in pure nitrate. As a result, electro-oxidation of $O^{-2}$ can occur at much less anodic potentials in the presence than in the absence of $CO_3^{-2}$.

Hydrogen reduction waves are well known in aqueous polarography (*6*); this completely analogous phenomenon brings out convincingly and tangibly the similar nature between oxide transfer chemistry in molten salts and proton transfer chemistry in conventional solvents.

Actually, the more interesting situation is (b) where the conjugate acid is an oxidizing agent (*12*). A striking demonstration of the interdependence of electron transfer and oxide transfer is inherent in the following observations. It is possible to prepare a solution of potassium iodide in a very pure nitrate melt and maintain

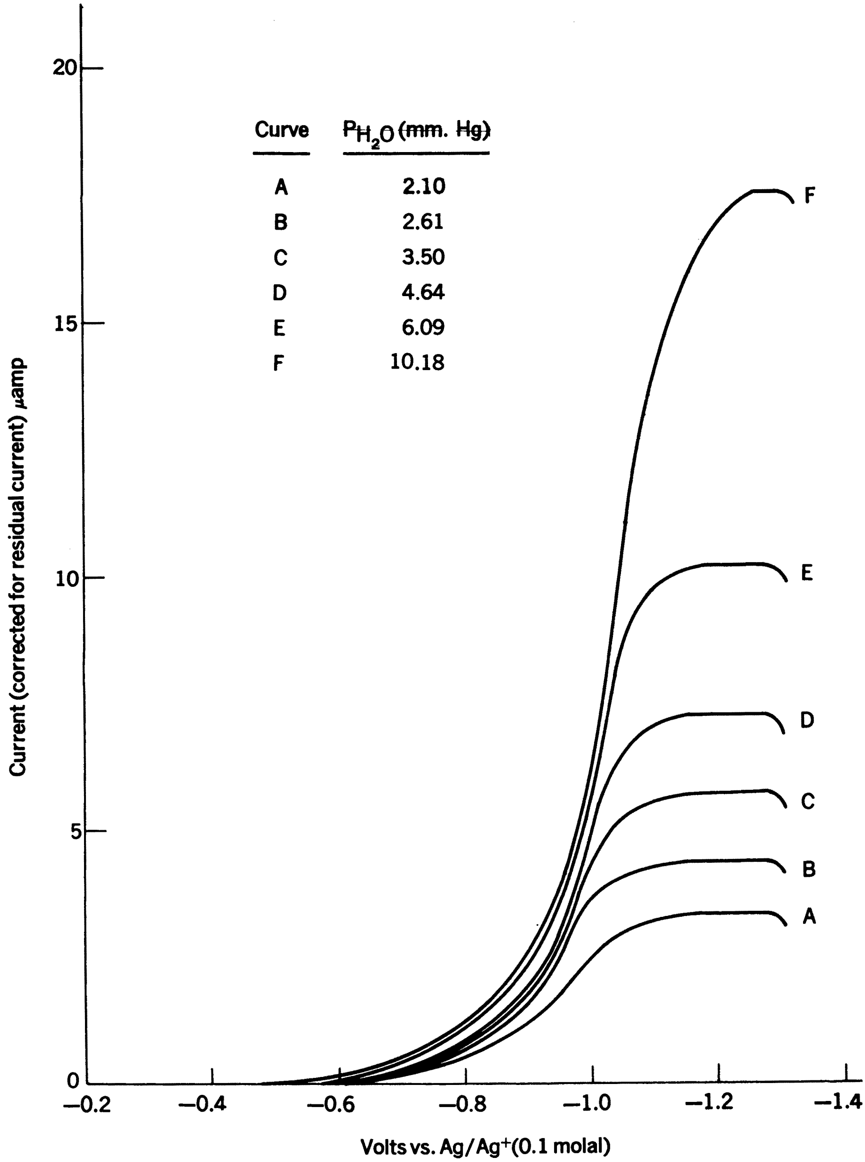

*Figure C. Polarograms for a nitrate alkali nitrate melt containing traces of water* stability indefinitely, in the sense that there is no oxidative loss of the iodide by conversion to iodine. If, however, the nitrate melt contains a trace of a heavy metal salt, such as lead or aluminum, one sees an instantaneous evolution of iodine. The reason for this is that lead and aluminum ions are Lux-Flood acids which abstract the oxide ion from the nitrate dissociation equilibrium, thus increasing the activity of the conjugate acid, $NO_2^+$. The nitronium ion functions as an electron acceptor which oxidizes iodide to iodine.

In order to illustrate the nature of interpretive problems which prevail in contemporary molten salt chemistry, I should like to describe an interesting catalytic reaction, viz., the reduction of nitrate to nitrite induced by the electro-reduction of traces of water. I believe that this may exemplify the mechanistic problems encountered typically in molten salt chemistry and hope that this will engender some discussion and research by this group which has so ably handled much more complex problems in aqueous chemistry. If one records a direct current voltage curve in a nitrate alkali nitrate melt which contains traces of water, one obtains the polarograms (*2*) shown in Figure C. The curves correspond to a cathodic reduction process, and the "wave heights" increase with the amount of moisture present. Similar findings have been reported previously from the University of Illinois (*11*). One of my graduate students, T. E. Geckle, became interested in this matter, because the question whether a water molecule can be electro-reduced directly as such (rather than via prior dissociation to a hydrogen ion) is a matter of considerable, fundamental importance. Mr. Geckle found that, while the limiting currents obtained in the nitrate melt were proportional to the concentration of water, the only products of the electrode reaction were nitrite ion and oxide ions (one half mole of each per faraday of electricity). The surprising thing was that no hydrogen was produced in any way or form. During electrolysis one could observe in the melt the yellow color of $NO_2$ which faded as soon as the electrolysis was stopped.

Mathematical analysis of the polarograms indicated that the overall electrode reaction involved one mole of reactant, two electrons, and three moles of product. The mechanism which accounts for the experimental results is illustrated in Figure D.

NET RESULT (from coulometry)

$$NO_3^- + 2e \rightarrow NO_2^- + O^{-2}$$

MECHANISM

$$H_2O^{\infty} \xrightarrow{\text{rate controlling}} H_2O^{\circ}$$

$$H_2O^{\circ} + 2e \rightarrow 2H^{\circ} + O^{-2}$$

$$2H^{\circ} \xrightarrow{\text{fast}} 2H^{\infty}$$

$$NO_3^- + 2H^{\infty} \rightarrow H_2O^{\infty} + NO_2^-$$

*Figure D. Mechanism of the electrode-reduction*

Water from the bulk of the melt is transported, by diffusion and forced convection, in a rate-controlling step to the electrode surface (this accounts for the proportionality of the limiting current to water concentration); at the electrode interface water is reduced to atomic hydrogen, which diffuses rapidly to the bulk of the solution; there it reacts with nitrate, producing nitrite and regenerating water; the water then "returns" (by diffusion and forced convection) to the electrode surface and controls the current.

The interesting reaction to this sequence is the last step: it must necessarily proceed via a mechanism which is consistent with the transient appearance of the color of $NO_2$ in the bulk of the solution. Figure E contains two alternatives which can account for this observation. The reaction sequence on the left is basically an oxide transfer mechanism and is consistent with some of Prof. Duke's ideas; hydrogen is assumed to reduce nitrate to $NO_2$; $NO_2$ acts as a "mixed acceptor" for oxide yielding nitrate plus nitrite; and hydroxyl ions are reconverted to oxide and water via a known reaction.

The second sequence in Figure E involves hydride as a reaction intermediate.

$$NO_3^- + 2H \rightarrow H_2O + NO_2^-$$

OXIDE TRANSFER

$$\begin{array}{rcl} 2NO_3^- + 2H & \rightarrow & 2NO_2 + 2OH^- \\ 2NO_2 + O^{-2} & \rightarrow & NO_3^- + NO_2^- \\ 2OH^- & \rightarrow & O^{-2} + H_2O \end{array}$$

HYDRIDE TRANSFER

$$\begin{array}{rcl} 2NO_3^- & \rightarrow & 2NO_2^+ + 2O^{-2} \\ 2O^{-2} + 4H & \rightarrow & 2H^- + 2OH^- \\ 2NO_2^+ + 2H^- & \rightarrow & 2NO_2 + 2H \\ 2NO_2 + O^{-2} & + & NO_3^- + NO_2^- \\ 2OH^- & \rightarrow & O^{-2} + H_2O \end{array}$$

*Figure E. Alternative mechanisms*

**Gilbert Haight:** I am glad that Prof. Duke has demolished a staid old organic mechanism. I would like to comment on this apparent nonparticipation of $NO_2^+$ in nitration reactions because there is now considerable kinetic evidence on what happens when $HNO_2$ is an oxidant in solution. The Ingold school, and specifically C. A. Bunton and G. Stedman in England, have elaborately studied the kinetics of the reaction of nitrous acid with azide ion. They conclude that the active intermediate, or an active intermediate is $H_2NO_2^+$. They offer evidence that $NO^+$, the anhydride of $H_2NO_2^+$, is not active in the kinetics, and in fact, only when $NO^+$ is attached to other things does it become labile and a good oxidant. There is further evidence for this. Hidden in the analytical literature (*9*) is an incredible method for $NO_3^-$. The method is to reduce nitrate in concentrated sulfuric acid with ferrous ion giving a quantitative two-electron reduction of the nitrate. To me, this means that $NO^+$ is at least a likely product and that it is inert.

Recently I have also heard from one of Szabo's collaborators (Bartha) at Szeged in Hungary that oxalate in concentrated sulfuric acid reduces nitrate by two equivalents, again indicating that $NO^+$ is inert.

Simply by inference, I suggested to one of my organic friends recently that maybe $NO_2^+$ is inert. It is isoelectronic with $CO_2$, has a higher charge on the central atom, and ought to be unreactive. By analogy with $HNO_2$ kinetics (*1*, *10*), $H_2NO_3^+$ may be the kinetically active species of nitrate. I think Prof. Duke has offered a strong indication that that is so.

**Dr. Duke:** I would like to warn Dr. Haight that organic mechanisms are not that easily destroyed. But I will let him go ahead and destroy if if he really chooses to do so.

**Harry Gray:** I would like to ask Dr. Gruen about the nitrate melts.

The nitrate ion itself has its first spin-allowed but orbitally-forbidden transition at about 3000 A. in aqueous solution, $\epsilon = 7$. Nitrate ion is planar in the ground state and in this $D_{3h}$ symmetry, the band at 3000 A., it is orbitally forbidden.

If the oxygens in nitrate are bent to form a pyramidal ion, one observes, not a substantial movement in energy of this band, but a substantial increase in intensity because the band becomes orbitally allowed if the planar symmetry is destroyed. I think the intensity is probably a fairly sensitive function of distortion, and I wonder if you have looked in this region to get additional information from the spectra on the structure of the nitrate ion in these melts.

I would also like you to speculate on whether the nitrate is bidentate or monodentate.

**Dr. Gruen:** We have not looked at this particular band, but other people have. Pedro Smith at Oak Ridge, for example, has made an extensive study of this particular band for pure alkali nitrates and finds substantial variations in intensity, depending on whether he is looking at lithium, sodium, or potassium nitrate. He interprets these effects, if I recall correctly, as owing to polarization effects resulting in slight distortions of the nitrate group. As far as our work is concerned we have not studied these charge transfer bands, and in fact we would not be able to pick up intensity changes because our transition metal ion concentrations are $10^{-2}M$. The effect of the transition metal ion on the nitrate absorption would be very difficult to measure. Your point certainly raises a very interesting problem. One may learn something about the structure of the nitrate group in the melt by detailed consideration of the first band.

**Dr. Gray:** I have observed that in some cases the $\epsilon$ of that band goes well over 1,000, in one case to 5,000.

**Dr. Duke:** All of these equilibrium constants involving oxide ion, such as a carbonate going to oxide ion in the nitrates, are much too large. I believe that we are getting orthonitrate here and would like to have some comments on that.

**Leonard Katzin:** My first point refers to the question of the nitrate absorption spectrum. If one goes back a decade or more in the literature, there are observations on this peak of a nitrate in nonaqueous solutions of inorganic salts, and I don't believe that the wave length stays fixed. It shifts toward shorter wave lengths—not a great deal, but perceptibly (*5*).

I have doubts about the nonplanarity. Our infrared studies (*4*) on some nitrate salts in nonaqueous systems indicate that we are taking one of these nitrates, tying it down, and shifting the vibrational pattern. But whether or not a nonplanarity occurs with this, I can't say.

I am intrigued by one aspect of Prof. Duke's work, namely, that a coordination number and configuration change of the cation occurs. This has certain analogies to metal ion situations. It raises interesting and provoking questions.

**Dr. Gruen:** I would like to address myself to the second part of Dr. Gray's question.

We have considered how many nitrate groups are around a metal ion. To get six-fold coordination one may have six nitrate groups or monodentate, or four with two bidentate and two monodentate, or three with three of them acting bidentate, or two with two of them acting tridentate.

To distinguish among these alternatives on the basis of melt spectra is impossible, I think. I have been interested in following the work of Piper I believe, who has isolated double salts of this type, or similar things, in which I believe this situation is found.

As far as I know, crystal structure studies have not been published on this kind of compound. But I think they would be revealing and by analogy perhaps tell us something about the melt situation. If one can determine—and I am sure it is possible by x-ray analysis of these compounds—what the nitrate coordination is around the metal ion, one might be able to infer something about the melt situation.

**Dr. Jordan:** I should like to reorient the discussion to the question Prof. Duke addressed to the audience. If I understood this question correctly it referred to the detailed nature, the form, in which the oxide ion may be present in molten nitrates. He suggested that this may well be the ion $NO_4^{-3}$. This is a nitrato solvate of the ion $O^{-2}$—i.e., $O^{-2}\cdot NO_3^-$. I presume that one can visualize in a massive carbonate melt a similar aggregate, viz., $O^{-2}\cdot CO_3^{-2}$, or $CO_4^{-4}$. This is related to the nature of the species actually present in conventional solvents, which are ignored in chemical formula-writing shorthand. The solvated hydrogen is quite different in aqueous solution from what it is in glacial acetic acid. Are there any suggestions regarding the nature of the "solvated oxide ion" in molten salts?

I feel that orthonitrate is very reasonable. For carbonate I would postulate the analog.

**Dr. Yalman:** Yes, the proton and the oxide ion are not analogous.

**Dr. Jordan:** I certainly agree that they are not analogous in all respects.

**Dr. Yalman:** The oxide does not have to be solvated in the same way that the proton or electron is solvated.

**Dr. Jordan:** Do you feel that the oxide ion is unsolvated in the melts? I did not intend to imply a complete analogy between oxide ions and protons.

**Dr. Yalman:** I think the analogy between the oxide and the proton is a bad one, and I don't think that the oxide ion has to be necessarily solvated in the same way that we accept the solvation of a proton or an electron.

**Arthur Adamson:** Actually, Dr. Harris is the better man to make this particular remark, I suspect. In the case of oxalate complexes it seems necessary to assume an ortho or hydrated formulation of one end of an oxalate as it detaches from the coordination sphere in order to explain the $O^{18}$ exchange. This is not exactly what you are talking about, but it is an illustration of one instance where ortho acid formation seems desirable.

**Michael E. Mirhej:** I propose that this might be a polymer of a structure similar to either tungstates or phosphates.

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# 10

# Spectrospecific Photolysis of Aqueous Cr $(en)_2(OH)_2{}^+$ Ion

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*University of Southern California, Los Angeles, Calif. 90007*

**The quantum yields for photoaquation and photoisomerization of *cis*-$Cr(en)_2(OH)_2{}^+$ vary in value and temperature dependence with the wave length of irradiating light over the region comprising the spin-allowed and the spin-forbidden transitions. The thermal lability of *cis*- and *trans*-$Cr(en)_2(OH)_2{}^+$ relates primarily to isomerization, and only secondarily to aquation. The cis form, although more stable, is more photosensitive, and photolysis yields a major portion of aquation product. From such comparisons and the wave length sensitivity of the photolytic behavior, the reaction path following excitation of a spin-allowed transition differs from that following excitation of a spin-forbidden transition, and both differ from the thermal reaction path.**

Several aspects of the photolytic behavior of aqueous complex ions have been studied in this laboratory over the past few years. One continually interesting question has been the extent to which the photochemistry of a complex depends on the absorption band irradiated. In the case of Co(III) acidopentamines, such as $Co(NH_3)_5Br^{+2}$, we found that irradiation of $({}^1A_{1g} \rightarrow {}^1T_{2g})$ bands showing appreciable charge transfer led to redox and aquation reactions which were competitive. It was reasonable to suppose that the common precursor was the species formed by a prompt heterolytic bond fission (*1*). The $({}^1A_{1g} \rightarrow {}^1T_{1g})$ band was far less photoactive, and in model cases, irradiation led only to aquation. Each excited state or excited state manifold thus tended to show a distinct photochemistry, which meant that conversion from one excited state to another was not important.

The situation has been less clear for Cr(III) complexes. Only substitution (*2*), (*6*), (*13*) (and isomerization (*15*)) photoreactions are observed, irrespective of which ligand field band is irradiated. It has been proposed that this uniform reaction mode (and nearly uniform quantum yield) could be accounted for if substantially complete conversion occurred of the ${}^4T_{2g}$ and ${}^4T_{1g}$ states to a lower lying doublet, presumably the $^2E_g$ state. This last, it was supposed, would be sufficiently long-lived to function as a chemical intermediate, exceptionally labile towards substitution (*13*). These designations of excited states are really for $O_h$ symmetry, but serve to identify loosely the absorption bands of complexes of descendent symmetry.

An alternative inclination has been to view the initial chemical act following excitation as a prompt heterolytic bond fission of some one chromium–ligand bond (*2*), (*15*). Both pictures adequately account for the so far not very elaborate data, the second perhaps more in keeping with the principle of scientific parsimony.

Probably the most sensitive diagnostic test of whether or not photolysis of a complex proceeds through an ubiquitous intermediate consists in determining the extent to which copresent reaction modes show different wave length dependencies. This type of test was available for Co(III) systems; the problem has been to find suitable Cr(III) systems. Following a report that $Co(en)_2(H_2O)_2^{+3}$ photoisomerized (*10*), it occurred to us that the analogous Cr(III) species might provide an answer.

If we denote *cis-* and *trans*-$Cr(en)_2(H_2O)_2^{+3}$ by $H_2C$ and $H_2T$, respectively, and the four acid dissociation products by HC, HT, C, and T, then there are four acidity constants ($K_{H_2C}$, $K_{HC}$, $K_{H_2T}$, and $K_{HT}$) and three isomerization constants ($K_{H_2T/H_2C}$, $K_{HT/HC}$, and $K_{T/C}$). All of these have been evaluated by Woldby (*17*), and some rate data on the T → C conversion has been reported by Olson and Garner (*12*). Preliminary experiments showed that both photoaquation and photoisomerization did indeed occur, and the detailed investigations described below were therefore carried out.

## *Experimental*

**Preparative Procedures.** The salts *cis*-$[Cr(en)_2(OH)(H_2O)]S_2O_6$ and *trans*-$[Cr(en)_2(OH)(H_2O)]Br_2$ were prepared from *cis*-$[Cr(en)_2Cl_2]ClO_4$ according to Woldbye (*17*), and the last complex by the procedures in "Inorganic Syntheses" (*7*). $Cr^{51}$ labelled complexes were similarly prepared. The ethylenediamine used was dried over sodium hydroxide and then distilled. Harshaw chromatographic alumina was used for the chromatographic separations. Lot No. K1773 behaved exceptionally well since clear effluents were obtained on elution with the $1M$ potassium chloride, $0.1M$ potassium hydroxide solution. Other chemicals used were of reagent grade.

The preparations proved to be 98 to 99% chromatographically pure, the contaminant always being the other isomer. The various absorption maxima are reported in Table I. All solutions were $0.01M$ in complex. Those designated as HC or HT were measured either in water at pH 5–6, or in $0.1M$ sodium acetate–acetic acid buffer at pH 5.5 (no spectral differences resulted); and those designated C or T were adjusted to pH 10.5 with ethylenediamine.

The values agree well in position with those of Woldbye (*17*) (which were for solutions $1M$ in sodium nitrate), but our extinction coefficients are consistently about 10% higher than his. In addition, we note a weak maximum for T at 330 mμ and report some information on the spectra in the doublet region. These last measurements were made on filtered $0.04M$ solutions, using 5 cm. cells. The general absorption curves were obtained by a Cary Model 14 spectrophotometer, but for most of the kinetic studies and analytical measurements, optical densities at selected wave lengths were determined by a DU Beckman spectrophotometer.

**Kinetic Studies.** There is some difficulty in unravelling the thermal reactions of the various forms, since not only does isomerization occur, but aquation is not negligible even at pH 10.5. The system, in fact, resembles classic reaction triangle

## Table I. Absorption Maxima

| *Complex* | λ, *mμ* | ε | λ, *mμ* | ε | λ, *mμ* | ε | λ, *mμ* | ε |
|---|---|---|---|---|---|---|---|---|
| $H_2C$ | 368 | 48 | 485 | 70 | | | 667 | 0.95 |
| | (367) | (42.5) | (495) | (67.0) | | | 640sh | 1.1 |
| HC | 392 | 47 | 515 | 72 | | | 681sh | 1.4 |
| | (391) | (43) | (512) | (69.3) | | | | |
| C | 377 | 69 | 528 | 65 | | | 692sh | 1.4 |
| | (378) | (66) | (525) | (63.6) | | | | |
| $H_2T$ | 365 | 43 | 445 | 32 | | | | |
| | (361) | (39.2) | (443) | (29.2) | (508) | (22.5) | | |
| HT | 398 | 49 | 495 | 38 | | | 680 | 2.1 |
| | (397) | (46) | (497) | (35.0) | | | | |
| T | 330 | 19 | 398 | 33 | 505 | 34 | 685sh | 1.4 |
| | | | (396) | (28.9) | (505) | (31.8) | | |
| Aquo (HC) | 415 | 33 | 570 | 31 | | | | |
| (HT) | 418 | 34 | 570 | 30 | | | | |
| (C) | 378 | | 548 | 37 | | | | |

Note: Values in parentheses are those reported by Woldbye (*17*). Those labelled Aquo are terminal spectra of solutions held at *ca.* 35°C. for six weeks.

(*14*), and even if it is assumed that the reverse of aquation is unimportant, solutions to a reaction triangle, while available, are difficult to use perceptively (*9*).

Fortunately, aquation occurred slowly enough, relative to isomerization, to be treated as a perturbation which gradually diminished the effect of equilibrium cis and trans concentrations without materially affecting their ratio. Applying this approach required parallel data for solutions initially all trans and initially all cis.

Assuming first-order kinetics, the optical density of the initially all cis solution for a path length of 1 cm. is given by:

$$D_C = \frac{a}{1+K}(\epsilon_C + K\epsilon_T) + \frac{aK}{1+K}(\epsilon_C - \epsilon_T)\,e^{-kt} \tag{1}$$

$K$ denotes the C → T equilibrium constant and $k = k_1 + k_2 = k_2(1 + K)$; the total concentration is given by $a$. Similarly, for a solution initially all trans:

$$D_T = \frac{a}{1+K}(\epsilon_C + K\epsilon_T) - \frac{a}{1+K}(\epsilon_C - \epsilon_T)\,e^{-kt} \tag{2}$$

It then follows that

$$D_{CT} = D_C + KD_T = a(\epsilon_C + K\epsilon_T) = \text{a constant} \tag{3}$$

Preliminary data have been obtained for $0.01M$ solutions at pH 2.0 (added hydrochloric acid) and solutions buffered to pH 5.5 with $0.1M$ acetate buffer. The principal interest, however, was in the C–T system (solutions brought to pH 10.5 with added ethylenediamine) for which most of the photochemical results were obtained. An example of the direct data for the C–T system is shown in Figure 1. Over the period of 120 hours, $D_{CT}$ decreased by about 3%, corresponding to about 6% aquation. The procedure was then to calculate from each measurement an effective $D^\infty$ value: $D^\infty = D_{CT}/(1 + K)$. Plots of $(D^\infty - D_T)$ and of $(D_C - D^\infty)/K$ *vs.* time should then superimpose. This was reasonably the case, as illustrated in Figure 2, for data at two wave lengths.

The insight provided by this approach led to the conclusion that an accurate $K$ value could not be obtained from isomerization data using just one form, and that

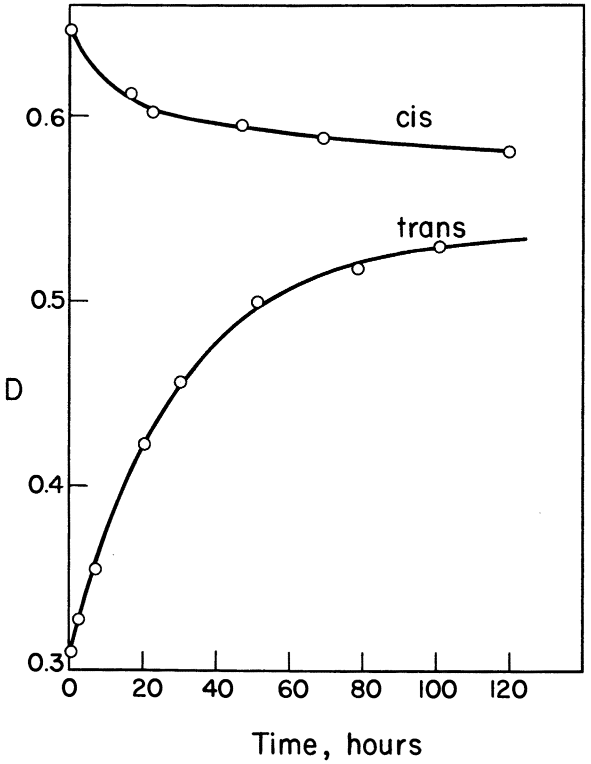

*Figure 1. Isomerization of 0.01M cis-and trans-Cr(en)$_2$-(OH)$_2^+$ at 25°C.; solutions adjusted to pH 10.5 with ethylenediamine; optical density at 525 mμ.*

even using the combined data for both forms, the relatively small aquation that occurred introduced a 50% uncertainty. Thus, for the 35°C. data of Figure 2, $K$ values of 0.2 and 0.3 represented the limits still giving acceptable straight line plots.

The results are summarized in Table II; $K$ values in parentheses are from Woldbye (*17*) (for 1*M* sodium nitrate medium).

**Table II. Isomerization and Aquation Kinetics**

| *System* | *t°C.* | *K* | *k (hr)* | *% Aquation in One Isomerization Half Life* |
|---|---|---|---|---|
| $H_2C$, $H_2T$<br>(pH 10.5) | 25 | 0.25 ± 0.05<br>(0.20) | 0.0425<br>(0.0245[a]) | 1 |
| | 35 | 0.25 ± 0.05 | 0.262<br>(0.104[b]) | 1 |
| | 42 | 0.25 ± 0.05 | 0.97 | 1 |
| HC, HT<br>(pH 5.5) | 25 | (0.41) | *ca.* 0.45 | 3 |
| $H_2C$, $H_2T$<br>(pH 2.0) | 25 | (0.078) | *ca.* 0.11 | 1.2 |

[a] Reported by Olson and Garner (*12*) for pH 10.9.

[b] Similarly reported for pH 10.6.

**Photochemical Experiments.** The general experimental procedure was that previously described (*15*). The bolometer was used as a relative intensity indicator since collimation in the cylindrical geometry of an AH6 lamp is poor, and allowance for scattering is difficult. Calibration at each wave length was by means of $KCr(NH_3)_2(NCS)_4$ solutions for which we now have accurate absolute quantum yields for wave lengths from 450 mμ to 750 mμ (*16*). For the runs at >680 mμ, a 500 watt tungsten lamp was used since the output of the AH6 mercury lamp was uncomfortably low at this wave length.

Wave length selection was by glass filters. For runs labelled 370 mμ, a Baird-Atomic filter with cut offs at 300 mμ and 400 mμ was used, so that absorption occurred mainly in the ($^4A_{2g} \rightarrow {}^4T_{1g}$) band. Runs labelled 550 mμ and 500 mμ were carried out with either Corning CS–2–64 or CS–3–71 filters whose short wave length cut offs were 530 mμ and 480 mμ, respectively; absorption thus occurred mainly in the ($^4A_{2g} \rightarrow {}^4T_{2g}$) type band. Finally, runs labelled >680 mμ were carried out using a Corning CS–3–69 filter whose cut off was at 680 mμ, so that absorption was primarily in the doublet region. We used absorbed light intensities of about $10^{-6}$ *E*/minute and irradiation time sufficient to produce 10 to 25% reaction (never more than an hour).

It was not certain that the aquation product would be identical in spectrum to that obtained by thermal reaction, and analysis was therefore carried out chromatographically, rather than spectrophotometrically. The procedure was that described by Woldbye, highly standardized to ensure maximum reproducibility. Parallel separations were carried out on unirradiated solutions, and the chromatographic yields of the cis and trans were in some cases determined by using $Cr^{51}$

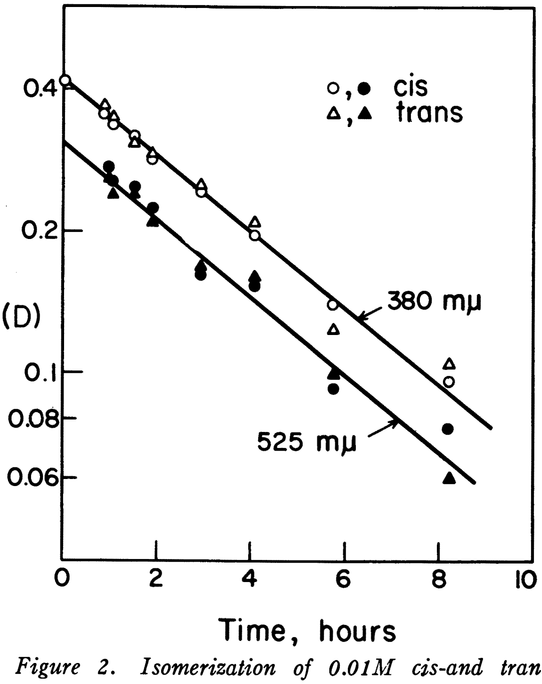

*Figure 2. Isomerization of 0.01M cis-and trans-$Cr(en)_2(OH)_2^+$ at 35°C.; solutions adjusted to pH 10.5 with ethylenediamine; $f(D) = D_T - D$ for the solution initially trans, and $f(D) = (D_C - D)/K$ for the solution initially cis, where $D = (D_C + K D_T)/(1 + K)$.*

labeled complex. The aquo product appeared as a narrow blue blue band which could not be eluted completely. The amount present therefore was determined by material balance (and qualitatively agreed with spectrophotometric estimates using the spectrum of the thermal aquation product).

### *Results*

The photosensitivity of all six forms was determined qualitatively, and the results are in Table III. The $H_2T$ and HT systems were difficult to work with because their high thermal lability made the dark reaction correction large. An additional complication was the secondary photolysis of cis isomer, which made it doubtful if the aquo product observed in the case of irradiated T was caused by primary photoaquation. The results in Table III are, therefore, qualitative and are displayed to provide a general picture of the situation.

**Table III. Photolysis Studies**

| *Complex* | *t°C.* | λ, *mμ* | *Quantum Yields* | |
|---|---|---|---|---|
| | | | *Aquation* | *Isomerization* |
| $H_2T$ (pH 2.0) | 25 | white light | Total yield *ca.* 0.04 | |
| | 25 | 370 | 0 | 0.4 |
| | | 500 | 0 | 0.3 |
| | | 680 | 0 | 0.05 |
| T (pH 10.5) | 18 | 500 | 0.003 | 0.01 |
| | 36 | 500 | 0.009 | 0.009 |
| $H_2C$ (pH 2.0) | 25 | 370 | 0.17 | 0.15 |
| HC (pH 5.5) | 25 | 550 | 0.04 | 0.05 |

The bulk of the data pertains to *cis*-$Cr(en)_2(OH)_2^+$ and fairly complete results were obtained. These are shown in Figure 3. Several points are actually the average of duplicate runs, and reproducibility was least for the aquation quantum yields (15 to 20%) for which the uncertainty in the chromatographic analyses was the greatest.

Where reasonably possible, straight lines are drawn to give apparent activation energies; while the temperature dependencies are undoubtedly complex, so that apparent activation energies could well be temperature dependent, the procedure serves to identify the qualitative behavior. The values are summarized in Table IV.

**Table IV. Apparent Activation Energies for the Photolysis of *cis*-$Cr(en)_2(OH)_2^+$**

| *Wave Length* *mμ* | $E\ddagger_{Aquation}$ (*kcal.*) | $E\ddagger_{Isomerization}$ (*kcal.*) |
|---|---|---|
| 370 | −2.7 | 9.2 |
| 550 | 3.5 | 10.2 |
| 680 | 20 | 12.7 |

A few qualitative experiments were made on the photolysis of $Cr(en)_3^{+3}$, on which Nikolaiski has reported in detail (*11*). Chromatographic analysis showed that both *cis*-and *trans*-bisethylenediamine complexes were formed, as well as some of the blue aquo species. Thus, a complete investigation of this system would be quite complex.

### *Discussion*

**Thermal *vs.* Photochemical Behavior.** The results of these investigations allow for comments at several levels of detail. First, it is quite evident that the photochemistry differs significantly from the thermal reaction chemistry. The latter displays isomerization as the predominant reaction for all forms, and perhaps for all temperatures, in the range normally available for aqueous systems. Thus, for the C–T system, the aquation mode remained relatively unimportant over a temperature range that provided a twenty-fold change in isomerization rate.

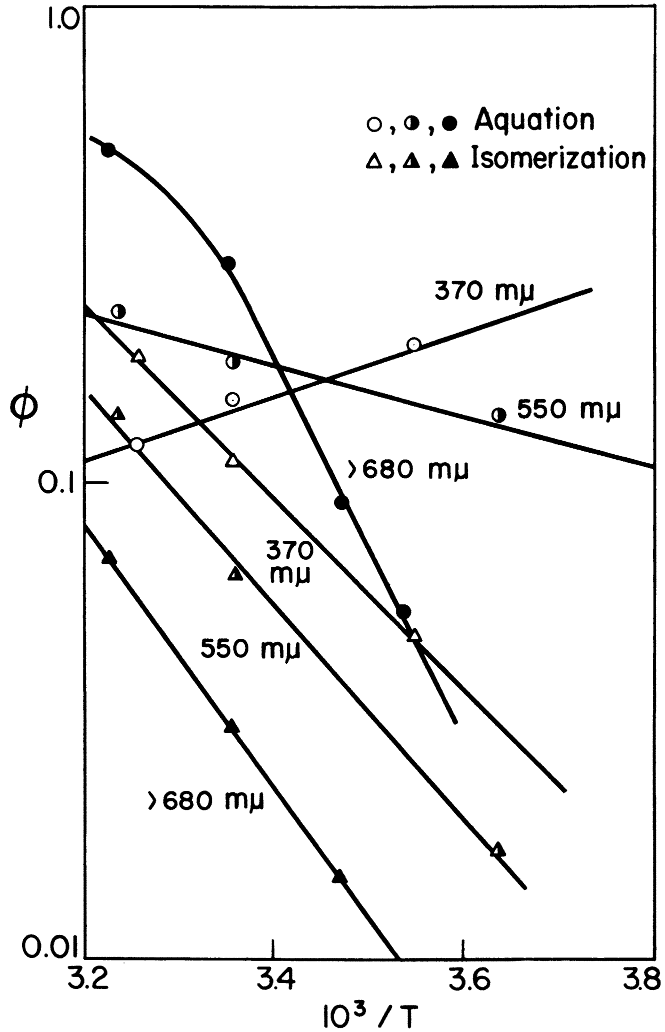

*Figure 3. Quantum Yields for Photoaquation and Isomerization of cis-Cr(en)$_2$(OH)$_2^+$; solutions adjusted to pH 10.5 with ethylenediamine.*

Contrariwise, the photochemistry is decidedly one of photoaquation for the cis species, and isomerization for the trans species.

As for the thermal isomerization of *cis*-$Cr(en)_2(OH)_2^+$, our values of $k$ are about twice those of Olson and Garner (although for somewhat different substrates), and our activation energy of 35 kcal. is definitely higher than their 32 kcal. However, using parallel runs with cis and trans isomers allowed us to correct for aquation, and made the values of $K$ and $k$ less interdependent. As noted under Experimental, the latitude in $K$ values, stemming from the presence of some aquation ($K$ and the aquation rate constant are again interrelated), was considerable. We can only delimit $\Delta H^\circ$ of isomerization as $0 \pm 2$ kcal.

Evidently then, $\Delta E\ddagger_{C\rightarrow T}$ and $\Delta E_{T\rightarrow C}$ are nearly the same, and likewise, $\Delta S\ddagger_{C\rightarrow T}$ and $\Delta S\ddagger_{T\rightarrow C}$ since $K$ itself is always close to unity. This implies that the transition state for isomerization is high in energy, high in entropy (possibly suggesting a loosely bonded arrangement), and conforms symmetrically to cis and trans geometries. The fact that $\Delta E\ddagger$ is more than twice that for the racemization of $Cr(C_2O_4)_3^{-3}$ (*15*) suggests that, in the present case, it is a Cr–N rather than a Cr–O bond that must loosen.

A second point of contrast between the thermal and the photochemical behavior is that, while the cis isomers are all thermodynamically favored, and consequently all the trans forms appear more labile, the situation on photolysis is varied. The quantum yields for C are ten to twenty times those for T; HT is more sensitive than HC (but only towards photoisomerization), and $H_2C$ is more photosensitive than $H_2T$.

Any attempt to explain the results unavoidably will require postulating significantly different intermediate states for the photochemical and thermal reaction sequences. Photoactivation must then carry its own stereospecificity and cannot be thought of as just an external solicitation of energy to ease an essentially thermal reaction sequence.

**Photolysis of *cis*-$Cr(en)_2(OH)_2^+$.** The temperature and wave length dependence studies on C provide a basis for some minimal conclusions. Consider first the contrast between photoisomerization and aquation at the 370 mμ and 550 mμ wave length regions. The former shows a considerable temperature dependence in quantum yield, the apparent activation energy averaging 9.6 kcal. for the two wave length regions, while the latter process obeys a small negative and a small positive apparent activation energy for these two regions, respectively.

It might be thought that photoisomerization and photoaquation could be competitive towards a common precursor excited state, but this explanation fails on quantitative testing. Briefly, the quantum yield for photoaquation is too high to accommodate its negative apparent activation energy. Photoaquation must then be competitive with some other process such as deactivation, or return to the original cis species.

Next is the contrast between the 370 mμ to 550 mμ behavior and that for wave lengths greater than 680 mμ. We are now comparing the consequence of exciting a quartet band and a doublet band. The activation energy for photoisomerization has increased to about 13 kcal., and there is a dramatic shift in the aquation behavior which now shows 20 kcal. apparent activation energy and quantum yields approaching unity at low temperatures. The minimal conclusion here is that irradiation of the doublet region produces an intermediate differently disposed towards aquation from that resulting from irradiation of a quartet band. Specifically, the quartet to doublet conversion mechanism, whereby all chemical consequences are filial to a long-lived doublet intermediate, cannot be in effect here.

Quantum yields for successive aquation steps of $Cr(NH_3)_6^{+3}$ have been reported by Edelson and Plane (*6*). The higher quantum yield for wave lengths in the doublet absorption region than for those in the quartet region was regarded as suggesting that the conversion mechanism applied. It seems likely that a detailed study of aquation and isomerization could yield observations and a final conclusion similar to those found here. Our data for photoaquation at 25°C. show the same trend of increasing quantum yield with decreasing wave length, and only the full picture shows that this particular correlation is trivial. Recent results in this laboratory show no increase in quantum yield in the case of $Cr(NH_3)_6^{+3}$ on irradiation of the doublet band.

**Mechanisms.** Since the above conclusions are minimum, it is interesting to see if a more detailed picture exists which can account for all of the observations. Four different sequences (at least) must be provided: thermal isomerization, photolysis in the doublet region of wave length, and photoaquation and photoisomerization in the quartet region.

In assembling this collection, may we first turn to some aquation studies of $KCr(NH_3)_2(NCS)_4$ (*3*). These led to the conclusion that substitution occurred by a concerted process, named $S_N2FS$, whereby arriving and departing groups interacted through hydrogen bonding. Figure 4b shows how this mechanism can be extended to the present instance. Hydrogen bonding interactions assist in shifting an $NH_2$ group from one position to another (needed to accomplish isomerization) but keep it sequestered so that the $NH_2$ group never loses rapport with the complex. Such loss of rapport would constitute the first step towards complete detachment or aquation.

The proposed intermediate has the symmetry suggested by the activation parameters, and many related configurations would be available to contribute to a high activation entropy. Possibly a similar detailed sequence holds for the racemization of $Cr(C_2O_4)_3^{-3}$, which again is much faster than aquation, yet involves the $-CO_2$ function participating with solvent to a degree leading to massive $O^{13}$ exchange (*15*). The case of $Co(en)_2(OH)_2^{+}$ may also be quite similar since isomerizazation was fairly concomittant with $O^{18}$ exchange (*10*), and entirely so in the case of $Co(en)_2(H_2O)_2^{+3}$. There is also a close resemblance of the activation thermodynamics for the Cr and Co systems.

Considering next the photochemistry of the doublet wave length region, it is helpful to accept the postulate that the real life time of the $^2E$ state (actually a vibronic state in all likelihood (*4*)) is long enough for it to function as a reaction intermediate. We now have a species able to bond, perhaps with some activation, to a seventh group (–e.g., using $d_{x^2}$, $d_{x^2-y^2}$, and $d_{xy}$ orbitals if the symmetry were $C_{5h}$) and the arrangement shown in Figure 4c is merely a suggestion. As Gillespie notes (*8*), the electrostatic prediction of heptacoordination geometry is ambiguous, and the arrangement shown could be a perspective either of a pentagonal bipyramid, or of Gillespie's 1,3,3 arrangement. In either case, small luxations could prepare this intermediate to return to hexacoordination by discharge of either an OH, or

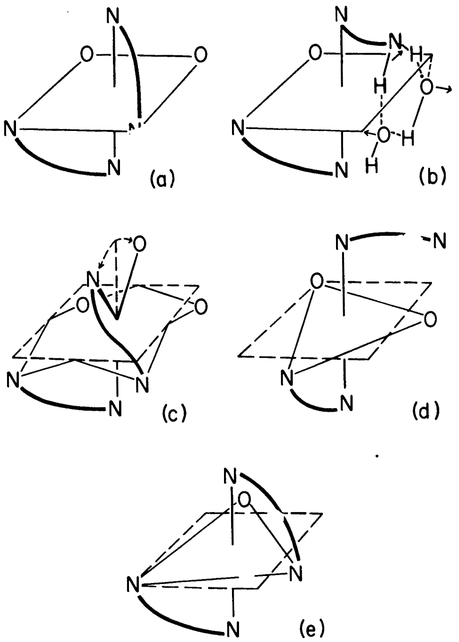

*Figure 4. Possible geometries; (a) cis-*$Cr(en)_2(OH)_2^+$*; (b) substitution by* $S_N2FS$ *mechanism; (c) a heptacoordinated intermediate; (d) a consequence of Cr–N bond fission; (e) a consequence of Cr–O bond fission.*

$NH_2$ from the coordination sphere. If the latter, an intermediate having monodendate ethylenediamine would result, and this in turn could proceed to the aquo product by substitutive detachment of the other end.

There is no present basis for deciding which or how many of the several isomers of Figure 4c might be involved; but we would conclude that heptacoordinated Cr(III) is stable enough to require activation to revert it to hexacoordination.

Lastly we will consider what happens when photolysis is occasioned by light of wave length corresponding to one of the spin-allowed transitions, and look at the possible consequences of homolytic bond fission. For the cis complex, two possibilities are shown in Figure 4d and 4e, assuming for simplicity that a prompt collapse to trigonal bipyramidal form occurs. If it is a Cr–O bond that is broken, then on regrouping, only isomerization can result, but not aquation. If, however, it is a Cr–N bond that fails, we again have a situation but one step removed from aquation, and, we would suppose, irreversibly committed.

It is also possible to account qualitatively for the greater photosensitivity of the of the cis form, especially towards aquation, than the trans. As Ballhausen (*4*) remarks, simple crystal field theory relates the energy positions of the spin-allowed transitions to a tetragonality parameter which depends on sums of axial charges.

For the cis complex, we have two O–N and one N–N type axis while for the trans there are two N–N and one O–O type axis. We can argue from the spectrochemical series that the effective crystal field along an axis increases in the order: O–O, O–N, and N–N. If, now, light absorption directly or eventually leads to bond weakening along the weakest ligand field axis, then for the cis complex, an O–N pair will be affected, leading to the dichotomous possibilities of Figure 4d and 4e. In the case of the trans form however, the O–O axis would be affected, and consequently this would lead only to isomerization.

It is thus possible to account for the general framework of observations. It does not seem possible, however, to specify any unique interpretation of the activation energy quantities. Following light absorption, there can be electronic return to the initial species by radiationless deactivation; there can be some conversion from one state to another. The chemical intermediates may retain the original configuration, may isomerize, and may aquate. Possibly solvent exchange studies would help reduce the plethora of possibilities.

We do conclude, however, that Cr(III) complexes can have a photochemistry which is spectrospecific as to mechanism, and we suspect that where this apparently is not the case, it is because only one product is possible or is sought for.

## *Acknowledgements*

The thermal isomerization and aquation rate studies were carried out by Mr. R. S. Hann and Miss L. B. Martinez.

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# Discussion

**Arthur Adamson:** There has been some discussion and comment on what I called a cage mechanism, and I want to say in a little more organized way what I think is involved.

First, I am not trying to attack the transition state theory. What I am aiming at is a little different.

Transition state theory itself is a beautiful union of wave mechanics in one respect and thermodynamics in the other. However, it cannot be applied fully to the systems that we have been discussing. In these circumstances the theory is used in an approximate way, it may even be used as a language to present results. Very often the entropy of activation that is reported for a reaction is not much more than a formal translation of data in a mechanical way, and it is dangerous to read all transition state implications into the result.

If we are going to talk about approximations and approximate situations, then I suggest using one or another emphasis or point of view as a useful approximation or language that renders less objectionable innuendoes.

One problem, I think, in a detailed acceptance of simple transition state theory regarding solution systems concerns the central supposition that the transition state is in equilibrium with the reactants. If the transition state is a species which proceeds irreversibly and on one vibration period to products, it is a little difficult to demonstrate, I think, that this thermodynamic equilibrium exists. The concept of equilibrium and the concept of an irreversible process at some point must be distinct.

One can retreat a step and talk about, say, a species whose energy content might be written as $\Delta H\ddagger$ minus a small increment, that is, a species below transition state in energy and argue that this is now in equilibrium with reactants. The added energy that carries this to products is then considered to be a small perturbation. But I think this is a debatable question since it argues that energy arrives in small increments. Maybe it does, but this is no longer a purely thermodynamic question.

I suggest that for certain types of reaction systems in solution it is useful to suppose that the energy, if it does arrive in increments, must arrive in a relatively short period of time compared to the lifetime of the cage.

Perhaps another way of looking at this is to consider the reaction's going in reverse (starting with a transition state which then breaks up into reactants) and to say that, in solution and perhaps especially with complex ions in hydrogen-bonded solvents, there is good communication between the molecule and its environment in a vibrational sense. Therefore, as a transition state decays backwards to reactants, its excess energy will be lost in reasonably large jumps and reasonably quickly. Consequently, the reactant species will be back to thermal energies in a time that is comparable, if not shorter, than the time it will take them to diffuse away.

I again emphasize that I am thinking primarily of complex ion reactions involving a fairly large molecule, and a lot of interaction with the solvents, usually through hydrogen bonding. I am not thinking of small molecules which may not be so intimately solvated.

Perhaps another way of explaining what I am trying to emphasize is that when reactants come together I think probably they will have diffused together before acquiring their activation energy.

It is reasonable to ask just what the operational meaning of the cage picture is. What differences does it really make? If there aren't any, why discuss it?

The first emphasis here is on the notion of a preassembly of reactants. In a bimolecular reaction A and B first diffuse towards each other. If A is a complex ion, then B, if a solvent species, must first diffuse into the solvation shell of A. If B is an ion, the situation would be described as ion pairing. In any event, A and B first diffuse into a common "cage"; then during this period of association, reaction will occur if a sufficient accidental confluence of energy occurs.

The second emphasis is that it is helpful and suggestive to suppose that the probability of forming a transition state favorable to the reaction is highly determined by the probability that a similar but nonactivated configuration is available in the preassembled or "caged" species. Thus, in the case of anation, the stereochemistry of the reaction would be determined partly by whether the initial ion pair had a favorable configuration. In the case of solvation in a mixed solvent, the solvent distribution in the solvation shell rather than the average composition should be the important variable determining reaction rate and order.

Some possible consequences of this emphasis are the following:

The concept of a preassembly focuses attention on the arrangement of potential reactants in the solvent cage and suggests that there is not much validity in using such formal labels as $S_N1$, limiting or nonlimiting, or $S_N2$ or the combination I have been guilty of—$S_N2FS$. It implies that these labels are too rigid, too constrictive, and too oriented towards gas phase reaction kinetics.

Another possible effect or difference is that ordinarily there is no real way independently to study the transition state—independently verify $\Delta H\ddagger$ or $\Delta S\ddagger$. But if one supposes, as a useful approximation, that configurations in the cage will include those of interest in the transition state, one can now study the solvation shell or the ion pair structure, or in other words, study the situation in the cage without requiring it to be activated. This means that one can study ion pair formation and consider this as a useful guide to substitution reactions and how they might proceed. In a mixed solvent system involving a substitutive solvation such as aquation, the reaction cage concept suggests that it would be helpful to study the solvent composition of the solvation cage. Ordinary physical chemical methods would now be applicable. We have been taking a particular complex whose absorption spectrum is somewhat sensitive to solvent environment and looking at this spectrum in mixed solvents to get at what seems to be the immediate solvent environment.

Another way of picturing the cage is as a large, loose molecule. In a sense, we are saying a bimolecular reaction forms a large, loose molecule in the case of complex ion, which then isomerizes; that is, the inner-outer sphere exchange is thought of as an isomerization or an intramolecular change.

In the case of mixed solvents, if the two solvents are about equally good, one may suppose that in the solvation shell there is very little fractionation around the complex. With isomerization or intramolecular changes as a view of what is occurring, one can argue that perhaps just the spatial occupancy, or roughly the volume fraction of the solvent component that will substitute, may be a good variable. The reaction rate should then be proportional to the volume fraction. In some cases this prediction seems to work out.

This is one of the specific suggestions that arises from the reaction cage concept, whereas transition state theory in its simple application would suggest that the activity of the solvent component, rather than its volume fraction, should be the proper variable.

Still another consideration is that this point of view, especially where at least one of the molecules is large and complex, lends itself readily to thinking in terms of more than one reaction path. That is, it is more apparent that there can be various similar configurations whose overall contribution to the rate may be similar, and hence competitive. Some may have a high activation energy but represent a very probable state of affairs; others may have a low activation energy but an improbable state of affairs. In other words, many related reaction paths can be present.

As an illustration, and not to draw specific conclusions about the particular set of reactions, the table that Prof. Taube showed (Table I) in his paper on rates of chromous reaction with various pentammine cobalt(III) complexes, provide a set of rate constants that are very similar, within a factor of two or three. Yet, activation energies suggest that the rates should vary a million-fold. The same is true for the entropies of activation. Somehow these two factors have managed just to balance each other. This is too monumental a coincidence to be only that. There must be an explanation and perhaps we can draw an analogy from the following situation in catalysis. For a particular reaction and a particular catalyst, but activated to different degrees, one often observes that the reaction proceeds at about the same rate for the variously activated catalysts, but with quite different activation energies. This was considered in detail by surface chemists sometime ago and they proposed a distribution of sites on the catalyst; those that are more active and reduce the activation energy are fewer in number so there is a compensation of frequency and activation factors.

I am suggesting that often the applicability of Barkley-Butler type plots, that is, the linear relationship between the entropy and enthalpy of activation in a series may come about because of there being a distribution of reaction paths. Small variations in the importance of low activation energy, low probability paths could then account for the data in Dr. Taube's table. By contrast, transition state theory in its approximate application, invariably leads to diagrams of energy *vs.* reaction path which, in spite of all protest, one reaction path, whatever it is, one transition state, and one energy.

Again let me say I am proposing a shift in emphasis and an approximation to deal with what is inevitably a state of approximation. I am not attempting to knock down the pillars of transition state theory (Figure A).

Over the past several years we have been interested in determining to what extent the photochemistry of complex ions of various transition metal ions resemble thermal reaction chemistry as to products, and to what extent the behavior varies with the wave length or type of excited state produced.

In the case of the cobalt complexes, and in particular a series of acetopentammines, generally irridation in the wave length vicinity of a charge transfer band led

First Stage

$$\mathrm{CoA_5X^{+2}} \xrightarrow{h\gamma} [\mathrm{Co(II)A_5{-}X}]^{+2} + \Delta$$

M—X bond weakened, vibrational energy, Δ, dissipated

Second State

$$[\mathrm{Co(II)A_5{-}X}]^{+2} \xrightarrow{k_1} \mathrm{CoA_5X^{+2}} + \Delta'$$

atom returns with
further Δ′ dissipated

$k_2$

$$\mathrm{CoA_5^{+2}{-}H_2O{-}X}$$

interposition of solvent

*Figure A. Suggested mechanism for photolysis of Co(III) complexes*

to a good deal of redox decomposition—i.e., oxidation of ligand and reduction of the cobalt. Accompanying this was often a good deal of substitution, but competitive to the redox mode of reaction. We proposed in 1957 that the primary act was a homolytic bond fission, and that either a redox or an aquation reaction ensued. This depended on whether the fragments escaped completely or whether, before complete escape, an electron returned to reverse the redox part but still allow the acido group to escape. On the other hand, irradiation, in the case of these cobalt complexes, of a purer ligand field band, led to very low quantum yields and aquation only. Thus, the choice of wave length or essentially the choice of type of band to irradiate made a considerable difference as to the photochemistry.

The general observation in the published work has been that for species such as hexamminechromium, thiocyanatopentammine, or the hexa-aquo ion where $O^{18}$ exchange was looked at, irradiation produced a substitution reaction and nothing else. Moreover the reaction mode was independent of wave length, and the quantum yields did not change much. From a morphological point of view, there are essentially three types of explanations. First all excited states independently lead to the same chemical sequence, and we suppose that the primary act is simply a heterolytic bond fission.

Second, the excited quartet states convert to the doublet state which then acts as a common chemical intermediate. This attractive suggestion, owing partly to to Plane and partly to Schlafer, is plausible because this conversion is known to occur in rigid media.

However, a third possibility is that various excited states are potentially different in their photochemistry, but that the systems chosen for study didn't have any means of reflecting this difference.

The present paper is concerned with choosing systems which reflect such differences if they exist. Figure B reproduces this summary of results.

The complex chosen for study was *cis*-dihydroxybis(ethylenediamine)chromium (III). Two types of substitution reactions can occur here: isomerization and aquation. We now are able to observe reaction ratios as well as overall quantum yields. We do see some differences with wave length. The most striking is that which occurs in the quantum yield for the aquation reaction. This is nearly temperature independent for short wave-length irradiations. At the longer-wave lengths where at least a fair proportion of light is being absorbed into the doublet transition, it is quite temperature dependent. The isomerization quantum yields given by the

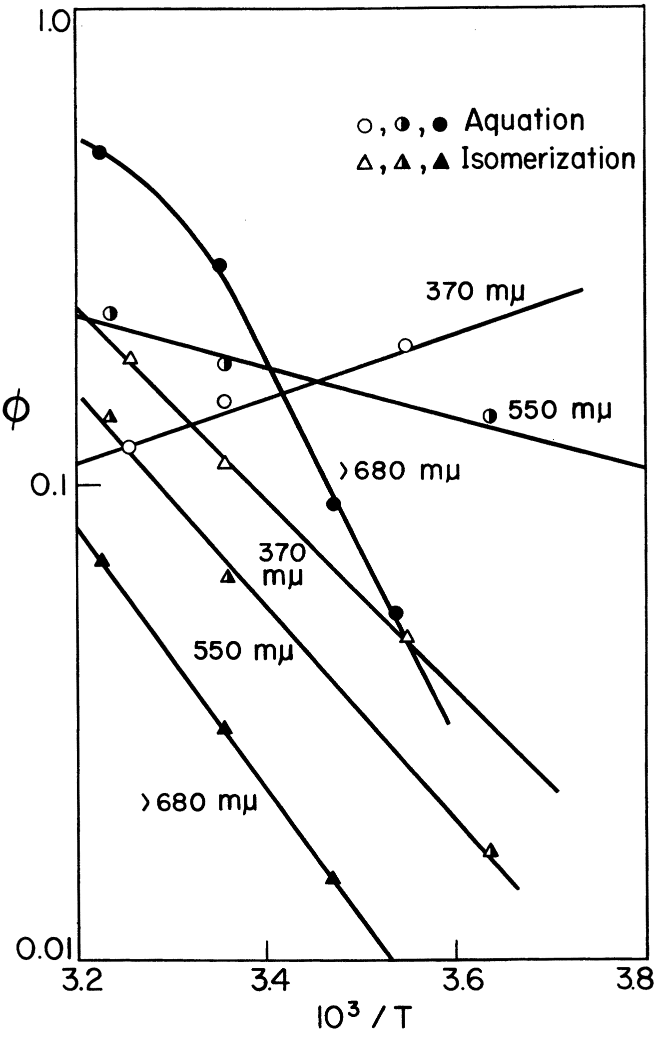

*Figure B. Quantum yields for photoaquation and isomerization of cis-$Cr(en)_2(OH)_2^+$*

triangles show rather similar behavior at all the wave lengths but with a gradually increasing temperature dependence as the wave length is decreased.

It is impossible to suppose that, in the case of photolysis at the shorter wavelengths, aquation and isomerization are competitive towards a common precursor. The argument is a quantitative one concerning the high quantum yields for both processes. The algebra of a competitive reaction scheme cannot explain two processes, one with a high temperature coefficient and one with an apparent zero-temperature coefficient, if both occur in comparable yields.

I proceed in the paper to speculate about intermediates that might be produced. These are essentially speculations, a frame for discussion. I will leave that aspect open for questions.

**Harry Gray**: Photochemistry is a new and exciting area in inorganic chemistry. I am sure the experts in the field, Prof. Adamson, Prof. Plane, and others here, will agree that the progress in inorganic photochemistry thus far has been a dog's dinner compared to organic photochemistry simply because we have attracted fewer people into this new field. I think it is going to be more complicted than the organic photochemistry since our systems are consistently more interesting and intricate.

I have some of our results to present. Also, I would like to point out some problems in this area. There are three problems that I think must be solved before we can do any significant photochemistry.

The first is the question of monochromatic light. Monochromatic light will have to be available, I think, at least ±100A., or even less.

The second problem is the identification of absorption bands, a problem that Prof. Adamson makes clear in the first page of his paper. In discussing transitions to the various *d-d* excited states in octahedral chromic complexes, he uses the usual octahedral designations. These designations serve to identify these bands loosely. But we must do considerably better than this. Thus, the second problem is certainly to identify the absorption bands in considerably more detail.

The third problem is to study systematically the various types of transitions involved in metal complexes. First, if one wants to study the photochemistry of *d-d* bands he should not study the photochemistry of *d-d* bands overlapped with charge transfer bands. That is, he should select systems which have *d-d* bands clearly separated from the other transitions. Second, there are two types of charge transfer. Ligand-to-metal charge transfer in the halides is one. Systems should be selected in which the L → M bands are isolated from the others, and one should study the quantum yields as a function of wave length. Metal-to-ligand charge transfer systems are third. This hasn't been stressed up to this point. Metal carbonyls, acetyl acetonates, and metal nitrosyls are interesting cases in which one can isolate the metal-to-ligand charge transfer bands from the other bands. Finally, the ligand-ligand transitions are types that the organic chemists have investigated thoroughly.

On the second problem the people in my area are responsible for the poor state of affairs. I take most responsibility because outside of octahedral and tetrahedral complexes no complete assignments have been made. But, we do have new results, and I think it is of some interest to present them. Cooper Langford and I at Columbia now have conclusive results on the energy levels in the distorted octahedral cobalt compounds. These are the $Co(NH_3)_5X^{+2}$ complexes.

The spectra of these complexes were carefully worked out by Lenhart and Weigel some time ago.

Dr. Langford and I decided to look at these spectra again. We remeasured the spectrum of $Co(NH_3)_5F^{+2}$ because this is the one in which to resolve the fourth *d-d* band. The band comes out nicely and we didn't even need a Gaussian analysis. A Gaussian analysis checked out Lenhart and Weigel's first three bands very nicely and thus we have resolved in one case, outside of octahedral and tetrahedral symmetry, all of the spin-allowed bands. The band from $xy$ to $x^2-y^2$ should have the

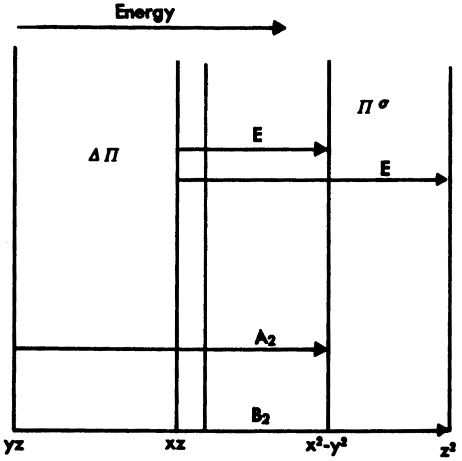

*Figure C: Energy levels in the distorted octahedral cobalt complexes*

same energy as in $Co(NH_3)_6^{+3}$ because the halide substitution is in a pole position. There are two allowed bands, the two E's, and two forbidden ones, $A_2$ and $B_2$. The polarizations had been done and interpreted by Carl Ballhausen and Moffitt, and all that remained was to get the fourth band. We have done the complete theoretical problem as well as possible in strong field with complete configuration interaction, and we now have, I think, the correct one-electron ordering for the halopentammines.

It turns out that $z^2$—a little surprising—is substantially above $x^2$—$y^2$. The $xz$—$yz$ level is further above $xy$, however, and the net effect places fluoride lower than $NH_3$ in the spectrochemical series. Fluoride gives stronger $\sigma$-antibonding but even stronger $\pi$-antibonding and thus net reduction.

$$\text{For } Co(NH_3)_5F^{+2},\ \Delta\pi = 3450/\text{cm.},\ \Delta\sigma = 2400/\text{cm.}$$

That is, $z^2$ is 2400 wave numbers above $x^2$—$y^2$. The chloropentammine, $\Delta\pi$ is 4000/cm. the bromopentammine, $\Delta\pi$ is 4550/cm., and the iodopentammine $\Delta\pi$ is 5550/cm.

**Dr. Adamson:** One can get 100A. resolution with interference filters. We use them mainly because of their high light intensity, but we do have detailed data by wave length region on one chromium compound, and we do see small dips and changes in the quantum yields. I am referring to some work by Dr. Begner in our department.

The development of theory is beautiful, and I would say that theoreticians have to be prompted by experimental results.

I showed, at a Faraday discussion in 1960, a slide depicting a spectrum of the fluoropentammine which showed the small peak. We weren't alert enough theoretically to see its significance.

I have one final comment on the chromium system. There is another doublet state, a doublet $T_{2g}$ that is supposed to be present and usually hidden by the quartet-quartet transitions.

Possibly some of our results involve conversion to that state. Do you have any comment?

**Robert Plane:** I would like to comment on the photochemistry of these complexes, particularly the chromium which I think are well chosen for at least two of Dr. Gray's reasons. First, in the case of chromium, unlike cobalt, the charge transfer band is well separated, so that one can study the *d-d* transitions, at least in certain systems where one has six ligands all alike, and there is no Jahn-Teller splitting, and one has a fairly good idea as to the assignment of bands.

The first theory to account for photochemistry in these series was that by Dr. Adamson which postulates the bond fission as the primary act. Simultaneously, H. L. Schlafer (*9*) and John Hunt and I (*8*) proposed the involvement of the doublet E state. Although these seemed similar, they were radically different suggestions. Schlafer's point was that on irradiation the molecule found itself ultimately in the spin-forbidden state where the energy was stored. On releasing energy during return from the doublet *E* state to the ground state, reaction occurred. Our postulate also involved the spin doublet state which is a spin-forbidden state. But our point was that the reaction occurred while the molecule was in the doublet state. In other words, we said that by irradiating the system we are studying the chemistry of an excited state of chromium. I think Prof. Adamson's data have shown very well that the thermal reaction and the photochemical reaction are different things. They lead to different products, and the temperature coefficients are very different. Such results are completely consistent with the postulate of reaction in the excited state. However, this postulate does not exclude the bond fission postulate. If you like, we are trying to decide what species is reacting: is it the doublet molecule or the ground state molecule? Also what is the mechanism by which the proper species finally reacts?

I would like to comment on the statement in Dr. Adamson's paper which says that our work as a function of wave length is trivial if we only knew all the facts. Perhaps this is true. But I am not willing to admit that it is trivial on the basis of any fact that I know yet. For the $H_2O^{18}$ exchange with $Cr(H_2O)_6^{+3}$, one can irradiate all three absorption bands separately, and the quantum yields are the same (*8*). This is reminiscent of what invariably happens in organic photochemistry when one excites to any of several spin-allowed states. The molecule immediately converts internally to the lowest state, and anything that is interesting happens from the lowest. Hence, it doesn't matter which state it goes to first. We believe it goes next into the doublet state and so we did the second part of the experiment. This could not be done with the hexaquo case because the spin doublet overlaps with one of the spin-allowed states. Instead we used $Cr(NH_3)_6^{+3}$ where we can irradiate the doublet directly and put the molecule into this state. When we do so, our quantum yield climbs to unity, which I think is significant (*1*). In this case the evidence is good that molecules are reacting in their excited states.

**Dr. Adamson:** This is a correction. I didn't say your results were trivial. I said that by having them at only one temperature possibly the ordering of the quantum yields with wave length led to a conclusion that was not general. At another temperature you might have found a different order.

**Dr. Plane:** We found them temperature independent.

**Cooper Langford:** My comment is not on photochemistry, but on Prof. Adamson's remarks on cage aggregates and the transition state theory.

I sympathize with the point of view he is advocating, and I hope that his suggestions would not be confused by misconstruing transition state theory. He singles out large molecule systems in condensed phases as places where the transition state theory would be in trouble.

My understanding of transition state theory is that this is where the approximations are most likely to be accurate, especially if the activation energy is large. The transition state theory, from the detailed statistical viewpoint, requires that all degrees of freedom but one be in equilibrium. This is most readily obtained in a condensed phase where energy transfer is rapid.

**Dr. Adamson:** You have a point there. I think that in the large molecule system, for example pentamminehalide and water, there will be more than one reaction path and not a single transition state. It is helpful to consider this as a kind of intramolecular rearrangement.

**Robert Connick:** Since the subject has been raised, I would like to comment on this general problem.

I agree with looking at these matters in different ways. As I understand it, you do not object to the transition state theory formulation. The one word of caution I would like to interject, though, is this: you spoke of the caged species before it had really reached the activated complex configuration, and you spoke of this concept's being particularly valuable.

In a formalistic sense the rate is controlled, according to the transition state theory, by the stability, concentration, and so on of the activated complex. This is the key configuration. This theory says that all other configurations may be interesting but they don't really count when it comes to determing the rate. Therefore, one is always in danger of incorrect predictions about a reaction rate if one deliberately strays from the activated complex configuration. I do not mean to say that one will always err, because in many reactions the configuration of the system as it approaches the activated complex is very similar to what it is in the activated complex. In fact, one believes that in most of these cases it is the accumulation of energy in particular bonds rather than changes in geometry which are occurring in the final activation. Nevertheless, such a situation does not always exist, and particularly if one talks about what caged species would form preferentially in a solution. Often the configuration which is thermodynamically preferable will not be the one which corresponds to the activated complex. In many cases there is no reason why they should be identical. It must be remembered that the activated complex is an unstable species, not a stable one. It is formed with a great expenditure of energy and therefore, one must not postulate properties about it based on general ideas of overall stability.

**Dr. Adamson:** It is possible that Dr. Connick and I have different viewpoints in this respect. He referred repeatedly to '*the* activated complex' and '*the* transition state.' I have said, that I feel in these types of reactions one may have a distribution of paths that are contributing comparably. They are not terribly different, but enough so that it is dangerous to compress ones thoughts to "the" transition state and "the" activated complex. I suspect that these Barkley-Butler sequences may indicate a distribution of reaction paths.

**Edward King:** Of course, if these different transition states have different composition, it appears in the rate law.

**Dr. Adamson:** Let's go back to the intramolecular rearrangement picture. The composition of the transition state is always the same.

**Daniel Leussing:** I want to pose a question. Is this picture open to experimental access? In other words, if there is a spectrum of transition states with different heats, will we not get the appearance of a heat capacity of the transition state; whereas if the model showed a single transition state predominating would not the heat of reaction be constant? Wouldn't this allow us to answer the question.

**Dr. Adamson:** If there is a distribution of reaction paths, then the apparent activation energy should indeed change with temperature, and the effect would appear as a heat capacity of activation. However, it does not seem possible to distinguish this situation from that of a single reaction path where the transition state heat capacity is different from that of the reactants. That is to say, the formal thermodynamics would be identical for the two cases.

**Gordon Atkinson:** I think there is, at least in principle, a way to examine a system for distribution of very similar paths. This is by relaxation technique, particularly ultrasonic absorption. A distribution of similar, though not identical paths, implies a distribution of relaxation times centered at a certain frequency. But there is a subtle experimental problem involved in distinguishing between a single relaxation time and a rather closely spaced distribution of relaxation times.

**Ronald Archer:** With regard to base hydrolysis, I think there is some stereochemical evidence that suggests both sides are probably somewhat correct. There is evidence of the type which John Bailar has been giving us for about 30 years regarding the so called $D \rightarrow L$ inversions of configuration (*2*, *3*, *4*). Fred Basolo has suggested several times that one does not see this inversion by a simple $S_N$1 type process (*6*, *7*). On the other hand, some of the work I have been doing in liquid ammonia suggests that not only does one see the inversion of configuration, but also the conjugate base path (*1*). Therefore, I think one must have a preorientation plus an intermediate that is probably basically an $S_N$1 type; no, I won't say $S_N$1—let's say there is possibly a five-coordinate intermediate of some sort in the middle.

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