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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO]

The Mechanisms of Substitution Reactions of Octahedral Complexes: The Induced Aquation of the Halogenopentamminecobaltic Ions by Metal Cations

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Observations on the fractionation of oxygen isotopes in the formation of the aquopentamminecobaltic ion from $Co(NH_3)_5Cl^{++}$, $Co(NH_3)_5Br^{++}$ and $Co(NH_3)_5I^{++}$ induced by metal ions, show that an intermediate of common properties is not formed when Ag^+ and Tl^{+++} are used to remove metal ion, but suggest that when Hg^{++} is used, a common intermediate is formed from the different halogeno cations. The results also suggest that an important source of the water added to the cobaltic ion in the case of Tl^{+++} is the hydration sphere of this cation. Data on the competition between the formation of $(NH_3)_5CoH_2O^{+++}$ and $(NH_3)_5CoSO_4^+$ (or $(NH_3)_5CoNO_3^{++}$) are presented, again for metal cations acting on halogenopentamminecobaltic ions. It is shown that when the reaction of $(NH_3)_5CoCl^{++}$ with Hg^{++} takes place in the presence of $SO_4^=$, this anion acts both by associating with the reactants and by entering the activated complexes. It is involved in the activated complex for aquation as well as for anation.

The difficulty in reaching definite conclusions about the mechanism of substitution in hexacoördinated complex ions has often been referred to. The particular difficulty when water is the solvent, that solvatization frequently intervenes as a step in the replacement of one ion for another, can perhaps be avoided by studying substitution reactions in other solvents. Thus, some of the most successful work in this field was done using CH_3OH as solvent.[1] Studies in other solvents, however, do not answer the questions about mechanism when reactions are carried out in water, although indirect light is thrown on this problem as more and more systems are understood.

In this paper we describe the results of a direct attack on the problem of the mechanism of aquation in water as a solvent. The method used attempts to distinguish those reacting systems on the one hand which make use of a common intermediate when a variety of groups are replaced by water, from those on the other, which do not involve a common intermediate. The relation to Ingold's[2] classification of mechanisms as SN1 and SN2 is that reactions of the first group are necessarily SN1 although those of the second group are not necessarily SN2. Studies of the general type implied have been found valuable in establishing the mechanism of substitution in organic molecules. In the systems we have explored, involving substitution in $Co(NH_3)_5X^{++}$, the attempts to learn the mechanism of simple aquation using competition for two different substances have failed because of the strong interaction between the ions undergoing substitution and the groups which qualify as competing effectively against water in the formation of products. A method entirely free from this complication and which shows promise is to observe the competition involved on aquation between isotopically distinct forms of the substituting ligand, water. The principle of using isotope fractionation data to characterize a chemical intermediate has been used in other systems,[3] and in the work to be described here, was used to search for evidence of the intermediate $Co(NH_3)_5^{+++}$.

The reactions in which oxygen-isotope fractionation studies were made are the aquations of $Co(NH_3)_5Cl^{++}$, $Co(NH_3)_5Br^{++}$ and $Co(NH_3)_5I^{++}$ under the influence of the ions, Hg^{++}, Ag^+ and Tl^{+++}. These cations greatly increase the rate of halide replacement, without appreciably increasing the rate at which isotopic equilibrium is reached in the water bound in the product ion. The spontaneous aquations are so slow that the exchange of the product aquo ion with the solvent may be a complication. During the course of this work, a

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(1) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Chapter VII, Sec. 23, Cornell University Press, Ithaca, N. Y., 1953.

(3) A. E. Cahill and H. Taube, THIS JOURNAL, **74**, 2312 (1952).

semi-micro method of isotopic analysis of the complex cations was refined, and there is hope of being able to extend the measurements to the spontaneous aquation reactions. The chemical competition studies were also done with the cations present, in some systems using $SO_4^=$ to compete against H_2O, and in others, NO_3^-. Although conceived as contributing to the solution of the same problem the results on the competition for isotopic forms of water, and competition for chemically distinguishable products feature distinct elements of interest, and therefore are presented and discussed separately, in Parts A and B, respectively.

Experimental

Apparatus.—CO_2 samples were analyzed for the ratio, O^{18}/O^{16}, by means of an isotope ratio mass spectrometer manufactured by the Consolidated Engineering Corporation (Model 21-201). Kinetic and chemical competition data were obtained using a Beckman model DU quartz spectrophotometer incorporating a thermostated cell compartment and cell holder. The temperature-controlling apparatus was such that absorption cells could be maintained at a constant temperature within ±0.05°. Absorption measurements in the visible region were made on solutions in matched, 10 cm. Vycor cells. For work in the ultraviolet region on the association reactions, matched, 10 cm. quartz cells were employed.

Materials.—Cobalt(III) complexes were used as the perchlorate form in all experiments. The salt $Co(NH_3)_5Cl(ClO_4)_2$ was prepared from $Co(NH_3)_5Cl_3$, which was prepared by the method of Hynes, Yanowski and Shiller.[4] $Co(NH_3)_5Br_3$ was used to prepare $Co(NH_3)_5Br(ClO_4)_2$ and was made by the method of Diehl, Clark and Willard.[5] The salt $Co(NH_3)_5I(ClO_4)_2$ was made by treating $Co(NH_3)_5I_3$, obtained by heating $(Co(NH_3)_5H_2O)I_3$ at 60°, with $HClO_4$ at 0°, followed by repeated crystallization in perchlorate medium. $Hg(ClO_4)_2$ stock solutions were prepared by dissolving weighed amounts of HgO in perchloric acid solution. An excess of $HClO_4$ was present to suppress hydrolysis of the Hg^{++} ions. $AgClO_4$ stock solutions were made by dissolution of Ag_2CO_3 in $HClO_4$ followed by boiling to expel CO_2. For preparation of a $Tl(ClO_4)_3$ stock solution, a weighed amount of metallic thallium was dissolved in perchloric acid to produce a solution of $TlClO_4$ through which ozone was bubbled to oxidize the thallium to the trivalent state. $HClO_4$ and H_2SO_4 solutions were prepared from acids and analyzed by titration with standard base. Na_2SO_4 stock solutions were made by dissolving weighed amounts of anhydrous salt in redistilled water. $NaHSO_4$ solutions were formed by combination of standard Na_2SO_4 and H_2SO_4 solutions. $NaClO_4$ solutions were prepared by neutralizing Na_2CO_3 in redistilled water with a slight excess of $HClO_4$ and boiling to expel CO_2. Excess acid was determined by titration and $NaClO_4$ content by drying aliquots to constant weight at 140°. Redistilled water was employed for the preparation of all stock solutions and test solutions and most chemicals were of analytical reagent grade.

Procedures and Treatment of Data

Definition of Symbols.—R is used to represent the radical $Co(NH_3)_5$. A formula such as $RH_2O^{+++}\cdot SO_4^=$ represents an outer-sphere[6] complex ion between $Co(NH_3)_5H_2O^{+++}$ and $SO_4^=$.

N_s represents the mole fraction of H_2O^{18} in the solvent water after completion of reaction, N_i is that in the water obtained from the inner sphere of coördination of the ion RH_2O^{+++} formed on aquation.

$f(\equiv N_s/N_i)$ is the isotopic fractionation factor on aquation.

$D(\equiv \log I_o/I)$ is the optical density. Subscripts o, t, and ∞ refer to time of measurement.

F is the fraction of the reacting complex RX^{++} converted to RSO_4^+ or RNO_3^{++}, the balance forming the aquo complex RH_2O^{+++}.

Isotopic Fractionation Studies.—The procedure was briefly as follows. Upon completion of the reactions at 25°, an aliquot of the solution was removed to be equilibrated with CO_2 for determination of the ratio O^{18}/O^{16} in the solvent. The remainder of the solution was cooled rapidly to 0° and HBr was added to precipitate $(Co(NH_3)_5H_2O)Br_3$. At this temperature the exchange of the aquo ion with the environment is negligible in the time necessary for complete precipitation and separation. This precipitate was filtered and dried in a vacuum desiccator. Analysis of precipitates prepared in this manner, both by determination of Co content and by dehydration on heating, proved them to possess only water bound in the coördination sphere of the cation. The thoroughly dried precipitate was weighed and placed in the high vacuum system and then heated at 110°. At this temperature the complex-bound water is released, leaving a residue of purple $Co(NH_3)_5Br_3$. The water collected was transferred to a sample tube and a known weight of CO_2 was added from a calibrated manometric device attached to the vacuum system. From the weight of the precipitate and the stoichiometry of RH_2OBr_3 the amount of water obtained from the salt was determined and, with the known weight of CO_2 added, the mole ratio of H_2O to CO_2 could be calculated. The aliquot of solution taken after completion of reaction was placed in an equilibration vessel, attached to the vacuum line and subjected to repeated cycles of freezing with liquid N_2, pumping and thawing to ensure complete removal of air. Then a known weight of CO_2 was added for equilibration. Sample tubes were stored for equilibration by immersion in a water-bath at 25.0°. The half-time for isotopic exchange between CO_2 and H_2O under these conditions is approximately 7 hr.[7] The equilibration vessels were allowed to remain in the water-bath for a period of 7–10 half-times for exchange, at the end of which time attainment of equilibrium is very nearly complete. Equilibrated CO_2 samples were separated from water samples on the vacuum system and transferred to sample tubes for measurement of the oxygen isotope ratio.

Relative values of isotope ratios were measured rather than absolute values, the procedure being adopted of normalizing all readings by a factor so as to yield a value of 2.000×10^{-3} for the ratio O^{18}/O^{16} in a standard of distilled water. Precise relative values suffice for the applications which have been made of the results.

Chemical Competition Studies.—The relative rates of reaction of $SO_4^=$ and H_2O and of $NO_3^=$ and H_2O with the halogenopentamminecobaltic complexes induced by the ions, Hg^{++}, Ag^+ and Tl^{+++}, were measured by a spectrophotometric technique. The differences in the extinctions of RH_2O^{+++} and RSO_4^+ over the range of wave lengths 590–490 mμ make possible the determination of the ratio of sulfate to aquo species formed during reaction with an estimated precision of ±2%. The analogous ratio of nitrato to aquo species, in experiments using NO_3^- instead of $SO_4^=$, could be determined with comparable precision by this method in the region 540–480 mμ.

All reactions were carried out under as nearly identical conditions as possible. In the competition experiments with Hg^{++}, RX^{++} and $SO_4^=$, reactions were run at constant ionic strength, replacing $NaClO_4$ by Na_2SO_4 to investigate the effect of variation in $(SO_4^=)$. Acid was necessarily present in sufficient amount to suppress hydrolysis of Hg^{++} ions. Sodium sulfate and sodium bisulfate were added in a pre-determined ratio which was fixed by the total acid present and the dissociation quotient of HSO_4^- at the prevailing ionic strength.[8]

In a typical experiment, the test solution contained 0.001 M RX^{++}, 0.005 M Hg^{++}, 0.010–0.050 M Na_2SO_4, 0.008–0.40 M $NaHSO_4$, 0.050 M $HClO_4$ and $NaClO_4$ in sufficient amount to make the ionic strength 0.338. Series of experiments with Ag^+ and Tl^{+++} were of necessity conducted at higher concentrations of metal ions, due to the slower rates of reactions in these systems. After complete reaction a portion of the test solution was placed in a 10 cm. absorption cell for comparison with a similar solution at the same ionic strength, but without added $SO_4^=$. The difference

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(4) W. A. Hynes, L. K. Yanowski and M. Shiller, THIS JOURNAL, **60**, 3053 (1938).

(5) H. Diehl, H. Clark and H. H. Willard, "Inorganic Syntheses," ed. by H. S. Booth, *et al.*, McGraw-Hill Book Co., New York, N. Y., 1939, p. 186.

(6) H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953).

(7) C. A. Mills and H. C. Urey, *ibid.*, **62**, 1019 (1940).

(8) W. C. Bray and H. A. Liebhafsky, *ibid.*, **57**, 51 (1935).

in extinctions of the solutions, when divided by the difference in extinctions of the RH_2O^{+++} and RSO_4^+ ions at any one wave length, yields the fraction of cobalt complex present in the sulfato form at the end of the aquation reaction. A similar procedure was followed in the experiments in which NO_3^- was substituted for $SO_4^=$.

The ratio of sulfato to aquo (or nitrato to aquo) forms, after completion of the induced aquation reaction, alters slowly with time because these ratios are in general not equilibrium values. Therefore, it was necessary to adjust the concentrations of reactants, increasing the reaction rate so that all measurements could be made in a time short compared to the half-time of the drive to equilibrium.

Kinetics of the Reaction of $Co(NH_3)_5Cl^{++}$ with Hg^{++} in the Presence of $SO_4^=$.—The extinctions of RH_2O^{+++} and RSO_4^+ are identical at the wave length 475 mμ while that of RCl^{++} differs, for $cd = 0.010$, by 0.132. Since all solution species except the cobalt complexes are transparent in this region, the wave length 475 mμ is convenient for following the kinetics of the net substitution reaction of RCl^{++} with $SO_4^=$ and H_2O. The reaction of RCl^{++} with Hg^{++} is much slower than the similar reactions of RBr^{++} and RI^{++} and, indeed, was the only one that could be followed conveniently by a spectrophotometric method, since the other reactions, at the concentration levels necessary to obtain precise results, are complete soon after mixing the reactants.

The procedure used in this study for preparation and measurement of solutions was essentially that used in the chemical competition studies, except that spectral differences between solutions containing $SO_4^=$ and those containing no $SO_4^=$ were followed as a function of time at the wave length 475 mμ. A plot of $(D_t - D_\infty)/(D_0 - D_\infty)$ *vs.* t, for any particular solution, yielded a value of the half-time for reaction, which could then be used with similar data at varying $(SO_4^=)$ to establish reaction kinetics.

Association of Hg^{++} with $SO_4^=$ and RCl^{++} with $SO_4^=$.—The importance of association between the reactants was indicated by the interesting kinetics of the reaction $RCl^{++} + Hg^{++} + SO_4^=$. The formulation of a complete rate law for the reaction requires a knowledge of the extent of association between the reactants, *i.e.*, between Hg^{++} and $SO_4^=$ and between RCl^{++} and $SO_4^=$ under the experimental conditions. Measurement of these quantities was accomplished by the method of Newton and Arcand,[9] using variations in the ultraviolet absorption bands of the cations on addition of $SO_4^=$ at constant ionic strength. The observed spectral changes may be interpreted by the equilibrium

$$Co(NH_3)_5Cl^{+} + SO_4^= \overset{K_1}{=} Co(NH_3)_5Cl^{++}\cdot SO_4^= \quad (1)$$

for the association of RCl^{++} with the $SO_4^=$ as an outer sphere complex ion. The association of mercuric ion with sulfate was measured in an analogous fashion, the major equilibrium involved being that expressed in eq. 2.

$$Hg^{++} + SO_4^= \overset{K_2}{=} HgSO_4 \quad (2)$$

The method does not distinguish, for the case of $Hg^{++} + SO_4^=$, between $SO_4^=$ bound directly to the cation and an outer sphere complex ion, but does yield an equilibrium quotient for the total association, which is the quantity of interest for the proposed application. Association quotients were measured at the ionic strength prevailing in the kinetic experiments, 0.32.

Spectral differences between solutions containing $SO_4^=$ and those containing no $SO_4^=$, all at constant ionic strength, were measured for solutions with varying amounts of sulfate ion. If the activity coefficients of all ions involved in the association equilibria are constant at constant ionic strength, but varying $(SO_4^=)$, the results may be interpreted with the aid of eq. 3.

$$D = D_c - (D - D_a)/K(SO_4^=) \quad (3)$$

Here D represents the optical density of a particular solution containing $SO_4^=$. D_c is the optical density of the 1:1 complex, and would represent the experimentally observed quantity if the cation under examination were completely complexed. D_a is the optical density of a solution containing no $SO_4^=$. K is the equilibrium quotient for the association reaction in question and $(SO_4^=)$ is the concentration of uncomplexed $SO_4^=$ at equilibrium. $(SO_4^=)$ differs but slightly from stoichiometric sulfate and the first plot of the data according to eq. 3, using stoichiometric $SO_4^=$, serves to fix $(SO_4^=)$ sufficiently well to make the second plot final.

Part A. Isotopic Fractionation Studies

Results

The results of the studies on oxygen isotope fractionation in the conversion of RCl^{++}, RBr^{++} and RI^{++} to the aquo form are shown in Tables I, II and III, respectively.

TABLE I

SUMMARY OF ISOTOPIC COMPETITION DATA FOR THE INDUCED AQUATION OF RCl^{++a}

Exp. no.	(RCl^{++})	(Hg^{++})	(H^+)	μ	$f = N_s/N_i$
1.01	0.06	0.58	0.01	1.93	1.011
1.02	.06	.58	.01	1.93	1.012
1.03	.01	.58	.01	1.78	1.012
1.04	.01	.05	.05	0.23	1.012
1.05	.01	.05	.05	.23	1.012
1.06[b]	.015	.10	.01	.45	1.010
1.07[c]	.015	.05	.05	.37	1.010
1.08[d]	.015	.05	.20	1.70	1.008
1.09[e]	.015	.10	.01	0.39	1.012
1.10[f]	.015	.05	.20	.46	1.012
1.11[g]	.015	.05	.20	1.40	1.009
1.12[h]	.06	..	.01	0.79	1.009
1.13[i]	.01	..	.10	.43	0.996

[a] Temperature = 25°. [b] $(SO_4^=) = 0.03$ *M*. [c] $(SO_4^=) = 0.03$ *M*, $(HSO_4^-) = 0.03$ *M*. [d] $(SO_4^=) = 0.10$ *M*, $(HSO_4^-) = 1.00$ *M*. [e] $(NaNO_3) = 0.030$ *M*. [f] $(NaNO_3) = 0.060$ *M*. [g] $(NaNO_3) = 1.00$ *M*. [h] $(Ag^+) = 0.60$ *M*. [i] $(Tl^{+++}) = 0.05$ *M*.

TABLE II

SUMMARY OF ISOTOPIC COMPETITION DATA FOR THE INDUCED AQUATION OF RBr^{++a}

Exp. no.	(RBr^{++})	(Hg^{++})	(H^+)	μ	$f = N_s/N_i$
2.01	0.01	0.05	0.05	0.23	1.012
2.02	.01	.05	.05	.23	1.012
2.03[b]	.01	..	.05	.18	1.007
2.04[c]	.01	..	.10	.19	0.993

[a] Temperature = 25°. [b] $(Ag^+) = 0.10$ *M*. [c] $(Tl^{+++}) = 0.01$ *M*.

TABLE III

SUMMARY OF ISOTOPIC COMPETITION DATA FOR THE INDUCED AQUATION OF RI^{++a}

Exp. no.	(RI^{++})	(Hg^{++})	(H^+)	μ	$f = N_s/N_i$
3.01	0.01	0.05	0.05	0.23	1.012
3.02	.01	.05	.05	.23	1.012
3.03[b]	.10	..	.05	.18	1.010
3.04[c]	.01	..	.10	.19	1.003

[a] Temperature = 25°. [b] $(Ag^+) = 0.10$ *M*. [c] $(Tl^{+++}) = 0.01$ *M*.

Discussion

An immediate conclusion from the results shown in Tables I, II and III is that a common intermediate having properties independent of the reaction used to generate it, is not formed in all the reactions. This follows from the observation that the values of f are not the same for all the different systems studied. Furthermore, the series with RX^{++} and Tl^{+++} as reactants, which because of differences in f observed for X = Cl, Br, and I cannot involve an intermediate of common properties,

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[9] T. W. Newton and G. M. Arcand, THIS JOURNAL, **75**, 2449 (1953).

shows the magnitude of the differences which can be expected when some memory of the halide is left while the bond to water is being formed. These considerations when applied to the results obtained with the series $RX^{++} + Hg^{++}$, for which f is essentially constant, makes it likely that in this series a common intermediate is involved, *i.e.*, the bond to water is not made until all memory of the effects of the halide ion removed has been wiped out. Thus for the series $RX^{++} + Hg^{++}$, the mechanism appears to be of the SN1 type. For the others we suggest that the reaction proceeds partly at least by SN2 mechanisms, *i.e.*, the bond with water is being formed while that with the halide is being broken. These conclusions are consistent with a feature of the chemistry of the cations used to remove the halide ion. Of them, Hg^{++} acts most rapidly. It seems reasonable that where the interaction of X with the metal ion is greatest, the necessity for exploiting the formation of the new bond to water in the activated complex is least. We are inclined to reject the interpretation that a free intermediate is formed in all the systems, but that for some the subsequent reactions are so rapid that a non-equilibrium environment is sampled. It is difficult to understand on this basis how the metal ion can determine the life-time of the intermediate; also it is not easy to understand why Hg^{++} and Tl^{+++} give extreme values for the fractionation factor.

The actual magnitudes of the values of f observed give some support to the interpretation advanced. A kinetic fractionation in the reaction of an intermediate $Co(NH_3)_5^{+++}$ with water can be expected because the water molecules are being removed from a partially bound state, in the liquid. The equilibrium fractionation for water transferred from the liquid to the vapor is approximately 0.8%; thus the value of 1.2% observed for the kinetic discrimination is reasonable. There is no equilibrium discrimination in the reaction of $Co(NH_3)_5^{+++}$ with water opposing the kinetic one. Studies[10,11] have shown that outer sphere interactions of cations with water do not appreciably affect the relative fugacities of H_2O^{16} compared to H_2O^{18}. The assumption of an SN2 mechanism provides a qualitative explanation of the remarkable observation that with Tl^{+++} and RBr^{++} or RCl^{++}, the heavy isotope of water is bound more rapidly than the light. This might result if the interaction of Tl^{+++} with the halide sets free inner sphere water which is consumed in making the new bond to Co(III) in a concerted mechanism.[12] The coördination sphere of Tl^{+++} can be expected to bind H_2O^{18} in preference to H_2O^{16} by as much as 2.5 to 3% while the effect with Ag^+ would be much less. In the absence of special circumstances provided by the presence of the cation while the bond between Co(III) and H_2O is being formed, H_2O^{16} would be expected to react more rapidly than H_2O^{18}, just as for the SN1 case. Some difference for X = Cl as compared to X = I is expected, but it is difficult to estimate from first principles how great the difference should be.

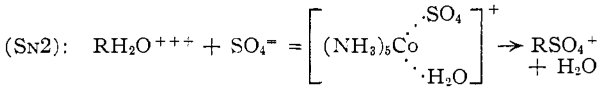
In the system $Hg^{++} + RCl^{++}$, the values of f were shown to be independent of the concentrations of RCl^{++}, Hg^{++} and H^+, as they must be if the values given truly represent fractionation factors. They do however depend on the nature of the anion, although at low concentration NO_3^- and ClO_4^- are indistinguishable. In the light of the results given in the next section which show that $SO_4^=$ (and presumably NO_3^- when at high concentration) are in the activated complex and/or associate with a cationic intermediate such as $Co(NH_3)_5^{+++}$, the effect of the anions is expected. The magnitude of the differences observed demonstrates the sensitivity of the isotopic fractionation method. On either the SN1 or SN2 mechanism, the anions can at most be present in the outer sphere of Co(III) for the aquation reaction. Their influence is not understood satisfactorily; it may be that they produce local breaking of the water structure, and therefore decrease the intensity of the H_2O–H_2O interactions. Such an effect has however escaped notice in direct studies of the influence of salts in the H_2O^{16}/H_2O^{18} fugacity ratio.[10,11]

Part B. Chemical Competition Studies

In an earlier paper[6] it was pointed out that attempts to reach conclusions about mechanisms of substitution by purely kinetic studies are vitiated in systems in which there are strong interactions between reactants. To illustrate: although the rate of substitution of H_2O by $SO_4^=$ in RH_2O^{+++} is almost constant over a considerable range of the concentration of $SO_4^=$, this kinetic behavior does not demonstrate that an SN1 mechanism operates. The particular form of the rate law described shows only that the compositions of the activated complex and of the dominant form of Co(III) are identical, and the latter is known on independent evidence to have the composition $RH_2O^{+++}\cdot SO_4^=$. Reasonable rate-determining steps with activated complexes of this formula for both SN1 and SN2 steps can be envisioned

(SN1): $RH_2O^{+++}\cdot SO_4^= \longrightarrow R^{+++}\cdot SO_4^= + H_2O$

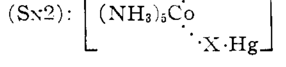
$R^{+++}\cdot SO_4^= \longrightarrow RSO_4^+$



(SN2): $RH_2O^{+++} + SO_4^= = \left[\begin{array}{l} \qquad\qquad\quad \cdot SO_4 \\ (NH_3)_5Co \\ \qquad\qquad\quad \cdot H_2O \end{array}\right]^+ \rightarrow RSO_4^+ + H_2O$

(in the SN1 mechanism above, $SO_4^=$ is involved as associating with the intermediate $Co(NH_3)_5^{+++}$, but is not admitted to the inner coördination sphere of the cation). For analogous reasons, the activated complex of composition $[Hg^{++}\cdot RX^{++}\cdot SO_4^=]$ encountered in the work to be described presently cannot be taken as demonstrating an SN2 mechanism. There are reasonable possibilities for locating $SO_4^=$ in activated complexes of this composition on SN1 as well as SN2 mechanisms. For example

(SN1): $[SO_4^=\cdot(NH_3)_5Co^{+++}\ldots X^-\ldots Hg^{++}]$ or $[(NH_3)_5Co^{+++}\ldots X^-\ldots HgSO_4]$



(SN2): $\left[\begin{array}{l} \qquad\qquad\quad \cdot SO_4 \\ (NH_3)_5Co \\ \qquad\qquad\quad \cdot X\cdot Hg \end{array}\right]^{++}$

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[10] H. Feder and H. Taube, *J. Chem. Phys.*, **20**, 1335 (1952).

[11] H. Taube, *J. Phys. Chem.*, **58**, 523 (1954).

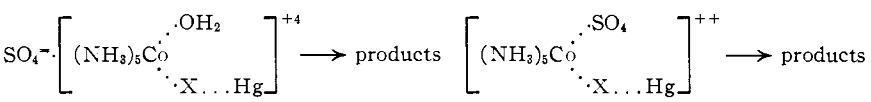
[12] This mechanism has features similar to that proposed by A. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1953), to explain effects observed on deuterium substitution.

We now turn to a consideration of what may be learned by measuring the distribution of Co(III) between the products, RH_2O^{+++} and RSO_4^+, as a function of ($SO_4^=$), for example, in the reaction of RCl^{++} with Hg^{++} in the presence of $SO_4^=$. It can be seen that if in fact $SO_4^=$ enters into outer sphere association with the SN1 intermediate $Co(NH_3)_5^{+++}$, no distinction may be possible[13] on the basis of such observations, between SN1 and SN2 mechanisms for paths which contain $SO_4^=$ in the corresponding activated complexes. Thus the composition $[SO_4 \cdot RX \cdot Hg]^{++}$ for the activated complex is common to all the following mechanisms.

(SN1) Aquation $SO_4^= \cdot RX^{++} \cdot Hg^{++} \longrightarrow R^{+++} \cdot SO_4^= + HgX^+$ Sulfate formation

$$R^{+++} \cdot SO_4^= + H_2O \longrightarrow RH_2O^{+++} \cdot SO_4^= \qquad R^{+++} \cdot SO_4^= \longrightarrow RSO_4^+$$

(SN2)



$$SO_4^= \cdot \left[(NH_3)_5Co \begin{matrix} \cdot OH_2 \\ \\ \cdot X \ldots Hg \end{matrix} \right]^{+4} \longrightarrow \text{products} \qquad \left[(NH_3)_5Co \begin{matrix} \cdot SO_4 \\ \\ \cdot X \ldots Hg \end{matrix} \right]^{++} \longrightarrow \text{products}$$

Furthermore it develops that paths involving $SO_4^=$ in the rate-determining steps are the dominant ones even at quite low $SO_4^=$ concentration. These paths having activated complexes containing the anion are not directly comparable to the pure aquation paths and the latter, which were of primary interest in undertaking this work, are fairly difficult to isolate. Finally, will be mentioned a feature complicating the interpretation of the product competition data obtained for a variety of reacting systems such as RCl^{++}, RBr^{++} and RI^{++} with Hg^{++}, Tl^{+++} and Ag^+, at constant sulfate ion concentration. Since a number of parallel paths operate, for their fullest use such data must be coupled with a study of the kinetics of the reaction, so that the product competition for each path can be determined. Variations in the ratios of products from system to system may be a result merely of the different contributions to the total reaction by the various paths, with a constant product ratio for each path.

The present results consist of a rather complete kinetic analysis of the system $Hg^{++} + RCl^{++} + SO_4^=$, including, of necessity, an independent study of the association of $SO_4^=$ with each of the cations, and measurement of the relative amounts of the products RSO_4^+ *vs.* RH_2O^{+++} and RNO_3^{++} *vs.* RH_2O^{+++}, for a variety of different reaction systems. For the reasons outlined in the previous paragraph, only limited conclusions can be drawn from the present data, still limited in scope. The data are offered as the beginning of a more complete study, and because the competition data as well as the data on association of reactants are of interest in themselves. When they are extended to a complete kinetic analysis of the other reacting systems, some further conclusions about mechanism may be possible, also for the paths involving anions. It can be seen that the SN1 paths mentioned above require the product ratio to be independent of the nature of the cation used to remove halide, and of the identity of the halide ion.

Results

Association of RCl^{++} and Hg^{++} with $SO_4^=$.—The results of the spectrophotometric study of the association of RCl^{++} with $SO_4^=$ are shown in Table IV and of Hg^{++} with $SO_4^=$ in Table V. A novel feature of the change in absorption for RCl^{++} when $SO_4^=$ is present in solution is that the extinction decreases. In the usual case, the "outer-sphere" influence of anions on the strong ultraviolet band of cations is to increase the absorption. Sulfate ion causes a decrease in the near ultraviolet extinction also of $(NH_3)_5Co\ SO_4^+$.[14] The conclusion that RCl^{++} associates with $SO_4^=$ is in agreement with the observation that more than one stage of association is indicated for $Co(NH_3)_6^{+++}$ with $SO_4^=$.[15] The value of 26 found spectrophotometrically for the first stage of association of Hg^{++} with $SO_4^=$ at $\mu = 0.33$ is in reasonable agreement with the value of 22 reported by Infeldt and Sillen[16] for $\mu = 0.50$, also at 25°. A second stage of association escaped notice in our work, perhaps because at the highest ($SO_4^=$) which was used, the ionic strength was also higher. This may have caused a partial cancellation of the effect produced by a second stage of association.

TABLE IV

SPECTROPHOTOMETRIC DETERMINATION OF THE ASSOCIATION OF RCl^{++} WITH $SO_4^=$

(at 25°; $\Sigma(RCl^{++}) = 0.001$; $\Sigma(H^+) = 0.001$; $\mu = 0.34$)

$\Sigma(SO_4^=)$	$(SO_4^=)$	$(RCl^{++}SO_4^=)/(RCl^{++})$	K
0.010	0.0098	0.046	4.7
.020	.0197	.094	4.9
.050	.0494	.238	4.8
.100	.0991	.475	4.8
		Av.	4.8 ± 0.5

λ	299	301	303	305
D_0	1.680	1.444	1.243	1.065
D_1	1.210	1.013	0.831	0.627

TABLE V

SPECTROPHOTOMETRIC DETERMINATION OF THE ASSOCIATION OF Hg^{++} WITH $SO_4^=$

(Temp. = 25°; $\mu = 0.33$ (0.43 when $\Sigma(SO_4^=) = 0.180$); Σ(Hg II) = 0.005)

$\Sigma(SO_4^=)$	$\Sigma(H^+)$	$(SO_4^=)$	(HSO_4^-)	(Hg^{++})	$(Hg^{++}\text{-}SO_4^=)$	K
0.036	0.066	0.0188	0.0156	0.0033_5	0.0016_5	26.2
.090	.090	.0475	.0397	$.0022_2$	$.0027_8$	26.4
.180	.130	.0985	.0779	$.0013_9$	$.0036_1$	26.4
					Av.	26.3 ± 0.6

λ	266	268	270	272	274	276
D_0	0.031	0.024	0.016	0.045	0.013	0.012
D_1	0.825	0.628	0.460	0.349	0.263	0.199

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(13) If however the dominant form of the intermediate in the sulfate concentration range covered is the uncomplexed form R^{+++}, or if there is a change in the degree of sulfate complexing in the concentration range in question, refined data on product competition could be used to distinguish SN1 and SN2 mechanisms. This point is referred to again in the Discussion.

(14) H. Taube, unpublished observations.

(15) F. A. Posey and H. Taube, THIS JOURNAL, **78**, 15 (1956).

(16) G. Infeldt and L. G. Sillen, *Svensk. Kem. Tid.*, **58**, 104 (1946).

Kinetics of the Reaction of RCl^{++} with Hg^{++} in the Presence of $SO_4^{=}$.—A preliminary kinetic survey of this system showed the reaction to be strictly first order with respect to RCl^{++} and first order with respect to Hg^{++}, with or without $SO_4^{=}$ present. The data recorded in Table VI have been used to determine the order of the reaction with respect to $SO_4^{=}$. A satisfactory analysis of the data in Table VI could not be achieved without taking into account association of $SO_4^{=}$ with Hg^{++} and with RCl^{++}. To interpret the data, a number of parallel paths must be assumed, differing with respect to the dependence on $(SO_4^{=})$

TABLE VI

KINETICS OF THE REACTION RCl^{++} WITH Hg^{++} IN THE PRESENCE OF $SO_4^{=}$

(Temp., 25°; $\mu = 0.30 \pm 0.03$; $\Sigma(RCl^{++}) = 0.001$; (Hg II) = 0.005)

$(SO_4^{=})$	$t_{1/2}$	Q
0.000	43.0	3.43
.0091	20.2	7.28
.0181	15.5	9.50
.0460	8.2	18.01

$$\frac{-d\Sigma(RCl^{++})}{dt} = k_1(RCl^{++})(Hg^{++}) + k_2(RCl^{++})(Hg^{++})(SO_4^{=}) + k_3(RCl^{++})(Hg^{++})(SO_4^{=})^2 \quad (4)$$

These paths will be referred to as 1, 2 and 3, respectively. Letting a and b represent the total initial concentration of RCl^{++} and Hg^{++}, c the equilibrium concentration of $SO_4^{=}$ and x the concentration of total RCl^{++} having undergone reaction at time t, eq. 4 on integration becomes

$$Q \equiv \frac{k_1 + k_2c + k_3c^2}{(1 + K_1c)(1 + K_2c)} = \frac{1}{(b - a)t} \ln \frac{a(b - x)}{b(a - x)} \quad (5)$$

Putting in the experimental values of a and b (Table VI), and treating c as being essentially constant ($SO_4^{=}$ is in considerable excess, and at low $SO_4^{=}$, little is incorporated into product as RSO_4^{+})

$$Q = \frac{2.303}{0.004t}\left[\log\left(\frac{D_0 - D_\infty}{D - D_\infty}\right)\left(\frac{4}{5} + \frac{1}{5}\left(\frac{D - D_\infty}{D_0 - D_\infty}\right)\right)\right] \quad (6)$$

Using this equation a value of Q can be calculated for each experimental point in a run. The values of Q recorded in Table VI are the mean values thus calculated for each experiment.

The value of k_1 is obtained directly from the experiments with no added $SO_4^{=}$; k_2 and k_3 are determined by solution of the simultaneous equations for the several values of Q. The results are $k_1 = 3.4_3 \pm 0.26$ l. mole^{-1}min.$^{-1}$, $k_2 = 4.8 \pm 0.1 \times 10^2$ l.^{2} mole^{-2}min.$^{-1}$, $k_3 = 1.11 \pm 0.14 \times 10^4$ l.^{3} mole^{-3}min.$^{-1}$.

Competition in Formation of Products.—The results of the chemical competition data are shown in Tables VII, VIII, and IX. When the kinetic data for the system $RCl^{++} + Hg^{++} + SO_4^{=}$ are combined with the competition data for this reaction, the fraction of the RCl^{++} reacting which appears as RSO_4^{+} can be calculated for each path. Table X shows the fraction of the RCl^{++} which reacts by each of the three rival paths at 25° at the various $SO_4^{=}$ concentrations of experiments 7.02, 7.03 and 7.04.

TABLE VII

THE PRODUCTS OF THE INDUCED AQUATION OF RCl^{++} IN THE PRESENCE OF $SO_4^{=}$ OR NO_3^{-}

$(RCl^{++}) = 1.00 \times 10^{-3}$ *M*, temperature = 25° except exps. 7.05 and 7.06

Exp. no.	Metal ion	Concn. × 10^3	(H^+)	$(SO_4^{=})$	(HSO_4^-)	(NO_3^-)	μ	F^a
7.01	Hg^{++}	20	0.02	0.06	0.03	..	0.29	21.5
7.02	Hg^{++}	5	.05	.05	.04	..	.34	20.6
7.03	Hg^{++}	5	.05	.02	.016	..	.34	14.7
7.04	Hg^{++}	5	.05	.01	.008	..	.34	10.1
7.05	Hg^{++}	5	.05	.02	.016	..	.34	15.0[b]
7.06	Hg^{++}	5	.05	.02	.016	..	.34	14.5[c]
7.07	Tl^{+++}	20	.05	.05	.04	..	.4	47
7.08	Hg^{++}	20	1.02	...	...	1.00	1.1	47.5
7.09	Hg^{++}	100	1.00	...	...	0.90	1.3	37

[a] F represents the per cent. of RCl^{++} which is converted to RSO_4^{+} or RNO_3^{++} on reaction. [b] At 15.5°. [c] At 34.0°.

TABLE VIII

THE PRODUCTS OF THE INDUCED AQUATION OF RBr^{++} IN THE PRESENCE OF $SO_4^{=}$ OR NO_3^{-}

$(RBr^{++}) = 1.00 \times 10^{-3}$ *M*, temperature = 25°

Exp. no.	Metal ion	Concn. × 10^3	(H^+)	$(SO_4^{=})$	(HSO_4^-)	(NO_3^-)	μ	F
8.01	Hg^{++}	10	0.01	0.02	0.02	..	0.11	11.5
8.02	Hg^{++}	5	.05	.05	.04	..	.34	15.3
8.03	Hg^{++}	5	.05	.02	.016	..	.34	11.8
8.04	Hg^{++}	5	.05	.01	.008	..	.34	8.2
8.05	Tl^{+++}	20	.05	.05	.04	..	.4	41
8.06	Ag^{+}	10	.01	.05	.05	..	.21	39
8.07	Hg^{++}	10	1.01	..	..	1.00	1.04	18.3

TABLE IX

THE PRODUCTS OF THE INDUCED AQUATION OF RI^{++} IN THE PRESENCE OF $SO_4^{=}$ OR NO_3^{-}

$(RI^{++}) = 1.00 \times 10^{-3}$ *M*, temperature = 25°

Exp. No.	Metal ions	Concn. × 10^3	(H^+)	$(SO_4^{=})$	(HSO_4^-)	(NO_3^-)	μ	F
9.01	Hg^{++}	5	0.05	0.05	0.04	..	0.34	12.4
9.02	Hg^{++}	5	.05	.02	.016	..	.34	9.5
9.03	Hg^{++}	5	.05	.01	.006	..	.34	7.3
9.04	Ag^{+}	10	.01	.015	.008	..	.08	49
9.05	Ag^{+}	25	.025	.010	.010	..	.09	37
9.06	Hg^{++}	25	1.03	...	...	1.00	1.03	19.2
9.07	Ag^{+}	100	1.10	...	...	1.00	1.20	21.4

TABLE X

FRACTIONS OF THE REACTION, $RCl^{++} + Hg^{++} + SO_4^{=}$, WHICH PROCEED BY VARIOUS PATHS

Path	Fraction		
1	0.070	0.217	0.393
2	.452	.553	.502
3	.478	.230	.105
$(SO_4^{=})$	.046	.181	.0091

Let the fractions of the reaction proceeding by each of the paths 1, 2 and 3 be B_1, B_2 and B_3. Assume for each of these paths that the fraction of RCl^{++} appearing as RSO_4^{+} is constant; let these constant fractions be X_1, X_2 and X_3. Then a series of simultaneous equations of the form

$$B_1X_1 + B_2X_2 + B_3X_3 = F$$

can be set up for the three experiments at differing $SO_4^{=}$ concentration. These equations when solved for X_1, X_2 and X_3 yield the values -1.1 ± 4, 14.9 ± 6, and $29 \pm 4\%$. Errors in the determination of specific rates and in the distribution of products have accumulated in the values of yields for the several paths.

Discussion

The results of the studies on chemical competition for systems with $SO_4^=$ present, suffice to show that an intermediate of common properties does not carry the reaction for all of them. This follows—even though the paths of differing order in $SO_4^=$ have not been resolved for all the systems—because the conversion of RX^{++} to RSO_4^+ in the presence of Ag^+ or Tl^{+++} *exceeds* in extent that observed with Hg^{++} acting on RCl^{++} by path 3, which is the most efficient one for the formation of RSO_4^+. It seems likely, moreover, that the reactions of RBr^{++} and RI^{++} with Hg^{++} are predominantly S_N1 in character, and that the reactions of RCl^{++} with Hg^{++} by the paths 1 and 2 are also predominantly S_N1. This conclusion, attractive because it is in agreement with that reached in Part A, finds this independent support in the present data. It seems unlikely that the fraction of reaction flowing by the paths 0, 1st and 2nd order in $SO_4^=$ will be much different for RCl^{++}, RBr^{++} and RI^{++} as reactants. The agreement in the values of F in the three systems when $SO_4^=$ is low therefore indicates a common intermediate. Furthermore, when NO_3^-, which presumably gives less kinetic interference than $SO_4^=$, is the competing reactant, the values of F for Hg^{++} acting on RBr^{++} and RI^{++} agree closely. If these conclusions are accepted, it means that the intermediate $Co(NH_3)_5^{+++}$ does not react particularly efficiently with $SO_4^=$. In the $(SO_4^=)$ region in which path 2 predominates, this intermediate would be present largely as $R^{+++}\cdot SO_4^=$; nevertheless, the reaction with H_2O is approximately seven times more rapid than with $SO_4^=$.

For reasons analogous to those stated in the previous section, the reactions with Ag^+ and Tl^{+++} are considered to differ because the new bonds are formed while the $Co(III)-X^-$ bond is being broken. In these paths, formation of the anion-containing products competes much more effectively against aquation. Since the reactions with Ag^+ and Tl^{+++} considered as being partly S_N2 at least, may also be S_N1 in part, it is not possible from the data to assign dependable values to the product competition ratios by the S_N2 paths.

It should be pointed out that for the systems in which S_N1 mechanisms operate, the treatment which was made of the product competition data may apply only approximately. The rate of consumption of ΣRX^{++} may be given correctly by an equation such as (4), but the fractional conversion to RSO_4^+ can only approximately be represented by assigning a constant (independent of $(SO_4^=)$) fractional conversion by each of the three independent paths. Thus it is possible that for path 1, which does not contain $SO_4^=$ in the activated complex for the formation of $Co(NH_3)_5^{+++}$, RSO_4^+ is nevertheless formed, and the fraction of $Co(NH_3)_5^{+++}$ converted to RSO_4^+ may depend on $(SO_4^=)$. Such kinetic features themselves would constitute strong evidence for the formation of an intermediate, but the present data are not sufficiently accurate to require modification of the method of treatment which was adopted.

Another feature of the kinetic data implied in the discussion introductory to this section is worthy of explicit mention: an anion such as $SO_4^=$ acts not only to increase the rate of formation of the sulfato complex but of the aquo complex as well. Thus at 0.05 M $SO_4^=$, the rate of reaction of RCl^{++} is almost 6 times the rate when no $SO_4^=$ is present, but the fraction of RCl^{++} converted to RSO_4^+ is only 20% of the total reacting.

The conclusion suggested by the present work, that an intermediate with properties independent of the reaction by which it is made, is realized only when the most reactive cation removes halide ion, in turn implies that in the absence of such an agent, *i.e.*, for the spontaneous processes, mechanisms of this extreme type will not be important. The conclusion that $R^{+++}\cdot SO_4^=$ reacts much more frequently to form RH_2O^{+++} than to form RSO_4^+, when applied to data[17] on the exchange of H_2O between RH_2O^{+++} and solvent in the presence of $SO_4^=$, shows that the intermediate $R^{+++}\cdot SO_4^=$, which is characteristic of the S_N1 mechanism, cannot explain completely the observations made for the $RH_2O^{+++}-RSO_4^+$ system. The reaction sequence on the basis of an S_N1 mechanism would be

$$RH_2O^{+++}\cdot SO_4^= \rightleftharpoons R^{+++}\cdot SO_4^= + H_2O \quad (k_1,\ k_{-1})$$

$$R^{+++}\cdot SO_4^= \rightleftharpoons RSO_4^+ \quad (k_2,\ k_{-2})$$

From this it follows that

$$\frac{k_1k_2}{k_{-1}+k_2} + \frac{k_{-1}k_{-2}}{k_{-1}+k_2} = k'$$

where k' is the specific rate for the approach to chemical equilibrium.[6]

$$\frac{k_1k_2}{k_{-1}k_{-2}} = K_{eq}$$

$k_1k_{-1}/(k_{-1}+k_2) = k''$ where k'' is the specific rate for the exchange of H_2O between RH_2O^{+++} and H_2O when RSO_4^+ is small. Then

$$\frac{k_2}{k_{-1}} = \frac{k'}{k''(1 + 1/K)}$$

k'' is known, and sufficiently good values for k'[6] and K[13] applicable to the conditions of the experiment in which k'' was measured can be interpolated. When these are substituted

$$k_2/k_1 = \frac{3.8 \times 10^{-4}}{4.3 \times 10^{-4}(1 + 0.9)} = 0.4$$

In the present work, k_2/k_1 is observed to be ~ 0.18. In an earlier paper,[17] on comparing the rate of exchange of water with and without $SO_4^=$ in the system, it was concluded that the reaction was in part at least S_N1. This conclusion was reached without giving proper consideration to the association of RH_2O^{+++} with $SO_4^=$; since such effects do exist it is not required by the data.[18] In the face of the present observations, it may be concluded that the S_N1 mechanism plays only a minor role. The effect of $SO_4^=$ in reducing the rate of water exchange (though only slightly) can be understood also on an S_N2 mechanism. This ion exerts an effect by

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(17) A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952).

(18) This was brought to the attention of the authors by Prof. W. K. Wilmarth, University of Southern California.

changing the distribution of Co(III) between the reactant RH_2O^{+++} and the activated complex $R(H_2O)_2^{+++}$. The outer-sphere affinity of these two forms for sulfate ion is expected to be approximately the same, and the present state of understanding of these effects would accommodate a slight preference in either direction.

The conclusions we have reached concerning mechanism for ions of the type $Co(NH_3)_5H_2O^{+++}$ and $Co(NH_3)_5X^{++}$ provide no basis for conclusions in other systems, or for the reactions under widely different conditions. Thus the reactants of the tetrammine series $Co(NH_3)_4X_2^+$ may much more readily adopt S_N1 mechanisms,[19,20] because a means of stabilizing a penta-coördinated intermediate, by making use of unshared electron pairs on the remaining group X, is available.

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Mechanisms of Electron Transfer in Aquo Cations—The Reaction of RH_2O^{+++} with Cr^{++}

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A kinetic study of the reaction of Cr^{++} with $(NH_3)_5CoH_2O^{+++}$ to form $Cr(H_2O)_6^{+++}$ and Co^{++} has been made, tracer experiments on the transfer of oxygen from $(NH_3)_5CoH_2O^{+++}$ to Cr^{++} have been done, and isotope fractionation effects on the oxygen and nitrogen in $(NH_3)_5CoH_2O^{+++}$ during reaction have been measured. The kinetic data are consistent with the rate law $-d(Cr^{++})/dt = k_1(Cr^{++})((NH_3)_5CoH_2O^{+++}) + k_2(Cr^{++})((NH_3)_5CoOH^{++})$. At 25° and $\mu = 1.$, $k_1 = 19$ l. mole^{-1} min.$^{-1}$, and $k_2 \sim 2 \times 10^7$ mole^{-1} min.$^{-1}$. $E_1 = 8.7$ kcal. mole^{-1} and $a_1 = 10^{8.7}$ l. mole^{-1} min.$^{-1}$. The reaction corresponding to the second term in the rate law proceeds by substantially complete transfer of oxygen from the oxidizing agent to the reducing agent. For the reaction corresponding to the first term, it can be stated that at least partial oxygen transfer is involved. The fractionation factor d ln O^{16}/d ln O^{18} for the oxygen in the bridging ligand OH^- is 1.03_4; and a substantial fractionation for nitrogen is also indicated. The efficiency of Cl^- acting as a bridging ligand and as a simple ligand in the activated complex of composition $Co(NH_3)_5^{+++}\cdot Cl^-\cdot Cr^{++}$ is compared.

In earlier work[1-4] in the general area of interest of this paper, the role of anions as bridging groups in certain electron transfer reactions was demonstrated. None of these observations, however, showed whether molecules of the solvent H_2O, or of the ion derived from it, OH^-, could also function as bridging ligands in a way analogous to that which was demonstrated for Cl^- and a number of other such groups. In the present paper is outlined work done on the reaction

$$RH_2O^{+++} + Cr^{++} + 5H^+ = Co^{++} + Cr(H_2O)_6^{+++} + 5NH_4^+$$

(R represents $Co(NH_3)_5$). The purpose of this work was to learn whether H_2O and OH^- can in fact act as bridging ligands in electron transfer reactions, and to learn other important features of the activated complex for this model reaction involving aquo cations. The considerations which guided the choice of the present system have already been outlined.

Experimental

The preparations $RH_2O(ClO_4)_3$, $RH_2O^*(ClO_4)_3$[5] and Cr^{++} aq.[2] were made following procedures described elsewhere.

The rate of the reaction of Cr^{++} and RH_2O^{+++} was followed by discharging known amounts of the reaction mixture into Fe^{+++} in excess, and determining the amount of Fe^{++} formed, by amperometric titration.

The tracer experiments were done by allowing Cr^{++} to react with RH_2O^{+++} in excess, in perchloric acid solution, precipitating the excess Co(III), the Zn(II) (formed in the reduction of Cr(III)) and Co(II) ions, then precipitating $Cr(H_2O)_6^{+++}$ as the phosphate,[6] heating this precipitate to obtain H_2O, and finally determining the isotopic composition of the H_2O by the CO_2 method.[7] At the concentrations of RH_2O^{+++} and of $HClO_4$ necessary to provide for the formation of $Cr(H_2O)_6^{+++}$ in reasonable quantity, the system contained solid $RH_2O(ClO_4)_3$ during most of the time the reaction proceeded.

For the fractionation work $R(H_2O)^{+++}$ was used in excess. After substantially complete reaction with Cr^{++}, the residual $R(H_2O)^{+++}$ was precipitated as the bromide. This salt was washed, dried and heated to yield water. Comparison of the final oxygen-isotope composition of the RH_2O^{+++}, with that of the salt initially, taking into account the fraction left unreacted, yielded values for the isotope fractionation.[8]

In connection with the experiments on the kinetics, which were completed toward the end of the research, there was evidence that precise stoichiometry in the reaction did not always obtain. Apparently some process for the destruction of Cr^{++} which does not involve Co(III) complex can interfere and the contribution of this additional reaction is not easily controlled. These effects have been more strikingly revealed in recent experiments in which Cr^{++} acts as catalyst rather than by being consumed in the reaction under study, and here the net destruction of Cr^{++}, presumably by ClO_4^-, but catalyzed by adventitious substances could be readily demonstrated. The effect described was almost completely absent in the experiments on the kinetics which have been reported, although it appears to have been present in earlier, preliminary work using a different batch of Cr^{++}. It should be mentioned that different batches of Cr^{++} show the side reactions to a differing extent, but other factors may also influence the extent to which it contributes.

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