TABLE V

MOLALITIES AND IONIC STRENGTHS OF THE AQUEOUS SOLUTIONS AT 427°K.

Sample	$K' \times 10^2$	$K'' \times 10^3$	(RH^+)	$(R^{\pm})$	(Na^+)	(HSO_4^-)	$(SO_4^=)$	$\frac{(R^{\pm})}{(R^{\pm}) + (RH^+)}$	$(\mu)^{1/2}$
M	0.96	1.1	0.141	0.029	1.42	0.34	0.61	0.17	1.48
O				.78				1.00	0.88
Q	2.9	0.60	.84	.26	2.80	.12	1.76	0.24	2.38
R	1.6	0.88	.58	.97	1.27	.03	0.91	0.63	1.93

the same as NaCl in calculating the ionic strengths listed in Table V.

The predominant molecular species present in solid alanine is the zwitterion which explains the fact that the melting point for alanine is greater than 297°. Considering the ionic species present in solution and in the solid phase and the fact that the first-order alanine decarboxylation reaction has about the same half-life in the presence as in the absence of water, there are two possible rate-determining steps for the decarboxylation reaction

$$R^{\pm} \longrightarrow CH_3{}^{-}CHNH_3{}^{+} + CO_2 \qquad (10)$$

and

$$RH^{\pm} \longrightarrow CH_3{}^{-}CHNH_3{}^{+} + CO_2 + H^+ \qquad (11)$$

both of which would be followed by the fast step

$$CH_3{}^{-}CHNH_3{}^{+} + XH \longrightarrow CH_3CH_2NH_3{}^{+} + X^- \qquad (12)$$

where XH is HOH or $R^{\pm}$.

Since the heat of ionization of RH^+ is about 0.74 kcal./mole,[18] reactions 10 and 11 have about the same change in enthalpy so the heat of activation for (11) could be equal to that for (10) even though an additional bond must be broken in (11). However, the entropy of activation for the formation of a solvated proton and a negative residue is about −15 to −25 e.u.,[19] so reaction 11 should have a steric factor at least 10^{-3} smaller than reaction (10). Also, there would be a much greater dependence of the half-life upon the ionic strength than is shown by comparing the half-lives in Table III to the ionic strengths in Table V if reaction 11 were involved in the mechanism.[20] In addition, if reaction 10 were the only mechanism for decarboxylation, the mechanism would be analogous to that found by Verhoek[21] and others for the trihaloacetic acids. The experiments in this Laboratory were not performed at sufficiently low *p*H's to determine whether the mechanism involves (10) or the assumed (10) and (11) combination. If (10) be the only mechanism, the half-lives quoted from about 373 to 427°K. must be multiplied by the factor $(R^{\pm})/[(R^{\pm}) + (RH^+)]$ (Table V for the 427°K. quantities) to obtain the true half-life for this species.

The Oxidation Reaction.—By the use of the experimental half-life for the oxidation reaction at 373°K. of 4.5 years determined with the J sample and the approximate Arrhenius activation energy for the oxidation reaction of 25 kcal./mole determined by runs with impure argon (results not tabulated), the half-life at room temperature for the oxidation reaction is estimated to be about 20,000 years.

Acknowledgment.—The authors wish to thank the Office of Scientific Research of the Air Research and Development Command, U. S. Air Force, for supporting the research; and P. H. Abelson, K. Kopple and T. F. Young for their helpful discussions.

CHICAGO, ILLINOIS

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[18] H. S. Harned and B. B. Owen, ref. 14, p. 514.

[19] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 128.

[20] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 361-362.

[21] F. H. Verhoek, THIS JOURNAL, **56**, 571 (1934); **67**, 1062 (1945).

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

Halides as Bridging Groups for Electron Transfer in the Systems $Cr^{++} + (NH_3)_5CrX^{++}$

BY ALLEN E. OGARD AND HENRY TAUBE

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The spontaneous reaction of the ions $(NH_3)_5CrX^{++}$ in acid solution leads to $(NH_3)_5CrOH_2{}^{+++} + X^-$ as products, but when Cr^{++} is present, reaction to form CrX^{++} and $NH_4{}^+$ takes place. The rate law for the Cr^{++} catalyzed dissociation of $(NH_3)_5CrCl^{++}$ has been established by a detailed kinetic study. The rate is proportional to the concentration of $(NH_3)_5CrCl^{++}$ and of Cr^{++} and is independent of the concentrations of H^+, $CrCl^{++}$ and of Cl^- at least at moderate concentrations. The second-order specific rate at 25° and $\mu = 1$ for X = F, Cl, Br and I are 0.016, 3.08, 19.4 and 330 ± 100 l. mole^{-1} min.$^{-1}$, respectively; the enthalpies of activation for the first three are 13.4, 11.1 and 8.5 kcal. mole^{-1}, respectively. The change in solvent from H_2O to 86% D_2O–14% H_2O for the reaction $Cr^{++} + (NH_3)_5CrCl^{++}$ causes a decrease in rate by a factor of 0.77.

A central point of interest in the subject of oxidation–reduction reactions of metal ions is the specific influence exerted on the rates of reaction by negative ions and other groups, and the mechanisms by which these influences are exerted. These influences are particularly interesting when the catalytic groups are not readily oxidized or reduced by the metal ions. Careful measurements of the effect of halide ions and hydroxide ion on the rate of the "electron exchange"[1] between Fe^{++} and Fe^{+++} have been made,[2,3] and rate coefficients

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[1] Used here without implication of mechanism, to describe oxidation-reduction systems in which no net chemical change takes place.

[2] J. Silverman and R. N. Dodson, *J. Phys. Chem.*, **56**, 869 (1952).

[3] J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

for terms such as $(FeX^{++})(Fe^{++})$ and $(FeX_2^{+}).(Fe^{++})$ have been reported. Because the complexes in question here are substitution labile, the relation of the catalytic group to the other reactants in the activated complex is not known with certainty. However, from the similarity of the catalytic effects of halides and hydroxide ion in the systems Fe^{++}–Fe^{+++} and Cr^{++}–Cr^{+++}, it has been inferred[4] that similar mechanisms operate. For the system Cr^{++}–Fe^{+++} it appears that the major part of the reaction takes place by a path having an activated complex in which Fe^{+++} and Cr^{++} share a common group.

Because of the simplicity of their structures, the halide ions are of conspicuous importance in theories of the mechanism of electron transfer. As the beginning of a systematic exploration of the influence of various groups on the rates of electron transfer, we have chosen to compare the efficiency of the halide ions in promoting oxidation–reduction reactions for some systems in which the nature of the activated complex is known with some certainty. The systems involve the reactions

$$(NH_3)_5CrX^{++} + 5H^+ = CrX^{++} + 5NH_4^+ \quad (I)$$

catalyzed by Cr^{++}. These reactions are particularly convenient to study because the catalyst Cr^{++} is conserved, and the half-life for the dissociation of the chromic complex can be adjusted to the desired level by adjusting the concentration of the catalyst. The reactions are obviously closely related to the reaction[5]

$$CrCl^{++} + Cr^{++} = Cr^{+++} + CrCl^{+} \quad (II)$$

except for this difference, that whereas in the former system Cr(III) is clothed by NH_3 and Cr^{++} by H_2O, so that on electron transfer a net change occurs, in the latter, both Cr(III) and Cr(II) are clothed by H_2O. Reactions of the type I are more convenient to study, because it is not necessary to resort to isotopic labelling to follow their rates.

The chemistry of the reactions of the type of (I) is remarkable in that, for the dissociation in the presence of Cr^{++}, the Cr–X bond is preserved and the Cr–NH_3 bonds are severed. (For the spontaneous dissociation, the reverse is true.) This chemistry, the analogy to reaction II as well as to reactions of $(NH_3)_5CoX^{++}$ with Cr^{++}, and the form of the rate law, as established in the present work, point to the conclusion that electron transfer *via* a halide bridge, with the bridging group being transferred from Cr(III) to Cr(II), is involved in this reaction

$$(NH_3)_3CrCl^{++} + Cr^{++} \xrightarrow{(+5H^+)} 5NH_4^+ + Cr^{++} + CrCl^{++}$$

A more direct proof of this conclusion using radioactive Cr was not possible, because the Cr^{++}–CrX^{++} exchange takes place more rapidly than the reaction of Cr^{++} with $(NH_3)_5CrX^{++}$, at least with Cl^- as the halide.

Experimental

Materials.—The only materials requiring special mention are the salts containing the ions $(NH_3)_5CrX^{++}$. The starting material for the preparation of all of them was the compound $(NH_3)_5CrCl_3$ which was prepared by the method of Christensen.[6] It was purified and converted to $(NH_3)_5CrCl_3^{++}$ by using cation-exchange resins, as was suggested by King[7] for the isolation of the various Cr(III)–Cl^- complexes in pure form. A solution of the salt in 0.15 *M* $HClO_4$ was poured through a column of Dowex 50-X4 in the acid form. Under these conditions, cations of charge two or higher are strongly held, while those of charge one wash through, and only ClO_4^- remains on the column as residual anion. Cations of charge two, and thus $Cr(NH_3)_5Cl^{++}$, are eluted by 1 *M* $HClO_4$, while those of higher charge, such as $Cr(NH_3)_6^{+++}$ remain on the column. The compound $(NH_3)_5CrCl(ClO_4)_2$ is readily precipitated from the eluent solution by adding concentrated $HClO_4$ and cooling.

The compound $(NH_3)_5CrH_2O(ClO_4)_3$ was an intermediate stage in the preparation of the fluoro and bromo compounds. It was prepared by allowing a solution of $(NH_3)_5CrCl(ClO_4)_2$ in 1 *M* $HClO_4$, kept in the dark, to aquate completely. The perchlorate salt was precipitated by pouring this solution into cold concentrated $HClO_4$ and was purified by recrystallization.

To prepare the fluoro salt, the aquopentamminechromium(III) perchlorate was dissolved in 48% HF and the solution heated until the volume was reduced by one half. During this process, the color changed from orange to deep red. The solution was cooled and at least an equal volume of acetone was added, whereupon $(NH_3)_5CrF_3$ precipitated. It was purified by dissolving in 0.15 *M* $HClO_4$, making use of the exchange resin technique. The ion was stored in solution rather than in the solid, because it was observed that acid retained on the solid causes hydrolysis during the drying procedure, and no means of removing acid without dissolving the fluoro compound was discovered.

The bromo compound was made by heating $(NH_3)_5CrH_2O(ClO_4)_3$ in concentrated HBr. The purple compound which precipitated, $Cr(NH_3)_5Br_3$, was filtered, washed and dried.

The iodo compound was prepared by the method of Christensen.[6] The product thus obtained was not completely pure and could not be purified by ion-exchange techniques because the spontaneous hydrolysis is too rapid.

The solution of Cr^{++} (containing also Zn^{++}) was prepared substantially as described earlier.[4]

Apparatus and Procedure.—In every case the color of the product CrX^{++} differs sufficiently from that of the reactant ion, to make it possible to follow the progress of the reaction spectrophotometrically. The only problem encountered was that of charging the spectrophotometric cell with the oxygen sensitive solution, and this was overcome in a simple and satisfactory way. The vessel used for making the reaction mixture is shown in Fig. 1, connected to the spectrophotometer cell in position for charging. After the system, including the cell, was thoroughly purged with O_2-free nitrogen, a measured amount of Cr^{++} solution was added to the reaction flask from a buret, the tip of which is

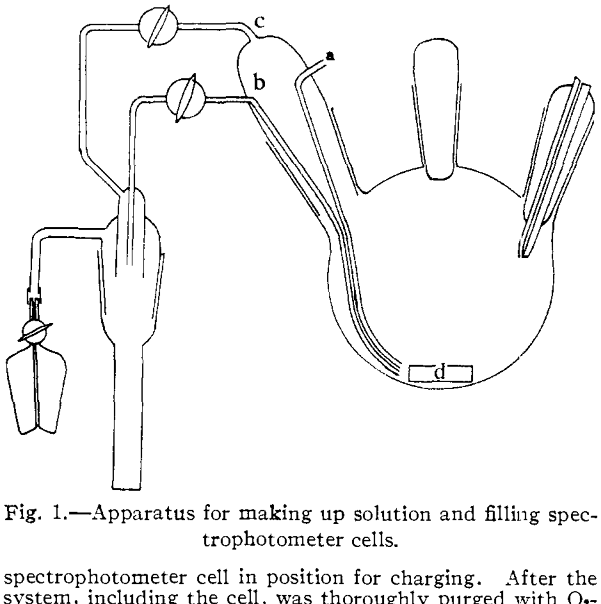

Fig. 1.—Apparatus for making up solution and filling spectrophotometer cells.

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[4] H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

[5] H. Taube and E. L. King, *ibid.*, **76**, 4503 (1954).

[6] O. T. Christensen, *Z. anorg. Chem.*, **4**, 229 (1893).

[7] E. L. King, private communication.

shown entering the reaction reservoir at the right. All other components of the reaction mixture had already been added to the reaction reservoir and were present during the purging stage. By means of gas pressure built up through the inlet tube a, the reaction mixture was charged into the cell through the delivery tube b, enough being added to fill it well up into the region of the standard taper. The cell was then disconnected, and the stopper shown at the extreme left was fitted into place. The excess solution, which includes that having come into contact with air is forced out through the center tube of the stopper, which was then closed, isolating the reaction mixture. The cell was transferred to the compartment of a Beckman spectrophotometer, for measurement of optical density, the compartment being thermostated at the desired temperature within 0.1°.

Definitions and Treatment of the Data.—The symbol R is used to represent the group $(NH_3)_5Cr$.

D represents the optical density as defined by the equation $D \equiv \log I_0/I$ (the cell thickness for all experiments was 1 cm.).

Although the main net change in all of the experiments can be represented by an equation of the type of (I), it was found necessary to make allowance for the independent side reaction III in the treatment of the data.

$$(NH_3)_5CrX^{++} = H_2O = (NH_3)_5CrOH_2^{+++} + X^- \quad \text{(III)}$$

The rate law used as basis for discussing the data takes the form

$$\frac{-\,d(RX^{++})}{dt} = k_1(RX^{++}) + k_2(RX^{++})(Cr^{++})$$

The first term on the right-hand side describes the reaction which produces RH_2O^{+++} and the second, the reaction producing CrX^{++}. Since (Cr^{++}) remains constant, equation 3 can be integrated to

$$\ln \frac{(RX)_0}{(RX)} = (k_1 + k_2(Cr^{++}))t \equiv kt$$

The specific rate k for a particular experiment is determined by taking the slope in a plot of $\ln(D_t - D_\infty)$ against time. k_1 is measured directly in an experiment in which no Cr^{++} is used, and thus k_2 can be calculated.

CrX^{++} in most cases dissociated slowly enough so that the appropriate value of D_∞ can be measured directly. It was found expedient however, in some cases to calculate D_∞—and, in any event, necessary in some instances to compare a calculated value of D_∞ to that observed experimentally as a check on the stoichiometry of the reaction. The products CrX^{++} and RH_2O^{+++} will be formed in the ratio $k_2(Cr^{++})/k_1$, and thus the expected final optical density is readily calculated.

Typical data are shown in Fig. 2 for the reaction of RCl^{++} in the presence of Cr^{++}. The upper curve shows the observed values of D *vs.* t in a semi-log plot, the next $(D - D'_\infty)$ (where D'_∞ is the value of optical density expected for $CrCl^{++}$ as sole product) and the lowest curve $D - D_\infty$ (where in this case D_∞ is the observed value). The curvature remaining in the second plot is removed by allowing for reaction to form CrH_2O^{+++}. For this experiment D_∞ calculated = 0.040 to be compared to 0.043 observed.

Results

1. RCl^{++} System. A. Hydrolysis Reaction.—Table I lists the results obtained on the rate of hydrolysis of $(NH_3)_5CrCl^{++}$ as a function of temperature. The reaction was found to be strictly first order in RCl^{++} over the concentration range investigated, corresponding to $(RCl^{++})_0 = 0.01$ *M*, decreasing during reaction to *ca.* 1/10 of this value.

TABLE I

HYDROLYSIS OF RCl^{++} IN 1.0 *M* $HClO_4$

Temp., °C.	25.2	30.3	32.8	40.8
$k_1 \times 10^3$, min.$^{-1}$	0.44	0.90	0.96	3.4

The data, except for the experiment at 32.8°, which is unaccountably aberrant, conform to the Arrhenius equation with E = 24 kcal. mole^{-1}.

The affinity of Cl^- for $(NH_3)_5CrH_2O^{+++}$ is quite low ($K_{ass.} < 3$ at 25° and $\mu = 1.0$) so that in the experiments reported in Table I, k_1 is substantially equal to the specific rate for dissociation of the complex.

B. **The Catalyzed Dissociation.**—Table II contains a summary of the results on the chromous ion catalyzed dissociation of the complex RCl^{++}.

TABLE II

THE KINETICS OF THE DISSOCIATION OF $(NH_3)_5CrCl^{++}$ CATALYZED BY Cr^{++}

(μ = 1.0-1.1; $(HClO_4)$ = 1.00 *M* except in experiment 2.08)

No.	Temp., °C.	(R-Cl$_2^{++}$) × 10^2	(Cr$_2^{++}$) × 10^2	k_2, l. mol.$^{-1}$ min.$^{-1}$	Special conditions
2.01	10.5	0.64	1.61	1.13	
.02	14.4	0.53	1.53	1.47	
.03	26	2.46	0.99	3.4	
.04	26.2	1.10	.54	3.28	
.05	26.2	1.07	.53	2.55	In 86.4% D_2O
.06	26.2	0.85	.92	3.29	
.07	26.2	0.93	1.08	3.28	
.08	26.0	1.15	0.92	3.22	(H^+) = 0.2 *M*, (Na^+) = 0.8 *M*
.09	26.8	0.69	.96	3.30	$(CrCl^{++})_0$ = 0.0072
.11	26.2	.50	.96	3.50	μ = 1.15, ClO_4^- only
.12	26.2	.50	.97	3.57	μ = 1.15, 0.1 *M* Cl^-
.13	26.2	.50	.97	3.57	μ = 1.15, 0.1 *M* Br^-
.14	26.2	.50	.97	3.54	μ = 1.15, 0.03 *M* HF
.15	38.6	1.11	.54	7.03	
.16	38.9	0.69	.39	7.58	

The group of experiments at 26° serve to establish the kinetics of the Cr^{++} catalyzed reaction. As shown by variation in initial (RCl^{++}), *ca.* 5-fold, and also by the variation in $(CrCl^{++})$ during an experiment, which sometimes was as much as ten-fold, the reaction is strictly first order in $(CrCl^{++})$. It is also first order in (Cr^{++}) (*cf.* expts. 2.04 and 2.07). The rate of the reaction is independent of the concentration of acid, at least in the range studied, 0.20 to 1.0 *M*. There is no marked effect on rate, of the accumulation of the product $CrCl^{++}$ (*cf.* exp. 2.09). Ligands such as Cl^- or Br^-, while they may have a small effect, certainly exert no marked effect on the rate of reaction. The specific rates show a proper exponential variation with temperature and yield for the parameters $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ in the equation[8]

$$k_2 = \frac{kT}{h}\, e^{\Delta S^{\ddagger}/R}\, e^{\Delta H^{\ddagger}/RT}$$

the values −23 e.u. and 11.1 ± 0.2 kcal. mole^{-1}.

2. RBr^{++} System. A. Aquation Reaction.—The data on the rate of aquation of RBr^{++} are shown in Table III. For this ion also, the reaction is strictly first order in RBr^{++}, and it proceeds essentially to completion.

TABLE III

AQUATION OF RBr^{++} IN 1 *M* $HClO_4$

Temp., °C.	24.8	28.0	34.0	39.1
$k_1 \times 10^3$, min.$^{-1}$	4.1	6.1	14.3	26.4

The data conform well to the Arrhenius equation and yield for the activation energy the value 24.5 kcal. mole^{-1}.

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[8] S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

B. Catalyzed Dissociation.—The results obtained in the study of the dissociation catalyzed by Cr^{++} are shown in Table IV.

TABLE IV

DISSOCIATION OF RBr^{++} CATALYZED BY Cr^{++}

(($HClO_4$) = 1.0 M, μ = 1.1 except where otherwise noted)

No.	Temp., °C.	(R-Br^{++}) × 10^2	(Cr^{++}) × 10^3	Other	k_2, l. mole^{-1} min.$^{-1}$
4.01	12.4	0.50	3.47		9.98
.02	24.1	0.40	2.34	0.9 M $HClO_4$ 0.1 M Br	20.7
.03	27.6	1.00	2.31		24.0
.04	28.3	1.00	2.24		22.8
.05	28.0	0.50	2.24	0.04 M $CrBr^{++}$ μ = 1.4	23.2
.06	34.0	1.00	1.13		30.4
.07	39.1	1.00	1.16		38.6

In a plot of log k_2/T *vs.* $1/T$, the points for experiments 4.01, 4.04, 4.06 and 4.07 fall precisely on a straight line. The value of $\Delta H^{\ddagger}$ which this plot defines is 8.5 kcal. and $\Delta S^{\ddagger}$ is -33 e.u. The points for experiments 4.02 and 4.05 are slightly above the line, and the deviation may be caused by the slightly different ionic environment. Experiment 4.05 shows that there is no striking effect $CrBr^{++}$, and 4.02, that while there may be slight catalysis by Br^-, this effect is by no means marked. The point for experiment 4.03 deviates slightly, without apparent reason.

RF^{++} System. Aquation Reaction.—The rate of aquation of RF^{++} is very slow, and the measurements of it were not very accurate. The specific rates reported in Table V are considered accurate only to a factor of 1.5. They are consistent with a value of 28 ± 3 kcal. mole^{-1} for the activation energy of the aquation reaction.

TABLE V

AQUATION OF RF^{++}

(In 1 M $HClO_4$); $(RF^{++})_0$ = 3.8 × $10^{-2}M$)

Temp., °C.	27.0	33.7	41.0
$k_1 \times 10^6$ l. mole^{-1} min.$^{-1}$	1.2	3.2	9.8

Cr^{++} Catalyzed Dissociation.—The relevant data are presented in Table VI.

TABLE VI

THE CATALYZED DISSOCIATION OF RF^{++}

($HClO_4$ = 1.00M, (Cr^{++}) = 3.8 × 10^{-2}, μ = 1.1)

Temp., °C.	(RF^{++}) × 10^3	k_2, l. mole^{-1} min.$^{-1}$
27.0	6.24	0.018
33.7	4.66	.032
41.0	4.66	.052

The rate law was not separately proven for this system (except insofar as the reaction is shown to be first order with respect to (RF^{++}) as the concentration of this ion diminishes during an experiment.) The analogy with the other systems is depended on to establish the reaction as first order in (Cr^{++}).

The data in Table VI lead to a value of $\Delta H^{\ddagger}$ = 13.4 ± 0.6 kcal. mole^{-1} and $\Delta S^{\ddagger}$ = -30 ± 2 e.u. mole^{-1}.

RI^{++} System.—The aquation of RI^{++} is so rapid that a good measure of the rate of this reaction was not obtained. From a single experiment at 26°, the specific rate for the aquation reaction is estimated as 0.047 ± 0.01 l. mole^{-1} min.$^{-1}$. The essential difficulty is not that the rate is too rapid for accurate measurement but rather that a pure salt is difficult to prepare, and that the rate of solution of the salt is not rapid enough compared to the dissociation.

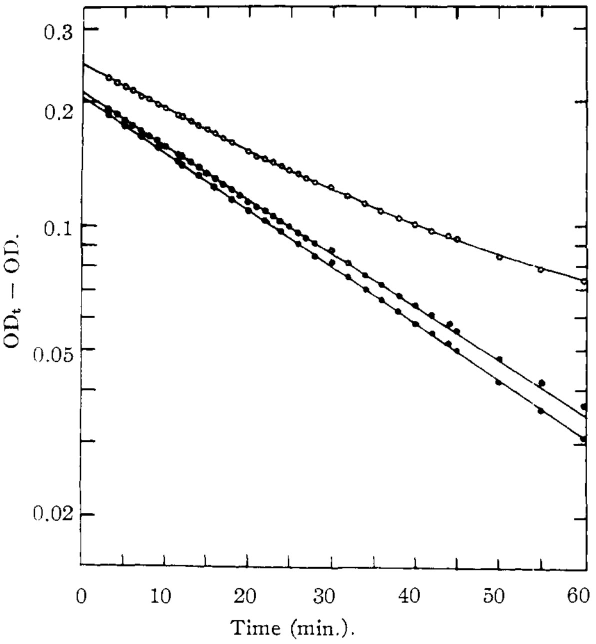

Fig. 2.—Typical data for reaction RCl^{++} + Cr^{++}. Ordinates for: upper curve, observed values of D; middle curve, $D_t - D_\infty$ where $D_\infty{}'$ makes no allowance for formation of RH_2O^{+++}; bottom curve, $D_t - D_\infty{}'$, where D_∞ makes allowance for formation of RH_2O^{+++}.

The rapid rate of the spontaneous dissociation makes itself felt in the efforts to measure the rate of the Cr^{++} catalyzed dissociation. Because of the large and uncertain correction for the spontaneous reaction only a small effort was expended on this system. In an experiment at 25.6° with RI^{++} at 5 × 10^{-3} M, Cr^{++} at 2.3 × 10^{-4} M, $HClO_4$ at 1 M and μ at 1.1, k_2 for the Cr^{++}–RI^{++} reaction was estimated at 330 ± 100 l. mole^{-1} min.$^{-1}$

Discussion

A summary of the data obtained on the Cr^{++} catalyzed dissociations is presented in Table VII.

TABLE VII

Reactant	k_2, l. mole^{-1} min.$^{-1}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
RF^{++}	0.016	13.4	-30
RCl^{++}	3.08	11.1	-23
RBr^{++}	19.4	8.5	-33
RI^{++}	330 ± 100	..	..

An important feature of the observations we have made is the qualitative one that the rates decline in the order from I^-–F^-. Thus, the rate of reaction is not determined simply by the efficiency of direct orbital overlap which is permitted as a consequence of the size of the negative ions, but other properties of the negative ions must be invoked. The trend in the rates is that which would be observed for the rate of removal of halogen from a carbon center by a free radical reagent. The inorganic case considered here, however, features additional elements of interest and is not to be dismissed simply with the statement that the bond energies decrease in order from Cr(III)–F^- to Cr(III)–I^-. While this correlation exists in the reactions under present study, it may well not obtain for the entire group of transition metal ions. An essential difference between the carbon and transition metal ion case is that the net changes for the transition metal ion case involves electrons which are differently concerned with bonds in the complexes.

In the case of a reaction such as CH_3Cl with Na, the electron left after the removal of Cl occupies the orbital vacated by this ligand. In the case of reaction of $(NH_3)_5CrCl^{++}$ with Cr^{++}, the analogous situation may be imagined, namely, that the configuration of NH_3's about Cr is essentially maintained on electron transfer (formally equivalent to removal of Cl), and an intermediate $(NH_3)_5Cr^{++}$, having one group missing from an octahedral position is formed as the primary product. Alternatively, it can be imagined that the electron accepted by the Cr(III) is accommodated in a d_z2 orbital which is made more accessible as the halide ion moves from Cr(III) to Cr(II), with simultaneous removal of the NH_3 *trans* to the halide. The former description was implied in the discussion of the similar case,[9] reaction of $(NH_3)_5$-$CoOH^{++}$ with Cr^{++}; the latter description has been made by Orgel[10] in his excellent analysis of reactions of this kind.

The experiments we have done, searching for an influence on the rate of the product $CrCl^{++}$ were directed to the point under discussion. It is conceivable that an intermediate such as $Cr(NH_3)_5^{++}$ would react more rapidly as

$$(NH_3)_5Cr^{++} + CrCl^{++} \longrightarrow (NH_3)_5CrCl^{++} + Cr^{++}$$

than it would dissociate to Cr^{++} and NH_4^+, and in this event, a diminution in rate as $CrCl^{++}$ accumulates would be observed. No effect of this kind was observed (experiment 2.09), and the experiments are thus inconclusive on the point at issue. The weight of other evidence does, however, support the view that important dislocations occur in the coördination sphere of Cr(III) to accommodate the incoming electron. The nitrogen isotope effect in the reactions of $(NH_3)_5CoOH^{++}$ with Cr^{++} was found to be considerable[11] and if, as seems possible, the effect is largely expended in the group *trans* to the OH^-, it is relatively as great as that observed for oxygen in OH. The hypothesis that a group *trans* to the halide is also concerned offers an explanation for the fact that the reaction $(H_2O)_5$-$CrCl^{++} + Cr^{++}$ takes place about 1100 times more rapidly[5,11] than does $(NH_3)_5CrCl^{++} + Cr^{++}$. Adopting crystal field language, because of the "stronger" field of NH_3, it must be moved to a greater distance than is necessary for H_2O, to lower the energy of the d_{z^2} orbital to the same extent.

The discussion of the influence of the bridging group is very complicated. Involved is a consideration of the energy required to stretch the Cr(III)–X^- bond, the energy of stabilization of a system such as $[CrXCr]^{+4}$ as a possible intermediate, as well as a factor which may loosely be called the conductivity of the bridging group. The importance of such a factor is clearly discernible in making a comparison of the relative efficiencies of succinate and maleate as bridging groups in electron transfer.[12]

The pure ligand effect of free halide ions in these reactions is shown to be small (expts. 2.11 to 2.14), a result which is not surprising in the context of the observation by Anderson and Bonner,[13] that Cl^- does not catalyze the reaction of Cr^{++} and Cr^{+++}, and of the observation that its effect in the reaction of $(NH_3)_5CoH_2O^{+++}$ with Cr^{++} is also very small.[9] It is conceivable that F^- would exert a strong ligand effect[12] but the concentration of the ion is suppressed in acid solution. The effect observed on the substitution of D_2O for H_2O can be construed as a ligand effect. In the process of transforming Cr^{++} to Cr^{+++}, Cr–OH_2 distances are decreased. The H_2O–D_2O isotope effect may arise simply from the circumstance that more energy is required to stretch D_2O–D_2O bonds than is required for H_2O–H_2O bonds. The appreciable solvent isotopic effect in a system which almost certainly does not involve hydrogen atom transfer, weakens the conclusion reached by Hudis and Dodson[14] on mechanism of electron transfer based on the hydrogen isotope solvent effect.

It is of interest that the entropies of activation do not change in a simple way as the size of the bridging group changes from F^- to Br^-. While the data are not accurate enough to maintain as a conclusion the indication that the entropy of activation for RF^{++}–Cr^{++} is lower than that for RCl^{++}–Cr^{++}, they are accurate enough to support the assertion that the increase in entropy of activation from RBr^{++} to RCl^{++} is much greater than it is from RCl^{++} to RF^{++}. Some of the implications of the magnitudes observed for the entropies of activation are perhaps revealed by comparing the two systems A and B below which have formally the same activated complexes but in which the first one involves an oxidation reduction reaction while the second involves substitution.

$$[(NH_3)_5CrBr\ldots Cr]^{+4} \qquad A$$
$$[(NH_3)_5CoBr\ldots Hg]^{+4} \qquad B$$

The entropy of activation for the first system at $\mu = 1$ is -33 e.u. For the second system $\Delta S^{\ddagger}$ can be estimated from the data of Brönsted and Livingston[15] as -16 e.u. at $\mu = 0$; at $\mu = 1$, $\Delta S^{\ddagger}$ can reasonably be expected[16] to be even less negative. General electrostatic effects which arise from the changes in the interaction of the charges with the

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(9) R. K. Murmann, H. Taube and F. A. Posey, THIS JOURNAL, **79**, 262 (1957).

(10) L. E. Orgel, "Rapport auxe Conseil de l'institut International de Chimie," Solvay, Bruxelles, Mai, 1950.

(11) The exchange reaction $CrF^{++} + Cr^{++}$ has been observed by D. L. Ball and E. L. King to proceed approximately 90 times more rapidly than the reactions $RF^{++} + Cr^{++}$ measured by us (private communication).

(12) H. Taube, THIS JOURNAL, **77**, 4481 (1955).

(13) A. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954).

(14) J. Hudis and R. W. Dodson, *ibid.*, **78**, 911 (1956).

(15) J. N. Brönsted and R. Livingston, *ibid.*, **49**, 435 (1927).

(16) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 11.

solvent as the dipositive ions approach should be similar for the two systems. It is tempting, therefore, to ascribe the much larger negative value observed for $(NH_3)_5CrBr^{++} + Cr^{++}$ to the circumstance that much more specific requirements are placed in this system on the motions of the groups in the first coördination sphere for each of the ions. There is, first of all, a considerably larger change in the dimensions of the coördination sphere for each of the metal ions in the electron-transfer reaction than in the substitution reaction. In addition, if indeed motion of NH_3 *trans* to Br, away from the original Cr(III), and of H_2O *trans* to Br toward the original Cr(II), simultaneous with transfer of Br is required, a large negative entropy of activation for system A as compared to B can be qualitatively understood.

The data on spontaneous aquation are incidental to the main purpose of the paper and in any event, are of good quality only for RCl^{++} and RBr^{++}. A comparison with data of Freundlich and Bartels,[17] obtained by a less direct method, is here appended

	k, at 25°		
	(O. and T.)	(F. and B.)	E
RF^{++}	0.7×10^{-5}	....	28
RCl^{++}	4.2×10^{-4}	5.8×10^{-4}	24.0
RBr	4.3×10^{-3}	3×10^{-3}	24.5
RI^{++}	4×10^{-2}	1×10^{-2} (at 0°)	..
$\mu = 1.1$		μ not defined; but note that Kl is probably not very sensitive to μ	

Acknowledgments.—This work was supported by the Atomic Energy Commission under contract AT (11-1)-378. Fellowship support for A. E. O. by the National Science Foundation, United States Rubber Co., and the du Pont Company is also gratefully acknowledged.

[17] H. Freundlich and R. Bartels, *Z. physik. Chem.*, **101**, 177 (1922).

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Calorimetric Determination of the Values of ΔH for Certain Chromium(III)—Chloride Complex Ion Reactions[1,2]

BY KENNETH SCHUG AND EDWARD L. KING

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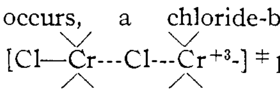
The values of ΔH for the complex ion formation reactions, $Cr(OH_2)_6^{+++} + Cl^- = Cr(OH_2)_5Cl^{++} + H_2O$ and $Cr(OH_2)_5Cl^{++} + Cl^- =$ *trans*-$Cr(OH_2)_4Cl_2^+ + H_2O$, have been determined by calorimetric measurements to be $+6.6 \pm 0.5$ and $+5.0 \pm 0.2$ kcal., respectively, at a value of $I \cong 5.1$ (I = ionic strength) at approximately 25°. The reverse of the second reaction is studied directly in experiments in which chromium(II) acts as a catalyst. The value of ΔH for the first reaction is obtained from the appropriate combinations of observed heats for the second reaction and the heats of conversion of $Cr(OH_2)_6^{+++}$ and *trans*-$Cr(OH_2)_4Cl_2^+$ to "chromite ion."

The chromium(III)-chloride inner-sphere complex ions which involve one and two chloride ions are inert species[3]; this makes possible the preparation of solutions containing single chromium(III)-chloride species. In particular, a solution prepared by dissolving solid green chromium(III)-chloride, $((Cr(OH_2)_4Cl_2)Cl \cdot 2H_2O)$ in dilute acid contains, at the time of preparation, *trans*-dichlorotetraaquochromium(III) ions as the only chromium(III) species.[4] Despite its general inertness, this ion undergoes certain reactions rapidly; such reactions are, therefore, amenable to direct calorimetric study. If treated with a trace of chromium(II) perchlorate, the reaction

$$trans\text{-}CrCl_2^+ = CrCl^{++} + Cl^- \qquad (1)$$

occurs, a chloride-bridged transition state  $[Cl{-}Cr{-}{-}{-}Cl{-}{-}{-}Cr^{+3}\text{-}]^{\ddagger}$ providing the reaction pathway.[5,6] In general, chromium(III) complex ions are rapidly converted by excess hydroxide ion to soluble "chromite ion" the nature of which is not well understood. If, however, the same species or the same mixture of species is produced in the reactions of hydroxide ion with hexaaquochromium(III) ion and with *trans*-dichlorotetraaquochromium(III) ion, the observed heat effects for these two reactions allow the calculation of the value of ΔH for the reaction

$$trans\text{-}CrCl_2^+ = Cr^{+++} + 2Cl^- \qquad (2)$$

Experimental Details

The Calorimeter.—The solution calorimeter employed in this work consists of a cylindrical Dewar flask of 400-ml. capacity with an evacuated ground joint cover; the flask contains a stirrer, a heater (*ca.* 80 ohms of No. 32 Nylon covered manganin wire), a resistance thermometer (*ca.* 80 ohms of No. 40 Formvar-coated copper wire) and a rod for mounting the sample bulbs. The heater and thermometer are contained in the annular space of a double-walled cylindrical copper stirring well which is painted with glyptal and coated with paraffin wax. The Dewar flask and cover are immersed in a large constant temperature bath maintained at 27.0 ± 0.005° during the calorimetric experiments. The heat capacity of the filled calorimeter is about 450 cal./degree.

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[1] Presented in part before the 129th National Meeting of the American Chemical Society, Dallas, Texas, April 12, 1956.

[2] This work was supported in part by grants from the United States Atomic Energy Commission and the Research Committee of the Graduate School, University of Wisconsin.

[3] The terms "inner-sphere" and "inert" are used in the sense suggested by H. Taube (THIS JOURNAL, **75**, 1463 (1953); *Chem. Revs.*, **50**, 72 (1952)); an inner-sphere complex is one in which the ligand is bonded directly to the central metal atom, and an inert complex is one in which metal-ligand bonds are made and broken slowly.

[4] E. L. King, Sr. M. J. M. Woods, O. P. and H. S. Gates, forthcoming publication.

[5] H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

[6] In general, the water molecules in the first coördination sphere of chromium(III) will not be shown; presumably chromium(III) exhibits coördination number 6 in all of the species under consideration here.