These results not only confirm the general reliability of Mathieu's data and the validity of equation 5 but show that ellipticity data can provide the necessary information for the resolution of rotatory dispersion curves into their individual components. If the curves can be resolved, it is then possible to correlate the rotatory dispersion data with spectral data and assign the transitions. The ellipticity curves permit one to detect small or very large splittings and make assignments in cases where no splitting is evident from absorption spectra.

The agreement between the calculated and the measured curves is very good. The addition of the expected contribution from the ultraviolet inversion center should make the calculated and measured curves coincide. It is indeed remarkable that Mathieu's extensive, but little recognized, work of thirty years ago gives such good agreement with modern theory. It should be kept in mind that the ellipticity data used here were read from graphs published by Mathieu. An improvement in the data might be expected to produce even better agreement between the calculated and the measured curve. When circular dichroism data are available in the region of the second visible absorption band (weak as it must be[6]) and the ultraviolet absorption bands, this approach should lead to an unambiguous resolution of the observed rotatory dispersion curves.

Work is planned to measure ellipticities and extend the calculations over a wider wave length range. The use of ellipticity parameters and rotational strengths in dealing with structural and stereochemical problems as well as the theoretical implications of these results to the mechanism of rotation and the nature of vibrations that bring about the optical absorption will be the subject of later papers.[29]

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Nucleophilic Substitution Reactions in Octahedral Complexes

BY RALPH G. PEARSON, DAVID N. EDGINGTON AND FRED BASOLO

RECEIVED JANUARY 26, 1962

The dissociation of octahedral tris-(acetylacetonato)-silicon(IV) cation is subject to catalysis by a variety of nucleophilic reagents. The relative rates form a series which is entirely reasonable if the mechanism of the slow step is an S_N2 displacement process in which the nucleophile pushes off one end of an acetylacetonate ligand. This seems to be the first clear-cut example of an S_N2 mechanism in an octahedral complex. Basicity, rather than polarizability, of the nucleophile is the dominant factor in determining its reactivity with this particular substrate.

Octahedral complexes, particularly of the transition metal ions, appear to have a strong preference for dissociation (S_N1) mechanisms in their substitution reactions.[1] At the present time there is no well substantiated case of a displacement (S_N2) mechanism in an octahedral system. A number of possible examples have appeared in the literature.[2] These all suffer from being fairly complex systems where alternative explanations are possible. Furthermore, generality has not been demonstrated in these cases. In a well behaved system it is expected that a variety of nucleophilic reagents (ligands) will be found to be effective and that their respective second order rate constants will bear some clear relationship to recognized nucleophilic properties.

The reaction of *cis*-$[Co(en)_2Cl_2]^+$ with a variety of reagents in methanol has been reported.[3] The apparently convincing result that some reagents (basic anions) react by an S_N2 mechanism is invalidated by recent observations. One is that the major influence of these basic ions is due to the methoxide ion which they generate by reaction with the solvent.[4] The small residual effect is almost certainly due to ion-pair formation in which the ion-pair is more reactive than the original complex cation. This is best shown by a recent study of the effect of basic anions on the rate of aquation of $[Cr(NH_3)_5Cl]^{2+}$ in water.[5] The rate constants for various basic anions correlate perfectly with the ion-pair association constants of the same anions with $[Co(NH_3)_6]^{3+}$. Also the product of reaction continues to be $[Cr(NH_3)_5H_2O]^{3+}$ instead of the expected product if the anion functioned as a nucleophile.

There are two possible reasons why displacement mechanisms are uncommon for octahedral complexes. One is that an expanded coördination number is a requirement for such a process. It may be sterically difficult to arrange seven groups around a central metal ion if the ion is small. Even for larger ions, six ligands may be much more stable than seven if the ligands are polyatomic. Hence, van der Waals and electrostatic ligand repulsions may hinder an S_N2 mechanism. The second barrier to S_N2 mechanisms is specific for the transition metal ions. Partly filled *d*-orbitals produce a crystal field stabilization in the ground state which usually resists the change from octahedral coördination to seven-

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(1) For discussions see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Ch. 3; F. Basolo and R. G. Pearson, "Substitution Reactions of Metal Complexes," Advances in Inorganic and Radiochemistry, Vol. III, H. J. Emeleus and A. G. Sharpe, Editors, Academic Press, Inc., New York, N. Y., 1961; R. G. Pearson, *J. Chem. Ed.*, **38**, 164 (1961); D. R. Stranks, "Modern Coördination Chemistry," R. G. Wilkins and J. Lewis, Editors, Interscience, New York, N. Y., 1960.

(2) A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 2981 (1961); A. L. Hope and J. E. Prue, *ibid.*, 2782 (1960); D. W. Cooke, G. A. Im and D. H. Busch, *Inorg. Chem.*, **1**, 13 (1962); D. W. Margerum and L. P. Morgenthaler, "Advances in the Chemistry of the Coördination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 481.

(3) D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2674 (1953).

(4) R. G. Pearson, P. M. Henry and F. Basolo, *J. Am. Chem. Soc.*, **79**, 5379, 5382 (1957).

(5) T. P. Jones, W. E. Harris and W. J. Wallace, *Can. J. Chem.*, **39**, 2371 (1961).

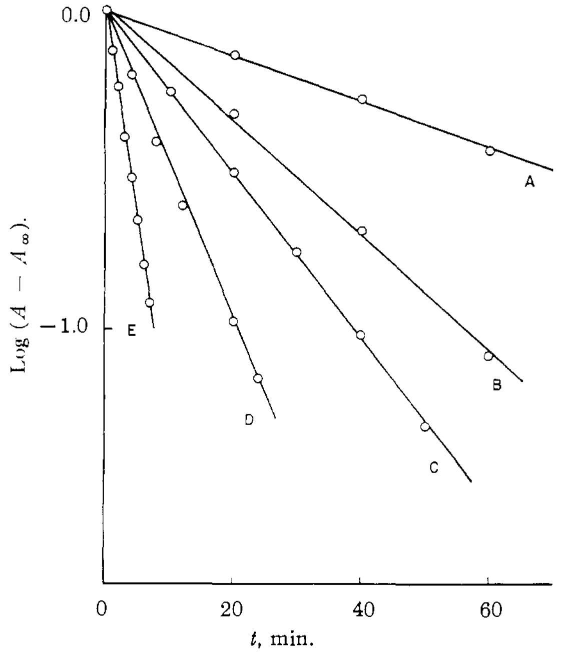

Fig. 1.—Typical first order plots of the experimental data: A, 0.050 *M* total phosphate + 0.100 *M* $NaClO_4$, pH = 5.66; B, 0.050 *M* total phosphate + 0.050 *M* $NaNO_2$, pH = 7.20; C, 0.050 *M* total phosphate + 0.100 *M* $NaClO_4$, pH = 7.62; D, 0.050 *M* total phosphate + 0.100 *M* $Na_2S_2O_3$, pH = 7.20; E, 0.050 *M* total phosphate + 0.0882 *M* H_2O_2, pH = 5.64; $[OOH^-] = 5.8 \times 10^{-8}$ *M*.

coördination of any geometry.[1] This is particularly true for the well studied d^3 and spin-paired d^6 metal ions. Furthermore in d^6 ions, such as cobalt(III), the *d* electrons fill up the octahedral faces and edges which are the natural points of attack for an incoming reagent.

To minimize the effects of the *d* electrons it was decided to study the substitution reactions of some octahedral complexes of the non-transition elements. Little work has been done in this area because relatively few systems are known and often they are extremely labile. The hydrolysis of SiF_6^{2-} is reported to be independent of the hydroxide ion concentration[6]; AsF_6^- and PF_6^- are completely stable in alkaline solution, even on boiling[7]; the triscatecholate of arsenic(V) does not show base acceleration of hydrolysis.[8]

All of the above systems have the disadvantage of being negatively charged and arsenic(V) also has a filled *d* shell for its outer electrons. A more promising example appears in the recent work of Dhar, Doron and Kirschner.[9] These workers have described the hydrolysis and racemization of the tris-(acetylacetonato)-silicon(IV) cation. They found that the rates of hydrolysis and racemization were the same and independent of acid concentration. However, they found that if the pH was increased to 9.2 there was a large increase in the rate of hydrolysis. If the solutions are not buffered there is a drop in pH during hydrolysis, and this can be accounted for by the reactions

$$Si(acac)_3^+ + 5H_2O \longrightarrow Si(OH)_4 + 3Hacac + H_3O^+$$

$$xSi(OH)_4 \longrightarrow (SiO_2)_x(H_2)_{2x-y} + yH_2O$$

We will show in this paper that this hydrolysis is an example of a true S_N2 reaction for an octahedral complex. The evidence will be that a variety of nucleophilic reagents catalyze the decomposition of the complex.

Experimental

The tris-(acetylacetonato)-silicon(IV) chloride hydrochloride, $[Si(acac)_3]^+ HCl_2^-$, was prepared as described by Dilthey.[10] The crude product was found to be stable over a long period of time, whereas if it were purified, it decomposed fairly rapidly on standing in a desiccator into a brown product of unknown composition. Small samples of the crude product were purified before each series of kinetic experiments. A pure sample was obtained by dissolving the impure material in a small amount of chloroform, filtering off the insoluble residue (presumably SiO_2) and then adding this solution very slowly into a briskly stirred large excess of ether. The pure complex separated out, was filtered off and air dried.

Kinetic Experiments.—All the kinetic experiments were carried out by following the decrease in the intensity of the absorption band of the complex in the ultraviolet using a Beckmann DB spectrophotometer linked to a recorder which gave a direct record of the change in optical transmission with time. Even though the absorption maximum for the complex was at 284 mμ, $\epsilon = 3.6 \times 10^6$, the experiments were carried out at a wave length of 305 mμ where the difference between the extinction coefficients of the reactants and products is greatest. This becomes more important at higher *p*H's where the spectra of the complex and the products are very similar. This is because the spectrum of the acetylacetone anion is almost identical with the spectrum of the complex. We have verified the work of Dhar, Doron and Kirschner in that the absorption spectrum of the acidified products is the same as that of the same concentration of acetylacetone, and also that, at the concentrations of complex being used for the experiments, 10^{-5} to 10^{-4} *M*, there are no difficulties due to the precipitation of hydrated silicon oxides.

The spectrophotometer cell was kept at a constant temperature of 25 ± 0.1°, and all the solutions required for the experiments were kept in a thermostat set at the same temperature. A typical experiment consisted of preparing a solution containing the required concentrations of buffer and neutral salt. Immediately after adding a suitable aliquot portion of the silicon complex, such that its concentration in the working solution was 5×10^{-5} *M*, a sample was placed in a 1 cm. quartz cell which was already in the cell compartment of the spectrophotometer. This minimized any errors due to changing temperatures of the solutions. Reagent blanks were always used in the reference cell.

The pH of the solution was determined sometime during the course of the reaction and at the end. The values always agreed within experimental error. Hydroxide ion concentrations were calculated from measured pH.

The variation of optical density with time was determined from the experimental curves and the data plotted according to the first order rate law

$$\log (A - A_\infty) = -kt/2.303$$

where *A* denotes optical density at time *t*, and A_∞ the optical density at infinite time. Typical experimental results are shown in Fig. 1. The reactions appear to be first order over the whole range that can be determined experimentally. This usually meant several half-lives.

Results

Preliminary experiments quickly confirmed the work of Dhar, Doron and Kirschner that in dilute acid media there was a slow hydrolysis which is independent of acid concentration. However, when the pH is above a value of six, there is an increase in the rate of hydrolysis, and this rate has been shown to be dependent on pH, or more specifically on the hydroxide ion concentration.

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[6] A. G. Rees and L. J. Huddleston, *J. Chem. Soc.*, 1334 (1936).

[7] W. Lange, *Ber.*, **63B**, 1058 (1930); H. M. Dess and R. W. Parry, *J. Am. Chem. Soc.*, **79**, 1589 (1957).

[8] J. H. Craddock and M. M. Jones, *ibid.*, **83**, 2839 (1961).

[9] S. K. Dhar, V. Doron and S. Kirschner, *ibid.*, **81**, 6372 (1959).

[10] W. Dilthey, *Ber.*, **36**, 932, 1595 (1903).

TABLE I

THE OBSERVED FIRST ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF $[Si(acac)_3]^+$ IN PHOSPHATE AND BORATE BUFFERS

0.005 M total phosphate, 0.1 M $NaClO_4$ (added salt), $T = 25°$

pH	<6	5.66	6.06	6.46	6.86	7.12	7.35	7.62	7.30[a]	8.65[a]
$[OH^-] \times 10^9$ (M)	..	4.6	11.5	28.8	72.4	132	224	417	199	4470
$k \times 10^4$, sec.$^{-1}$ obsd.	2.69	2.69	2.76	3.07	4.06	4.96	6.55	10.1	6.9	76.7

[a] 0.005 M borate in place of the phosphate.

The results in phosphate and borate buffers are given in Table I and can be represented by an equation

$$k_{obsd} = k_{H_2O} + k_{OH}[OH^-] \qquad (1)$$

where $k_{obsd.}$ = experimentally determined pseudo first order rate constant, k_{H_2O} = rate constant in acid media and k_{OH} = rate constant due to basic hydrolysis, a second order rate constant. Values of $k_{obsd.}$ plotted against $[OH^-]$ are shown in Fig. 2, the intercept giving the value of k_{H_2O} and the slope the value of k_{OH}. The results fit the equation over the whole range measured experimentally. From the graph $k_{H_2O} = 2.6 \times 10^{-4}$ sec.$^{-1}$ (*cf.* Dhar, Doron and Kirschner who found 2.4×10^{-4} sec.$^{-1}$) and $k_{OH} = 1.7 \times 10^3$ sec.$^{-1}$ M^{-1}.

In addition it was found that the rate of reaction depended on the composition of the reaction medium. Whereas increasing the concentration of perchlorate ion in the reaction medium reduced the rate of reaction, the converse was true for the phosphate ion. These results are shown in Table II. From the table it is apparent that the increase in rate with increasing total phosphate concentration becomes greater as the pH increases. Below pH 7 the concentration of the buffer anion has little effect on the observed rate. The increase in rate with increase in total phosphate ion concentration and pH is greater than would be predicted from the change in $[OH^-]$ alone, so this is evidence that HPO_4^{2-} ion is acting as a nucleophilic reagent. The observed rate for this nucleophile (and others) can be represented by a similar equation to (1), except that it now has at least three terms.

TABLE II

THE VARIATION OF THE SPECIFIC REACTION RATES IN PHOSPHATE BUFFERS. $T = 25°$

$[ClO_4^-]$	$[PO_4]$total	pH	$[OH^-] \times 10^7$	$k_{obsd.}$, sec.$^{-1}$ $\times 10^4$
0.100	0.05	7.42	2.63	8.79
.050	.05	7.50	3.16	10.0
.045	.05	7.48	3.02	10.4
.025	.05	7.50	3.16	11.7
.000	.05	7.52	3.31	13.1
.100	.05	7.17	1.49	5.69
.100	.025	7.17	1.49	5.49
.100	.050	7.42	2.63	8.79
.100	.025	7.42	2.63	8.29

$$k_{obsd.} = k_{H_2O} + k_{OH}[OH^-] + k_X[X] \qquad (2)$$

where X is the nucleophilic reagent. Several other possible nucleophilic reagents were added to phosphate buffers and in each case an increase in rate was observed. From the increase an approximate value of k_X could be calculated. The results are shown in Table III.

TABLE III

THE EFFECT OF VARIOUS NUCLEOPHILES ON THE RATE IN PHOSPHATE BUFFERS. $T = 25°$

$[PO_4]_t = 0.05$ M

Nucleophile X	[X]	pH	$[OH^-] \times 10^7$	$k_{obsd.} \times 10^4$	$k_{corr} \times 10^{4a}$	$k_X \times 10^4$ M^{-1} sec.$^{-1}$
Thiourea[b]	0.100	5.40	0.025	2.87	0.18	1.8
Iodide	.100	7.25	1.78	5.99	0.30	3.0
Fluoride	.100	7.25	1.78	7.44	1.75	17
Nitrite	.050	7.20	1.58	7.44	1.75	35.0
Thiosulfate[b]	.100	7.22	1.66	18.4	12.7	130
Hydrogen	2.21	1.00	10^{-6}	3.18	0.49	0.22
peroxide	4.42	1.00	10^{-6}	3.87	1.18	0.26

[a] $k_{corr} = k_{obsd} - (k_{H_2O} + k_{OH}[OH^-] + k_{HPO_4}[HPO_4^{2-}])$.
[b] Duplicate runs reproduced to better than 5%.

The value of k_X for the HPO_4^{2-} was found by using the difference between the observed rate constants in Table II and rate constants at the same pH interpolated from the data in Table I. For the other nucleophiles it was necessary to correct for the rates due to water, hydroxide ion and phosphate ion. It is clear that in several cases the values of k_X are not very reliable because they are small. The nucleophiles OOH^-, NH_2OH and NH_2NH_2 were examined in more detail as they were found to give very large increases in the rate of reaction. On varying the concentration, results such as shown in Fig. 3 were found. From such plots the values of k_X were calculated.

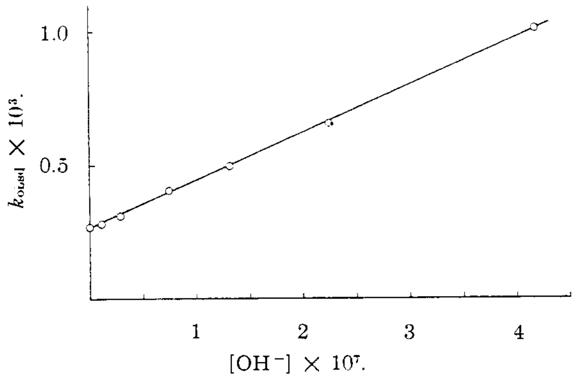


Fig. 2.—The variation of k_{obsd} with hydroxyl ion concentration.

The data for all the nucleophiles studied are shown in Table IV, together with the values for their acid dissociation constants.

Discussion

The results of Table IV show that a variety of reagents can influence the rate of dissociation of $[Si(acac)_3]^+$. It remains to show that the relative catalytic constants follow an order consistent with

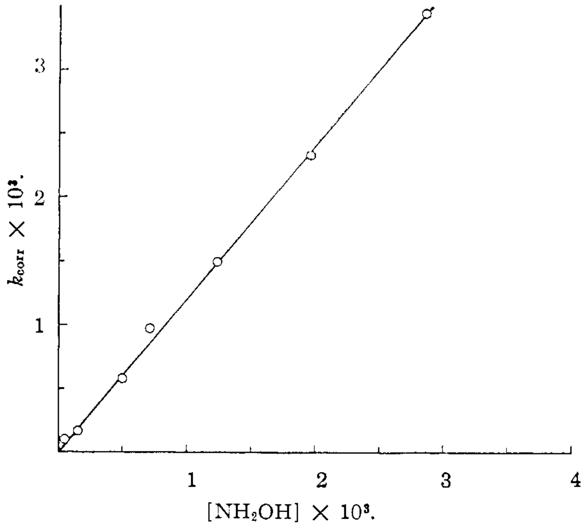


Fig. 3.—The variation of k with hydroxylamine concentration, $k = k_{obsd} - k_{H_2O} - k_{OH}[OH]$.

the initial mechanism being a nucleophilic attack on octahedral silicon(IV). One end of an acetylacetonate group would be displaced in the rate determining step and a rapid loss of the remaining ligands must follow. The latter statement follows from the observed first order kinetics. It is not expected that stable products would be formed in which X is bonded to silicon, and SiO_2 would be the final product. The possibility that nucleophilic attack occurs at a carbonyl group of the ligands is discounted because the final spectra are clearly those of acetylacetone or its anion. Reaction at the carbonyl group would lead to carbon–carbon bond cleavage with the formation of acetone and acetic acid.[11]

TABLE IV

SUMMARY OF DATA OBTAINED FOR THE EFFECT OF VARIOUS NUCLEOPHILIC REAGENTS ON THE RATE OF REACTION

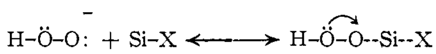
Nucleophile	K_A	k_X M^{-1} sec.$^{-1}$	k_X M^{-1} sec.$^{-1}$ calcd.
OH^-	1.1×10^{-16}	1.7×10^3	1.7×10^3
HOO^-	1.5×10^{-12}	8.0×10^4	17.5
NH_2NH_2	3.98×10^{-9}	18	3.81×10^{-1}
HPO_4^{2-}	7.5×10^{-8}	3.2×10^{-2}	9.3×10^{-2}
HOOH	....	2.4×10^{-5}	....
NH_2OH	1.58×10^{-6}	1.2	2.15×10^{-2}
F^-	1.8×10^{-5}	1.7×10^{-3}	6.5×10^{-3}
NO_2^-	4×10^{-4}	3.5×10^{-3}	1.5×10^{-3}
$S_2O_3^{2-}$	1.38×10^{-2}	1.3×10^{-2}	2.7×10^{-4}
$(NH_2)_2CS$	8.7	1.8×10^{-4}(?)	1.2×10^{-5}
H_2O	55.5	4.9×10^{-6}	4.9×10^{-6}
I^-	(10^9)	3.0×10^{-4}(?)	(10^{-9})

In a recent paper Edwards and Pearson[12] have shown that three factors determine nucleophilic reactivity, exclusive of steric and solvation effects. These are basicity, polarizability and the presence of unshared pairs of electrons on an atom adjacent to the nucleophilic atom, the Alpha Effect. As a starting point to assess the importance of basicity, the Brönsted equation may be used.[13] Arbitrarily

$$k_X = GK_{BX}^{\beta} = G(1/K_{AX})^{\beta} \qquad (3)$$

using water and hydroxide ion as a basis, G was found to be 3.4×10^{-5} M^{-1} sec.$^{-1}$ and β was equal to 0.48. The other values of k_X using these values were calculated and are shown in the last column of Table IV. It is seen that a fair correlation exists. The polarizable reagents $S_2O_3^{2-}$, I^- and thiourea are more reactive than predicted, though the observed rate enhancements for the last two are so small that the true values of k_X may be much less than those reported.

The hydroperoxide ion, hydroxylamine, hydrazine and, probably, hydrogen peroxide are all much more reactive than expected on the basis of basicity or polarizability. These enhanced reactivities are examples of the Alpha Effect.[11] The reagents all have a pair of unshared electrons on the atom alpha to the nucleophilic atom. The explanation given for the increased reactivity is that this pair of electrons stabilizes the transition state by compensating for the electron loss suffered by the nucleophilic atom,[11] *e.g.*



$$\text{H–}\ddot{\text{O}}\text{–}\overset{-}{\text{O}}\text{:} + \text{Si–X} \longleftrightarrow \text{H–}\ddot{\text{O}}\text{–O--Si--X}$$

The Alpha Effect has been noted in nucleophilic displacements on activated esters, peroxides, nitriles, tetrahedral phosphorus and activated double bonds.[12] This is the first example reported for a metal or semi-metal complex.

This silicon(IV) system, from the large value of β in equation 3, is one which shows a very high dependence on basicity compared to, say, tetrahedral carbon substrates. The low reactivity of iodide ion and thiourea shows that the effect of polarizability is small compared to tetrahedral carbon. The strong dependence on the basicity of the nucleophile is entirely as expected according to the criteria discussed in reference 11; a high positive charge on the central atom and empty outer d orbitals of low energy permit the ready acceptance of reagents such as hydroxide ion. Thus silicon(IV) is a substrate in the same class as the proton, carbonyl carbon, tetrahedral sulfur, tetrahedral phosphorus, trigonal boron and tetrahedral halogen.[14]

The naïve expectation that hydroxide ion will be a good nucleophilic reagent for all metal complexes is invalidated by studies of the planar complexes of platinum(II). For planar complexes, S_N2 mechanisms have been found without exception and a well defined nucleophilic reactivity series exists.[1] In this series hydroxide ion is found to have no measurable nucleophilic power, being indistinguishable from water as far as rate of reaction is concerned. In fact basicity as such seems to be playing no role for platinum(II) complexes and unsaturation, or polarizability, in the nucleophile is the dominant factor. This can be reasonably explained in terms of interaction with the d orbital electrons of the metal ion.[15]

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[11] R. G. Pearson, D. H. Anderson and L. L. Alt, *J. Am. Chem. Soc.*, **77**, 527 (1955), and earlier papers referenced therein.

[12] J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962); see also W. P. Jencks and J. Carriuolo, *ibid.*, **82**, 1778 (1960).

[13] J. N. Brönsted and K. Pedersen, *Z. physik. Chem.*, **A108**, 185 (1923).

[14] To the examples previously discussed,[12] that of tetrahedral iodine (V) in the iodate ion may be added. See M. Anbar and S. Guttman, *J. Am. Chem. Soc.*, **83**, 781 (1961).

[15] Ref. 1 and R. G. Pearson, H. B. Gray and F. Basolo, *ibid.*, **82**, 787 (1960).

Thus divalent platinum is an example of the class of substrates which includes peroxide oxygen, divalent sulfur, monovalent halogen, and to a considerable extent, tetrahedral carbon.[11] These substrates respond chiefly to polarizability in the nucleophile and basicity is of little or no importance. It is expected that other metal complexes in which the metal atom is of low positive charge and surrounded by many *d*-orbital electrons, will fall into the same category.

In summary then, the rate data of Table IV show a nucleophilic series whose order can be interpreted according to well established principles. It seems quite reasonable to say that the values of k_X refer to S_N2 displacement processes, the first well established cases for an octahedral system. Other cationic octahedral complexes of high positive charge for the central atom and with few or no *d* electrons should show similar behavior.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

Ligand Exchange. I. Equilibria

BY F. HELFFERICH

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Sorption of complexing agents from solutions by ion exchangers containing a complexing metal ion as the counter ion ("ligand sorption") and exchange of complexing agents between solutions and such ion exchangers ("ligand exchange") are investigated. Equations for ligand-sorption and ligand-exchange equilibria are derived. The equations can be used for predicting equilibria from tabulated complex stability constants. Experimental results with Amberlite IRC-50 in Ni^{2+}, Cu^{2+}, Zn^{2+} and Ag^+ forms and ammonia and 1,3-diaminopropanol-2 as the ligands are in satisfactory agreement with the theory.

Introduction

"Ligand exchange"[1] is a novel application of ion exchangers and provides a useful technique for separating and isolating compounds which can form complexes or adducts with metal ions. An ion exchanger containing a complexing metal ion such as Cu^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Co^{3+}, Fe^{3+}, etc., as the counter ion is used as a solid sorbent. The potential ligands, for example ammonia, amines, polyhydric alcohols, olefins, amino acids, etc., are sorbed from solutions or gases and form complexes with the metal in the ion exchanger ("ligand sorption"), or displace other ligands that have previously complexed the metal ("ligand exchange"). By virtue of the strength and specificity of complex formation, high capacities and selectivities can be achieved. Ligand-exchange capacities and selectivities and their theoretical prediction are the subject of the present study.

Ligand sorption by cation exchangers containing complexing metal ions was observed as early as 1954 by Stokes and Walton.[2] Separations of ligands by virtue of differences in complexing strength occasionally have been achieved by other authors.[3–5] The idea of exploiting chemical interactions for separations by means of ion exchangers has also been applied in various other ways; for example, silica has been removed from water by anion exchange after addition of F^- ions which form $[SiF_6]^{2-}$,[6,7] and carbohydrates and other carbonyl compounds which form adducts with borate or bisulfite anions have been separated with anion exchangers in the borate[8] or bisulfite[9] forms. However, no systematic study of ligand exchange has so far been reported. In particular, the striking effect of the coördinative valences of the ligands[1] has apparently been overlooked in the past.

General Aspects

Ligand exchange resembles ion exchange in that molecular species are exchanged—usually in stoichiometrically equivalent amounts—between the solid ion exchanger and an external solution. The essential difference is that in conventional ion exchange, counter ions are exchanged, whereas in ligand exchange, ligands are exchanged while the counter ion remains in the solid. Typical ligand-sorption and ligand-exchange reactions are, for example (boxes indicate that the respective species is in the ion exchanger).

$$\boxed{Cu(H_2O)_4^{2+}} + 4NH_3 \longrightarrow \boxed{Cu(NH_3)_4^{2+}} + 4H_2O \quad (1)$$

$$\boxed{Cu(NH_3)_4^{2+}} + 2NH_2RNH_2 \longrightarrow \boxed{Cu(NH_2RNH_2)_2^{2+}} + 4NH_3 \quad (2)$$

Reaction 1 is sorption of ammonia by a cation exchanger in (aqueous) Cu^{2+} form; alternatively, this reaction can be viewed as a ligand exchange of ammonia for water of hydration. Reaction 2 is a ligand exchange of a (bidentate) diamine for ammonia on a resin in Cu^{2+} form.

Analogous to the ion-exchange capacity (number of fixed ionic groups per unit weight or unit volume of the resin) a *"ligand-exchange capacity"* of

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(3) C. L. Thomas, U. S. Pat. 2,865,970 (1958).

(4) J. Giesen and F. Müller, U. S. Pat. 2,916,525 (1959).

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