stable disubstituted species of $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$[3,12] are the trans isomers, while amine-substituted compounds are of the cis geometry.[14] In these phosphorus-containing ligands, the trans isomer allows for the increase in metal–phosphorus π bonding necessary to stabilize the compounds, especially for the tungsten complex, by taking the ligand out of direct competition with a CO for the metal π-electron density. On the other hand, the cis isomer allows for maximum metal–CO π bonding in the case of the poor π-accepting amine ligands.

We are currently studying the coordination chemistry of $(CH_3)_2PN(CH_3)_2$ to determine what effect having only one $-N(CH_3)_2$ group on a phosphorus will have on the donor–acceptor properties of phosphorus.

Complexing Tendency of Trifluoromethylsulfonate Ion As Measured Using Chromium(III)

BY ARTHUR SCOTT AND HENRY TAUBE*

By using cation-exchange resins, a species which answers to the properties expected of $CrCF_3SO_3^{2+}$ can be separated from a solution in which Cr(III) has reached equilibrium in 9.1 M CF_3SO_3H. The rate constant for aquation of the complex at 25° and 1 M acid is $(7.6 \pm 0.2) \times 10^{-4}$ sec^{-1}, which is about tenfold slower than that of $CrClO_4^{2+}$ but in turn about tenfold more rapid than that of $CrNO_3^{2+}$. On the basis of the weak nucleophilic power for $CF_3SO_3^-$ thus indicated and its resistance to reducing agents, it shows great promise as an indifferent anion. Higher complexes of Cr(III) with $CF_3SO_3^-$ form at high acid concentration. The complex formed in 11.1 N acid is shown to aquate much less rapidly than the 1:1 complex referred to above.

Introduction

Perchlorate ion is widely used in research on metal and other cations in solution because of its weak tendency to form complexes. It is well suited to this use except for a serious limitation arising from the fact that it is strongly oxidizing. Because reduction reactions are often slow, the ion is compatible with many strongly reducing species under a wide range of conditions. It does, however, oxidize Ti(III), V(II), and Eu(II) rapidly enough even at room temperature severely to restrict its use in the presence of these species. With metal ions of the second- and third-row transition elements, interference by ClO_4^- acting as an oxidizing agent becomes quite common. More serious are the consequences of the great oxidizing capacity of ClO_4^- in dealing with perchlorate salts. Particularly when organic matter is present, these materials have proven to be extremely hazardous.

The description[1] of trifluoromethylsulfonic acid as a strong acid suggests that the anion may be a sufficiently weak nucleophile to replace ClO_4^- for many purposes. It appears to be indefinitely stable with respect to hydrolysis, at least under ordinary conditions,[1,2] and has the advantage over ClO_4^- that it is much more difficult to reduce. The present work was undertaken to gauge the nucleophilic power of $CF_3SO_3^-$. To do this, we chose Cr(III) as a representative of cations having a tendency to associate with oxygen bases. It is convenient for study because it is colored and also because its complexes are substitution inert. Moreover, the ClO_4^- complex has been described[3] and its rate of aquation measured. Taking advantage of the general conclusion[4] that the rates of formation of complexes of a given metal ion are nearly the same for different ligands of the same class and charge type, the relative affinities for a metal ion can then be assessed simply from the relative rates of aquation.

Experimental Section

Trifluoromethylsulfonic acid was supplied by courtesy of the 3M Corp. The acid as supplied was found by titration to be 11.2 N (pure anhydrous acid is 11.305 N). Some samples of the acid contained significant amounts of SO_4^{2-}. On redistilling the acid and rejecting the final one-eighth of liquid, it was found to be free of SO_4^{2-} as tested using Ba^{2+}. Formation of $CrSO_4^+$ is itself a test for the presence of SO_4^{2-}. Whereas, without untreated acid, in some cases there were complications arising from the formation of this species, no interference was observed for the distilled acid. The concentration of SO_4^{2-} in the purified acid (10 M) appears to be less than 10^{-3} M.

Cr(III) solution was made up by reducing chromium trioxide with hydrogen peroxide in CF_3SO_3H. Ten grams of Baker and

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(1) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 4228 (1954).

(2) T. Gramstad and R. H. Haszeldine, *ibid.*, 4069 (1957).

(3) K. M. Jones and N. Bjerrum, *Acta Chem. Scand.*, **19**, 974 (1965).

(4) (a) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965); (b) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

Adamson reagent grade CrO_3 was dissolved in 125 ml of 4.5 N CF_3SO_2H in a three-neck flask with dropping funnel and reflux condenser. Hydrogen peroxide (30%) was added dropwise. The reaction is exothermic and was initially violent; to moderate it, the system was cooled in an ice bath. The reaction became continually less violent and larger aliquots of H_2O_2 were added. The mixture changed color to muddy green and eventually to the deep violet-blue color characteristic of $Cr(H_2O)_6{}^{3+}$. Excess peroxide was added, about 60 ml in all. The mixture was then refluxed for 24 hr to destroy excess peroxide.

Water.—Tap distilled water was doubly distilled, the first time from alkaline permanganate.

Analyses.—The total Cr(III) concentration was determined by making an aliquot basic with NaOH and then adding excess 30% H_2O_2. Excess peroxide was destroyed by boiling and the solution was made up to a known volume. The optical density at 373 mμ was determined and the concentration of $CrO_4{}^{2-}$ calculated using an extinction coefficient of 4815 M^{-1} cm^{-1}.[5] The total chromium concentration was found to be 0.32 M.

The free acid concentration in the stock Cr(III) solution was determined by a cation-exchange method and by using oxalate to complex Cr^{3+}. The methods agreed in yielding the value 0.64 N for the acid concentration.

The final acid and chromium concentrations give at once the concentration of $CF_3SO_3{}^-$, since it is the only anion present.

For some work a stock solution more concentrated in Cr(III) was needed. This was made up by the same method as before, with higher initial concentrations of CrO_3 and acid. After reaction the solution was concentrated on a rotary evaporator until material began to precipitate. Just sufficient water was then added to dissolve the solid. Chromium and free acid concentrations were determined as before, with the following results: Cr(III), 1.56 M; H^+, 1.88 M.

Kinetic Studies.—Solutions of Cr(III) in concentrated CF_3SO_3H were made up by pipetting 1 ml of the 0.32 M Cr(III) stock solution into a 10-ml volumetric flask, adding the desired amount of neat acid, and diluting to volume with water. When it was desired to keep the heat of solution to a minimum, the acid was first diluted in water and the diluted acid was then added to the stock chromium solution. The solution was kept cold in an ice bath except where otherwise noted.

To follow the aquation of the complex, 3 ml of concentrated solution was measured out with the buret and the solution was diluted to 25 ml with water. The water and solution were kept cold in an ice bath until spectra were run.

Chromatographic Techniques.—Separation of ionic chromium species was done on a column of Dowex 50W-X2 cation-exchange resin obtained from Bio-Rad. The column, approximately 6 in. long with a 1-cm diameter, was kept cold by circulating ice water through a water jacket surrounding it. Ten milliliters of a concentrated solution of chromium complex was transferred to 1 l. of cold water and the solution was kept in an ice bath until all of the solution was passed through the column. To reduce the rate of aquation further while charging the column, the reservoir at the top was packed in ice and the elution was sped by compressed air.

The +2 complex species was eluted from the column with 1 N perchloric acid (occasionally 0.5 N acid was used when a less concentrated eluent was desired). The eluent was kept cool until it was transferred to the spectrophotometer cell. Appropriate choice of cell length made further dilution or concentration of the eluent unnecessary.

Spectra.—Most spectra were run on a Cary 14 (a few on a Cary 15) visible–uv spectrophotometer in the region 200–800 nm. An appropriate wavelength for kinetic observations was chosen by repeatedly scanning the entire spectrum at intervals. The kinetic data were obtained by recording continuously, or at spaced intervals when the spectral change was slow, at the chosen wavelength. Kinetic runs done with the cell cavity thermostated at 25.0 ± 0.2 or 9.0 ± 0.2°. Ten minutes was allowed for the

solution to come to room temperature before the first point was taken.

Results

When the Cr(III) stock solution was made up to be 7 M in CF_3SO_3H, no change in color was discernible from that of $Cr(H_2O)_6{}^{3+}$ in a more dilute medium. At 8 M the solution took on a definite blue-green color, and at 9.12 M the solution was a bright green. The rapidity with which the color change occurred depended on how the solution was made up. Mixing CF_3SO_3H with water is an extremely exothermic process, and if acid in quantity was added rapidly to the chromium stock solution, the green color appeared immediately. If the acid was partially diluted before mixing, cooled, and added slowly to the solution in an ice bath, the green color would appear over a period of a few hours at room temperature.

Chromium(III) in a 10.2 M CF_3SO_3H solution was initially yellow-green, but after standing at room temperature for about 2.5 days, it turned a straw brown color. By using the more concentrated Cr(III) stock solution, it was possible to increase the acid concentration to 11.1 M. After achieving equilibrium in a few days, this solution was a rosy pink. A small amount of water added to this solution produced the brown color in about 15 min.

The color changes described suggest that, at least at high concentration of acid, complexes of Cr(III) with $CF_3SO_3{}^-$ are formed, and attention was then directed to characterizing the complexes and to studying their rates of aquation.

A solution containing Cr(III) in 9.12 M CF_3SO_3H was left to reach equilibrium. It was then diluted 1:100 with water at 0° and passed through a column of Dowex 50W-X2 cation-exchange resin, the column being kept cold by means of ice water. Two bands were observed, a narrow blue band at the top and a broad green band below it. Initially only the green appeared, and thus the blue band presumably arises from the aquation of the green species during the period of 1.5 hr needed to pass the solution through the column.

After charging, the column was eluted with 1 M $HClO_4$. The elution properties of the resin are well known from the studies by Cady and Connick[6] on ruthenium(III) chlorides and by King and Dismukes[7] on chromium(III) thiocyanates. Species of charge +2 are readily eluted by 1 N acid and those of +1 charge are difficult to hold on the column and are readily eluted by 0.1 M, while +3 species are tightly bound but rapidly eluted at about 5 M acid. When 1 M acid was passed through the column, the green band was rapidly displaced while the blue band was spread only slightly. We thus conclude that a +2 species makes up the green band. The solution passed through on charging the column showed a small amount of chromium to be present, but the concentration was not determined quantitatively.

The solution of green complex eluted by the 1 N

(5) E. A. Deutsch, Ph.D. Thesis, Stanford University, 1967.

(6) H. H. Cady and R. E. Connick, *J. Amer. Chem. Soc.*, **80**, 2646 (1958).

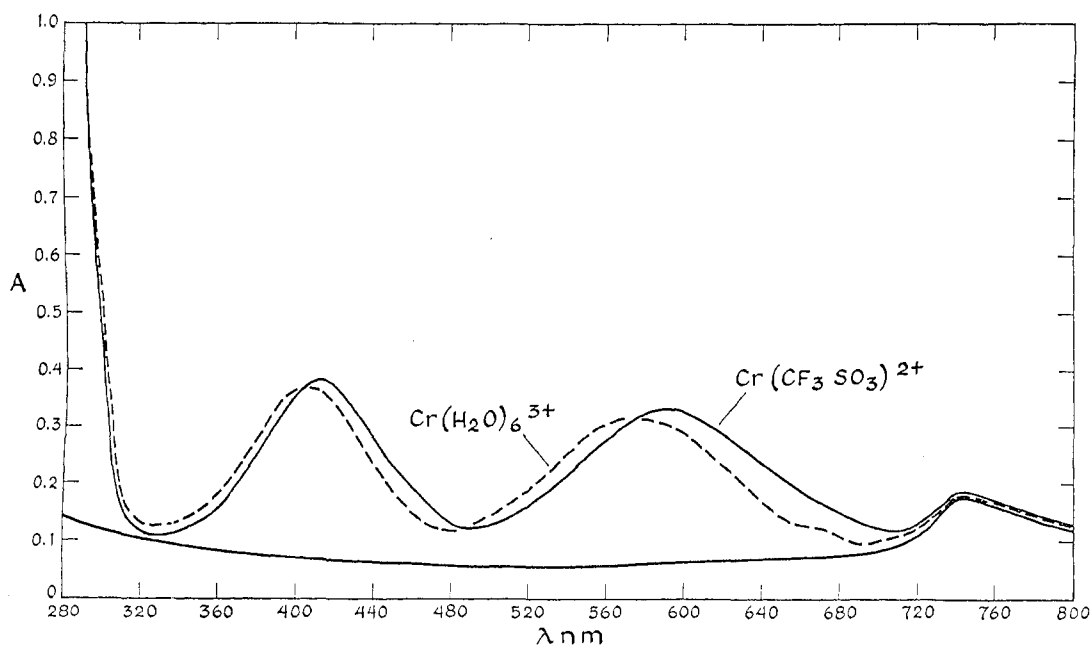(7) E. L. King and E. B. Dismukes, *ibid.*, **74**, 1674 (1952).

Figure 1.—Spectra of $Cr(CF_3SO_3)^{2+}$, as eluted from ion-exchange column, and of $Cr(H_2O)_6^{3+}$, at 25°, in 1.1 M HClO$_4$. Lowest line is base-line absorption.

HClO$_4$ was brought to temperature and its visible–uv spectrum was run. The spectrum is shown in Figure 1, along with the spectrum of hexaaquochromium after completion of the aquation reaction. The green complex spectrum is seen to be slightly displaced toward longer wavelength with maxima at 590 and 413 nm *vs.* 575 and 408 nm for the $Cr(H_2O)_6^{3+}$. Quite similar shifts were reported by Fogel, *et al.*,[8] for the spectrum of CrSO$_4^+$, and it is reasonable to expect that the spectra of $Cr(CF_3SO_3)^{2+}$ and CrSO$_4^+$ will be alike. Values of extinction coefficients *vs.* wavelength for the green complex are shown in Table I.

The aquation of the complex (*ca.* 4.5 $\times$ 10^{-3} M) in 1.1 M HClO$_4$ was followed by observing the change of absorbance at 650 nm with time. Good first-order behavior was observed in plots of log $(A_0 - A_\infty)/(A - A_\infty)$ against time.

The values obtained for the first-order rate constant are $k_1 = (7.6 \pm 0.2) \times 10^{-4}$ sec^{-1} at 25° and $k_1 = (1.0 \pm 0.3) \times 10^{-4}$ sec^{-1} at 9°. Using the Eyring equation, $\Delta H^{\ddagger}$ for the reaction is calculated as 21 kcal mol^{-1} and $\Delta S^{\ddagger}$ as -3 cal mol^{-1} deg^{-1}.

Some qualitative experiments were done to assess the extent of complex formation in the range 6–9 M CF$_3$SO$_3$H. Solutions were prepared and left at room temperature for 1 week to reach equilibrium. After this time they were analyzed by the cation-exchange technique described earlier. At 7.44 M acid and below, no green complex could be observed, but at 8.00 M some green appeared, the predominant component still being Cr^{3+}. As already noted, in 9.12 M acid very little $Cr(H_2O)_6^{3+}$ remains at equilibrium.

Some studies were also done on the complex formed in the highest range of acid concentration. A spectrum

(8) N. Fogel, J. M. J. Tai, and J. Yarborough, *J. Amer. Chem. Soc.*, **84**, 1145 (1962).

TABLE I
SPECTRUM OF Cr(III) IN 11.1 M ACID[a]

λ, nm	ϵ, M^{-1} cm^{-1}	λ, nm	ϵ, M^{-1} cm^{-1}
		580	2.86
780	8.49		
		560	3.70
760	11.94		
		540	7.17
740	15.77		
		520	13.14
720	18.57		
710[b]	19.08	500	19.41
700	18.88		
		483[b]	21.76
680	14.03		
670[b]	16.10	460	18.04
660	13.85		
		440	10.56
640	10.13		
		420	4.95
620	6.17		
		400	2.98
600	3.57		
380	2.58		
360	2.86		
340	5.43		
320	12.07		
300	15.31		

[a] [Cr^{3+}] = 0.0392 M; 1-cm cell; temperature 25°. [b] Maximum.

of Cr(III) in the most highly concentrated solution, 11.2 M CF$_3$SO$_3$H, is shown in Figure 2. The spectrum is radically different from that of $Cr(H_2O)_6^{3+}$. For this species, prominent maxima in the visible region occur at 408 and 575 nm; in the strongly acidic medium the maxima appear at 483, 640 (sh) and 670, 710 nm.

The brown species, on diluting the solution 1:100 and passing it through a column, does not adhere at all, and the charge on the species is therefore less than +2.

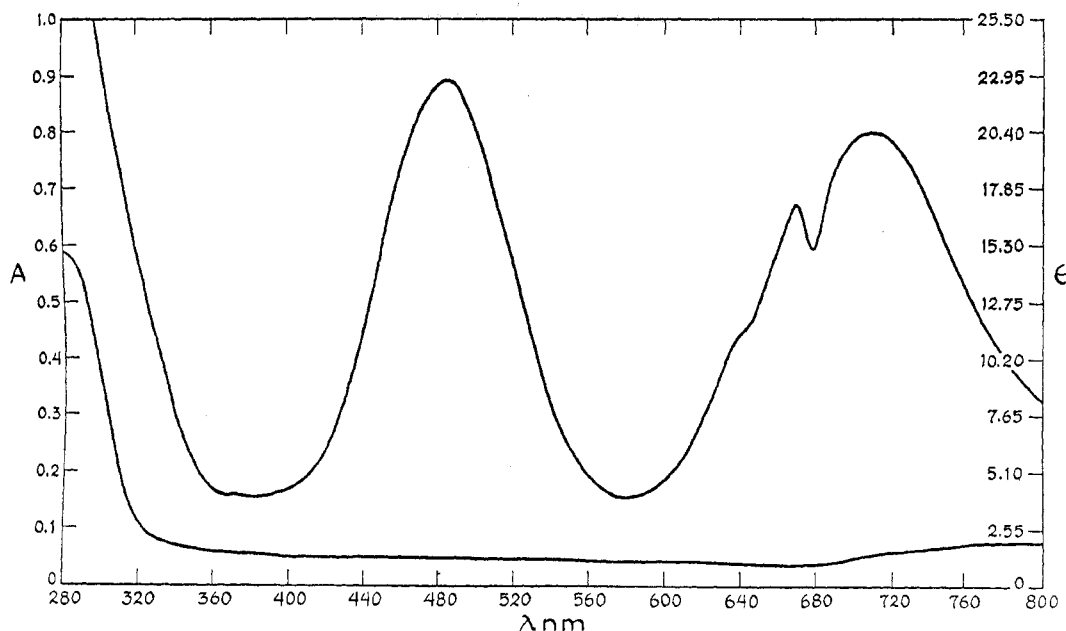The aquation of a solution of Cr(III) made up and

Figure 2.—Spectrum of pink-brown material in 11.1 M HCF$_3$SO$_3$ at 25° using a 1-cm cell.
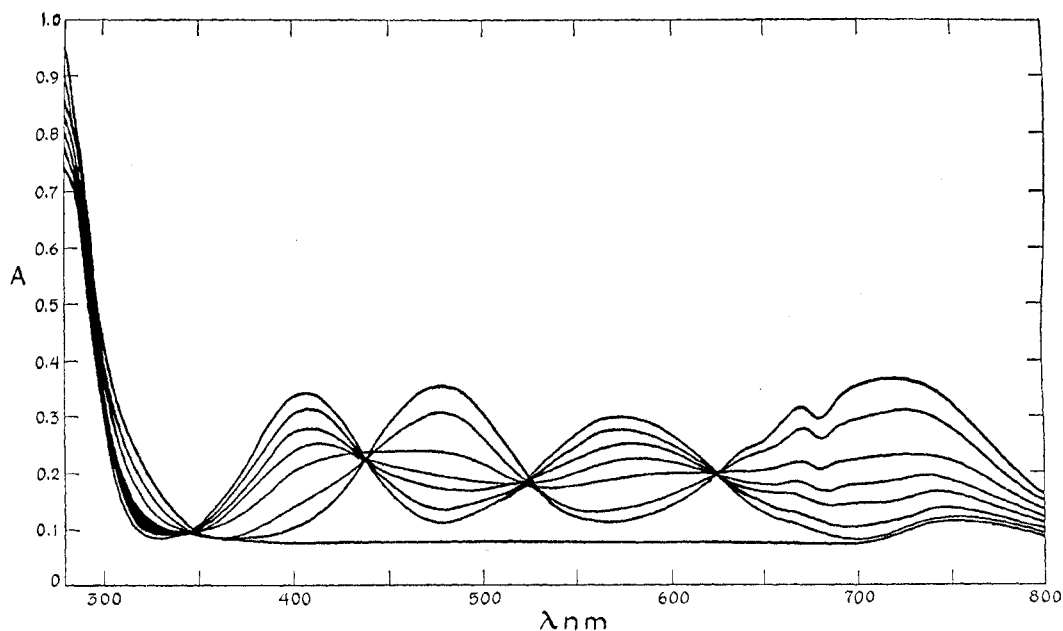

Figure 3.—The progress of the aquation of a solution, originally brown, in 10.2 M HCF$_3$SO$_3$, on dilution to 1.22 M acid, at 25° using a 5-cm cell. The time intervals reading from the top in the long-wavelength band are 0, 178, 601, 954, 1350, 2123, and 4100 min, respectively.

equilibrated in 10.2 M CF$_3$SO$_3$H (this solution is also brown) after dilution to 1.2 M CF$_3$SO$_3$H was followed by scanning the spectrum as a function of time. The results are shown in Figure 3. Considering that the initial complex contains at least two anions per Cr(III) and the final spectrum is that of Cr(H$_2$O)$_6$$^{3+}$, the isosbestic behavior observed is very remarkable. It implies that the initial complex aquates less rapidly than any intermediate species, and this relation, at least in respect to CrCF$_3$SO$_3$$^{2+}$, was demonstrated in measuring the half-life for the aquation of the brown species. The rate was followed in 1.2 M CF$_3$SO$_3$H both at 710 and at 580 nm. The kinetic plots conformed well to

first-order behavior, and the values of k were determined as 1.8×10^{-5} and 1.5×10^{-5} sec^{-1}, respectively, to be compared to 7.6×10^{-4} sec^{-1} for CrCF$_3$SO$_3$$^{2+}$ under the same conditions.

Discussion

In view of its ion-exchange behavior, the green species eluted from the column is in all likelihood CrCF$_3$SO$_3$$^{2+}$. Its rate of aquation, $k = 7.6 \times 10^{-4}$ sec^{-1} at 25° in 1.1 M HClO$_4$, can be compared to that of CrClO$_4$$^{2+}$. The rate for the perchlorate complex is calculated from the data at 9.8 and 20° to be 7.6×10^{-3} sec^{-1} at 25°. The values for CrClO$_4$$^{2+}$ were measured at high perchloric

acid concentration (5.3–10.6 M) and were corrected[3] to unit activity of water. As another significant comparison, the kinetic data for the aquation of $CrNO_3^{2+}$ can be cited. Swaddle[9] reported $k = 7.4 \times 10^{-5} sec^{-1}$ at 25° and $\mu = 1$ for this species ($\Delta H^{\ddagger} = 21.6 \pm 0.1$ kcal mol^{-1}).

Despite the somewhat indeterminate nature of the comparison between $CrClO_4^{2+}$ and $CrCF_3SO_3^{2+}$, it is certain that $CF_3SO_3^-$ is more nucleophilic toward Cr^{3+} than is ClO_4^-. It is still more certain that $CF_3SO_3^-$ is less nucleophilic toward Cr^{3+} than is NO_3^-. Even with NO_3^-, except at high concentrations, the extent of complexation of metal ions is small. The equilibrium constants for the association of Cr^{3+} with NO_3^-, $CF_3SO_3^-$, and ClO_4^- can be expected[4] to be inversely proportional to the rates of aquation, and on this basis a tenfold greater concentration of $CF_3SO_3^-$ than of NO_3^- is needed to produce the same degree of complex formation. The direct experiment done in a search for evidence of complex formation at 7.4 M CF_3SO_3H suggests that there is less than 10% conversion to a complex under these conditions. Thus it seems safe to conclude that when $CF_3SO_3^-$ is at ordinary concentration levels, say 2 M or less, the formation of a complex with Cr^{3+} is insignificant in extent. On this basis and on the basis of its other properties, the use of $CF_3SO_3^-$ as an indifferent anion appears to be very promising.

(9) T. W. Swaddle, *J. Amer. Chem. Soc.*, **89**, 9338 (1967).

The decreasing lability with increased extent of complexation is unprecedented for Cr^{3+} as the central ion. Further work will need to be done in characterizing the complex species formed before this behavior is understood. The possibility that $CF_3SO_3^-$ can be a chelating ligand will need to be taken into account in considering the various alternatives. Almost as remarkable as the kinetic stability of the most highly complexed species is its spectrum (see Figure 2). The absorption properties displayed do, however, have precedent. Jones and Bjerrum[3] reported for the equilibrium spectrum of $Cr(H_2O)_6(ClO_4)_3$ in 13 M H_2SO_4 features which closely resemble those shown in Figure 2, there being peaks at 460 and 640 nm, and the long-wavelength band showing structure. In 13 M H_2SO_4, coordinated SO_4^{2-} is in all likelihood protonated; HSO_4^- and $CF_3SO_3^-$ are undoubtedly much alike in respect to their affinities for cations. The splitting of the long-wavelength band indicates a lowering of the symmetry about Cr(III).

A reasonable candidate for the complex formed at high acid is $trans$-$Cr(H_2O)_4(CF_3SO_3)_2^+$; if $CF_3SO_3^-$ has a weaker trans-labilizing effect than H_2O, the relative rates of aquation can be understood.[10]

(10) This suggestion, made by one of the reviewers, seems to us to be more reasonable than our own earlier hypothesis which involved chelation by the ligand.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA 19104

Kinetics of the Aquation of Dichlorotetraaquochromium(III) Catalyzed by Monosubstituted Mercury(II) Complexes

BY JAMES P. BIRK

The kinetics of the aquation of cis-$Cr(H_2O)_4Cl_2^+$ catalyzed by $HgCl^+$ and of $trans$-$Cr(H_2O)_4Cl_2^+$ catalyzed by HgX^+ (X = Cl, Br, I, CN) have been examined at 15–35° and 0.50 M ionic strength. In each reaction, except for X = CN, the rate equation is of the form $-d \ln [Cr(H_2O)_4Cl_2^+]/dt = (k_0 + k_{-1}[H^+]^{-1})[HgX^+]$. Values of the activation parameters were determined for each term and were used in an attempt to elucidate energetic and structural features of the transition state. The reaction of $trans$-$Cr(H_2O)_4Cl_2^+$ with $HgCN^+$ follows the rate equation $-d \ln [Cr(H_2O)_4Cl_2^+]/dt = (a[H^+] + b)[HgCN^+]/(c + [H^+])$, which is interpreted in terms of several mechanisms which are consistent with this form of rate equation.

Introduction

As part of a continuing study[1–4] of the mechanism of aquation of chromium(III) complexes catalyzed by metal ions, in particular Hg(II), the aquations of cis- and $trans$-$CrCl_2^+$ catalyzed by HgX^+ (X = Cl, Br, I, CN) have been examined. In a previous study[3] of the reaction between $CrCl_2^+$[5] and Hg^{2+}, evidence was found for binuclear complex formation with the cis but not with the trans isomer. It was suggested that a binuclear complex would be formed only when it is possible to achieve a double-bridged configuration. The reaction between cis-$CrCl_2^+$ and $HgCl^+$ was examined to test further this proposal. Since the coordination of a third chloride to mercury(II) is not a particularly favorable process,[6,7] it would be expected that a bi-

(1) J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **4**, 527 (1965).
(2) J. P. Birk and J. H. Espenson, *ibid.*, **7**, 991 (1968).
(3) J. P. Birk, *ibid.*, **9**, 735 (1970).
(4) J. P. Birk and C. M. Pasquale, submitted for publication.
(5) In general, coordinated water molecules will not be shown in chemical formulas.

(6) L. D. Hansen, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, **2**, 1243 (1963).
(7) L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949), and papers cited therein.