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A Survey of Solvolytic Reactions of Some Cobalt(III) Complexes in Various Solvents

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The rates of solvolysis of the complexes *trans*-$[Co(en)_2NO_2Br]^+$, *trans*-$[Co(en)_2NO_2Cl]^+$, and *trans*-$[Co(en)_2Cl_2]^+$ in dimethyl sulfoxide solution are reported. These rates are compared to solvolysis rates in water and dimethylformamide. Some solvolysis rates in aqueous methanol are correlated with Winstein's Y parameter. It is seen that the effect of solvent change is similar for all of the complexes, and it is inferred that the mechanism of solvolysis is the same for all of the complexes even though they contain ligands of opposite electronic effect. The use of the solvent effects as aids in diagnosing the mechanism is discussed.

Introduction

Recent reviewers have commented on the paucity of data on reactions of transition metal complexes in nonaqueous solvents.[1,2] It is significant that until quite recently the few studies that were reported involved solvents either very like water or not reactive solvolytically, but the situation is changing as a result of the recognition that a number of dipolar aprotic solvents are suitable media for reactions of transition metal complexes.[3-5] This report describes the solvolysis of complexes of the type *trans*-$[Co(en)_2AX]^+$ (en = ethylenediamine, A = a nonlabile ligand, and X = a labile ligand) in dimethyl sulfoxide and presents a comparison of dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and water as solvolytic reagents for these complexes. In addition, some rates in aqueous methanol are given and correlated with Y.[6]

The aquation rates for this family of complexes have been studied in the past as a function of the nature of the nonlabile ligand A and the conclusion has been generally accepted that electron donor A ligands facilitate SN1 solvolyses and electron acceptor A ligands facilitate SN2 solvolyses.[1,7,8] In this work, a complex with –Cl as an electron donor A and two complexes with $-NO_2$ as an electron acceptor A were studied.

Experimental

New Complexes.—When *trans*-$[Co(en)_2NO_2Cl]ClO_4$ in dimethyl sulfoxide solution was treated with excess silver perchlorate, silver chloride precipitated slowly. The spectrum of the solution after precipitation was complete is similar to the spectrum of *trans*-$[Co(en)_2NO_2OH_2]^{+2}$ (see Fig. 1). It is assumed that the complex present is *trans*-$[Co(en)_2NO_2DMSO]^{+2}$. This assignment is reasonable since it has been shown that DMSO lies near water in the spectrochemical series,[9] and it is known that complexes containing the nitro group usually undergo substitution without geometrical isomerization. In addition, the *cis*-chloro–nitro complex was subjected to similar treatment producing the spectrum labeled *cis*-$[Co(en)_2NO_2DMSO]^{+2}$ in Fig. 1 which conforms to expectations for that form. Unfortunately, attempts to precipitate the complexes containing DMSO failed. This experience is reminiscent of the difficulty encountered in attempting to precipitate *trans*-$[Co(en)_2NO_2OH_2]^{+2}$. Tobe and Watts[10] have prepared a complex, $[Co(en)_2ClDMSO]^{+2}$, by a procedure similar to that described above. It precipitated from aqueous solution as the nitrate perchlorate. Following a suggestion of Tobe and Watts, *trans*-$[Co(en)_2Cl_2]ClO_4$ was dissolved in DMSO and treated with one equivalent of silver perchlorate. After precipitation was complete, the solution was violet and had a spectrum very similar to, but distinguishable from, *cis*-$[Co(en)_2Cl_2]^+$ (see Table I). This is taken to be the spectrum of $[Co(en)_2ClDMSO]^{+2}$.

Other Materials.—*cis*- and *trans*-dichlorobis(ethylenediamine)-cobalt(III) chlorides were prepared and purified by standard methods.[11] *cis*- and *trans*-chloronitrobis(ethylenediamine)cobalt-(III) chlorides were prepared by Werner's method[12] and *trans*-bromonitrobis(ethylenediamine)cobalt(III) bromide was prepared following Tobe's method.[13] All of these salts were converted to perchlorates by precipitation from cold aqueous solution with concentrated perchloric acid. The identity of the samples was verified by comparison of spectra and kinetic parameters with data in the literature.

Dimethyl sulfoxide (J. T. Baker, 99.9%) was fractionally distilled at 20 mm. pressure from anhydrous potassium carbonate. A middle fraction, comprising about 50% of the total, was retained for use. Distilled water was passed through a mixed bed ion-exchange column prior to use in preparing solvent mixtures. Methanol was obtained as Fisher reagent grade and used without further purification. Simple salts were dried reagent grade materials.

Spectra.—The most important spectral features of all of the complexes in dimethyl sulfoxide solution are given in Table I. Several more complete spectra are displayed in Fig. 1. Spectra of complexes which solvolyze appreciably and rapidly in dimethyl sulfoxide were recorded in the presence of excess ligand to repress the solvolysis reaction.

Kinetic Studies.—Except as noted, kinetic studies were carried out spectrophotometrically on a Beckman DU spectrophotometer equipped with a thermostated cell chamber maintained at the stated temperature ±0.1°. Other reaction conditions are detailed in the following sub-sections.

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(1) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).

(2) D. R. Stranks in J. Lewis and R. C. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 125.

(3) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

(4) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 4614 (1962).

(5) C. Langford and P. Langford, *Inorg. Chem.*, **2**, 300 (1963).

(6) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(7) M. L. Tobe, *Sci. Progr.*, **48**, 483 (1960).

(8) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

(9) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(10) M. L. Tobe and D. W. Watts, to be published. These workers have studied the *cis-trans* isomerization of the dichloro complex in DMSO. The author is indebted to Dr. Tobe for calling his attention to the fact that the DMSO complex could be prepared and pointing out that the reaction which occurred when *trans*-$[Co(en)_2Cl_2]ClO_4$ was dissolved in dimethyl sulfoxide was *not* primarily isomerization to the *cis* form.

(11) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).

(12) A. Werner, *Ann.*, **386**, 251 (1912).

(13) C. H. Langford and M. L. Tobe, *J. Chem. Soc.*, 506 (1963).

TABLE I

MAJOR SPECTROSCOPIC FEATURES OF SOME Co(III) COMPLEXES IN DIMETHYL SULFOXIDE SOLUTION (400–700 mμ)

Complex	λ_{max}, mμ	ε
trans-$[Co(en)_2NO_2Br]ClO_4$	508	114
trans-$[Co(en)_2NO_2OH_2][ClO_4]_2$[a]	470	93
trans(?)-$[Co(en)_2NO_2DMSO]^{+2}$	484	109
cis(?)-$[Co(en)_2NO_2DMSO]^{+2}$	462	108
cis-$[Co(en)_2Cl]ClO_4$	540	108
$[Co(en)_2ClDMSO]^{+2}$	530	108

[a] The solvent contained 9% (by volume) H_2O.

(1) **Aquation of *trans*-$[Co(en)_2NO_2Br]ClO_4$ in Dimethyl Sulfoxide–Water Mixtures.**—Solutions containing 2.2 to 55 *M* H_2O were thermostated at 25° in the cell chamber. Solid *trans*-$[Co(en)_2NO_2Br]ClO_4$ was added and the absorbance change at 500 mμ followed. The reaction does not go to completion when the H_2O concentration is <11 *M*. The first-order rate constant was calculated from the function

$$\frac{k(2a - x_e)t}{x_e} = 2.30 \log \frac{ax_e + x(a - x_e)}{a(x_e - x)}$$

where a is the initial concentration of $[Co(en)_2NO_2Br]^+$ and x and xe are the concentrations of the aquo complex at time t and equilibrium, respectively. This expression is valid if the aquo complex *only* is formed in a process opposed by a second-order reverse reaction. The assumption that aquo complex was the only species formed was checked by recording the spectra of the reacting solutions on a Cary Model 14 spectrophotometer and looking for an isosbestic point. From the spectra of the complexes (recorded on the Beckman DU) an isosbestic point is predicted at 478 mμ (ε 94). At water concentrations as low as 3.3 *M* the observed point is at 480 mμ (ε 96). The last point quoted in this study deviated somewhat. At 2.2 *M* H_2O the isosbestic point is at 482 mμ (ε 98). The associated rate constant may be subject to significant error.

(2) **Solvolysis of *trans*-$[Co(en)_2NO_2Br]ClO_4$ in Dimethyl Sulfoxide.**—Weighed samples of the solid complex were added to DMSO thermostated at 25° in the cell chamber. The change in absorbance was followed at 520 mμ. Since the reactions did not go to completion, the forward rate constants were calculated from the reversible reaction expression given above. The equilibrium quotient for the solvolysis was also calculated. The lowest initial concentration of bromo complex was 1.4×10^{-3} *M* and the highest was 4.4×10^{-3} *M*. The rate constants obtained were independent of the complex concentration and reproducible to better than 10%.

(3) **"Solvolysis" of *trans*-$[Co(en)_2NO_2Cl]ClO_4$ in Dimethyl Sulfoxide.**—Direct solvolysis of this compelx does not proceed far enough for kinetic study. However, Pearson, Schmidtke, and Basolo[14] report that nitrite substitution for chloride is nitrite-independent in DMSO from 0.0012 to 0.097 *M* $[NO_2]$. They do not quote a rate constant, but if the reaction is strictly nitrite-independent, nitrite entry must be preceded by a rate-determining step that is either solvolysis or its mechanistic equivalent. Pearson, Schmidtke, and Basolo's experiment was imitated at 35° using nitrite concentrations in the range 0.01 to 0.07 *M* and concentrations of the chloro–nitro complex from 1 to 3×10^{-3} *M* (the complex was introduced as a solid). The reaction was followed at 435 mμ. The product spectrum corresponded to that of a synthetic sample of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ dissolved in DMSO. The rate constants obtained from first-order plots were nitrite-independent and reproducible to better than 3%.

(4) **Solvolysis of *trans*-$[Co(en)_2Cl_2]ClO_4$ in Dimethyl Sulfoxide.**—Solid samples of the complex were dissolved in DMSO thermostated at 35° in the cell chamber and the change of absorption was followed at 520 mμ. At this wave length, excellent linear first-order plots were obtained. The molar absorptivity of $[Co(en)_2ClDMSO]^{+2}$ at 520 mμ is 103 and that of *cis*-$[Co(en)_2Cl_2]^+$ is 96. The molar absorptivity at infinity time in the kinetic studies was 102, indicating that the product is at least 80% solvolysis product and no more than 20% *cis*-dichloro. The total complex concentration in these experiments was varied from 1.2×10^{-3} to 3.2×10^{-3} *M*. The range is intentionally small to stay within the range where solvolysis predominates.

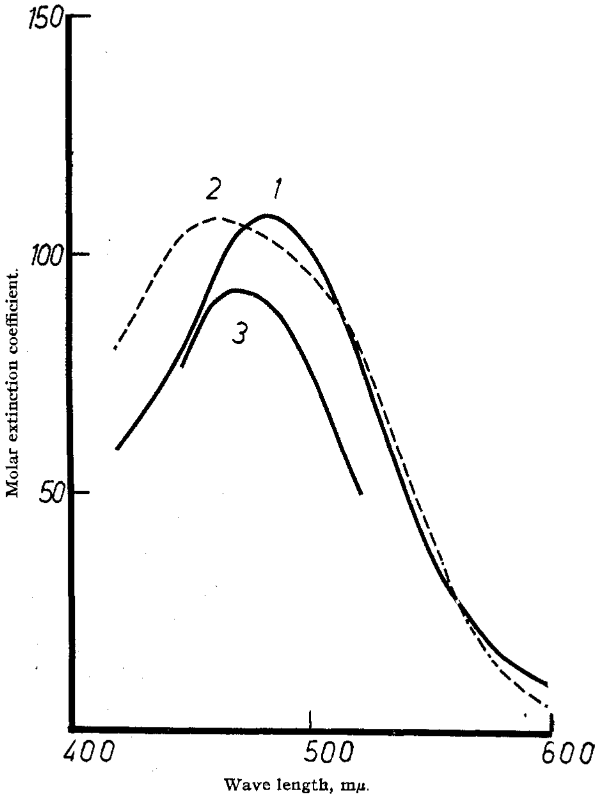

Fig. 1.—Spectra of some complexes in dimethyl sulfoxide: 1, *trans*(?)-$[Co(en)_2NO_2DMSO]^{+2}$; 2, *cis*(?)-$[Co(en)_2NO_2DMSO]^{+2}$ 3, *trans*-$[Co(en)_2NO_2OH_2]^{+2}$.

(5) **Aquation of *trans*-$[Co(en)_2NO_2Br]ClO_4$ in Aqueous Methanol.**—The complex concentration was 1×10^{-3} *M* added as a solid; 70% (by volume) methanol was the highest methanol concentration. In this solution (and those containing more water), the aquation reaction goes to completion. First-order rate constants were obtained in the usual way using 520 mμ data.

(6).—The initial rate of chloride release from *trans*-$[Co(en)_2Cl_2]Cl$ was studied in aqueous methanol (up to 60% by volume CH_3OH) by the titrimetric method of Brown and Ingold.[15] The complex concentration was 5×10^{-3} *M* and the reactions were followed for the first 25% of the reaction. The temperature was 25°.

Results

The reaction conditions and methods of treatment of data have been detailed in the Experimental section. Table II contains the first-order solvolysis rate constants for the three complexes *trans*-$[Co(en)_2NO_2Cl]^+$, *trans*-$[Co(en)_2NO_2Br]^+$, and *trans*-$[Co(en)_2Cl_2]^+$ in dimethyl sulfoxide. The solvolysis rates in water and dimethylformamide are included for comparison. The water values are taken from Tobe's review[7] and Langford and Tobe[13]; the DMF data from Langford and Langford.[5] The DMF rate constants, like the rate constant for the chloro–nitro complex in DMSO,

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[14] R. G. Pearson, H. H. Schmidtke, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4434 (1960).

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

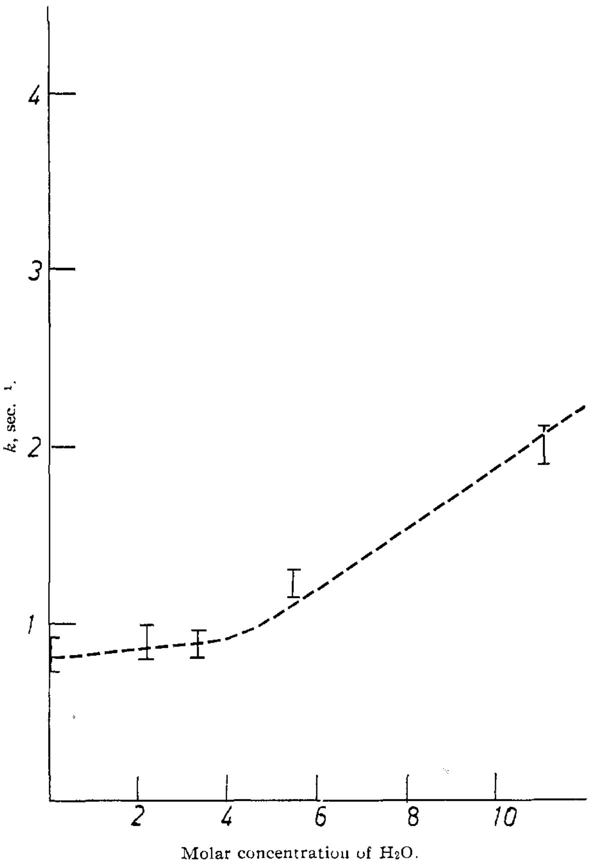

Fig. 2.—The first-order aquation rate of *trans*-$[Co(en)_2NO_2Br]^+$ in dimethyl sulfoxide–water mixtures as a function of the water concentration. (Intercept is rate of solvolysis by dimethyl sulfoxide.)

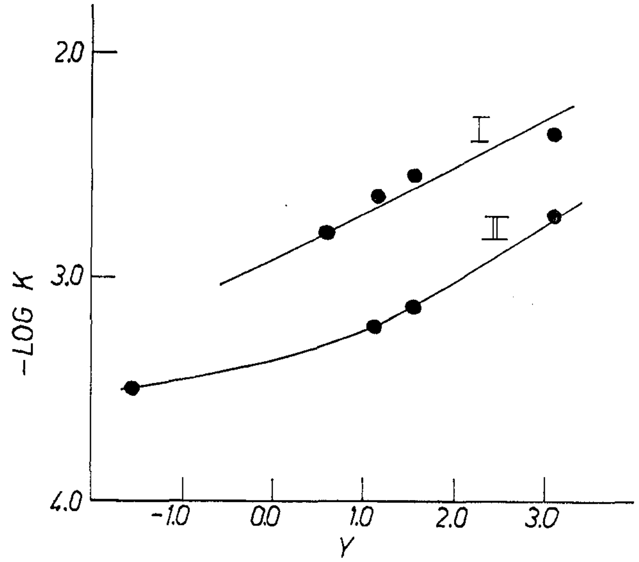

Fig. 3.—Rates of aquation of two complexes in methanol–water mixtures as a function of the Grunwald–Winstein solvent ionizing power parameter *Y*: I, *trans*-$[Co(en)_2NO_2Br]^+$, *k* in sec.$^{-1}$; II, *trans*-$[Co(en)_2Cl_2]^+$, *k* in min.$^{-1}$.

are actually values for entering anion independent anion substitution reactions. The evidence for considering these as indirect measures of the solvolysis rate has been presented in ref. 5. The final column of Table II quotes the rate constants for the chloride-independent radiochloride exchange of $[Pt(py)_2Cl_2]$ taken from Pearson, Gray, and Basolo.[3] These data are interesting in this context because it is clear that the solvent attacks Pt(II) in a reaction with some SN2 character.

Figure 2 shows the dependence of the rate of solvolysis of *trans*-$[Co(en)_2NO_2Br]^+$ on the water content of dimethyl sulfoxide–water mixtures. The points at water concentrations above 1.0 *M* are rates of *aquation*. The intercept is the experimental solvolysis rate in dry dimethyl sulfoxide. It is especially interesting that the aquation rate falls to approximately the DMSO solvolysis rate at low water concentration. Plots made of the rate as a function of the several different ways of expressing the composition of the mixed solvents revealed no simpler form than the plot given.

The equilibrium quotient for the reaction *trans*-$[Co(en)_2NO_2Br]^+$ + DMSO = *trans*-$[Co(en)_2NO_2\text{-}DMSO]^{+2}$ + Br^- is $9 \pm 1 \times 10^{-4}$ *M* at 25°.

Figure 3 shows the aquation rates in aqueous methanol at 25° of *trans*-$[Co(en)_2NO_2Br]^+$ and *trans*-$[Co(en)_2Cl_2]^+$ as a function of Grunwald and Winstein's solvent ionizing power parameter, *Y*.[6] The points given are for 0, 50, 60, and 70% (by volume) methanol except that the last point on the curve for the dichloro complex is the methanolysis rate (pure CH_3OH) given by Pearson, Henry, and Basolo.[16] Although good straight line correlation between log *k* and *Y* is not obtained, slopes for the water-rich parts of the curves can be estimated. This slope is the *m* value, Grunwald and Winstein's measure of susceptibility of a reaction to solvent ionizing power. The reaction of the bromonitro complex has an *m* of about 0.18; the reaction of the dichloro complex has an *m* of about 0.25.

Finally, the stereochemical results in dimethyl sulfoxide and dimethylformamide parallel those in water. The nitro complexes react with retention of geometry. The dichloro complex reacts with considerable geometrical isomerization.

Discussion

These data seem to support the idea that solvolysis in nonaqueous, coordinating solvents is not radically different from solvolysis in water. The rates are altered, but only moderately. The stereochemistry parallels the familiar stereochemistry of aquation. However, the surest conclusion to be drawn from these data is that the effect of solvent change is indifferent to the presence of an electron-donating or an electron-withdrawing nonlabile substituent in the complex. This was not expected. It has been widely argued[1,7,8] that the electron-withdrawing nitro group facilitates aquation by facilitating a nucleophilic attack at cobalt (SN2 mechanism), whereas the electron donor chloro group facilitates aquation by facilitating dissociation (SN1 mechanism). These two processes should be responsive to different properties of the solvent. Nucleophilic attack should vary proportionately to

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

TABLE II[a]

RATES OF SOLVOLYSIS OF COMPLEXES IN VARIOUS SOLVENTS

First order rate constants in sec.$^{-1}$

Solvent	*trans*-$[Co(en)_2Cl_2]^+$ (35°)	*trans*-$[Co(en)_2NO_2Cl]^+$ (35°)	*trans*-$[Co(en)_2NO_2Br]^+$ (25°)	$[Pt(py)_2Cl_2]$ (25°)
H_2O	1.2×10^{-4} (1)[b]	2.8×10^{-3} (1)	4.2×10^{-3} (1)	3.5×10^{-5} (1)
Dimethyl sulfoxide	3.7×10^{-5} (0.31)	1.4×10^{-4} (0.04)	8.0×10^{-4} (0.19)	3.8×10^{-4} (11)
DMF	5.8×10^{-6} (0.05)	5.4×10^{-5} (0.02)	6.9×10^{-4} (0.16)	$<1 \times 10^{-5}$ (<0.3)

[a] Sources of data given in the text. [b] Numbers in parentheses are relative solvolysis rates (aquation rate = 1.0).

solvent nucleophilicity. (That, perhaps, being measured by the order of solvolysis rates at Pt(II).) Dissociation rates should respond to the ability of the solvent to solvate the ions produced. The similar behavior of the complexes argues for a *single* mechanism for solvolysis. (Comparison with the Pt(II) data suggests that this common response is not to nucleophilicity.)

Parker[17] has given an excellent discussion of the ability of solvents to solvate anions. The solvolysis rates reported here are in the right *order* to suggest that leaving anion solvation is the major determinant of solvolysis rate, but the differences seem a little small. This last point is clearly made in connection with *m* values. Alkyl halides which undergo SN1 solvolysis yield *m* values about five times as large as the ~0.2 reported here. That is, their reactions are more sensitive to "solvent ionizing power." Yet it does not follow that we should exclude a predominantly SN1 mechanism for the solvolysis of cobalt(III) complexes. The Co–X (X = halide) bond is no doubt more ionic than the C–X bond. Thus, the *increase* in anion solvation in the transition state as compared to the ground state may be much greater in the alkyl halide case, leading to a greater "ionizing power" sensitivity in SN1 solvolysis rates.

Note that adoption of a primarily SN1 process as a description of these reactions would agree with a large body of work on the reactions of *trans*-$[Co(en)_2Cl_2]^+$, but would require revision in ideas about the electronic effect of the nitro group.[18] Actually, there is some evidence that electron-withdrawing groups (otherwise known as π-bonding groups with metal to ligand electron donation) may stabilize five-coordinate species similar to the required SN1 intermediate. For example, Haim and Wilmarth[19] have presented strong evidence for a limiting SN1 mechanism in the water exchange reaction of $[Co(CN)_5OH_2]^{-2}$.

Acknowledgment.—The author is indebted to the Research Corporation for financial support and to Mrs. P. O. Langford for assistance with several experiments. The author is also indebted to a referee for helpful criticism.

[17] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[18] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, Chapter 3.

[19] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573, 583 (1962).

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The Photochemical Aquation of Chromium(III)–Ammonia Complexes

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The photochemical aquation of $Cr(NH_3)_6^{+3}$ was shown to proceed in a stepwise manner, and quantum yields were determined for each step. For light absorption by the non-spin-forbidden ligand field bands, the quantum yields for the substitution of a single NH_3 by H_2O were determined to be: 0.32 for $Cr(NH_3)_6^{+3}$, 0.18 for $Cr(NH_3)_5H_2O^{+3}$, 0.15 for $Cr(NH_3)_4(H_2O)_2^{+3}$, 0.018 for $Cr(NH_3)_3(H_2O)_3^{+3}$, and 2.0×10^{-3} for $Cr(NH_3)_2(H_2O)_4^{+3}$. These quantum yields were independent of which of the two main absorption bands were irradiated and also independent of temperature, concentration, light intensity, and acidity in the range 1 to 0.05 *M*. The final product of long irradiation was not $Cr(H_2O)_6^{+3}$. If perchlorate was the only anion present, the final product had a spectrum consistent with that for $Cr(NH_3)(H_2O)_5^{+3}$. If either sulfate or nitrate was present the product appeared to be polynuclear. The photochemical mechanism seems to involve reaction from an excited spin-forbidden (doublet) state. Strong support for the mechanism was found by irradiating $Cr(NH_3)_6^{+3}$ only at the position of its doublet absorption (6500 Å.) and obtaining quantum yield unity.

Earlier studies[2] have concerned the photochemical substitution of solvent water molecules into $Cr(NH_3)_6^{+3}$, $Cr(NH_3)_5H_2O^{+3}$, and $Cr(H_2O)_6^{+3}$. In those cases quantum yields (molecules reacted/quantum absorbed) were found which were significantly smaller than unity and the explanations offered placed great emphasis on a direct involvement of a spin-forbidden (doublet) electronic state. To further test the ideas postulated and to follow the aquation through the entire series of

[1] Presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] R. A. Plane and J. P. Hunt, *J. Am. Chem. Soc.*, **79**, 3343 (1957); M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, **63**, 327 (1959).