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]

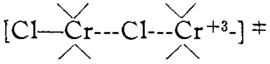
BY KENNETH SCHUG AND EDWARD L. KING

RECEIVED AUGUST 12, 1957

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  $[\mathrm{Cl{-}Cr{-}{-}{-}Cl{-}{-}{-}Cr^{+3}\text{-}}]^{\ddagger}$ 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.

---

[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.

A Mueller bridge (Leeds and Northrup No. 8067) is used to measure the resistance of the copper resistance thermometer, and a potentiometer (Rubicon Type B, with volt box) is used to measure the potential supplied to the calibration heater by a series circuit of seven low-discharge storage batteries (Willard Type DD-5-1). A d.c. galvanometer (Leeds and Northrup No. 2430) is used as a null instrument in each type of measurement. The electrical calibration periods are timed by an electric timer (Standard Electric Time Co., Type SIA) connected to the output from a frequency standard (American Time Products, No. 2005). The estimated uncertainties in the measured values of the potential, the temperature and the duration of the electrical heating periods are ±0.01 volt, ±0.0005° and ±0.02 second, respectively. In the present experiments, the quantity with the greatest relative uncertainty is the temperature.

The amount of heat accompanying a given reaction is determined in the usual way by comparing the change in resistance of the thermometer during the electrical calibration and the reaction periods. (The results are given in thermochemical calories, 1 cal. = 4.1840 joules.) The magnitude of the resistance changes in the calibration and reaction periods are made nearly the same; a calibration is generally carried out both before and after the chemical reaction, since it is observed that the calibration factor (energy input ÷ change in thermometer resistance) is a mild linear function of the temperature within the calorimeter (*ca.* +1% per degree).

In each calorimetric experiment, the initial temperature of the solution in the calorimeter is several degrees below the temperature of the thermostat; at the end of an experiment the temperature is generally still one degree below the temperature of the thermostat.

Two reactions were studied to provide a chemical calibration of the calorimeter. Measurements of the heat evolved upon dissolving magnesium metal in 1.000 *M* hydrochloric acid gave values in the range 108.2 to 112.6 kcal./gram atom of magnesium in five experiments in which approximately 300 cal. were evolved(7); a correction was made for the heat effect associated with vaporization of water accompanying the hydrogen evolution.(8) (Less reliable values of −102 and −114 kcal./gram atom were obtained for the value of ΔH in trial calibration experiments.) A value of −111.32 kcal./gram atom has been reported for this reaction.(8)

In a series of seven experiments involving smaller amounts of heat liberated per experiment (20–60 cal.), the heats of dilution of small amounts (1–3 ml.) of 4 *M* sulfuric acid into 400 ml. of water were found to agree, with an average deviation of 2.4%, with values calculated from data in the literature.(9)

Reagents.—Solid green chromium(III) chloride hydrate ($(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O$) which is used in these experiments was obtained in several different ways. The compound was prepared from chromium(VI) oxide and hydrochloric acid and was also obtained as a reagent grade chemical from several manufacturers; while most of the experiments reported here have been performed using the commercially available material which had been reprecipitated from cold concentrated hydrochloric acid solution by the addition of hydrogen chloride gas, the results of calorimetric experiments using the material from the other sources are the same. The $(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O$ was stored in a desiccator over 80% sulfuric acid(10) and was transferred to the sample bulbs in a dry box.

Solid violet chromium(III) chloride hydrate, which contains the hexaaquochromium(III) ion, was prepared by addition of cold concentrated hydrochloric acid to a cold saturated solution of chromium(III) perchlorate. The precipitate was washed with acetone and ether, and stored over 80% sulfuric acid.

Concentrated solutions of sodium perchlorate, prepared by the neutralization of reagent grade perchloric acid with reagent grade sodium carbonate or sodium hydroxide, were used to adjust the value of electrolyte concentration of the solutions used in the calorimeter runs.

Chromium(II) perchlorate solutions were prepared by the electrolytic reduction at a mercury cathode of chromium(III) in perchloric acid solution.(11) The chromium in the solutions prepared in this way remains in the reduced (+2) state for many months (in contrast to chromium(II) solutions prepared by the use of amalgamated zinc).

The Nature of "Chromite Ion."—If a solution of a chromium(III) salt is treated with excess sodium hydroxide, a green solution results. In general, a precipitate forms and redissolves in this procedure. The chromium(III) species present in such solutions is referred to as "chromite ion," although its nature is uncertain. It has been reported that "chromite ion" does not pass through a semipermeable membrane(12) and this observation is confirmed in the present work.(13)

The absorption spectrum of the chromium(III) species which is present in alkali has, in common with the spectra of many other chromium(III) species, two peaks in the visible region. Tracings of the spectrum of "chromite ion" prepared in different ways were obtained using a Cary spectrophotometer; the "chromite ion" solutions in 0.36 *M* sodium hydroxide were prepared using either an acidic solution of chromium(III) perchlorate, solid violet $Cr(OH_2)_6Cl_3$, or solid green $(Cr(OH_2)_4Cl_2)Cl_2\cdot 2H_2O$. In the range 550 to 300 mμ, the spectrum of the "chromite ion" in each of these solutions was essentially the same; there was an average difference of 1.8% between the individual values of $\bar{a}$ ($\bar{a} \times b \times (Cr^{III}) = \log I_0/I$; b = cell length) measured at 10 mμ intervals and the average value of $\bar{a}$ at each of these wave lengths. While this does not constitute proof that the chromite species are the same regardless of whether the chromium(III) was initially $Cr(OH_2)_6^{+++}$ or *trans*-$Cr(OH_2)_4Cl_2^+$, neither does it suggest that the calorimetric experiments involving "chromite ion" are doomed to fail.

Experimental Procedure and Results for Reaction 1. The value of ΔH for reaction 1 has been determined in solutions of varying electrolyte concentration. To do this, a weighed portion of solid $(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O$ is first added to the calorimeter vessel containing about 350 ml. of dilute perchloric acid which contains sufficient sodium perchlorate to give the desired electrolyte concentration. This solution is then deaerated by a stream of carbon dioxide which has been freed of oxygen by passing through a vanadium(II) sulfate solution.(14) As soon as a constant rate of temperature rise is attained, a small bulb containing sufficient chromium(II) perchlorate to make its final concentration in the range 2×10^{-4} to 2×10^{-3} molar is broken against the bottom of the calorimeter vessel. The catalyzed reaction is complete within 2 to 3 minutes after the addition of the chromium(II). In the calculation of a value of ΔH, a correction is made for the 5 to 7% of the uncatalyzed reaction 1 which occurs during the time interval (up to 20 minutes) between the dissolving of the solid green chromium(III) chloride and the addition of the catalyst. The results are given in Table I for those experiments which satisfied two criteria: (1) the visible absorption spectrum of the final solution closely resembled that of $Cr(OH_2)_5Cl^{++}$ (as previously determined)(15) and (2) the time temperature curve from the calorimetric run showed a steep temperature rise upon addition of the catalyst and leveled off sharply after the reaction period.

Experimental Procedure and Results for Reaction 2. Six reactions have been studied in order to evaluate ΔH for reaction 2 at ~24°. These are

$$Cr(ClO_4)_3\ (2.34\ M) \longrightarrow Cr(ClO_4)_3\ (0.034\ M)\ (\text{in acid}) \quad (a)$$

$$Cr(ClO_4)_3\ (2.34\ M) \longrightarrow \text{"chromite"}\ (0.034\ M)\ (\text{in base}) \quad (b)$$

$$\text{violet}\ (Cr(OH_2)_6)Cl_3(s) \longrightarrow Cr(OH_2)_6^{+++}\ (0.034\ M) + 3Cl^-\ (\text{in acid}) \quad (c)$$

---

(7) Some of these experiments were performed by Mr. Patrick Gallagher.

(8) C. H. Shomate and E. H. Huffman, THIS JOURNAL, **65**, 1625 (1943).

(9) "Selected Values of Chemical Thermodynamic Properties," Circular No. 500, National Bureau of Standards, p. 41.

(10) N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907).

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

(12) W. Fischer and W. Herz, *Z. anorg. Chem.*, **31**, 352 (1902).

(13) In an experiment with 0.03 *M* "chromite ion" and 0.36 *M* sodium hydroxide dialyzing against 0.36 *M* sodium hydroxide, very little chromium(III) diffused through the membrane (cellulose dialyzing tubing). In a similar experiment, chromate ion in 0.6 *M* sodium hydroxide rapidly diffused through the membrane.

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

(15) H. S. Gates, Ph.D. thesis, University of Wisconsin, 1956.

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

$$\text{green } trans\text{-}(\mathrm{Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O} \longrightarrow trans\text{-}\mathrm{Cr(OH_2)_4Cl_2^+}\ (0.034\ M) + \mathrm{Cl^-} \text{ (in acid)} \quad \text{(e)}$$

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

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*-$\mathrm{CrCl_2^+} \rightarrow \mathrm{CrCl^{++}} + \mathrm{Cl^-}$

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

Mean value of I[a]	Initial concn., moles/l. ($\mathrm{HClO_4}$)	Initial concn., moles/l. (*trans*-$\mathrm{CrCl_2^+}$)	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 $\mathrm{(Cr(OH_2)_6)Cl_3(s)}$ and $\mathrm{(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O(s)}$ (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*-$\mathrm{CrCl_2^+}$ 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 $\mathrm{Cr(OH_2)_6^{+++}}$ 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 $\mathrm{Cr^{+++}}$ and $\mathrm{CrCl_2^+}$.

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 ~25°, the values of ΔH are $+6.6 \pm 0.5$ and $+5.0 \pm 0.2$ kcal./mole for the formation of $\mathrm{CrCl^{++}}$ and $\mathrm{CrCl_2^+}$, 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 $\mathrm{CrCl^{++}}$ into $\mathrm{CrCl_2^+}$.

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 $\mathrm{Cr^{++}}$ and $\mathrm{CrF^{++}}$ 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 $\mathrm{Cr^{++}}$ and $\mathrm{CrN_3^{++}}$ proceeds $>10^4$ fold more rapidly than the exchange of $\mathrm{Cr^{++}}$ and $\mathrm{CrNCS^{++}}$. 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).