violet $(Cr(OH_2)_6Cl_3(s) \longrightarrow$
"chromite" (0.034 M) + $3Cl^-$ (in base) (d)

green *trans*-$(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O \longrightarrow$
trans-$Cr(OH_2)_4Cl_2^+$ (0.034 M) + Cl^- (in acid) (e)

green *trans*-$(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O \longrightarrow$
"chromite" (0.034 M) + $3Cl^-$ (in base) (f)

In all cases, the chromium compound, as a solid or in concentrated solution, is in the bulb which was broken to initiate the reaction.

TABLE I

VALUES OF ΔH FOR THE REACTION *trans*-$CrCl_2^+ \rightarrow CrCl^{++} + Cl^-$

Catalyst: $\sim 0.002\ M\ Cr^{++}$; $T = 23.5 \pm 1°$

Mean value of I[a]	Initial concn., moles/l. (HClO₄)	(*trans*-$CrCl_2^+$)	ΔH (kcal.)
0.136	0.02	0.055_1	−5.69
.145	.02	.061	−5.55
.186	.10	.042	−5.90
.212	.105	.053	−5.58
$.25_4$	.107	$.072_5$	−5.63[b]
.270	.106	.080	−5.70
.459	.10	.174	−3.81
$.65_5$	.10	$.065_3$	−5.43[b]
1.01	.10	.122	−5.52
1.01_5	.10	$.174_5$	−5.27
1.11	.10	$.063_2$	−5.37
3.46	.50	.079	−5.22
3.49	.50	.096	−5.39
4.47	.09	$.082_1$	−4.34
5.16	.50	.086	−4.87
5.18	.50	$.090_5$	−5.11[b]

[a] The ionic strength on the molar concentration scale is I.
[b] The average value of ΔH from the results of two very similar experiments. In each case, the two values which are averaged are within 2% of one another.

A total of 20 successful calorimetric experiments, each involving approximately 11 mmoles of chromium(III), have been run on these reactions. The concentration of perchloric acid or sodium hydroxide (whichever is appropriate) is 0.5 M in each experiment and in some of the experiments a high electrolyte concentration exists (5.0 M sodium perchlorate). The observed values of ΔH (in kcal./mole) for reactions a, b, e and f in the absence of added sodium perchlorate are −5.25, -25.9_2, +0.70 and -31.3_0, respectively. The observed values of ΔH (in kcal./mole) for reactions a, b, c, d, e and f in the presence of added sodium perchlorate are −5.47, -25.9_9, -10.8_3, -32.0_3, +1.60 and -30.9_2, respectively. It is worthy of note that the four sets of "chromite ion" experiments were run in duplicate with agreement to 0.6% or better in each pair despite the indefinite nature of the "chromite ion" formed. The values of ΔH for the solution of $(Cr(OH_2)_6)Cl_3(s)$ and $(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O(s)$ (reactions c and e) have been determined by Recoura[16] to be −12.0 and 0.0 kcal./mole, respectively.

One calculates for the value of ΔH for the conversion of *trans*-$CrCl_2^+$ to "chromite ion" −32.0 and −32.5 kcal./mole at the low and high values of the electrolyte concentration, respectively. The derived values of ΔH for the conversion of $Cr(OH_2)_6^{+++}$ to "chromite ion" are -20.6_7 kcal./mole at the low electrolyte concentration and −20.5 and −21.2 kcal./mole at the high electrolyte concentration. (These two values are independent, being derived from the pairs of reactions b-a and d-c.) The derived values of ΔH for reaction 2 are calculated to -11.3_3 kcal./mole at the low electrolyte concentration and -11.6_5 kcal./mole at the high electrolyte concentation. Recoura[16] has obtained a value of −9.4 kcal./mole for the heat of this reaction from values of the heat of precipitation of chromium(III) hydroxide from solutions of Cr^{+++} and $CrCl_2^+$.

Conclusions

It is of interest to compare the values of ΔH for the successive replacement of water molecules in the first coördination sphere by chloride ion. At $I \cong 5.1$ and $\sim 25°$, the values of ΔH are $+6.6 \pm 0.5$ and $+5.0 \pm 0.2$ kcal./mole for the formation of $CrCl^{++}$ and $CrCl_2^+$, respectively, each being formed from the species with one fewer chloride ion. A value of +6.0 kcal./mole can be obtained for the value of $\Delta H°$ for the conversion of $CrCl^{++}$ into $CrCl_2^+$.

The authors wish to acknowledge the assistance of Professors Paul Bender and Z Z. Hugus in planning the design of the calorimeter.

[16] M. A. Recoura, *Ann. chim. phys.* [6], **10**, 1 (1887).

MADISON, WISCONSIN

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

The Exchange Reactions of Chromium(II) Ion and Certain Chromium(III) Complex Ions[1]

BY DONALD L. BALL AND EDWARD L. KING

RECEIVED AUGUST 12, 1957

The rate of exchange of chromium(II) and the inert monofluoride, -chloride, -bromide, -thiocyanate and -azide complex ions of chromium(III) is the subject of the present paper. The observed "electron-transfer" reactions of chromium(II) and the chromium(III) complexes preserve the inert chromium(III) complexes and thus occur *via* transition states which involve the complexing anion as a bridging unit between the chromium(II) and chromium(III) atoms. The observed temperature coefficient of the rate of exchange of Cr^{++} and CrF^{++} allows the calculation of the values 13.7 kcal. and −20 e.u. for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Limited experimental data suggest the exchange of Cr^{++} and CrN_3^{++} proceeds $>10^4$ fold more rapidly than the exchange of Cr^{++} and $CrNCS^{++}$. The latter exchange reaction, unlike the other exchange reactions, is believed to occur either in two steps or *via* a transition state in which the chromium atoms have a coördination number of less than six.

The influence of specific anions on the rate of exchange of metal atoms between two different oxidation states of the metal in aqueous solution has been investigated for several elements.[2-5] The role of

---

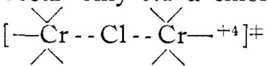
[1] Supported in part by a grant from the United States Atomic Energy Commission.

[2] Iron(II)-iron(III): (a) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952); (b) J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

[3] Thallium(I)-thallium(III): (a) R. J. Prestwood and A. C. Wahl, *ibid.*, **71**, 3137 (1949); (b) G. Harbottle and R. W. Dodson, *ibid.*, **73**, 2442 (1951).

[4] Cerium(III)-cerium(IV): (a) J. W. Gryder and R. W. Dodson, *ibid.*, **73**, 2890 (1951); (b) H. C. Hornig and W. F. Libby, *J. Phys. Chem.*, **56**, 869 (1952); (c) F. R. Duke and F. R. Parchen, THIS JOURNAL, **78**, 1540 (1956).

[5] Europium(II)-europium(III): D. J. Meier and C. S. Garner, *J. Phys. Chem.*, **56**, 853 (1952).

the anions is not completely understood; the incorporation of an anion into the transition state lowers the otherwise high positive charge on the transition state and thus would increase its stability. The form of the rate law does not, however, establish the geometry of the transition state. In particular the question of whether the anion is present as a bridging group in the transition state, *i.e.* $[\text{M-X-M}']^{\ddagger}$, or is located in some other position is not answered for those systems[2-5] in which the metal ion–anion association reactions occur rapidly. The observed exchange of chromium(II) ion and monochlorochromium(III) ion can occur only *via* a chloride-bridged transition state  $[\text{—Cr - - Cl - - Cr—}^{+4}]^{\ddagger}$.[6] Any other transition state for "electron-transfer" with a configuration in which the chloride ion is not bonded to both of the chromium atoms is a transition state for the net chemical change[7] $CrCl^{++} \rightarrow Cr^{+++} + Cl^-$. In addition to extending the study of the exchange of Cr^{++} and $CrCl^{++}$, the present paper deals with the exchange of Cr^{++} and CrX^{++}, where $X^- = F^-$, Br^-, SCN^- and N_3^-. These CrX^{++} species, like $CrCl^{++}$, are inert and thus the observed appearance of the chromium tracer, initially present as Cr^{++}, in the CrX^{++} fraction demonstrates that a bridged transition state also accomplishes "electron-transfer" in these systems.

Experimental Methods

Reagents.—Conductivity water has been used in the kinetic studies; it is prepared by redistilling ordinary laboratory distilled water from an alkaline permanganate solution using a Barnstead still.

Chromium(III) perchlorate has been prepared by the reaction of chromium trioxide with formic acid in the presence of excess perchloric acid. The product is twice recrystallized from 0.10 *M* perchloric acid.

Lithium perchlorate, which is used to maintain a constant ionic strength, has been prepared by the reaction of perchloric acid with lithium carbonate. The product is twice recrystallized from conductivity water.

The solution of chromium(II) perchlorate has been prepared by the electrolytic reduction of a solution of chromium(III) perchlorate in 0.10 *M* perchloric acid.[8] During the electrolysis, the solution is kept under an inert atmosphere (carbon dioxide or nitrogen). The chromium(II) solution is stored in a sealed vessel under an excess pressure of purified nitrogen. The storage vessel is a round bottomed flask, the neck of which is sealed to a section of a graduated pipet. The vessel is sealed with a vacuum stopcock. The solution of chromium(II) ion in 0.10 *M* perchloric acid stored in this manner is stable over a period of three months.

The reagents used in the preparations described above and in the rest of this work were of reagent grade quality.

Traces of oxygen were removed from tank carbon dioxide and nitrogen by passing the gas through an acidic solution of vanadium(II).[9]

The Cr^{51} tracer is obtained from the Oak Ridge National Laboratory in the form of a solution of chromium(III) chloride in hydrochloric acid. The tracer is converted to chromium trioxide by fuming in nitric acid and then by fuming in perchloric acid in which medium chromium trioxide is insoluble. The chromium trioxide is washed with 72% perchloric acid and then dissolved in water. The solution of chromic acid obtained is reduced to chromium(III) with excess hydrogen peroxide, the excess of which is decomposed by the insertion of a small piece of platinized platinum into the solution. In the present exchange experiments, the chromium tracer is always initially in the form of chromium(II) ion, this oxidation state being produced by the electrolytic procedure already described. The measured values of the half-life for the radioactive decay of the two samples of tracer used in this work are $28._4$ and $27._7$ days. These values agree well with the reported value of 27.8 ± 0.3 days.[10]

Solutions containing chromium(III) complexes of fluoride, chloride, bromide and thiocyanate are prepared by heating chromium(III) and the appropriate anion in dilute perchloric acid, a procedure which is unsuccessful with the more basic azide ion. Monoazidochromium(III) ion is prepared by the reaction of chromium(II) and iron(III) azide complex(es) in $\sim$0.3 *M* azide ion in dilute perchloric acid solution[11]; thereafter hydrogen peroxide is added to oxidize the iron(II) which is formed. The desired complex of charge +2 is, in each case, separated from other chromium(III) complexes and aquochromium(III) ion (or iron(III) ion) present in the preparation by the use of a Dowex-50 cation exchange resin method, which has been demonstrated to be effective for the cases $X^- = Cl^-$, F^-, Br^- and SCN^-. The dipositive complexes are eluted with 1 *M* perchloric acid after the column has been washed free of species of lower charge with 0.1 *M* perchloric acid; hexaaquochromium(III) ion of charge +3 is not eluted by 1 *M* perchloric acid. The stock solutions of each complex are used before appreciable aquation has occurred.

Analyses.—The concentration of the chromium(III) complex in each stock solution is assumed to be equal to the total concentration of chromium in the solution. The latter is obtained by oxidizing the chromium present to chromate ion in alkaline solution using hydrogen peroxide. The chromate concentration is measured with a Beckman DU spectrophotometer; an absorbancy index of 4830 at a wave length of 372 mμ is used.[12]

The chromium(II) concentration of the stock solution enriched with tracer is measured by the reaction of chromium(II) with excess standard iodine solution; a back titration is performed using standard thiosulfate solution. All other analyses have been performed by the customary procedures.

Experimental Procedure.—The reaction vessel is a 250-ml. three-necked flask similar to that used by Anderson and Bonner.[13] Prior to the start of a run, the chromium(III) complex in an aqueous solution of perchloric acid and lithium perchlorate is added to the reaction flask. The flask is immersed in the constant temperature bath and flushed out with purified carbon dioxide for about 1.5 hours; at least twice during this period the flask is sealed, evacuated and then refilled with carbon dioxide to continue the flushing. Subsequently, a measured amount of chromium(II) solution is added to the vessel and the run commenced. The flask is either sealed under excess pressure or the flushing is continued and the outlet gas passes through a mercury trap to ensure that a pressure in excess of one atmosphere is maintained inside the reaction vessel. The aliquots are blown out at appropriate time intervals. In the case of the experiments using the chloride and bromide complexes of chromium(III), the reaction aliquots are quenched with excess iron(III). In the case of all other runs, the reaction aliquots are quenched with a stream of oxygen. Iron(III) very rapidly oxidizes chromium(II) to hexaaquochromium(III) ion; oxygen rapidly oxidizes chromium(II) to a polymeric form of chromium(III) which is believed to have a charge of plus four.[14]

A known amount of "untagged" chromium(III) complex is added to the quenched aliquot and 50 to 80% of the complex separated from the higher charged chromium(III) species by ion exchange. The eluted chromium(III) species is oxidized by hydrogen peroxide in alkaline solution to chromate ion. This solution is analyzed spectrophotometrically to permit a calculation of the fraction recovery from the ion-exchange separation. An aliquot of the chro-

---

(6) H. Taube and E. L. King, THIS JOURNAL, **76**, 4053 (1954).

(7) Water molecules in the first coördination shell will not, in general, be shown.

(8) R. Flatt and F. Sommer, *Helv. Chim. Acta*, **25**, 684 (1942).

(9) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(10) W. S. Lyons, *Phys. Rev.*, **87**, 1126 (1952).

(11) This preparative method is suggested by the analogous preparation of monochlorochromium(III) ion described by H. Taube and H. Myers (THIS JOURNAL, **76**, 2103 (1954)).

(12) G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

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

(14) M. Ardon and G. Stein, *J. Chem. Soc.*, 2095 (1956).

mate solution is acidified to a *p*H of *ca.* 2.5; the chromium is precipitated as lead chromate and mounted on filter paper discs; filtration is performed using glass filter chimneys of standard diameter (27 mm.). The lead chromate is washed with a 50-50 mixture of *t*-butyl alcohol and methyl alcohol and dried in air prior to mounting on a square of cardboard under a strip of Scotch tape.[15]

The mounted sample is inserted under a thin window Geiger–Mueller tube for counting. The corrected counting rate and the data obtained previously permit the calculation of the specific activity of the chromium(III) complex. The "infinity value" for the specific activity is determined by calculation using the known specific activity of the chromium(II) in the stock solution and the known concentrations in the reaction solution.

Experimental Results

In general, the results of each experiment in which a measurable rate of exchange is exhibited conform to the equation

$$-\ln(1 - x/x_\infty) = Rt\,[(\mathrm{Cr^{++}}) + (\mathrm{CrX^{++}})]/(\mathrm{Cr^{++}})(\mathrm{CrX^{++}})$$

where x is the specific activity of the Cr complex and a formula in parentheses, is molar concn. of the species; that is, plots of the logarithm of the quantity (1 –*fraction exchange*) versus *time* are linear with zero intercept.[16] That R, the rate of exchange, is proportional to the product $(\mathrm{Cr^{++}})(\mathrm{CrX^{++}})$ has been demonstrated for the fluoride and chloride systems; the exchange reactions in the other systems are assumed to be second order. Values of the concentration conditions and the second-order rate constants (calculated using the equation $k = R/(\mathrm{Cr^{++}})(\mathrm{CrX^{++}})$) are present in Table I. The lower limits for the rate constants for the exchange of $\mathrm{Cr^{++}}$ and $\mathrm{CrBr^{++}}$ or $\mathrm{CrN_3^{++}}$ have been calculated under the assumption that the observed exchange is not induced during the quenching procedure.

The temperature dependence of k for the exchange reaction involving $\mathrm{CrF^{++}}$ allows the calculation of the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ which are 13.7 kcal. and –20 e.u. It is particularly interesting to note that the value of the entropy of activation for the exchange of $\mathrm{FeF^{++}}$ and $\mathrm{Fe^{++}}$ ($\Delta S^{\ddagger} = -21$ e.u. at $I = 0.5$) found by Hudis and Wahl[2b] is essentially equal to the value found in the present work for the exchange of $\mathrm{CrF^{++}}$ and $\mathrm{Cr^{++}}$ ($\Delta S^{\ddagger} = -20$ e.u. at $I = 1.0$). Since the transition state for the chromium exchange reaction involves the fluoride ion as a bridge, this result suggests, but does not prove, a similar geometry for the fluoride-containing transition state for the iron exchange reaction.[17]

TABLE I

KINETICS OF THE EXCHANGE REACTION

$$\mathrm{CrX^{++}} + \overset{\otimes}{\mathrm{Cr}}{}^{++} = \overset{\otimes}{\mathrm{Cr}}\mathrm{X^{++}} + \mathrm{Cr^{++}}$$

I (the ionic strength) = 1.0 ($\mathrm{LiClO_4}$ is added inert salt)

Temp., °C.	$(\mathrm{H^+})$	$(\mathrm{CrX^{++}}) \times 10^3$	$(\mathrm{Cr^{++}}) \times 10^4$	k(in moles^{-1} l. sec.$^{-1}$)
		$\mathrm{X^-} = \mathrm{F^-}$		
0	0.93	6.4	6.9	$2.5_5 \times 10^{-3}$[a]
27	.97	3.3	3.5	$2.6_4 \times 10^{-2}$[a]
43	.97	3.1	3.6	8.8×10^{-2}
	.95	5.0	7.4	8.5×10^{-2}
	.99	5.3	0.88	9.3×10^{-2}
	.95	0.50	7.3	10.2×10^{-2}
	.10	3.2	3.7	8.4×10^{-2}[a]
		$\mathrm{X^-} = \mathrm{Cl^-}$		
0	0.95	0.23	0.11	11.
	0.97	.47	.072	11.
	.88	.28	.072	7.0
	.82	.47	.21	7.2
	.29	.15	.098	9.7
	.29	.31	.10	8.2
	.28	.14	.26	9.2
	.27	.28	.077	7.3
	.054	.28	.074	7.7
	.062	.47	.27	8.5
	.057	.055	.51	10.3[b]
	.072	.055	.49	11.2
	.057	.28	.28	9.7
		$\mathrm{X^-} = \mathrm{Br^-}$		
0	1.0	0.42	1.1	>60[c]
		$\mathrm{X^-} = \mathrm{NCS^-}$		
~24	1.0	9.6	6.7	1.2×10^{-4}
27.0	1.0	8.7	4.9	1.8×10^{-4}
		$\mathrm{X^-} = \mathrm{N_3^-}$		
0	1.0	1.8	3.8	>1.2[d]

[a] This value is the average of the values obtained in two duplicate experiments; the two values agree within less than 7%. [b] An experiment which duplicated this one yielded a value of k which is approximately 60% greater than the average value of k; this value was not used in obtaining the average. [c] In this experiment, exchange is essentially complete at the time of removal of the first aliquot (25 sec.). It is assumed that exchange is >90% complete at this time in the calculation of this lower limit for k. [d] In this experiment, exchange is essentially complete at the time of removal of the first aliquot (330 sec.). It is assumed that exchange is >90% complete at this time in the calculation of this lower limit for k.

The contrast in the tentatively established rates of the exchange of $\mathrm{Cr^{++}}$ with $\mathrm{CrNCS^{++}}$ and $\mathrm{CrN_3^{++}}$ is marked, differing by more than 10^4-fold.[18] This undoubtedly is related to the unsymmetrical nature of $\mathrm{NCS^-}$ in contrast to the symmetrical nature of $\mathrm{NNN^-}$. The exchange of $\mathrm{CrN_3^{++}}$ and $\mathrm{Cr^{++}}$ can be accomplished *via* the

---

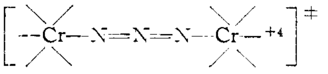
[15] This procedure was developed by Dr. Carl Altman of this Laboratory.

[16] In approximately 10% of the experiments, the "best" straight line through the first few points does not go through the origin but rather corresponds to up to as much as 15% exchange at $t = 0$; the cause of this has not been investigated. In approximately 25% of the experiments, there is some curvature in the line for the latter part of the run. In determining the rate of exchange for such experiments, the straight line is drawn through the early points.

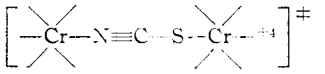
[17] The strength of this argument is somewhat weakened by the apparent insensitivity of $\Delta S^{\ddagger}$ for iron exchange reactions on the nature of the iron(III) species from which the transition state is formed. The transition state containing $\mathrm{Fe^{++}}$ and either $\mathrm{Fe^{+++}}$, $\mathrm{FeOH^{++}}$, $\mathrm{FeF^{++}}$, $\mathrm{FeCl^{++}}$, $\mathrm{FeF_2^+}$ or $\mathrm{FeCl_2^+}$ are formed from these ions in a medium with $I = 0.5$ with a value of $\Delta S^{\ddagger} = -22 \pm 2$ e.u. (Hudis and Wahl, ref. 2b). The direct comparison of the iron system and the chromium system involves the assumption that the variation of $\Delta S^{\ddagger}$ with ionic strength in the range $I = 0.5$ to $I = 1.0$ is small. The values of the entropies of dilution of various strong electrolytes in this same ionic strength range suggest that the correction might amount to as much as –3 to –4 e.u., this figure to be added to the value –20 e.u. for the chromium reaction.

[18] Dr. Kenneth Schug has performed some additional experiments which demonstrate that thiocyanate ion does not effectively fill the role of a bridging group for the "electron-transfer" between chromium(II) and chromium(III). In an experiment at $(\mathrm{Cr^{++}}) = (\mathrm{Cr(NCS)_2^+}) = 0.008$ M, 0.001 M $\mathrm{HClO_4}$, less than 1% of the dithiocyanatochromium(III) ion aquates in ten minutes at room temperature, as judged by the absence of detectable free thiocyanate ion.

symmetrical transition state



in which each chromium has coordination number six. On the other hand, the unsymmetrical transition state for "electron-transfer"

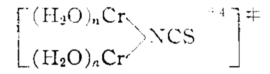


leads to products, Cr^{++} and $CrSCN^{++}$, which are less stable than the reactants Cr^{++} and $CrNCS^{++}$.[19] The necessarily symmetrical reaction pathway for the exchange of Cr^{++} and $CrNCS^{++}$ *via* such a transition state would involve the two steps

$$CrNCS^{++} + Cr^{++} \longrightarrow Cr^{++} + CrSCN^{++}$$

$$CrSCN^{++} + Cr^{++} \longrightarrow Cr^{++} + CrNCS^{++}$$

the intermediate $CrSCN^{++}$ being present at a very low relative concentration.[19] The transition state involving chromium(III)–sulfur bonds is expected to be less stable than one involving only chromium(III)–nitrogen bonds (*i.e.*, the transition state for exchange in the azide system) since the species involving chromium(III)–sulfur bonds are less stable than species involving chromium(III)–nitrogen bonds. The symmetrical transition state for "electron transfer"



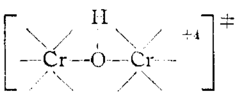
is sterically impossible if $n = 5$ and has a high energy if $n < 5$; thus exchange *via* this transition state is expected to be slow. Which of these two possible mechanisms is the mechanism for the exchange of Cr^{++} and $CrNCS^{++}$ is not known. It is not surprising, however, that this exchange is slower than the exchange of Cr^{++} and CrN_3^{++}.

The low rate of exchange of $CrNCS^{++}$ and Cr^{++} is to be contrasted with the greater rate of the reaction of $(H_3N)_5CoNCS^{++}$ and Cr^{++}, which also produces $CrNCS^{++}$ as the final product.[20] This oxidation reaction, unlike the exchange reaction, is accompanied by an appreciable decrease in free energy; one might expect that the transition state for the production of the unstable intermediate $CrSCN^{++}$ would, therefore, have a lower free energy relative to the reactants.

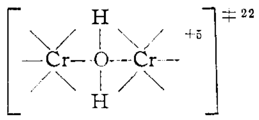
Of the exchange reactions studied, only the exchange of $CrNCS^{++}$ and Cr^{++} proceeds at a rate comparable to the rate of the exchange of the aquoions in the same reaction medium. In the thiocyanate exchange experiment, run at 27°, the half time for exchange is ~78 hours; under the same concentration conditions, the half-time for exchange of the aquo ions is ~52 hours.[13] In this particular experiment involving $CrNCS^{++}$, the reaction was followed for 90 hours and showed no evidence of the induced aquation which would occur if "electron-transfer" occurs between $CrNCS^{++}$ and Cr^{++} in any way other than *via* a thiocyanate-bridged transition state. There are two probable reasons for the absence of induced aquation: (1) the exchange of the aquoions in 1 *M* perchloric acid goes predominantly *via* a hydroxide ion-containing transition state; the presence of the thiocyanate anion would undoubtedly lower the stability of the hydroxide ion-containing transition state, and (2) a transition state for "electron-transfer" between $CrNCS^{++}$ and Cr^{++} which is not a thiocyanate-bridged transition state produces chromium(II) and thiocyanate ion in intimate contact with one another; in the absence of evidence for appreciable association of thiocyanate ion and chromium(II) ion, it is assumed that such a configuration is unstable and the transition state producing it is expected to be relatively unstable.[21]

The absence of a hydrogen ion dependence of the rates of the exchange of Cr^{++} with CrF^{++} and $CrCl^{++}$ is to be noted as is the agreement of the values of the rate of exchange in the chloride system at 0° observed in the present work ($k = 9.1 \pm 1$ moles^{-1} l. sec.$^{-1}$) and in the earlier study[6] ($k = 8.3 \pm 2$ moles^{-1} l. sec.$^{-1}$).

The exchange of chromium(II) and chromium(III) in perchloric acid solution proceeds very predominantly *via* a transition state involving hydroxide ion.[13] This transition state and the much less stable transition state of charge +5 containing no hydroxide ion may involve oxygen bridging



and



Assuming this to be the case, it is of interest to make a provisional arrangement of the bridging groups in order of their efficiency in facilitating the "electron-transfer" between chromium(II) and chromium(III). This order is: Br^-, $N_3^- > Cl^- > OH^- > F^- > NCS^- > H_2O$.

MADISON, WISCONSIN

---

[19] Y. Saito, Y. Takeuchi and R. Pepinsky (*Z. Krist.*, **106**, 476 (1955)) find that the nitrogen end of thiocyanate ion is bound to chromium(III) in the compound $NH_4(Cr(NCS)_4(NH_3)_2)\cdot{}^2/_3H_2O$. It is assumed that the same configuration is predominantly present in the aquothiocyanatochromium(III) ions.

[20] H. Taube, THIS JOURNAL, **77**, 4481 (1955).

[21] This point was suggested by Professor Henry Taube.

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