# KINETICS AND MECHANISM OF REPLACEMENT REACTIONS OF CO-ORDINATION COMPOUNDS

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## 1. Introduction and Value of Subject

THIS subject has been well documented in recent years[1-10] and in greater detail than is the intention of this Reviewer. The salient features of the subject will be covered, however, and references to key papers and accounts will be included. Inevitably many of the ideas previously propounded will be recounted. The Review will be mainly concerned, necessarily, with co-ordination compounds of the transition elements since it is this group of complexes, with its variety of stereochemical behaviour, which has primarily interested the investigator, further stimulated in recent years by the application of the powerful ligand-field theory.[4,9] It is about fifty years since the earliest kinetic study of a complex-ion reaction.[11] It is, however, only in the past decade that anything approaching a concerted attack on the problem of the mechanism of these reactions has been made. One of the challenges of investigating co-ordination compounds is understanding the variety of chemical intermediates and transition states possible for the reactions of four- (planar and tetrahedral), five-, six-, and eight-co-ordinate complexes. Many fundamental problems remain unanswered but increasing attention from a number of quarters is being paid to the subject.

Apart from their intrinsic interest, the reactions of co-ordination compounds have been investigated to test some of the theories of chemical reactivity. Thus the base hydrolysis of bromopenta-amminecobalt(III) ion:

$$[Co(NH_3)_5Br]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Br^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

has been used to study the effects of hydrostatic pressure,[12] ionic strength,[13]

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[1] Taube, *Chem. Rev.*, 1952, **50**, 69.

[2] Basolo, *Chem. Rev.*, 1953, **52**, 459.

[3] Basolo, *Rec. Chem. Progr.*, 1957, **18**, 1.

[4] Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958.

[5] Pearson, *J. Phys. Chem.*, 1959, **63**, 321.

[6] Ingold, "Substitution of Elements other than Carbon," Weizmann Science Press, Jerusalem, 1959, Chapter 1.

[7] Tobe, *Sci. Progr.*, 1960, **48**, 483.

[8] Stranks in "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960, p. 78.

[9] Pearson, *J. Chem. Educ.*, 1961, **38**, 164.

[10] Basolo and Pearson in "Advances in Inorganic Chemistry and Radiochemistry," ed. Emeléus and Sharpe, Academic Press, Inc., New York, Vol. III, 1961, Chapter 1.

[11] Lamb and Marden, *J. Amer. Chem. Soc.*, 1911, **33**, 1873.

[12] Burris and Laidler, *Trans. Faraday Soc.*, 1955, **51**, 1497.

[13] Brönsted and Livingston, *J. Amer. Chem. Soc.*, 1927, **49**, 435.

and ion-pairing[14] on reaction rate. The rate of the second-order reaction:

$$Fe^{2+} + [Co(C_2O_4)_3]^{3-} \rightarrow Fe^{3+} + Co^{2+} + 3C_2O_4{}^{2-} \quad . . . . . . . (2)$$

can be measured conveniently by using $\mu$M-concentrations of reagents.[15] Salt effects can thus be studied in the region of low ionic strength in which the Brönsted theory is applicable and can thus be tested. Many of these oxidation–reductions whose rates have been measured involve complex ions, and a knowledge of the lability* of these ions is often important for understanding the detailed mechanism of electron-transfer processes.[16]

Metal ions can act as important catalysts in organic and biological systems. Reactivity may form the basis for this behaviour; the profound difference between calcium and magnesium ions as enzyme-activators may arise[17] from the much faster reaction of calcium discovered recently with ligands such as adenosine 5′-diphosphate, adenosine 5′-triphosphate,[18] and a metal indicator, metal phthalein.[19] The *modus operandi* of the catalytic effect often involves a metal ion's attacking the substrate to form a transient complex in which the drain of electrons to the co-ordination centre results in facilitated reaction at another point of the substrate.[20,21]

A knowledge of reaction mechanism can aid in the synthesis of new metal complexes and improve older methods. Basolo,[22] in a readable account, outlines how, for example, the hitherto unknown nitrito-complex ions of rhodium(III), iridium(III), and platinum(IV), $[M(NH_3)_5ONO]^{n+}$ were prepared as a direct sequel to kinetic studies. The successful use of some of the procedures for complexometric estimation of metals depends on the difference in rates of complex reactions,[23] although insufficient attention appears to have been paid to the rate aspect in analytical procedures.

One of the least ambiguous methods for assigning the solvation number of a metal ion involves exchange studies, *e.g.*,

$$[M(H_2O)_n]^{m+} + nH_2{}^*O \rightleftharpoons [M(H_2{}^*O)_n]^{m+} + nH_2O \quad . . . (3)$$

Provided the rate of exchange is measurable, and flow methods[24,25] can

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*A kinetic term.[1] Complex ions reacting within 1 minute at room temperature involving ~ 0·1M-solutions are termed "labile"; otherwise they are "inert".

[14] Davies and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1547; Davies, "Progress in Chemical Kinetics," ed. Porter, Pergamon Press, London, 1961, p. 175.

[15] Barrett and Baxendale, *Trans. Faraday Soc.*, 1956, **52**, 210.

[16] Halpern, *Quart. Rev.*, 1961, **15**, 207. These processes will not be discussed further in this Review.

[17] Diebler, Eigen, and Hammes, *Z. Naturforsch.*, 1960, **15b**, 554.

[18] Eigen and Hammes, *J. Amer. Chem. Soc.*, 1960, **82**, 5951.

[19] Czerlinski, Diebler, and Eigen, *Z. phys. Chem. (Frankfurt)*, 1959, **19**, 246.

[20] Ref. 4, Chapter 8.

[21] Martell and Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, 1952, Chapter 8.

[22] Basolo, *Chem. Eng. News*, 1961, **39**, 86.

[23] Schwarzenbach, "Complexometric Titrations," transl. by Irving, Methuen, London, 1957.

[24] Baldwin and Taube, *J. Chem. Phys.*, 1960, **33**, 206.

[25] Sutter and Hunt, *J. Amer. Chem. Soc.*, 1960, **82**, 6420.

help attain this, the value of *n* can be determined. In this way the hexa-co-ordinated structures for $[Al(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ in water,[24,26] as well as for $[Co(NH_3)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ in liquid ammonia,[27] have been deduced.

## 2. Experimental Background

**(a) The Measurement of Rates.**—A wide range of rates and a variety of reactions of metal complexes are known. For example, cupric ions react "instantaneously" at −100° with ammonia or pyridine in methanol[28] whereas the hydrolysis of $[Ir(NH_3)_5Cl]^{2+}$ has to be studied at 95° to obtain measurable rates.[29]

Some idea of the extent of rate constants encountered is shown in Table 1, where examples are also given of the variety of methods which must be used to encompass the large time scale for reactions.[8] The importance of the recently developed techniques for measuring very fast processes

TABLE 1. *Reactions, rate constants and techniques used in kinetic studies of co-ordination compounds: illustrative examples.*

| Reaction[a] | Rate constant[b] | Technique applied | Ref. |
|---|---|---|---|
| $Cd^{2+} + Br^- \rightleftharpoons CdBr^+$ | $k_2 = 1{\cdot}4 \times 10^9$<br>$k_1 = 1{\cdot}0 \times 10^7$ | NMR (line broadening of Br nuclei) | 30 |
| $Cd(CN)_3^- + CN^- \rightleftharpoons Cd(CN)_4^-$ | $k_2 = 5 \times 10^8$ | Polarographic | 31 |
| [c]$Mg^{2+} + ADP^{3-} \rightleftharpoons MgADP^-$ | $k_2 = 0{\cdot}3 \times 10^7$<br>$k_1 = 2{\cdot}5 \times 10^3$ | Temperature jump | 18 |
| $Co_{aq}^+ + SO_4^{2-} \rightleftharpoons CoSO_{4aq}$ | $k_1 = 2 \times 10^5$ | Ultrasonic relaxation spectroscopy | 32 |
| $Ni\ en_3^{2+} + 2H^+ \rightarrow$<br>$Ni\ en_2^{2+} + enH_2^{2+}$ | $k_1 = 86{\cdot}6$ | Stopped-flow | 33 |
| [d]*cis*-*l*-$[Co\ en_2Cl_2]^+ + X^- \rightarrow$<br>$[Co\ en_2ClX]^+ + Cl^-$ | $k_1 = 1{\cdot}4 \times 10^{-4}$ | Polarimetric (X = SCN or $Cl^-$), spectral (X = SCN) and radiochemical (X = $^{35}Cl$) | 34 |

[a] All reactions in water except last (MeOH).

[b] $k_1$, first-order rate constant in sec.$^{-1}$; $k_2$, l. mole$^{-1}$ sec.$^{-1}$; at ∼25° unless otherwise indicated.

[c] ADP = adenosine 5′-diphosphate; temperature of reaction 13°.

[d] Temp. 35·8°.

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[26] Hunt and Taube, *J. Chem. Phys.*, 1951, **19**, 602.

[27] Wiesendanger, Jones, and Garner, *J. Chem. Phys.*, 1957, **27**, 668.

[28] Bjerrum and Poulsen, *Nature*, 1952, **169**, 463.

[29] Lamb and Fairhall, *J. Amer. Chem. Soc.*, 1923, **45**, 378.

[30] Hertz, *Z. Elektrochem.*, 1961, **65**, 36.

[31] Gierst and Hurwitz, *Z. Elektrochem.*, 1960, **64**, 36.

[32] Eigen, *Z. Elektrochem.*, 1960, **64**, 115; Eigen and Tamm, *ibid.*, 1962, **66**, 93,107.

[33] Ahmed and Wilkins, *J.*, 1960, 2901.

[34] Brown and Ingold, *J.*, 1953, 2680.

with half-lives of reaction in the micro- or millimicro-second range cannot be over emphasised.[35] Estimates of the lability of certain metal complexes (*e.g.*, aquo, ammines, halides) have been assessed by electrochemical methods[35b] and from nuclear magnetic resonance data.[30,36,37] In the latter case the resonance line broadening of nuclei such as $^{1}H$, $^{17}O$, $^{35}Cl$, and $^{127}I$ which is produced by paramagnetic ions can be interpreted in terms of the rate at which these nuclei (as water or halide ions in the examples above) are entering the co-ordination sphere of the paramagnetic ion (*i.e.*, the exchange rate). In addition the elegant relaxation methods pioneered by Eigen and his colleagues[38] can be used, in which a chemical equilibrium is rapidly perturbed by some physical process. Here, the temperature-jump method appears to be particularly applicable to the study of co-ordination compounds[18,19] (for reaction rates in the range $10^{-5}$—1 second) in which light-absorption changes arising from rapid temperature elevations can be related to a kinetic rate (for example, dissociation). The interpretation of the results from these rapid methods can, however, be difficult for the mere chemist (see, *e.g.*, ref. 30), especially if more than one stage is involved. This is not so true of the well-known flow techniques[39] but these cover only the millisecond—second time range, although their extension to low-temperature work has considerable potentiality for study of a wide range of complex ions.

Undoubtedly the most important property of a complex ion which has been used for kinetic measurements is its absorption spectrum and the changes, often large, which occur in the visible, ultraviolet, or even infrared region can be extremely useful, not only in measuring rate, but also for clarifying detailed mechanism, importance of intermediates, etc. Thus an understanding of the steric course of reactions (4)[40] and (5)[41] was

$$cis\text{-}[\mathrm{Co\ en_2Br(SCN)}]^+ + \mathrm{H_2O} \rightarrow 100\%\ cis\text{-}[\mathrm{Co\ en_2(H_2O)(SCN)}]^{2+} + \mathrm{Br^-} \quad . \; . \; . \; . \quad (4)$$

$$trans\text{-}[\mathrm{Co\ en_2Br(SCN)}]^+ + \mathrm{OH^-} \rightarrow 81\%\ cis\text{-},\ 19\%\ trans\text{-}[\mathrm{Co\ en_2OH(SCN)}]^+ + \mathrm{Br^-} \quad . \quad (5)$$

aided considerably by the observation during the reaction of a constant optical density at a certain wavelength. This isosbestic point indicated that the original substance was being replaced by either (*a*) one other substance or (*b*) two or more substances which were in constant ratio and once formed underwent no further change.

[35] (*a*) Eigen and Johnson, *Ann. Rev. Phys. Chem.*, 1960, **11**, 307; (*b*) Bewick and Fleischmann, *Ann. Reports*, 1960, **57**, 90.

[36] Pearson, Palmer, Anderson, and Allred, *Z. Elektrochem.*, 1960, **64**, 110.

[37] Connick in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 15; Connick and Stover, *J. Phys. Chem.*, 1961, **65**, 2075.

[38] For a general account see Eigen in "Advances in the Chemistry of the Coordination Compounds," ed Kirschner, Macmillan, New York, 1961, p. 371.

[39] Roughton and Chance in "Investigation of Rates and Mechanisms of Reactions," ed. Friess and Weissberger, Interscience Publ., Inc., New York, 1st edn., 1953, Chapter 10.

[40] Baldwin and Tobe, *J.*, 1960, 4275.

[41] Ingold, Nyholm, and Tobe, *J.*, 1956, 1691.

Conductivity, polarography, and pH measurements have also featured in kinetic studies of co-ordination compounds and, like the spectral methods, allow continuous examination of the reaction system. This is not usually possible with the other methods which have been used, involving chemical analysis and the important isotopic-exchange reactions (Table 2).[42]

TABLE 2. *Some isotopic exchange reactions of co-ordination complexes.*

| Reaction (see text) | Reactants | Rate law (25°) |
|---|---|---|
| (8) | $[Cr(NH_3)_6]^{3+} + {}^*H_2O$ | $R = 2{\cdot}6 \times 10^6[Cr(NH_3)_6{}^{3+}][OH^-]^a$ |
| (8) | $[Cr(NH_3)_6]^{3+} + H_2O$ | $R = 2{\cdot}1 \times 10^6[Cr(NH_3)_6{}^{3+}][OH^-]^b$ |
| (23) | $[Ni(CO)_4] + {}^*CO$ | $R = 7{\cdot}5 \times 10^{-4}[Ni(CO)_4]^c$ |
| (31) | $[Pt\ en_2Cl_2]^{2+} + {}^*Cl^-$ (presence of $[Pt\ en_2]^{2+}$) | $R = 15{\cdot}0[Pt(\textsc{iv})][Pt(\textsc{ii})][Cl^-]^d$ |
| (31) | $[{}^*Pt\ en_2Cl_2]^{2+} + [Pt\ en_2]^{2+}$ (presence of $Cl^-$) | $R = 12{\cdot}1[Pt(\textsc{iv})][Pt(\textsc{ii})][Cl^-]^d$ |

[a] L. mole$^{-1}$ sec.$^{-1}$, from H exchange in $DC_2H_3O_2/C_2H_3O_2^-$ buffers.
[b] L. mole$^{-1}$ sec.$^{-1}$, from NMR line broadening in 0·02M-NaOH.
[c] Sec.$^{-1}$, in toluene at 0°. [d] L.$^2$mole$^{-2}$ sec.$^{-1}$.

**(b) Kinetic Behaviour.**—The rate data encountered so far in studies of co-ordination compounds are relatively straightforward. In the successive-replacement or decomposition reactions of complexes containing more than one ligand, there is often sufficient difference in the reactivity of succeeding stages to prevent difficulties in interpretation. Thus the hydrolysis in acid solution of both $[Ni\ en_3]^{2+}$ and $[Cr\ en_3]^{3+}$ slows down as successive ethylenediamine molecules are removed.[33,43] Even so, if the properties of intermediates (*e.g.*, spectral) are unknown then several interpretations of the data are possible, and resort must often be made to plausibility.[44] In addition it is sobering to realise that the decomposition of hexa-amminechromium(III) ion in acid solution:

$$[Cr(NH_3)_6]^{3+} + 6H_3O^+ \rightarrow [Cr(H_2O)_6]^{3+} + 6NH_4^+ \qquad (6)$$

consists of twenty consecutive and simultaneous exchanges of ammonia by water and *cis–trans*-isomerisations. The complete solution is complicated but can be partially resolved by resort to matrix algebra.[45] There has been little investigation of reactions involving successive formation of complex ions which, being commonly of the second-order, may well prove even less simple.

An important mechanism noted in complex-ion studies involves slow rate(s) preceded by equilibrium, *e.g.*, in the formation of trisbipyridyliron(II) ion:[46]

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[42] Stranks and Wilkins, *Chem. Rev.*, 1957, **57**, 743.
[43] Schläfer and Kollrack, *Z. phys. Chem.* (*Frankfurt*), 1958, **18**, 348.
[44] Jørgensen and Bjerrum, *Acta Chem. Scand.*, 1959, **13**, 2075.
[45] Jørgensen and Bjerrum, *Acta Chem. Scand.*, 1958, **12**, 1047.
[46] Baxendale and George, *Trans. Faraday Soc.*, 1950, **46**, 736.

$$Fe^{2+} + \text{bipy} \rightleftharpoons [\text{Fe bipy}]^{2+} \quad \text{fast, } K_1 \quad \text{(7a)}$$

$$[\text{Fe bipy}]^{2+} + \text{bipy} \rightleftharpoons [\text{Fe(bipy)}_2]^{2+} \quad \text{fast, } K_2 \quad \text{(7b)}$$

$$[\text{Fe(bipy)}_2]^{2+} + \text{bipy} \rightleftharpoons [\text{Fe(bipy)}_3]^{2+} \quad \text{slow, } k_3 \quad \text{(7c)}$$

The rate of formation of $[Fe(bipy)_3]^{2+}$ was shown to equal $k_t[Fe^{2+}][bipy]^3$, with the value of $k_t$ independent of temperature from 0° to 35°. This unusual circumstance arises because $k_t(=K_1K_2k_3)$ incorporates the heats of (7*a*) and (7*b*) and the energy of activation of (7*c*) and these cancel one another.[47]

## 3. The Mechanisms of Replacement Reactions

All reactions of co-ordination compounds with the exception of those involving redox processes may be regarded as replacements (substitutions). Reactions in which only part of the ligand is replaced include the important hydrogen exchange processes occurring between aquated and ammonated metal ions and solvent, *e.g.*:

$$[Cr(NH_3)_6]^{3+} + {}^*H_2O \rightleftharpoons [Cr(N^*H_3)_6]^{3+} + H_2O \quad . \; . \quad (8)$$

This reaction is catalysed by hydroxide ion, with a rate equal to $k_2$[Complex][$OH^-$] over a wide range of hydroxide concentration from about $10^{-10}$M (where it has been studied by conventional deuterium-exchange experiments[48]) to $10^{-2}$M (where it has been studied by proton magnetic resonance line-broadening[36]) (see Table 2). Hydrogen-exchange experiments have value in assessing lability of solvated ions,[36,37,49] detecting metal–ligand bond rupture in certain chelate complexes,[50] and disclosing processes of the type[51]

$$[\text{Cu en}_2]^{2+} + \text{en} \rightleftharpoons [\text{Cu en}_3]^{2+} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

even where the thermodynamic equilibrium lies very much to the left-hand side.

Reactions may involve the replacement of one metal by another, and these are termed electrophilic reactions and designated $S_E$, *e.g.*,

$$[\text{Ni EDTA}]^{2-} + Cu^{2+} \rightarrow [\text{Cu EDTA}]^{2-} + Ni^{2+} \quad . \; . \; . \quad (10)$$

where EDTA = $(O_2C{\cdot}CH_2)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_2{\cdot}CO_2)_2{}^{4-}$.

By far the most important substitution reactions involve the ligand, and (1)—(9), except (2), constitute examples of such nucleophilic, $S_N$, reactions.

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[47] Bjerrum, Poulsen, and Poulsen, "Proceedings of the Symposium on Coordination Chemistry," Danish Chemical Society, 1954, p. 51.

[48] Palmer and Basolo, *J. Inorg. Nuclear Chem.*, 1960, **15**, 279; they measured the exchange rate of a number of metal ammines, studying the effect of electron configuration of metal, charge, and co-ordination number.

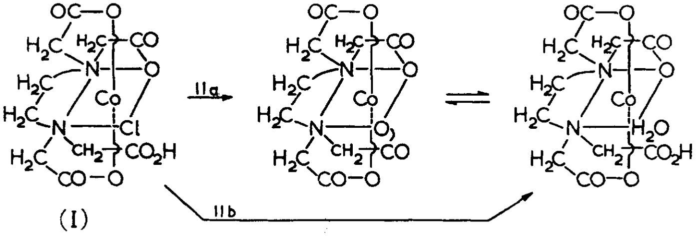
[49] *E.g.*, Bernheim, Brown, Gutowsky, and Woessner, *J. Chem. Phys.*, 1959, **30**, 950.

[50] Ahmed and Wilkins, *J.*, 1959, 3700.

[51] Morgan, Murphy, and Cox, *J. Amer. Chem. Soc.*, 1959, **81**, 5043; Cox and Morgan, *J. Amer. Chem. Soc.*, 1959, **81**, 6409.

It will emerge in subsequent discussion that there are several variants or sub-classifications. Most kinetic studies refer to aqueous solutions, since water is, by far, the most common solvent for co-ordination compounds. Two types of reaction can be studied involving (*a*) replacement of ligand by water and (*b*) replacement of water in an aquo-complex, which includes formation reactions.

**(a) The Replacement of Ligand by Water (Hydrolysis* Reactions).**— This is an important process since replacement of one ligand by another almost invariably proceeds initially by hydrolysis. Thus, the substitution of chlorine by glycine, aniline, or pyridine in *trans*-$[Pt(NH_3)_2Cl_2]$ is controlled by the hydrolysis of the latter, followed by rapid replacement of water by the substituting group. Chloride ion, however, appears to be able to effect direct entry as well as *via* hydrolysis, judging from some $^{36}Cl^-$ exchange experiments (see Table 6).[52] Similarly, hydrolysis may play an important role in the reactions of certain cobalt(III) complexes containing quinquedentate EDTA, which revert in solution to complexes containing sexadentate EDTA,[53,54] *e.g.*:



(I)

It is difficult experimentally to distinguish between two possible paths (11a) or (11b) because equilibration is rapid compared with the slow step.[53b] This means therefore that the observation that compound (I) and its carboxylate form lose chloride at the same rate is not necessarily significant.

Ingold, Nyholm, Tobe, and their colleagues[7,55] have investigated the orienting, rate, and mechanistic effect of a non-participating group A on the hydrolysis of octahedral complexes of cobalt:

$$cis\text{- or } trans\text{-}[\mathrm{Co\ en_2AB}]^{n+} + \mathrm{H_2O} \rightarrow cis\text{- or } trans\text{-}[\mathrm{Co\ en_2A(H_2O)}]^{n+} + \mathrm{B} \quad . \quad . \quad (12)$$

Some results are shown in Table 3 but a discussion of their significance will be deferred. In the reactions of type (12) which have been assigned the

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*The terms hydrolysis, aquation, and dissociation are synonymous in this field. The reaction is often referred to as solvolysis in non-aqueous solvents.

[52] Martin and Adams in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 579.

[53] (*a*) Shimi and Higginson, *J.*, 1958, 260; (*b*) Dyke and Higginson, *J.*, 1960, 1998.

[54] Morris and Busch, *J. Phys. Chem.*, 1959, **63**, 340.

[55] Ingold, Nyholm, and Tobe, *Nature*, 1960, **187**, 477, and references cited therein; Baldwin, Chan, and Tobe, *J.*, 1961, 4637, and previous Parts of that series.

TABLE 3. *First-order constants* ($k_1$, *sec.*$^{-1}$ *at* 25°) *and steric course of reaction* $[\text{Co en}_2\text{ACl}]^{n+} + H_2O \rightarrow [\text{Co en}_2\text{A}(H_2O)]^{(n+1)+} + \text{Cl}^-$.[a]

| *cis*-A | $10^7k_1$ | *cis* (%) | Suggested mechanism |
|---|---|---|---|
| OH | 130,000 | 100 | $S_N1$ |
| $N_3$ | 2400 | 100 | |
| Cl | 1250 | 100 | |
| NCS | 114 | 100 | |
| $NH_3$ | ~2 | 100 | $S_N2$ |
| $H_2O$ | ~150 | ? | |
| $NO_2$ | 1120 | 100 | |
| *trans*-A | | | |
| OH | 14,000 | 75 | $S_N1$ |
| $N_3$ | 2500 | 20 | |
| Cl | 160 | 35 | |
| NCS | ~1 | 50—70 | |
| $NH_3$ | ~2 | 0 | $S_N2$ |
| $NO_2$ | 8000 | 0 | |

[a] Data taken from refs. 7, 40, and 55, which should be consulted for fuller details.

mechanism $S_N1$ (Substitution, Nucleophilic, Unimolecular), the Co–B bond is commonly pictured as lengthening to a critical distance, whence water slips in to occupy the position held by B, which is then expelled. Thus, because the 5-co-ordination complex which would result from a "pure" $S_N1$ reaction is unstable, water must play a significant part in the hydrolysis and indeed the term "solvent-assisted $S_N1$" has been suggested for this mechanism;[56] it has, however, always been appreciated that solvation is important in an $S_N1$ reaction. In certain cases (B = halide) the hydrolysis can be assisted by metal ions and with certain of these, *e.g.*, $Hg^{2+}$, the reaction may indeed be of $S_N1$ type, the bond to water not being made "until all memory of the effects of the halide ion removed has been wiped out."[57] Similarly under the influence of mercuric ion, reaction (11a) is assured.[53b] In an $S_N2$ (Bimolecular) mechanism, the binding of the water is considered more important than the liberation of B. The difference is thus often a question of degree, dependent on whether bond-breaking or bond-making takes the lead. Since the reactant is always in large excess, kinetics are not helpful in deciding the molecularity of hydrolytic reactions. This has been assigned by the usual procedures, well tried in physical-organic chemistry, of examining steric, electron-displacement, and ligand effects, as well as from considerations of changes in entropy and volume of activation accompanying these reactions.[4,7,58] However, some doubt as to their correctness remains.

*Effect of acid.* These hydrolyses will not be acid-catalysed unless a protonated species can be formed as a reactive intermediate. Thus the

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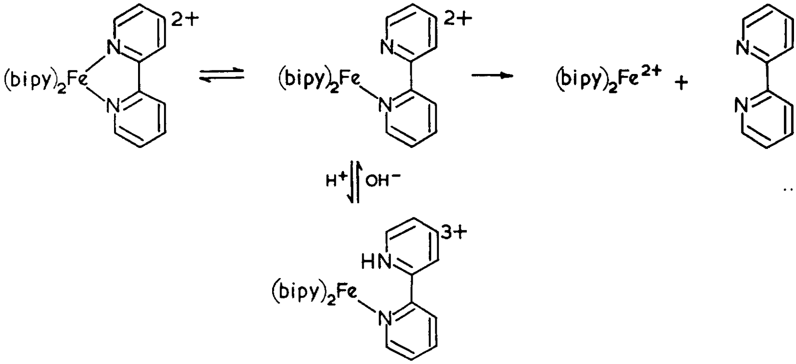
[56] Jones, Harris, and Wallace, *Canad. J. Chem.*, 1961, **39**, 2371.
[57] Posey and Taube, *J. Amer. Chem. Soc.*, 1957, **79**, 255.
[58] Hunt and Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 2642.

rates of hydrolysis of $[Co(CN)_5N_3]^{3-}$ {but not $[Co(CN)_5Br]^{3-}$}[59] and of $[Co(Cr)en_2F_2]^+$ (but not the corresponding chloro-complexes)[69,61] are acid-dependent. A mechanism such as:[60]

$$\begin{array}{lll} [Co\ en_2F_2]^+ + H^+ \rightleftharpoons [Co\ en_2F(FH)]^{2+} & \text{fast, } K_1 & \ldots\ldots (13a) \\ [Co\ en_2F_2]^+ + H_2O \rightarrow [Co\ en_2F(H_2O)]^{2+} + F^- & \text{slow, } k_2 & \ldots\ldots (13b) \\ [Co\ en_2F(FH)]^{2+} + H_2O \rightarrow [Co\ en_2F(H_2O)]^{2+} + HF & \text{fast, } k_3 & \ldots\ldots (13c) \end{array}$$

can account for the observed rate equation, $k_{\text{observed}} = k_2[Co\ en_2F_2^+] + k_3K_1[Co\ en_2F_2^+][H^+]$. Hydrolyses involving $H_2O$ as the entering ligand are often referred to as acid hydrolyses to distinguish them from base hydrolyses.

Our discussion thus far has been concerned with the removal of unidentate ligands, since this is the easier to understand and the associated complexes are used for molecularity assignment. In general, the effect of acid on the hydrolysis of complexes containing multidentate, even simple bidentate, ligands is decidedly more complicated. There is a dependence on $[H^+]$ for the rates of hydrolysis of $[Fe(bipy)_3]^{2+}$,[62] $[Ni\ en(H_2O)_4]^{2+}$,[50] and $[Cr(C_2O_4)_3]^{3-}$[63] which can be explained on the basis of small amounts of reactive intermediates which have one ligand linked by only one donor atom, nitrogen or oxygen: *e.g.*,



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The kinetic behaviour can also be explained by assuming *larger* amounts of a "protonated" species, without invoking bond rupture, but this idea appears chemically feasible only for the bipyridyl complexes. Although it is a less likely explanation it cannot be dismissed, especially in view of recent

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[59] Grassi, Haim, and Wilmarth in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 276.

[60] Basolo, Matoush, and Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 4883.

[61] Fehrmann and Garner, *J. Amer. Chem. Soc.*, 1961, **83**, 1276; MacDonald and Garner, *J. Inorg. Nuclear Chem.*, 1961, **18**, 219.

[62] Baxendale and George, *Trans. Faraday Soc.*, 1950, **46**, 736; Basolo, Hayes, and Neumann, *J. Amer. Chem. Soc.*, 1953, **75**, 5102; Krumholz, *J. Phys. Chem.*, 1956, **60**, 87.

[63] Graziano and Harris, *J. Phys. Chem.*, 1959, **63**, 330; Krishnamurty and Harris, *J. Phys. Chem.*, 1960, **64**, 346; Krishnamurty and Harris, *Chem. Rev.*, 1961, **61**, 213.

experimental support for such "protonated" species.[64] With the hydrolysis of $[Cr\ en_3]^{3+}$ in 0·1M-perchloric acid:

$$[Cr\ en_3]^{3+} + 2H_3O^+ \rightarrow cis\text{-}[Cr\ en_2(H_2O)_2]^{3+} + enH_2^{2+} \quad \ldots\ldots \quad (15)$$

the intermediate species (in which one ligand is attached to the chromium by only one $-NH_2$ group) probably has little independent stability although the kinetic data are ambiguous.[44,65]

The dissociative behaviour of metal complexes of polyamines[66] and polyamino-carboxylates represented by ethylenediaminetetra-acetate[67] is examined in the neutral pH region, where there is no net chemical reaction, by isotopic exchange studies. One obtains a rate composed from hydrolysis and formation rate constants and its unravelling in terms of simple processes is extremely difficult. If, alternatively, net decomposition is examined, *e.g.*, by addition of protons,[67,68,69] cyanide,[70] or a different metal ion* [*e.g.*, reaction (10)], complex rate data are obtained which must be interpreted in terms of intermediates containing the decomposing substituent. It is thus a problem to get at the unassisted (or solvent-aided) dissociative rates. When it is difficult to produce stepwise rupture (which may arise because there is little flexibility in the chelate, as in the metal phthalocyanines or porphyrins) kinetic inertness often results.

*Effect of base.* The hydrolysis of many acidoamminecobalt(III) complexes is markedly accelerated by the addition of hydroxide ion (base hydrolysis). These reactions are often easily measurable at low alkalinity (*e.g.*, pH ~9) but resort must be made to continuous-flow methods to investigate the reaction rates in stronger alkaline solution.[73] Concomitant with the base hydrolysis, and with similar rate characteristics (*i.e.*, Rate = $k_2[\text{Complex}][OH^-]$) and dependence of rate on substituent effects,[74] is a very much faster hydrogen exchange, analogous to reaction (8). Indeed the complex mechanism shown below ($S_N1CB$; substitution, nucleophilic, unimolecular, conjugate base) which includes the hydrogen exchange as a rapid pre-equilibrium (16*a*) may be the actual route for base hydrolysis:

$$[Co(NH_3)_5X]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4(NH_2)X]^+ + H_2O \quad \ldots\ldots \quad (16a)$$

$$[Co(NH_3)_4(NH_2)X]^+ \rightarrow [Co(NH_3)_4(NH_2)]^{2+} + X^- \quad \ldots\ldots \quad (16b)$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \rightarrow [Co(NH_3)_5OH]^{2+} \quad \ldots\ldots\ldots \quad (16c)$$

*There have been several studies of this type; see refs. 67, 71, 72.

[64] Murmann and Healy, *J. Amer. Chem. Soc.*, 1961, **83**, 2092.

[65] Schläfer and Kling, *Z. phys. Chem.* (*Frankfurt*), 1958, **16**, 14.

[66] Hogg, Melson, and Wilkins in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 391.

[67] Margerum, *J. Phys. Chem.*, 1959, **63**, 336.

[68] Tanaka, Tamamushi, and Kodama, *Z. phys. Chem.* (*Frankfurt*), 1958, **14**, 141.

[69] Papoff, *J. Amer. Chem. Soc.*, 1959, **81**, 3254.

[70] Margerum, Bydalek, and Bishop, *J. Amer. Chem. Soc.*, 1961, **83**, 1791.

[71] Tanaka and Kato, *Bull. Chem. Soc. Japan*, 1960, **33**, 1236, and previous work cited therein.

[72] Bydalek and Margerum, *J. Amer. Chem. Soc.*, 1961, **83**, 4326.

[73] Pearson, Meeker, and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 709.

[74] Basolo, Palmer, and Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 1073.

This mechanism can give the observed second-order kinetics with certain conditions.[7,75] Attempts have been made to distinguish this from a simple $S_N2$ mechanism[34] by examining the effect of adjusting the molecular structure of the reacting molecule (displaced group changes, steric and isotope effects, etc.) but the results can be usually explained on either mechanism. The arguments in support of these mechanisms are well documented.[3,4,6,7,10] It does appear that a simple $S_N2$ mechanism can be ruled out in certain solvents,[76] *e.g.*, dimethyl sulphoxide, but for water the problem remains unsolved. Even with this question settled, the behaviour of other metal complexes may be different. There is, for example, a striking difference in the onset of base hydrolysis of $[Co(NH_3)_5X]^{2+}$ and $[Cr(NH_3)_5X]^{2+}$ which is at pH 5 and 10, respectively.[77] An interpretation of this result in terms of the $S_N1CB$ mechanism has been suggested.[78]

The base hydrolysis of metal chelates has been little studied. Since $[Fe(phen)_3]^{2+}$ has no acidic hydrogen the marked base-catalysed hydrolysis *cannot* proceed *via* an $S_N1CB$ mechanism. Since, in addition, the hydrolysis of the *very similar* ion $[Ni\ phen_3]^{2+}$ is little affected by hydroxide, other mechanisms can also probably be dismissed, including $S_N1IP$ (see p. 339) and those involving stepwise rupture.[79] Consequently attention is focused on the $d^6$ configuration of iron(II) and a 7-co-ordinate reaction intermediate, stabilised by this particular electronic configuration, is postulated for the reaction with $OH^-$ (and $CN^-$ and $N_3^-$) ions.[79] A 7-co-ordinate species is also postulated for the base-catalysed hydrolysis of $[Co\ EDTA]^-$[80] and some credence is given to these ideas by the establishment (by means of *X*-ray structural analysis) of 7-co-ordinated metal in certain ethylenediaminetetra-acetate complexes.[81] An illustration of the interpretative difficulties facing the investigator is the observation that the rate of hydrolysis of the corresponding cobalt(III) propylenediaminetetra-acetate complex is *not* affected by addition of hydroxide ion.[80] Thus such an important difference is produced by simply placing a methyl group on the periphery of the complex ion.

**(b) The Replacement of Water in an Aquo-complex.**—Insight into the mechanism of the replacement of co-ordinated water in aquo-complexes has been obtained from water and ligand exchange.

*Water exchange.* The exchange of water between bulk solvent and the aquated metal ion is the simplest experiment in principle but, because of its

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[75] Pearson and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 4878.

[76] Pearson, Schmidtke, and Basolo, *J. Amer. Chem. Soc.*, 1960, **82**, 4434.

[77] Levine, Jones, Harris, and Wallace, *J. Amer. Chem. Soc.*, 1961, **83**, 2453.

[78] Ref. 4, p. 136.

[79] Margerum and Morgenthaler in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 481.

[80] Busch, Cooke, Swaminathan, and Young Ae Im, in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 139.

[81] Hoard, Smith, and Lind in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 296; Hoard, Lind, and Silverton, *J. Amer. Chem. Soc.*, 1961, **83**, 2770.

rapidity generally, it is most difficult to measure in practice. Resort is made to nuclear magnetic resonance experiments, these however introducing difficulties of interpretation. The broadening of the nuclear magnetic resonance signal of $^{17}O$ in water by the addition of paramagnetic metal ions sheds information on the mobility of oxygen and hence on the water-exchange process.[37] Lower limits for the first-order rate constant ($k_{H_2O}$) for the process:

$$[M(H_2{}^*O)]^{n+} + H_2O \rightleftharpoons [M(H_2O)]^{n+} + H_2{}^*O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

have been recently obtained (see Table 4).[37] $1/k_{H_2O}$ represents the lifetime of a particular water molecule on a metal ion. By studying the temperature effect on the relaxation process it is possible in principle to determine the *actual* rate constant, and the agreement between this value for $Mn^{2+}$ ($5 \times 10^7$ sec.$^{-1}$) with the proton exchange rate from nuclear magnetic resonance data ($4 \times 10^7$ sec.$^{-1}$)[49] shows, that with this metal ion at least, protons do not move independently of the water molecules. The results of these experiments are important in the interpretation of the mechanism of formation reactions (see next section). By studying the methyl- and hydroxyl-proton magnetic resonance of methanol solutions of metal ions, the *actual* exchange rates of copper(II) and nickel(II) solvated ions have been determined. Comparison with water-exchange data shows that methyl alcohol molecules undergo exchange more slowly.[36]

TABLE 4. *Kinetic data for water exchange (reaction* 17)[24,37] *and for sulphate reaction* (20)[38] *with metal aquo-complexes.*

| $M^{n+}_{aq}$ | $Al^{3+}$ | $Be^{2+}$ | $Mg^{2+}$ | $Mn^{2+}$ |
|---|---|---|---|---|
| $k_{H_2O}{}^a$(sec.$^{-1}$). | $<35$ | — | — | $2 \times 10^7$ |
| $k_{SO_4{}^{2-}}$(sec.$^{-1}$) | $\sim 1$ | $1 \times 10^2$ | $1 \times 10^5$ | $3 \times 10^6$ |

| $M^{n+}_{aq}$ | $Fe^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ |
|---|---|---|---|---|
| $k_{H_2O}{}^a$(sec.$^{-1}$). | — | $3 \times 10^5$ | $3 \times 10^4$ | $3 \times 10^6$ |
| $k_{SO_4{}^{2-}}$(sec.$^{-1}$) | $1 \times 10^6$ | $2 \times 10^5$ | $1 \times 10^4$ | $>10^7$ |

[a] *Lower*[36] limit for first-order rate constants.

The slow exchange of water between certain chromium(III) or cobalt(III) aquo-complexes and solvent has been measured by conventional oxygen-18 exchange experiments. By studying the rate of the reaction (18)

$$[Co(NH_3)_5H_2O]^{3+} + H_2{}^*O \rightleftharpoons [Co(NH_3)_5H_2{}^*O]^{3+} + H_2O \quad . \; . \; . \; . \quad (18)$$

at various temperatures and pressures, the volume and entropy of activation were determined as $+ 1{\cdot}2 \pm 0{\cdot}2$ ml. (independent of pressure) and $+ 6{\cdot}7 \pm 1$ e.u., respectively. These values appear to eliminate a compact $S_N2$ mechanism. The reasonable conclusion was drawn that an $S_N1$ designation more nearly applied, in which the cobalt–water bond stretched to a definite critical distance in the activated complex and that this was rapidly followed by bonding with the incoming water.[58] The higher positive entropies of activation for water exchange with *cis*- and *trans*-$[Co\ en_2(H_2O)_2]^{3+}$ and $[Co\ en_2(OH)_2]^+$ is in agreement with this concept.[82] The results of such water-exchange experiments can also aid in understanding isomerisation[82] and racemisation[83] processes (see section 5).

*Formation* reactions.* The important question posed by these reactions concerns the part played by the entering ligand Y:

$$[MX_m(H_2O)_n] + Y \rightarrow [MX_mY(H_2O)_{n-1}] + H_2O \quad . \; . \; . \quad (19)$$

where $(m + n)$ commonly equals six, and charges are omitted for clarity. The answer can be anticipated—there is little evidence, in the studies so far, for the reactant "forcing" an entry in a direct $S_N2$ reaction and the rate appears to be controlled by the water-exchange process. For such an $S_N1$ mechanism:

$$[MX_m(H_2O)_n] \rightleftharpoons [MX_m(H_2O)_{n-1}] + H_2O \qquad k_1, k_{-1} \quad . \; . \quad (19a)$$

$$[MX_m(H_2O)_{n-1}] + Y \rightarrow [MX_mY(H_2O)_{n-1}] \qquad k_2 \quad . \; . \; . \quad (19b)$$

it is easily shown, by assuming steady-state conditions, that

$$\frac{d}{dt}([MX_mY(H_2O)_{n-1}]) = \frac{k_1k_2[MX_m(H_2O)_n][Y]}{k_{-1} + k_2[Y]}$$

Various situations can arise:

(*a*) $k_{-1} \approx k_2$. In this case, the kinetics observed may well be dependent on the concentration of [Y]. At low [Y], $k_{-1} > k_2[Y]$ and a second-order kinetic expression, rate $= (k_1k_2/k_{-1})[MX_m(H_2O)_n][Y]$, is obtained. At high [Y], the reaction becomes of the first-order, with a rate $= k_1[MX_m(H_2O)_n]$. Thus with this mechanism prevailing a rate should be obtained which is dependent on small concentrations of Y, but independent of the concentration and nature of Y at higher concentrations, and, with a limiting formation rate constant $k_1$, equal to the corresponding value for water exchange, since (19*a*) is the path for such exchange. This behaviour has been observed only recently in the reaction of $[Co(CN)_5H_2O]^{2-}$ with $N_3^-$ and $SCN^-$ ions.[59] Earlier attempts to show the effect in the reactions of cationic cobalt(III) ammines with $N_3^-$ and $SCN^-$ ions[84] or with $SO_4^{2-}$ ions[57] and of $Cr^{3+}_{aq}$ with $SCN^-$ ions[85] were thwarted by ion-pairing between reactants at the high anion concentrations apparently necessary to reach the limiting region.† Summarising then, second-order kinetics do not *necessarily* indicate an $S_N2$ direct replacement, unless the rate can be shown to be

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*Often termed *anation* in the common circumstance that the entering substituent is anionic.

†The very little studied reactions with neutral ligands may, as with the anionic reactants, circumvent this difficulty.

[82] Kruse and Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 1280.

[83] Bailar, *J. Inorg. Nuclear Chem.*, 1958, **8**, 165.

[84] Basolo, Stone, Bergmann, and Pearson, *J. Amer. Chem. Soc.*, 1954, **76**, 3079.

[85] Postmus and King, *J. Phys. Chem.* 1,955, **59**, 1216.

very much faster than corresponds to $k_1$, and this so far has not been observed.

(*b*) $k_2 \gg k_{-1}$. The limiting condition appears to have been reached with certain reactions. Thus Hamm and his co-workers[86] found that the rates of reaction of $Cr^{3+}_{aq}$ with certain unidentate and bidentate ligands, *e.g.*, acetate, lactate, oxalate, were similar and their energies of activation close to that for water exchange. An even more penetrating example of reactions where water release dominates the entry of ligand is well shown by some formation-rate studies of complexes of certain bivalent metal ions, particularly of the first transition series, in which sound-absorption relaxation methods were used.[32,38] The rate constant for the formation of the sulphate complex (from the ion pair; sulphate considered a unidentate ligand):

$$[M(H_2O)_n]^{2+} \ldots . SO_4^{2-} \rightleftharpoons [M(H_2O)_{n-1}SO_4] + H_2O \quad k_1,k_{-1} \quad . \quad . \quad (20)$$

is similar to that for water exchange of the corresponding aquo-ion[37] (see Table 4). The value is also independent of the entering anion, in the light of some limited results for other ligands containing oxygen donor atoms, namely, thiosulphate, chromate, and EDTA. This emphasises the small specificity and role of the entering ligand. The corollary of these observations is that it is the reverse reactions (hydrolysis or dissociation, represented by $k_{-1}$) which are responsible for the differences in stability constants usually observed for complexes of a particular metal with various ligands[19,32,38] or of a particular metal with different numbers of ligands.[33] The values for the second-order rate constants for the formation of $[Ni(SCN)]^+$ [87] and $[Ni(NH_3)]^{2+}$ [88] suggest that here also metal–aquo bond-breakage is an almost controlling factor. The same may be true (although the situation is at present unclear) of some formation reactions involving iron(III) which, although rapid, have been studied by using rapid-flow devices:

$$[Fe(H_2O)_6]^{3+} + X^{(2 \text{ or } 1)-} \rightleftharpoons [Fe(H_2O)_5X]^{(1 \text{ or } 2)+} + H_2O \quad . \quad . \quad (21)$$

with X = $SO_4$, Cl, Br, or SCN.[38,89-91]* The common rate-law for these reactions, rate (forward) = $k_1[Fe^{3+}][X^{n-}] + k_2[Fe^{3+}][X^{n-}][H^+]^{-1}$ can be interpreted in terms of two reacting iron(III) species, the aquo- and the (significantly more reactive) monohydroxy-species. The rough parallelism between kinetic and thermodynamic parameters observed for the reaction of the aquo-complex (for example, between rate and stability constant of product;[89,90] see Table 5) suggests that the transition and the final state

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* These reactions have recently been studied by the pressure-jump relaxation method (Wendt and Strohlow, *Z. Electrochem.*, 1962, **66**, 228).

[86] Hamm, Johnson, Perkins, and Davis, *J. Amer. Chem. Soc.*, 1958, **80**, 4469, and previous work cited therein.

[87] Davies and MacF. Smith, *Proc. Chem. Soc.*, 1961, 380.

[88] Melson and Wilkins, unpublished observations.

[89] Connick and Coppel, *J. Amer. Chem. Soc.*, 1959, **81**, 6389.

[90] Matthies and Wendt, *Z. phys. Chem. (Frankfurt)*, 1961, **30**, 137.

[91] Below, jun., Connick, and Coppel, *J. Amer. Chem. Soc.*, 1958, **80**, 2961.

TABLE 5. *Kinetic data for formation of* $[FeX]^{n+}$ *at* 25° (*reaction* 21).

| X | $k_1$ (l. mole$^{-1}$ sec.$^{-1}$) | $k_2$ (sec.$^{-1}$) | $K^a$ (l. mole$^{-1}$) | Ref. |
|---|---|---|---|---|
| Cl | 9·4 | 18 | 4 | 89 |
| Br | 20 | 31 | 0·6 | 90 |
| NCS | 127 | 20 | 150 | 91 |
| $SO_4$ | ~3000 | ~500 | 100 | 38 |
| F | 5400 | — | $10^5$ | 92 |

[a] Approximate value for association constant appropriate for the conditions of the kinetic experiments, as used in cited reference.

have similar characteristics, *i.e.*, that a true $S_N2$ reaction is involved. Similar arguments had been used with the $Fe^{3+}_{aq}$–$F^-$ reaction, which however, perhaps not surprisingly with this ligand, has different rate characteristics.[92] However, whether an $S_N1$ mechanism can be ruled out, at least with the faster reactions of the series, awaits further study of the $Fe^{3+}_{aq}$–water exchange rate from nuclear magnetic resonance measurements.[37] There is a relation between rate ($k_1$) and the basicity of the ligand for the aquo-complex. In addition, the hydroxy-species is the more reactive (the second-order rate constants for the reaction, $k_2/K_h$,[91] are all approx. $10^4$—$10^5$ l. mole$^{-1}$ sec.$^{-1}$). Eigen[38] has therefore suggested a mechanism for the reaction of the aquo-species, in which the hydroxy-species is generated by transfer of a proton from the aquo-complex to the substituting ligand. This idea has affinities to the $S_N1CB$ mechanism which has been proposed for base hydrolysis. This phenomenon of co-ordinated ligands being labilised more by a hydroxy- than by an aquo-group has also been observed in the Cr(III)–$SCN^-$ reaction [85] and in the hydrolysis of $[Co(NH_3)_4(H_2O)(NO_3)]^{2+}$ ion.[93]

## 4. The Geometry and Characteristics of Intermediates and Transition States

The discussion of this aspect of the mechanism of reaction of co-ordination compounds has become more profitable as more results become available. In addition, resort is being increasingly made to consideration of available orbitals and the crystal-field theoretical approach.[4,94] The configuration of the possible transition states and chemical intermediates for reactions of octahedral and planar complexes has been considered by various investigators.

**(a) Seven-co-ordinate.**—In the transition state for a bimolecular reaction, the incoming and the outgoing group must have a similar geometrical relation to the rest of the molecule so as not to violate the principle of

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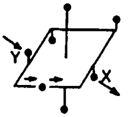
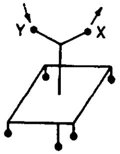
[92] Pouli and MacF. Smith, *Canad. J. Chem.*, 1960, **38**, 567.
[93] Brönsted, *Z. phys. Chem.* (*Leipzig*), 1926, **122**, 383.
[94] Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," Methuen, London, 1960, Chapter 7.

microscopic reversibility. Two structures which satisfy this requirement for an $S_N2$ reaction for an octahedral complex are as shown in (II) and (III).[95] Any kind of observed stereochange (*e.g.*, *cis*⟷*trans*; *D*⟷*L*) can be ascribed to an *edge-displacement* or *edge-shift*[6] or *trans*-attack.[4] For such a reaction the transition state is pictured as (II). It is not possible to accommodate a *trans* → *trans*-conversion within this concept so that the transition state for this (and possibly the other non-stereochemical changes) must be represented differently for these processes involving *non-edge-displacement* or *cis*-attack (III). Since different orienting effects can be observed in similar molecules, the energies associated with (II) and (III) must be similar. A third possible transition state, the pentagonal bipyramid,[96] in which entering and the displaced ligands are symmetrically located represents a somewhat uneven change in the original octahedral structure and is therefore less favoured. In the special case of solvolysis, assumed specific hydrogen-bond interaction between the entering hydroxylic substituent, departing ligand, and amine group may modify the simple concept of a bimolecular mechanism so that a six-co-ordinate metal complex more closely represents the transition state.[7,77,97]

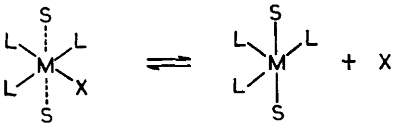
(II)





(III)

**(b) Five-co-ordinate.**—This concerns the intermediate and the transition state for both an $S_N1$ mechanism with an octahedral complex and an $S_N2$ mechanism with a planar complex. Indeed the four-co-ordinate complex can be considered as an octahedral complex with easily replaceable solvent molecules occupying the two extra positions at longer bond distances. The mechanism of the reaction is then "dissociative," the solvent molecules moving in to help push off the departing ligand.[98]



X and L represent the departing and the remaining ligands and S a solvent molecule. The five-co-ordinate species then rapidly reacts with various potential ligands.

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[95] Ašperger and Ingold, *J.*, 1956, 2862.
[96] Basolo, Stone, and Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 819.
[97] Adamson, *J. Amer. Chem. Soc.*, 1958, **80**, 3183.
[98] Banerjea, Basolo, and Pearson, *J. Amer. Chem. Soc.*, 1957, **79**, 4055; cf. ref. 52.

There are two plausible structures associated with this co-ordination number. These are the tetragonal pyramid and the trigonal bipyramid, both probably modified by a ligand in a sixth distant position. Both structures have support and which pertains may well depend on the particular reaction. The tetragonal pyramid is the more easily attained and is favoured on crystal-field and orbital considerations.[4,99] In the trigonal bipyramid arrangement,[53,56,100,101] however, there is less repulsion between ligands and in the special case that one of the five groups can form $\pi$-bonding, it is favoured in many respects.[75]

(c) **Three-co-ordinate.**—There is little evidence for planar complexes [and this refers currently and specifically to platinum(II)] reacting by an $S_N1$ mechanism. Isomeric change is usually very slow with platinum(II) in the absence of catalysts. Examination of Table 6 shows that the charge on the platinum(II) complex has little effect on the rate[4,53] while steric hindrance above and below the metal atom has a profound influence.[102,103] The latter is shown[102] by examining the reaction:

TABLE 6. *Kinetic data at 25° for the reactions of certain platinum*(II) *complexes showing aquation, charge, and ligand effects.*[52,102]

| Reactants | Products | Rate law ($R$ =) (sec.$^{-1}$ or l. mole$^{-1}$ sec.$^{-1}$) |
|---|---|---|
| $[PtCl_4]^{2-}$ + $H_2O$ | $[PtCl_3(H_2O)]^-$ + $Cl^-$ | $3{\cdot}9 \times 10^{-5}[PtCl_4{}^{2-}]$ |
| *trans*-$[Pt(NH_3)_2Cl_2]$ + $H_2O$ | $[Pt(NH_3)_2Cl(H_2O)]^+$ + $Cl^-$ | $9{\cdot}8 \times 10^{-5}[Pt(NH_3)_2Cl_2]$ |
| *trans*-$[Pt(NH_3)_2Cl_2]$ + aniline | $[Pt(NH_3)_2(\text{aniline})Cl]^+$ + $Cl^-$ | $9{\cdot}5 \times 10^{-5}[Pt(NH_3)_2Cl_2]$ |
| *trans*-$[Pt(NH_3)_2Cl_2]$ + $^*Cl^-$ | $[Pt(NH_3)_2Cl^*Cl]$ + $Cl^-$ | $9{\cdot}8 \times 10^{-5}[Pt(NH_3)_2Cl_2]$ +<br>$7{\cdot}8 \times 10^{-4}[Pt(NH_3)_2Cl_2][Cl^-]$ |
| $[Pt(PEt_3)_2ACl]$ + py $\rightleftharpoons$ $[Pt(PEt_3)_2A(py)]^+$ + $Cl^-$ | | $k_1 + k_2[py]$ |
| A = *cis*-$C_6H_5$ | | $k_1{}^a = 3{\cdot}8 \times 10^{-2}$ |
| A = *cis*-$C_6H_3(CH_3)_2$ | | $k_1{}^a = 4{\cdot}2 \times 10^{-7}$ |
| A = *cis*-$CH_3$ | | $k_1{}^a = 6{\cdot}0 \times 10^{-2}$ |
| A = *cis*-Cl | | $k_1{}^a = 1{\cdot}7 \times 10^{-2}$ |
| A = *trans*-H | | $k_1{}^a = 1{\cdot}8 \times 10^{-2}$ |
| A = *trans*-$CH_3$ | | $k_1 = 1{\cdot}7 \times 10^{-4}$ |
| A = *trans*-Cl | | $k_1 = 1{\cdot}0 \times 10^{-6}$ |

[a] At 0°.

$$[M(PEt_3)_2ACl] + py \rightleftharpoons [M(PEt_3)_2A(py)]^+ + Cl^- \qquad \ldots\ldots \quad (22)$$

The pseudo-first-order rate constant $k_{obs} = k_1 + k_2[py]$, where $k_1$ refers

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[99] Dyatkina and Syrkin, *Russ. J. Inorg. Chem.*, 1959, **4**, 579.
[100] Hamm, Kollrack, Welch, and Perkins, *J. Amer, Chem. Soc.*, 1961, **83**, 340.
[101] Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 137.
[102] Basolo, Chatt, Gray, Pearson, and Shaw, *J.*, 1961, 2207.
[103] Pearson, Gray, and Basolo, *J. Amer. Chem. Soc.*, 1960, **82**, 787.

to the solvent(ethanol)-controlled reaction and $k_2$ is a second-order rate constant for reaction with pyridine. For M = Pt, A = phenyl, $k_1$ is some $10^5$ higher than for M = Pt, A = mesityl, two methyl groups occupying positions in the latter above and below the plane of the complex. All the above facts militate against a dissociative mechanism for reactions of platinum(II). On the other hand, the little study that has been made of tetrahedral complexes suggests that these reactions involve an $S_N1$ mechanism. Thus, the rate of exchange of carbon-14 between tetracarbonylnickel and carbon monoxide in toluene is independent of the concentration of carbon monoxide (Table 2):[104]

$$[Ni(CO)_4] + {}^*CO \rightleftharpoons [Ni(CO)_3({}^*CO)] + CO \quad . \; . \; . \; . \; . \quad (23)$$

That panacea of inorganic ills ($\pi$-bonding) can be invoked to account for this difference in behaviour.

## 5. Stereochemical Changes accompanying Replacement Reactions

One of the interesting facets of co-ordination chemistry is the study of geometrical isomerisation and racemisation,[105] *e.g.*:

$$d\text{-}cis\text{-}[Co\ en_2F_2]^+ \xrightarrow{\text{Mutarotation}} d\text{-}cis\text{-}[Co\ en_2F(H_2O)]^{2+}$$

$$\xrightarrow{\text{Racemisation}} trans\text{-}[Co\ en_2F(H_2O)]^{2+} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (24)$$

Only the relevance of the results to the understanding of the mechanism of substitution will be mentioned here. Although all possible stereochemical changes have been observed in cobalt(III) chemistry,[106] it is important from an interpretative point of view that the *initial* product is observed and not one produced later in the reaction or one chemically isolated. This care is necessary since *cis*⟷*trans*, and *D*⟷*L* changes can often occur as readily as the substitution process itself. Even armed with the correct stereochemical result, it is difficult to assign mechanism. The calculation of the likely proportions of isomers produced with octahedral complexes from an $S_N1$ (with trigonal-bipyramidal or tetragonal-pyramidal intermediates) or an $S_N2$ mechanism has been undertaken.[9] A number of other factors are, however, involved and there are at present many limitations to the stereochemical approach to elucidation of mechanism.

Although an $S_N2$ reaction always produces quantitative stereochemical changes with tetrahedral carbon, the same is not true of octahedral complexes [*e.g.*, base hydrolysis of cobalt(III); Table 8] and with platinum(II), reaction with *retention* of configuration is usual, this itself aiding a mechanistic discussion (see previous section). In general, however,

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[104] Basolo and Wojcicki, *J. Amer. Chem. Soc.*, 1961, **83**, 520.

[105] Wilkins and Williams in "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960, p. 174.

[106] Werner, *Annalen*, 1912, **386**, 1.

stereospecific reactions will result more from $S_N2$ than $S_N1$ mechanisms. Both *cis*- and *trans*-cobalt(III) complexes aquate with full retention of configuration for an $S_N2$, but only *cis* for an $S_N1$ reaction (Table 3). Circumstantial evidence for mechanism can sometimes be obtained from racemisation and isomerisation studies. The fact that, for example, the rate of reaction of optically active *cis*-$[Co\ en_2Cl_2]^+$ with certain anions in methanol (see Table 1) equals the rate of concurrent racemisation, supports the postulate of an intermediate $[Co\ en_2Cl]^{2+}$ or $[Co\ en_2Cl(CH_3{\cdot}OH)]^{2+}$ ion which is symmetrical or can rearrange before reaction. Contrariwise, the observation that $[Co\ en_2(NH_3)(H_2O)]^{2+}$ exchanges water without racemising suggests that the intermediate must be asymmetric, in which case it is more likely to have the tetragonal-pyramidal configuration.[83] Experiments in which $H_2{}^{18}O$ was used show that in the isomerisation of *trans*-$[Co\ en_2(H_2O)_2]^{3+}$ one molecule of water is brought into exchange with solvent water, whereas in the isomerisation of $[Co\ en_2(OH)_2]^+$ only a fraction of one oxygen per ion undergoes exchange for each act of isomerisation. This and the fact that the energy of activation varies with temperature indicate that more than one mechanism operates in the isomerisation of $[Co\ en_2(OH)_2]^+$.

## 6. Important Factors influencing Rate and Mechanism[5]

**(a) Nature of Central Metal Atom.**—It would be expected from electrostatic considerations that there would be a slowing down of rate as the charge of the central metal increases and its size decreases.[5,9] It is thus understandable that, *e.g.*, $Be^{2+}$ and $Al^{3+}$ react more slowly than $Mg^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ ions with $SO_4{}^{2-}$ (see Table 4) and thenoyltrifluoroacetone.[107] Some attempt has been made to correlate the rates of these reactions with the ionic charge and radius of the reacting metal aquo-ion.* Such relations will, however, be disturbed by considerations of the electronic configuration of the metal involved.

Although attention had been drawn[28,108] to the importance of the electronic configuration of the metal ion on the rates of reaction of its complexes, it was Taube[1] who first tabulated the scattered and fragmentary data on the rates of reaction of co-ordination complexes. Attention was focused on the relation between lability and electronic configuration, on the basis of the valence-bond theory. Although these ideas have been somewhat superseded by the crystal-field approach their importance in drawing attention to this area of research cannot be exaggerated.

The systems which are highly stabilised crystal-fieldwise are likely to

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*The "effective ionic charge" allows for ions with a large number of *d*-electrons to have effective charge some 10—20% *greater* than the nominal value and in *part* explains why metals in second and third transition series react more slowly than those in the first.[9]

[107] Taft, jun., and Cook, *J. Amer. Chem. Soc.*, 1959, **81**, 46.

[108] Adamson, Welker, and Volpe, *J. Amer. Chem. Soc.*, 1950, **72**, 4030; Adamson, Welker, and Wright, *J. Amer. Chem. Soc.*, 1951, **73**, 4786.

react slowly on either an $S_N1$ or an $S_N2$ basis, since in formation of the transition state there will be a loss of crystal-field stabilisation energy which will be an extra (but important) contribution to the energy of activation, compared with that for similar ions not so stabilised. This is the basis for understanding the slow reactions of $d^3$ [Cr(III)], low-spin $d^6$ [Co(III) and certain Fe(II)] complexes, and $d^8$ [Ni(II)] systems. The advantage of the crystal field over the valence-bond treatment (in the simple form visualised by Taube) is its ability to predict, at least semi-quantitatively, differences in energies of activation for the reactions of a series of similar complexes. The difference $\Delta E$ in the crystal-field stabilisation energy (C.F.S.E.) has been calculated for the octahedral (reactant state) and square-pyramidal (transition state) configurations for various $d^n$ systems (Table 7).[4] For the reactions of the bis(terpyridine) complexes[109]

TABLE 7. *Kinetic data and C.F.S.E. for the dissociation of terpyridine complexes at* pH $\sim$ 7 *at* 25°, $k = A \exp(-E/RT)$.[109]

| Electronic system | Complex ion | $10^5k$ (sec.$^{-1}$) | log $A$ (sec.$^{-1}$) | $E$ (kcal. mole$^{-1}$) | $\Delta E(Dq)$ |
|---|---|---|---|---|---|
| $d^5$ | [Mn terpy]$^{2+}$ | Fast | — | — | 0 |
| $d\epsilon^6\, d\gamma^0$ | [Fe terpy$_2$]$^{2+}$ | 0·017 | 14·3 | 28·7 | 4 |
| $d\epsilon^4\, d\gamma^2$ | [Fe terpy]$^{2+}$ | 670 | 11·0 | 18·0 | 0 |
| $d^7$ | [Co terpy$_2$]$^{2+}$ | 67 | 7·7 | 14·8 | 0 |
| $d^8$ | [Ni terpy$_2$]$^{2+}$ | 0·167 | 9·5 | 20·8 | 2 |
| $d^9$ | [Cu terpy]$^{2+}$ | Fast | — | — | 0 |
| $d^{10}$ | [Zn terpy]$^{2+}$ | Fast | — | — | 0 |

there are increasing energies of activation in the sequence, cobalt, nickel, and iron. The increments are about 6—8 kcal. mole$^{-1}$ and this is in good agreement with the estimated increasing C.F.S.E. losses ($\Delta E \approx 2Dq \approx 6$ kcal. mole$^{-1}$). The estimation of the energies of activation for the $d^5$, $d^9$, and $d^{10}$ systems (which should resemble that for $d^7$) will have to be made by using rapid-reaction techniques. A really striking difference is between low-spin [Fe terpy$_2$]$^{2+}$ and high-spin [Fe terpy]$^{2+}$. On either a displacement or a dissociation mechanism, a much larger C.F.S.E. loss would be expected for the diamagnetic than for the paramagnetic iron complex. The difference, 11 kcal. mole$^{-1}$ in the energies of activation, agrees nicely with prediction.

From considerations then of both charge and crystal field, cobalt(III) complexes would be expected to react slowly. This is often observed and any digression from such behaviour can be usually ascribed to the fact that the cobalt–ligand link is not actually being broken during the reacion,[110] *e.g.*, in the rapid decomposition of the amminecobalt(III) hydrogen carbonate complex by acid:[111]

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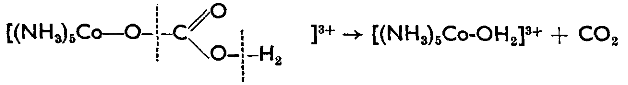
[109] Hogg and Wilkins, *J.*, 1962, 341.

[110] Murmann and Taube, *J. Amer. Chem. Soc.*, 1956, **78**, 4886.

[111] Hunt, Rutenberg, and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 268; Bunton and Llewellyn, *J.*, 1953, 1692.

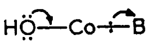


$$[(NH_3)_5Co{-}O{-}C(=O){-}O{-}H_2]^{3+} \rightarrow [(NH_3)_5Co{-}OH_2]^{3+} + CO_2 \quad . \; . \; . \quad (25)$$

Most comparisons have been made so far between elements of the first transition series. Only fragmentary results exist for the second and the third row but when similar compounds can be compared it is usually found that the heavier elements react the more slowly. This is certainly true of the Ni, Pd, Pt triad.[102,112] For example, the ratio of the rates of the reaction (22) for A = *o*-tolyl and M = Ni, Pd, and Pt is $5 \times 10^6:10^5:1$.[102] Some very early kinetic studies showed that rhodium(III) and iridium(III) complexes react much more slowly than the corresponding ones of cobalt(III).[8] This increasing inertness may have crystal-field and "effective ionic charge" behaviour as its basis.[9] Lest one should become too confident of this truth, however, it is worth recalling some recent results of Hertz,[30] where the order of formation rates for bromide and iodide complexes is Hg > Cd > Zn. Finally, the stereochemistry of the metal complex will have some influence. Apart from the considerations outlined above, metals which tend to form planar complexes (or tetragonal structures), *e.g.*, copper(II), may be expected to react rapidly for reasons already considered (see Table 4).[38]

**(b) Ligand Specificity.**—The effect of ligand change is rarely as drastic as that of the metal. However, in the reaction $[MA_nB] + X \rightarrow [MA_nX] + B$, we find that A, B, and X can influence the rate and mechanism of the reaction. Predictions as to the effect on the rate of charge and size of these groups can be made.[4,9] In all cases we must rely on experiments with cobalt(III) and platinum(II).

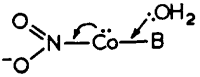
*Substituent present* (A) *but not replaced.* Systematic work on this aspect has been carried out on the hydrolysis of $[Co\ en_2AB]^{n+}$ (reaction 12). The rates are very dependent on the nature and to a smaller extent the position (*i.e.*, *cis* or *trans*) of the non-participating group A (Table 3).* As the electron supply of A diminishes—and this may operate through conjugative (electron-transfer) or inductive (electron-deformation) processes—the ability to promote an $S_N1$ mechanism, *e.g.*:



by assisting the departure of B, diminishes. The rate thus falls to a minimum, OH > $N_3$ > Cl > SCN ~ $NH_3$. A group which can withdraw electrons from cobalt can promote a bimolecular mechanism, *e.g.*:

*A full discussion has been given of the polar effects which influence rate and orientation.[55]

[112] (*a*) Basolo, Gray, and Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 4200; (*b*) Basolo, Bergmann, and Pearson, *J. Phys. Chem.*, 1952, **56**, 22.



and since a conjugative effect such as this is more important than an inductive one, the increased rate can be understood.

Base hydrolysis is much less dependent on the nature of A (see Table 8) and since there is now a *reduced* rate with the nitro-group, the $S_N2$ process assigned is considered one of synchronous bond-fission and -formation, rather than reagent in the lead as in the hydrolysis reaction. Reasons for this behaviour have been suggested.[6] The steric course of base hydrolysis is, however, profoundly influenced by the non-participating ligand.

TABLE 8. *Second-order rate constants* ($k_2$, *l. mole*$^{-1}$ *sec.*$^{-1}$ *at* 0°) *and steric course of reaction* $[\text{Co en}_2\text{ACl}]^{n+} + \text{OH}^- \rightarrow [\text{Co en}_2\text{A(OH)}]^{n+} + \text{Cl}^-$ (ref. 7,113).

| | *cis*-A | | *trans*-A | |
|---|---|---|---|---|
| A | $k_2$ | *cis* (%) | $k_2$ | *cis* (%) |
| OH | 0·37 | 97 | 0·017 | 94 |
| Cl | 15 | 37 | 85 | 5 |
| Br | 23 | 40 | 110 | 0 |
| NCS | 1·4 | 80 | 0·36 | 76 |
| $NH_3$ | 0·50 | 85 | 1·25 | 76 |
| $N_3$ | 0·17 | 51 | 0·41 | 13 |
| $NO_2$ | 0·03 | 66 | 0·08 | 6 |

It has been known for many years that with platinum-(II) and -(IV) complexes a *trans*-effect operates which reflects the tendency of a ligand to direct an incoming group into the *trans*-position. An order of *trans*-effect has been constructed on the results of preparative studies. The kinetic basis of the effect is currently being explored. By examining the ease of replacement of chlorine by pyridine with different A substituents (reaction 22, M=Pt) it was shown in a very interesting study[102] that there are probably two electronic mechanisms of the *trans*-effect. These produce polarisation of metal ion by (*a*) $\pi$-bonding and/or (*b*) electrostatic effects. Both of these enhance nucleophilic attack at the *trans*- and have little effect on the *cis*-position. Examples of (*a*) and (*b*) are phosphine and hydride ion, respectively, both of which are strongly labilising. Table 6 illustrates these points.

*Substituent replaced* (B). In the reaction:

$$[\text{Pt dien X}]^+ + \text{py} \rightarrow [\text{Pt dien py}]^{2+} + \text{X}^- \quad \ldots\ldots\ldots \quad (26)$$

the observed rate constant equals $k_1 + k_2(\text{py})$,[112a] much as with (22). By using either $k_1$ or $k_2$, the following order of decreasing ease of removal is observed: $NO_3 > Cl > Br > I > N_3 > SCN > NO_2 > CN$. This indicates that strong *trans*-activating groups are themselves difficult to

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[113] Chan and Tobe, personal communication.

dislodge. A similar order obtains with cobalt(III) except that the halides are reversed.[112a] However, changes of B (a series of substituted acetates[112b]) in $[Co(NH_3)_5B]^{2+}$ influence markedly the rate of base, but not of acid, hydrolysis, so that the nature of entering nucleophile will also have an influence. From their studies on exchange reactions of platinum(II) complexes, Martin and his colleagues conclude that $H_2O > Cl > NH_3$ in decreasing ease of replacement.[114] Groups already present may, however, modify these sequences.[115] The steric course of acid or base hydrolysis of cobalt(III) appears little affected by the nature of B.

Chelated ligands are usually replaced with more difficulty than unidentate ligands unless strain factors are involved.[44] Substitution within a ligand has predictable effects on the rates of bond cleavage involving it or other ligands.[102,116]

*Entering substituent* (X). It is difficult to set up a scale of nucleophilic power for cobalt(III) because of the overriding complexing power of water, except *via* the rate of substitution of an aquo-complex. By studying the rates of reaction of $[Co(CN)_5H_2O]^{2-}$ with a series of ligands a nucleophilic scale was built up.[59] The value for $k_2/k_{-1}$ (see equation, p. 328) was used and thus the nucleophilicity refers to the 5-co-ordinate intermediate: $OH > N_3 > SCN > SC(NH_2)_2 > I > NH_3 > Br > S_2O_3 > CNO > H_2O$. This agrees with the more limited series in methanol for the reaction[34]

$$[Co\,en_2Cl_2]^+ + X^- \rightarrow [Co\,en_2ClX]^+ + Cl^- \quad \ldots\ldots \quad (27)$$

where, although the usurping power of water is avoided, complications due to ion-pairing may arise. The situation is simpler with platinum(II) since the complexes are often soluble in organic solvents and $S_N2$ reactions are more common. It is thus easier to construct an order of nucleophilic power, roughly:[98] $R_3P$, $SC(NH_2)_2$, SCN, I > $N_3$ > $NO_2$ > py > aniline > olefin, $NH_3$, Br > Cl > glycine, OH, $H_2O$, which shows a general similarity to the Co(III) series, and for that matter the sequence found with organic halides,[117] except in the position of hydroxide which is a very much weaker nucleophile for platinum(II).

The removal of bromine from cobalt(III) complexes:

$$[CoEDTA\,Br]^{2-} \rightarrow [CoEDTA]^- + Br^- \quad \ldots\ldots\ldots \quad (28)$$

in which the ethylenediaminetetra-acetate changes from a 5- to a 6-co-ordinate ligand, see (11), is accelerated by metal ions. The order of increasing electrophilic effect $Fe^{3+} > Cd^{2+} > Tl^+$ is expected on charge considerations.[118]

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[114] Elleman, Reishus, and Martin, jun., *J. Amer. Chem. Soc.*, 1959, **81**, 10.

[115] Grinberg and Kukushkin, *Russ. J. Inorg. Chem.*, 1959, **4**, 139.

[116] Ellis, Hogg, and Wilkins, *J.*, 1959, 3308; Aprile, Caglioti, and Illuminati, *J. Inorg. Nuclear Chem.*, 1961, **21**, 325.

[117] Edwards and Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16; they compare nucleophilic reactivities at saturated carbon and platinum(II) atoms.

[118] Dyke and Higginson, personal communication.

(c) **Change of Solvent.**—It is apparent that a study of reactions in non-aqueous solvents would obviate the problems of ubiquitous water, so apparent from previous sections. At the same time ion-pairing might then become a more important consideration and the necessity to remove even traces of water be important.[119] The very few systematic studies which have been undertaken of reactions in a variety of solvents[97,103] emphasise the key role that solvent plays in the reactions of co-ordination compounds. Adamson[97] showed that the rate constant for removal of the first thiocyanate group from $[Cr(NH_3)_2(SCN)_4]^-$ by solvolysis was approximately constant for hydroxyl solvents but negligibly small for solvents such as nitromethane, where hydrogen bonding was impossible. The kinetic importance of the solvent and the inability of strong nucleophiles to accelerate the rate suggested to Adamson that "pure" $S_N1$ or $S_N2$ reactions could be ruled out and an alternative mechanism was proposed in which the role of the hydroxyl group was paramount.

The strong interaction of solvent and metal ion in the rate-determining step (as required by the "dissociation" mechanism for a planar complex[98]) is shown by the importance of the solvent on the reaction order for the simple exchange process:[103]

$$trans\text{-}[Pt\ py_2Cl_2] + {}^*Cl^- \rightleftharpoons trans\text{-}[Pt\ py_2{}^*Cl_2] + Cl^- \quad . \quad . \quad . \quad . \quad (29)$$

Solvents with potentially vacant orbitals, *e.g.*, nitromethane, were particularly effective in aiding the rate, probably because of their ability to $\pi$-bond with the platinum(II), and thus approach nearer and help displace the chlorine.

The second-order substitution of $N_3^-$ into *cis*-$[Co\ en_2Cl_2]^+$ (but not the *trans*-isomer) in methanol can be interpreted as either an $S_N2$ or an $S_N2IP$ (or $S_N1IP$) reaction, with *ion-pairing* (30a) an important pre-equilibrium in the latter cases:

$$[Co\ en_2Cl_2]^+ + X^- \rightleftharpoons [Co\ en_2Cl_2]^+ \ldots X^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30a)$$

$$[Co\ en_2Cl_2]^+ \ldots X^- \xrightarrow{\text{Slow}} [Co\ en_2ClX]^+ + Cl^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30b)$$

In the special case of $X = OMe^-$, an $S_N1CB$ mechanism is also possible. For these reactions in methanol, first-order kinetics observed with certain nucleophilic reagents (see Table 1) are more likely to arise from an $S_N1$ than from an $S_N2$ reaction involving the weakly nucleophilic methanol.[120] The advantages of thus studying substitution, racemisation, and isomerisation phenomena in non-aqueous solvents without accompanying hydrolysis are still offset by interpretative difficulties.

(d) **Catalysis.**—Homogeneous, heterogeneous, and photo-catalysis have all been observed in kinetic studies involving co-ordination compounds.

*Homogeneous.* Acceleration of rate by added ligand or metal ion can

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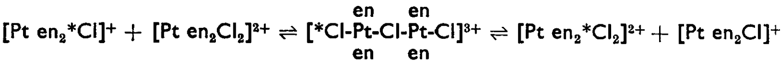
[119] Slaten and Garner, *J. Phys. Chem.*, 1959, **63**, 1214.

[120] Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379, 5382.

occur in certain circumstances.[121] $10^{-6}$M-Hg(II) ion accelerates the hydrolysis of $\mathrm{Fe(CN)_6}^{4-}$.[122] Probably the most important catalysis, however, involves redox processes. Thus $\mathrm{Cr}^{2+}_{q}$ (labile) catalyses $\mathrm{Cr}^{3+}_{aq}$–$\mathrm{H_2O}$ exchange *via* the rapid $\mathrm{Cr}^{2+}_{aq}$–$\mathrm{Cr}^{3+}_{aq}$ electron transfer,[123a] and cobalt(II) catalyses reactions of cobalt(III).[123b] A study of the reaction kinetics of platinum(IV) is fraught with dangers from traces of Pt(III)[52,124] or Pt(II).[125] Thus exchange of chloride with $[\mathrm{Pt\ en_2Cl_2}]^{2+}$ occurs only in the presence of Pt(II), and the rate law $R = k_3[\mathrm{Pt(IV)}][\mathrm{Pt(II)}][\mathrm{Cl^-}]$ can be explained by:[126]

$$[\mathrm{Pt\ en_2}]^{2+} + {}^*\mathrm{Cl}^- \rightleftharpoons [\mathrm{Pt\ en_2{}^*Cl}]^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (31a)$$



$$[\mathrm{Pt\ en_2{}^*Cl}]^+ + [\mathrm{Pt\ en_2Cl_2}]^{2+} \rightleftharpoons [{}^*\mathrm{Cl}\text{-}\overset{\mathrm{en}}{\underset{\mathrm{en}}{\mathrm{Pt}}}\text{-}\mathrm{Cl}\text{-}\overset{\mathrm{en}}{\underset{\mathrm{en}}{\mathrm{Pt}}}\text{-}\mathrm{Cl}]^{3+} \rightleftharpoons [\mathrm{Pt\ en_2{}^*Cl_2}]^{2+} + [\mathrm{Pt\ en_2Cl}]^+ \quad (31b)$$

*Heterogeneous.* Certain substances (for example, active charcoal and mercury) appear capable of labilising metal–ligand bonds. This has been observed particularly with cobalt(III) complexes, although even here the studies are fragmentary. Isomerisation[127] and racemisation[128] of cobalt(III)–ethylenediamine complexes can be markedly accelerated by addition of active charcoal. This solid appears to have a dual role:[129] (*a*) it converts small amounts of the low-spin $[\mathrm{Co\ en_3}]^{3+}$ into a high-spin state, which it can then reduce to high-spin $[\mathrm{Co\ en_3}]^{2+}$ and (*b*) it catalyses the electron-transfer process

$$\begin{aligned} d\text{-}[\mathrm{Co\ en_3}]^{3+}\ (\text{low-spin}) + l\text{-}[\mathrm{Co\ en_3}]^{2+}\ (\text{high-spin}) &\rightarrow \\ l\text{-}[\mathrm{Co\ en_3}]^{3+} + d\text{-}[\mathrm{Co\ en_3}]^{2+} &\rightleftharpoons l\text{-}[\mathrm{Co\ en_3}]^{2+} \quad . \; . \; . \; . \quad (32) \end{aligned}$$

Small amounts of cobalt(II) are found. That the charcoal is involved in a redox process is indicated by the fact that *l*-$[\mathrm{Pt\ en_3}]^{4+}$ is less readily racemised, while *l*-$[\mathrm{Rh\ en_3}]^{3+}$ is stable to charcoal treatment even on boiling for some time.[130] Certain polarographic observations on the rate of reduction of $[\mathrm{Co(NH_3)_5X}]^{2+}$ at the dropping-mercury electrode can be understood on the basis that the substitution $[\mathrm{Co(NH_3)_5X}]^{2+} + \mathrm{Cl^-} \rightarrow [\mathrm{Co(NH_3)_5Cl}]^{2+} + \mathrm{X^-}$ occurs at the mercury surface much faster than in bulk solution.[131]

*Photocatalysis.* Once again, little systematic investigation of this often-

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[121] Beck, *J. Inorg. Nuclear Chem.*, 1960, **15**, 250; he classifies and discusses homogeneous and heterogeneous catalysis of complex formation.

[122] Ašperger and Pavlovic, *J.*, 1955, 1449.

[123] (*a*) Plane and Taube, *J. Phys. Chem.*, 1952, **56**, 33; (*b*) Ellis, Wilkins, and Williams, *J.*, 1957, 4456.

[124] Rich and Taube, *J. Amer. Chem. Soc.*, 1954, **76**, 2608; Pöe and Vaidya, *J.*, 1961, 2981.

[125] Ellison, Basolo, and Pearson, *J. Amer. Chem. Soc.*, 1961, **83**, 3943.

[126] Basolo, Wilks, Pearson, and Wilkins, *J. Inorg. Nuclear Chem.*, 1958, **6**, 161; see also Cox, Collins, and Martin, jun., *J. Inorg. Nuclear Chem.*, 1961, **17**, 383.

[127] Bjerrum and Rassmussen, *Acta Chem. Scand.*, 1952, **6**, 1265.

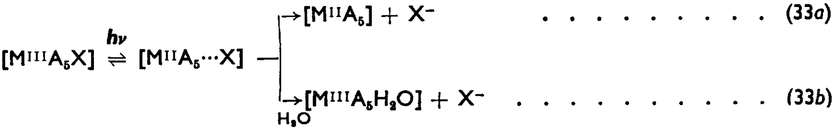
[128] Douglas, *J. Amer. Chem. Soc.*, 1954, **76**, 1020.

[129] Dwyer and Sargeson, *Nature*, 1960, **187**, 1022.

[130] Sen and Fernelius, *J. Inorg. Nuclear Chem.*, 1959, **10**, 269.

[131] Vlcek and Kuta, *Nature*, 1960, **185**, 95; Watt and Vaughn, *Nature*, 1960, **186**, 309.

observed phenomenon can be reported. The photochemical reactions of metal complexes can be understood on the basis of a chemical mechanism[132] in which absorption of a light quantum results in homolysis of the ligand–metal bond. If the products are formed with sufficient energy to escape completely, the net result is a redox reaction (33*a*). If re-formation occurs the total quantum yield is reduced, and if "back-electron transfer" occurs (33*b*) aquation results, *e.g.*:



$$[\mathrm{M^{III}A_5X}] \overset{h\nu}{\rightleftharpoons} [\mathrm{M^{II}A_5\cdots X}] \begin{cases} \rightarrow [\mathrm{M^{II}A_5}] + \mathrm{X^-} & \ldots\ldots\ldots\ldots (33a) \\ \xrightarrow[\mathrm{H_2O}]{} [\mathrm{M^{III}A_5H_2O}] + \mathrm{X^-} & \ldots\ldots\ldots\ldots (33b) \end{cases}$$

This simple idea can account for the facts that photochemical reactions of cobalt(III) and iron(III) are often of redox type while those of chromium(III) and iron(II) usually result in aquation. In certain cases the energy of the light quantum and the ease of oxidation of the acido-group will be important.[133] However some role surely must be ascribed to the photochemically excited state and, with chromium(III) at least, photocatalysis may involve reaction when the complex is in the lowest spin-forbidden electronic state.[134]

**(e) Thermodynamic Stability and Kinetic Reactivity.**—It is often stressed that there is not necessarily any connection between kinetic and thermodynamic behaviour, and there are certainly examples with co-ordination compounds where this is true. Thus, the inertness of complex cyanides does not parallel their stability.[108,135] Nevertheless, since in simple cases the stability constant is equal to the ratio of formation and dissociation rate constants ($K = k_1/k_{-1}$)

$$\mathrm{A + B} \overset{K}{\rightleftharpoons} \mathrm{AB} \qquad k_1, k_{-1} \qquad \ldots\ldots (34)$$

should $k_1$ (or $k_{-1}$) remain sensibly constant with change of structure in A or B, then obviously the other rate constant will parallel concomitant changes in $K$. This behaviour is observed with the formation of metal sulphate and nickel diamine complexes and has been referred to in Section 3(*b*).

Some other examples, necessarily incomplete, of observed relations between kinetic and thermodynamic parameters are shown by rates of reaction of diamine complexes of nickel,[136] ethylenediaminetetra-acetate complexes of metals,[67] halide complexes of chromium,[77] iron,[89,90] cobalt,

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[132] Adamson and Sporer, *J. Amer. Chem. Soc.*, 1958, **80**, 3865; Adamson, *J. Inorg. Nuclear Chem.*, 1960, **13**, 275.

[133] Adamson, *Discuss. Faraday Soc.*, 1960, **29**, 163.

[134] Plane and Hunt, *J. Amer. Chem. Soc.*, 1957, **79**, 3343; Edelson and Plane, *J. Phys. Chem.*, 1959, **63**, 327.

[135] MacDiarmid and Hall, *J. Amer. Chem. Soc.*, 1954, **76**, 4222.

[136] Ahmed and Wilkins, *J.*, 1960, 2895.

and platinum[112,124b] and zinc, cadmium, and mercury.[30] In the last case, for example, attention is drawn to a rough relation between increasing formation rate and stability with bromide and iodide complexes.

## 7. General Conclusions and Future Developments

It will be apparent from the foregoing that a surplus of conflicting mechanisms exists, even for the simple hydrolytic processes in acid and base solution. Obviously it will be necessary to devise key experiments to resolve these problems. Here there will be scope for experiments with both conventional apparatus and the techniques for fast reactions. Indeed, in the latter respect, the subject is on the threshold of exciting developments since so many of the reactions of complexes, especially of the first transition series, are rapid and hitherto unmeasured. The impact of the results on the understanding of inorganic, analytical, and biological problems can be imagined.

More intensive examination of complexes of elements other than those of the transition series is also required (a start having been made with, for example, boron,[137] silicon,[138] and arsenic[139]) and of complexes containing ligands (such as carbon monoxide and phosphines[140]) where interesting questions of bonding arise and which may be answered in part by kinetic studies. The examination of polynuclear hydroxy-complexes by rapid techniques[141] has begun but here, as elsewhere, the kinetic aspects have lagged behind the thermodynamic work. There are signs that this has been recognised and an attempt is being made to reduce the leeway. The rewards will surely be great.

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[137] Ryschkewitsch, *J. Amer. Chem. Soc.*, 1960, **82**, 3290.

[138] Dhar, Doron, and Kirschner, *J. Amer. Chem. Soc.*, 1959, **81**, 6372.

[139] Craddock and Jones, *J. Amer. Chem. Soc.*, 1961, **83**, 2839.

[140] Ref. 10, p. 68; Strohmeier and Mittnacht, *Z. phys. Chem. (Frankfurt)*, 1961, **29**, 339.

[141] Schwarzenbach and Meier, *J. Inorg. Nuclear Chem.*, 1958, **8**, 302; Wendt, *Z. Electrochem.*, 1962, **66**, 235.