TABLE IV

CONDUCTIVITY OF BROMINE TRIFLUORIDE IN CHLORINE TRIFLUORIDE AT 25°

Concn, *M*	Specific conductivity × 10^3, ohm^{-1} cm^{-1}	Molar conductivity × 10^3, ohm^{-1} cm^2	Concn, *M*	Specific conductivity × 10^3, ohm^{-1} cm^{-1}	Molar conductivity × 10^3, ohm^{-1} cm^2
20.5[a]	8.01	391	12.95	0.717	55.4
19.39	5.09	263	8.13	0.209	25.7
18.29	2.88	157	2.92	0.00403	1.28
17.19	2.52	147	1.32	0.000412	0.312

[a] Pure BrF_3.

our measurements. As seen from Figure 5, initial addition of chlorine trifluoride produces a sharp drop in the conductance which becomes more gradual in solutions containing ~85 mol % bromine trifluoride. It appears, therefore, that our conductance data support the postulate that the high electrical conductivity of pure bromine trifluoride is due to a chain-conducting mechanism.[6] (See also Table IV.)

It is evident from the above results that the fluoride ion transfer in bromine trifluoride–chlorine trifluoride mixtures does take place and leads to the formation of BrF_4^- and ClF_2^+ ions, but, at room temperature, the extent of the reaction is quite limited.

Acknowledgment.—T. S. gratefully acknowledges support from an Associated Midwest Universities–Argonne National Laboratory predoctoral fellowship.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF COLORADO, BOULDER, COLORADO 80302

The Interaction of Chromium(III) Ion with Bromide Ion in Hydrobromic Acid Solution[1]

BY LARRY O. SPREER[2] AND EDWARD L. KING*

Received June 9, 1970

The inner-sphere association of chromium(III) ion and bromide ion has been studied in aqueous hydrobromic acid solution (~0.5–9.0 *M*) at 45, 60, and 75° and in aqueous hydrobromic acid–perchloric acid solution (I = 7.14 *M*, 45°). Outer-sphere interactions of oppositely charged ions also occur in the concentrated electrolyte solutions studied, thereby complicating greatly the interpretation of the data. The association reaction to form pentaaquobromochromium(III) ion occurs to a greater extent at high electrolyte concentration; this is due, in part, to the low activity of water in these solutions. The association reaction is endothermic (ΔH = +7.5 kcal mol^{-1} at 0.50–2.0 *M* hydrobromic acid; ΔH = +5.9 kcal mol^{-1} at 8.0 *M* hydrobromic acid). The rate of formation of pentaaquobromochromium(III) ion has been studied at 45°.

The interaction of a metal ion and an anionic ligand in solution may produce two (or more) definable types of species: inner-sphere species with direct bonding of the ligand to the metal ion and outer-sphere species (ion pairs) with one (or more) solvent molecules separating the metal ion and the ligand. In addition, there are ion atmosphere effects in electrolyte solution; it is unnecessary and inappropriate to describe such interaction in terms of the formation of new species.[3] Distinguishing inner-sphere and outer-sphere interaction is facilitated for chromium(III) ion by the large difference in rates of establishment of equilibrium in the two types of interaction. Distinguishing outer-sphere interaction from ion atmosphere effects is aided by no such experimental criterion; the basis for establishing the extent of outer-sphere interaction is usually an assumption which cannot be proved (*e.g.*, the validity of the ionic strength principle).

The present paper deals with studies on chromium(III) bromide in aqueous solutions of hydrobromic acid or perchloric acid–hydrobromic acid mixtures. The interactions investigated are *the inner-sphere interactions*[4]

$$Cr(OH_2)_{7-n}Br_{n-1}{}^{4-n} + Br^- = Cr(OH_2)_{6-n}Br_n{}^{3-n} + H_2O \qquad (n = 1, 2, 3(?))$$

with equilibrium quotients Q_n and *the outer-sphere interactions*

$$Cr(OH_2)_{6-n}Br_n{}^{3-n} + Br^- = Cr(OH_2)_{6-n}Br_n{}^{3-n}\cdot Br^- \qquad (n = 0, 1)$$

with equilibrium quotients q_{n1} and

$$Cr(OH_2)_{6-n}Br_n{}^{3-n} + ClO_4^- = Cr(OH_2)_{6-n}Br^{3-n}\cdot ClO_4^- \qquad (n = 0, 1)$$

with equilibrium quotients q_{n2}. In addition, the presence of outer-sphere species containing more than one ion-paired anionic ligand (*e.g.*, $Cr(OH_2)_6{}^{3+}\cdot(Br^-)_2$) is possible in media of high electrolyte concentration. These several equilibria must be considered simultaneously, resulting in difficulties which will be explored in the interpretation of the data.

The following system of notation will be used in concentration terms in equilibrium quotients and rate laws: C_{Cr}, total stoichiometric concentration of chromium(III); $[Cr(OH_2)_6{}^{3+}]$, molarity of hexaaquochromium(III) ion; $[Cr^{3+}] = [Cr(OH_2)_6{}^{3+}] + [Cr(OH_2)_6{}^{3+}\cdot Br^-] + \ldots$; $[Cr(OH_2)_5Br^{2+}]$, molarity of pentaaquobromochromium(III) ion; $[CrBr^{2+}] = [Cr(OH_2)_5Br^{2+}] + [Cr(OH_2)_5Br^{2+} \cdot Br^-] + \ldots$, etc. That is, a chromium(III) chemical formula without the first coordination shell specified completely stands for the sum of all of the species, free ion and ion pairs, with the same number of bromide ions in the first coordination shell.

---

[1] Based on the Ph.D. thesis of L. O. Spreer, University of Colorado, 1969; work supported by grants from the National Science Foundation (Grants GP-680 and GP-7185X).

[2] National Science Foundation Predoctoral Trainee, 1968–1969.

[3] T. F. Young and A. C. Jones, *Ann. Rev. Phys. Chem.*, **3**, 275 (1952); O. Redlich and G. C. Hood, *Discuss. Faraday Soc.*, **24**, 87 (1957).

[4] J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

Column cation-exchange procedures have allowed separation of the species with different numbers of bromide ions in their first coordination shells. The lability of outer-sphere species prevents their separation by such means.

Experimental Methods and Results

Reagents.—Doubly distilled water was used in the preparation of all solutions. Before the second distillation, made with an all-Pyrex still, the water was passed through a Barnstead ion-exchange demineralizer. Reagent grade hydrobromic acid (48%) was distilled at atmospheric pressure (~630 Torr) under a nitrogen atmosphere. Reagent grade perchloric acid was used without further purification. Hydrated chromium(III) perchlorate was prepared from reagent grade chromium(VI) oxide and hydrogen peroxide;[5] the relative light absorption of this stock solution at 230 and 260 nm ($A_{230}/A_{260} = 0.22$) shows the presence of negligible amounts of polymeric chromium(III) species.[6] Tetraaquodibromochromium(III) bromide was prepared from chromium(VI) oxide and hydrobromic acid by a procedure similar to that used by Recoura.[7] (Based upon observations on the analogous chloride system,[8,9] this solid probably contains the trans isomer of dibromochromium(III) ion.) Solutions containing pentaaquobromochromium(III) ion as the only chromium(III) species were prepared by the reaction of chromium(II) with bromine[10] followed by purification using cation-exchange procedures.[11] (The chromium(II) solution in perchloric acid was prepared by dissolving 99.9+% pure chromium metal in perchloric acid.[12])

Dowex 50W-X12, 50–100 mesh cation-exchange resin was used in the separation procedures. It was purified before use by treatment at steam bath temperatures with 2 *M* sodium hydroxide containing dilute hydrogen peroxide (~0.01 *M*) and then with 3 *M* hydrochloric acid; then there was a repeat of the treatment with basic peroxide, followed by rinsing at room temperature first with 3 *M* hydrochloric acid and then with 0.05 *M* perchloric acid until no chloride ion was detectable.

Spectral measurements were made using a Cary Model 15 spectrophotometer with provision for thermostating the cell.

Analytical Procedures.—Chromium was determined spectrophotometrically in alkaline solutions containing chromate ion;[13] chromium(III) species were converted to chromate ion by alkaline hydrogen peroxide.

Spectrophotometric Study of Outer-Sphere Association.—Spectrophotometric studies of perchloric acid–hydrobromic acid solutions of chromium(III) perchlorate over a range of wavelengths were made at 25, 35, and 45° at a series of electrolyte concentrations. The chromium(III)-containing solution was measured against a perchloric acid–hydrobromic acid blank of the same concentration. The formation of inner-sphere chromium(III) species is slow under the conditions of these experiments; to obtain the light absorption in the absence of any contribution from inner-sphere species, the observed values of log (I_0/I) were extrapolated to the time of mixing. These extrapolated data from solutions of varying concentration of bromide ion at constant ionic strength were treated by plotting $\tilde{a}$ *vs.* $(\tilde{a} - a_0)/[Br^-]$ in which $\tilde{a}$ is the apparent molar absorbancy index of chromium(III) in the solution in question, $(\log (I_0/I))/(C_{Cr}b)$ (where b is the cell length), and a_0 is the corresponding quantity for chromium(III) in perchloric acid solutions of the same ionic strength.[14] These plots were approximately linear[15]

$$\tilde{a} = a - \frac{\tilde{a} - a_0}{[Br^-]} \frac{1}{q_0'} \qquad (1)$$

and they allowed evaluation of two parameters: the intercept, a, an apparent molar absorbancy index, and the negative of the reciprocal of the slope, q_0', an apparent equilibrium quotient. Discussion of the exact physical significance of these parameters will be deferred, but a summary of their values, obtained by the method of averages, is given in Table I. In each series, five different concentrations of bromide ion were studied ranging from a low of 0.68 *M* (0.34 *M* in a few of the series) to a high of the value of the ionic strength. The concentration of hexaaquochromium(III) ion was varied from 0.027 to 0.067 *M* at some of the concentrations of bromide ion; Beer's law was obeyed.

TABLE I

VALUES OF q_0', THE APPARENT EQUILIBRIUM QUOTIENT FOR OUTER-SPHERE ASSOCIATION OF HEXAAQUOCHROMIUM(III) ION AND BROMIDE ION, AND a, THE APPARENT MOLAR ABSORBANCY INDEX OF THE OUTER-SPHERE SPECIES $Cr(OH_2)_6 \cdot Br^{2+}$ [a]

λ, nm	*I*, *M*	25°	35°	45°
280	8.2			0.36 (38)
270	8.2		0.27 (92)	0.29 (100)
	7.2			0.24 (61)
	5.8			0.16 (47)
260	8.2	0.27 (215)	0.26 (225)	0.24 (257)
	7.2	0.21 (150)	0.32 (140)	0.20 (176)
	5.8	0.18 (87)	0.16 (108)	0.14 (134)
	4.1	0.15 (50)	0.15 (56)	0.23 (54)
	3.1			0.26 (36)
255	8.2	0.26 (340)	0.22 (373)	
	7.2	0.21 (230)	0.32 (220)	0.20 (280)
	4.1			0.21 (89)
	3.1			0.19 (68)
250	8.2	0.24 (533)		
	7.2	0.23 (344)	0.32 (338)	
	5.8	0.17 (231)	0.15 (289)	
	4.1	0.15 (126)	0.15 (152)	0.18 (160)
	3.1	0.13 (144)		
245	5.8	0.18 (360)	0.15 (470)	
	4.1	0.16 (200)	0.12 (290)	

[a] Values of a (in l. mol^{-1} cm^{-1}) are given in parentheses.

Similar series of experiments were run with pentaaquobromochromium(III) ion in perchloric acid–hydrobromic acid solution. In these studies, like those involving hexaaquochromium(III) ion, slow chemical changes occur (the concurrent conversion of bromochromium(III) ion to hexaaquochromium(III) ion or dibromochromium(III) ion), and the spectral measurements were extrapolated to zero time to obtain the effects due solely to the rapidly established outer-sphere association equilibria involving pentaaquobromochromium(III) ion.[14] The correlations in a plot of $\tilde{a}$ *vs.* $(\tilde{a} - a_0')/[Br^-]$, in which a_0' is the molar absorbancy index of pentaaquobromochromium(III) ion, were of appreciably lower quality than those for the outer-sphere association of hexaaquochromium(III) ion.

The best data were obtained at $I = 4.1$ *M*, 45°, where q_1' was evaluated to be 0.23 (250 nm), 0.29 (255 nm), and 0.25 (260 nm); at $I = 7.1$ *M*, 45°, where q_1' was evaluated to be 0.46 (255 nm) and 0.44 (260 nm); and at $I = 7.1$ *M*, 35°, where q_1' was evaluated to be 0.33 (250 nm) and 0.28 (255 nm).

Studies of Inner-Sphere Association.—Solutions of chromium(III) bromide (concentration 2.6×10^{-3}–8.9×10^{-2} *M*) in hydrobromic acid were equilibrated at 45, 60, and 75° in sealed Pyrex tubes. The minimum times of equilibration follow: 45°, 8 days; 60°, 10 hr; and 75°, 5 hr. Most solutions were equilibrated appreciably longer than these minimum times. After equilibration, a measured volume of the reaction mixture was

---

(5) D. W. Kemp and E. L. King, *J. Amer. Chem. Soc.*, **89**, 3433 (1967).

(6) C. Altman and E. L. King, *ibid.*, **83**, 2825 (1961).

(7) M. S. Recoura, *C. R. Acad. Sci.*, **110**, 1193 (1890).

(8) E. L. King, M. J. M. Woods, and H. S. Gates, *J. Amer. Chem. Soc.*, **80**, 5015 (1958).

(9) I. F. Dance and H. C. Freeman, *Inorg. Chem.*, **4**, 1555 (1965); B. Morosin, *Acta Crystallogr.*, **21**, 280 (1966).

(10) H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

(11) F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

(12) J. P. Fackler, Jr., and D. G. Holah, *ibid.*, **4**, 954 (1965).

(13) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

(14) Detailed tables of data are available as Document NAPS-01215 from ASIS National Auxiliary Publication Service c/o CCM Corp., 909 3rd Ave., New York, N. Y. 10022. Remit $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make check payable to: CCMIC-NAPS.

(15) T. W. Newton and G. M. Arcand, *J. Amer. Chem. Soc.*, **75**, 2449 (1953).

quenched by rapid dilution (5–10-fold) with cold water (0–5°). The resulting solution with an electrolyte concentration of 0.1–0.25 N was passed through a cation-exchange column held at ~1°. Species of charge 0 and 1+ ($CrBr_3$ and $CrBr_2^+$) are not held in the resin phase under these conditions; continued rinsing with 0.15 M perchloric acid removed completely the species of charge $\leq 1+$. Species of charge 2+ ($CrBr^{2+}$) then were eluted with 1.0 M perchloric acid. In most experiments, hexaaquochromium(III) ion was not eluted; its concentration in an equilibrated solution was obtained from material balance ($[Cr^{3+}] = C_{Cr} - [CrBr^{2+}] - [CrBr_2^+]$). (As will be pointed out, the concentration of tribromochromium(III) is very low; in the preceding equation its concentration is combined with the dibromochromium(III) ion.) At high concentrations of bromide ion, the relative equilibrium concentration of hexaaquochromium(III) ion is low, and this calculation leads to an uncertain value for the concentration of this species. Under these conditions, hexaaquochromium(III) ion was determined directly after it had been eluted from the resin phase with 4 M hydrochloric acid. (Use of hydrochloric acid was advantageous; evaporation of the eluate reduced the amount of acid which had to be neutralized before conversion of chromium(III) to chromate for analysis.) The ion-exchange procedures were carried out at low temperatures (+1°) as promptly as possible; independent experiments showed that recovery of bromochromium(III) ion (prepared by the reaction of chromium(II) and bromine) and dibromochromium(III) ion (the species present in crystalline green hydrated chromium(III) bromide) under these conditions was essentially qualitative (99 ± 2% for bromochromium(III) ion and 97 ± 4% for dibromochromium(III) ion). In the solutions of highest concentration of hydrobromic acid, some tribromochromium(III) may be formed. The ion-exchange procedures are not capable of separating tribromochromium(III) and dibromochromium(III) ion in solutions containing extra electrolyte.

The data,[14] treated provisionally under the assumption that no tribromochromium(III) is present, will be summarized in terms of two empirical equilibrium quotients

$$Q_1' = \frac{[CrBr^{2+}]}{(C_{Cr} - [CrBr^{2+}] - [CrBr_2^+])(C_{Br} - [CrBr^{2+}] - 2[CrBr_2^+])}$$

$$Q_2' = \frac{[CrBr_2^+]}{[CrBr^{2+}](C_{Br} - [CBr_2^+] - 2[CrBr_2^+])}$$

At most concentrations of hydrobromic acid, duplicate or triplicate independent samples were run. At some concentrations of hydrobromic acid, samples were run at different concentrations of chromium(III). There was no appreciable dependence of the values of the equilibrium quotients upon the stoichiometric concentration of chromium(III); *e.g.*, at 75° and 2.43 M bromide ion, $Q_1' = 0.0143$ at both 2.6×10^{-2} and 4.6×10^{-2} M chromium(III), and at 75° and 8.83 M bromide ion, $Q_1' = 0.465$ at 1.40×10^{-2} M chromium(III) and $Q_1' = 0.472$ at 6.49×10^{-2} M chromium(III). Checking this point was appropriate since in a study of the chromium(III)–chloride system,[16] a mild dependence of the value of the equilibrium quotient corresponding to Q_1' was observed. In the absence of evidence for a dependence of Q_1' and Q_2' upon the stoichiometric concentration of chromium(III) bromide, the average of the observed values will be reported, even if this includes values from experiments at different concentrations of chromium(III). The values reported as a function of the concentration of free bromide ion are as follows ($[Br^-]$, $10^2Q_1'$, $10^2Q_2'$, including an uncertainty in the values of Q which represents a measure of the scatter of values): for 45°: 0.442 M, 0.484 ± 0.015, . . .; 0.674 M, 0.432 ± 0.015, . . .; 1.16 M, 0.446 ± 0.030, . . .; 2.10 M, 0.466 ± 0.015, . . .; 4.11 M, 1.05 ± 0.015, . . .; 5.69 M, 2.84 ± 0.05, 1.19 ± 0.08; 7.00 M, 6.53 ± 0.10, 2.40 ± 0.16; 8.93 M, 28.4 ± 0.6, 7.26 ± 0.15; for 60°: 0.51 M, 0.731 ± 0.015, . . .; 0.79 M, 0.639 ± 0.015, . . .; 1.18 M, 0.670 ± 0.015, . . .; 2.03 M, 0.814 ± 0.020, . . .; 4.20 M, 1.79 ± 0.05, 0.672 ± 0.015; 6.42 M, 6.68 ± 0.11, 1.99 ± 0.05; 8.92 M, 37.9 ± 0.3, 8.41 ± 0.15; for 75°: 0.51 M, 1.31 ± 0.02, . . .; 0.79 M, 1.07 ± 0.02, . . .; 1.22 M, 0.21 ± 0.02, . . .; 2.42 M, 1.49 ± 0.03, . . .; 4.21 M, 2.56 ± 0.15, 1.03 ± 0.04; 5.99 M, 7.59 ± 0.15, 1.90 ± 0.15; 7.00 M, 14.0 ± 0.5, 3.69 ± 0.20; 8.81 M, 48.4 ± 1.0, 10.2 ± 0.25. No value of Q_2' is given for solutions in which the concentration of dibromochromium(III) was not high enough to be measured with reasonable accuracy.

A series of measurements was made on perchloric acid–hydrobromic acid solutions of approximately constant ionic strength ($I = 7.14$ M) at 45°. These solutions containing 6×10^3–4×10^{-2} M chromium(III) bromide were equilibrated and analyzed in the same manner as the hydrobromic acid solutions. The values of $10^2Q_1'$ as a function of the concentration of bromide ion are 93 (0.68 M), 56 (2.0 M), 22 (4.25 M), 10.5 (6.25 M), and 6.95 (7.14 M).

The Activity of Water in Aqueous Hydrobromic Acid.—In the balanced equation for the stepwise formation of inner-sphere bromochromium(III) species, a molecule of water appears on the product side. This will be taken into account in calculating the equilibrium quotients Q_1 and Q_2 from the values of Q_1' and Q_2': $Q_1 = Q_1'a_w$ and $Q_2 = Q_2'a_w$. Values of the activity of water in hydrobromic acid solution at 25° were obtained up to a concentration of 3 M from published values of osmotic coefficients;[17] above this concentration, calculation of the activity of water was based upon the activity of hydrobromic acid as a function of concentration.[18] The activity of water was evaluated at temperatures of this study using values[19] of $\bar{L}$, which were assumed to be independent of temperature. Values calculated in this way for particular molalities of hydrobromic acid follow (given as m, a_w at 45°, a_w at 60°, a_w at 75°): 0.50, 0.982, 0.983, 0.983; 1.00, 0.963, 0.963, 0.963; 2.00, 0.915, 0.916, 0.917; 4.00, 0.778, 0.781, 0.783; 6.00, 0.634, 0.642, 0.649; 8.00, 0.514, 0.525, 0.536; 10.00, 0.385, 0.399, 0.441; 12.00, 0.275, 0.289, 0.302. To allow calculation of the activity of water at the molarities of hydrobromic acid studied, the densities of hydrobromic acid solutions of various concentrations were determined at each of the temperatures studied in this work. In correlation of the data obtained at constant ionic strength, it was assumed that the activity of water was constant.

The Rate of Formation of Bromochromium(III) Ion.—The dependence of light absorption upon time in perchloric acid–hydrobromic acid solutions initially containing hexaaquochromium(III) ion allows calculation of the rate of formation of bromochromium(III) ion. In calculating values of the rate, $d[CrBr^{2+}]/dt$, absorbancy indices for hexaaquochromium(III) ion and bromochromium(III) ion appropriate for each medium were used. The reaction was followed only to a slight extent (<5%) in any particular experiment, and the rate was essentially constant. In each run, six to ten measurements were made at each of three different wavelengths in the region 250–280 nm. Values of the rate derived from the three different wavelengths agree within ~10%. Table II summarizes values of the pseudo-first-order rate constant ($k' = [Cr^{3+}]_{av}^{-1}(d[CrBr^{2+}]/dt)$) as a function of the concentration of bromide ion.

TABLE II

THE PSEUDO-FIRST-ORDER RATE CONSTANT FOR FORMATION OF BROMOCHROMIUM(III) ION[a]

$$d[CrBr^{2+}]/dt = k'[Cr^{3+}]$$

	$10^7k'$, sec^{-1}		
$[Br^-]$, M	$I = 4.1$ M	$I = 5.8$ M	$I = 7.1$ M
0.34		0.776	
0.68	0.497	1.39	
1.36	0.820	2.30	
2.04	0.920		9.45
2.72		3.50	
3.06	1.25		
4.08	1.38		12.5
5.78		4.11	13.3
7.10			14.7

[a] At 45°.

Interpretation of Results

Spectrophotometric Study of Outer-Sphere Association.—Conventional interpretation of the parameters q_0' and a obtained by linearization of data from the spectral study of solutions of hexaaquochromium-

---

(16) C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967).

(17) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(18) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1959, p 481; "International Critical Tables," Vol. 3, E. W. Washburn, Ed., McGraw-Hill, New York, N. Y., 1928, p 55.

(19) *Nat. Bur. Stand. (U. S.), Tech. Note*, **270-3**, 32–33 (1968).

(III) ion in hydrobromic acid–perchloric acid solutions identifies q_0' as q_{01}, the equilibrium quotient for formation of the outer-sphere species $Cr(OH_2)_6^{3+}\cdot Br^-$, and a as the molar absorbancy index of this species. If this interpretation is correct, the calculated value of q_0' should not depend upon the wavelength studied, and the value of a should not depend dramatically upon the medium.

The values of q_0' presented in Table I satisfy reasonably well the first of these criteria, although the values obtained at 45° at most of the ionic strengths studied show a mild dependence upon the wavelength. The dramatic dependence of a upon the ionic strength suggests that the simplest interpretation of the data ($q_0' = q_{01}$ and $a = a_{01}$) is not correct.[20]

Outer-sphere association species of hexaaquochromium(III) ion and perchlorate ion may be present.[21,22] The form of the equation relating the apparent molar absorbancy index of chromium(III), $\tilde{a}$, to the concentration of bromide ion *is not* altered by the presence of such a species. This is a consequence of the linear relationship between the concentration of perchlorate ion and bromide ion in solutions of constant ionic strength: $[ClO_4^-] \cong I - [Br^-]$ (the concentration of chromium(III) is small compared to the total ionic strength). Appropriately rearranged to the form given earlier, the equation becomes

$$\tilde{a} = \frac{a_{01}q_{01} - a_{02}q_{02}}{q_{01} - q_{02}} - \frac{\tilde{a} - \dfrac{a_{00} + a_{02}q_{02}I}{1 + q_{02}I}}{[Br^-]}\,\frac{1 + q_{02}I}{q_{01} - q_{02}} \qquad (2)$$

in which a_{00}, a_{01}, and a_{02} are the molar absorbancy indices of the species $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_6^{3+}\cdot Br^-$, and $Cr(OH_2)_6^{3+}\cdot ClO_4^-$, respectively. In a plot of $\tilde{a}$ *vs.* $\{\tilde{a} - (a_{00} + a_{02}q_{02}I)/(1 + q_{02}I)\}]/[Br^-]$ the intercept, called a in the simple treatment (eq 1), is a weighted difference of the absorbancy indices of the outer-sphere species, $a = (a_{01}q_{01} - a_{02}q_{02})/(q_{01} - q_{02})$, and the reciprocal of the slope, called q_0' in the simple treatment, is a function of the equilibrium quotients for formation of the two kinds of outer-sphere species: $q_0' = (q_{01} - q_{02})/(1 + Iq_{02})$. It is to be noted that the quantity subtracted from $\tilde{a}$ in the numerator of the quantity plotted as abscissa, called a_0 in the simple treatment, is the apparent extinction coefficient of hexaaquochromium(III) ion in a solution containing perchlorate ion at a concentration equal to the ionic strength of the solution; it is the weighted average of the extinction coefficients of free hexaaquochromium(III) ion and the outer-sphere perchlorate species. Comparison of values of the parameter identified as the molar absorbancy index (a in the simple treatment and $(a_{01}q_{01} - a_{02}q_{02})/(q_{01} - q_{02})$ in the complete derivation) obtained in solutions of different electrolyte concentration supports the view that ion pairs involving perchlorate ion play a role. This parameter increases greatly with an increase in the electrolyte concentration (as is seen in Table I). If the values of q_{01} and q_{02} become closer to one another as the electrolyte concentration increases, the quotient involving $(q_{01} - q_{02})$ as a denominator might be expected to increase. (The dependence is also a function of the magnitude of a_{01} and a_{02} and their dependences upon electrolyte concentration.)

Inner-Sphere Association of Bromide Ion with Chromium(III) Ion.—Evaluation by the ion-exchange procedure of the concentration of pentaaquobromochromium(III) ion present at equilibrium is unambiguous. If no ion pairing (outer-sphere interaction) complicated the problem, conversion of the empirical equilibrium quotient Q_1' to the equilibrium quotient for the reaction

$$Cr(OH_2)_6^{3+} + Br^- = Cr(OH_2)_5Br^{2+} + H_2O$$

$$Q_1 = \frac{[Cr(OH_2)_5Br^{2+}]a_w}{[Cr(OH_2)_6^{3+}][Br^-]}$$

would be straightforward: $Q_1 = Q_1'a_w$. Once the existence of ion pairs is admitted, the problem becomes much more complicated if it is to be handled rigorously. For solutions containing chromium(III) bromide, hydrobromic acid, and perchloric acid it can be shown that

$$Q_1\frac{1 + Iq_{12}}{1 + Iq_{02}} = Q_1'a_w\,\frac{1 + [Br^-]\dfrac{q_{01} - q_{02}}{1 + Iq_{02}}}{1 + [Br^-]\dfrac{q_{11} - q_{12}}{1 + Iq_{12}}} \qquad (3)$$

For the solutions containing no perchloric acid, the terms involving q_{02} and q_{12} can be dropped from eq 3.

The coefficients of $[Br^-]$ in the numerator and denominator of the right-hand side of the equation are the same functions evaluated in the spectrophotometric study of freshly prepared perchloric acid–hydrobromic acid solutions, and one can, therefore, evaluate the quantity $Q_1(1 + Iq_{12})/(1 + Iq_{02})$. As one might anticipate, if perchlorate ion pairing occurs, it eliminates the possibility of evaluation of Q_1 involving only free (*i.e.*, non-ion-paired) species. Since the values of q_0' and q_1' are close to one another, the value of the quotient will be close to unity (see eq 4), and conversion of

$$\frac{1 + [Br^-]q_0'}{1 + [Br^-]q_1'} = \frac{1 + [Br^-](q_{01} - q_{02})/(1 + Iq_{02})}{1 + [Br^-](q_{11} - q_{12})/(1 + Iq_{12})} \qquad (4)$$

the empirical equilibrium quotients Q_1' and Q_2' to the composite quotients $Q_1(1 + Iq_{12})/(1 + Iq_{02})$ and $Q_2\cdot(1 + Iq_{22})/(1 + Iq_{12})$ will be accomplished simply by multiplication by the activity of water.

The apparent enthalpy changes associated with these composite quantities are as follows: for $Q_1'a_w$ at I = 0.50–2.0 M, ΔH = 7.5 ± 0.5 kcal mol^{-1} (the dependence of ΔH upon electrolyte concentration is within the experimental uncertainty), at I = 4.0 M, ΔH = 6.5 kcal mol^{-1}, and at I = 8.0 M, ΔH = 5.9 kcal mol^{-1}; for $Q_2'a_w$ at I = 4.0 M, ΔH = 3.0 kcal mol^{-1}, and at 8.0 M, ΔH = 2.7 kcal mol^{-1}.

As indicated earlier, the analytical procedures do not separate tribromochromium(III) from dibromochromium(III) ion. The apparent value of Q_2' is, therefore, the composite

$$Q_2'(\text{app}) = Q_2' + Q_2'Q_3'[Br^-] \qquad (5)$$

Since the correction of Q_2'(app) to obtain Q_2' is not large, an approximate value of Q_3' is adequate If one assumes[23] that $Q_3'/Q_2' = Q_2'/Q_1'$, this relationship, after rearrangement, becomes

$$Q_2' = \frac{Q_2'(\text{app})}{1 + [Br^-](Q_2')^2Q_1'} \qquad (6)$$

---

[20] F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, **78**, 15 (1956).

[21] M. Alei, Jr., *Inorg. Chem.*, **3**, 44 (1964).

[22] K. M. Jones and J. Bjerrum, *Acta Chem. Scand.*, **19**, 974 (1965).

[23] A statistical factor should be incorporated into this quotient. Since the relative concentrations of isomeric species are not known, the correction cannot be made correctly (E. L. King, *J. Chem. Educ.*, **43**, 478 (1966)), and it will be omitted.

To correct Q_2'(app) to Q_2', one can use $Q_2' = Q_2'$(app) in the denominator of the right-hand side of the equation. Successive approximations are needed only at the highest concentration of bromide. The correction is not particularly sensitive to temperature; values of the quantity $(1 + [\mathrm{Br}^-](Q_2')^2/Q_1')$ as a function of the concentration of bromide ion are 1.13 (8.9 *M*), 1.07 (7.0 *M*), 1.04 (6.4 *M*), 1.03 (5.8 *M*), and 1.01 (4.2 *M*).

The values of the quantity Q_1' obtained in the series of experiments at 45° run at constant ionic strength ($I = 7.14$ *M*) show an appreciable dependence upon the composition of the solution. The approximately 13-fold change in Q_1' as the concentration of bromide ion increases from 0.68 to 7.14 *M* is not due to differences in ion pairing of hexaaquochromium(III) ion and pentaaquobromochromium(III) ion by bromide ion and perchlorate ion. This follows from eq 3 and 4; the spectrophotometrically evaluated parameters q_0' and q_1' (which are approximately equal) should allow appropriately for ion pairing. Nonspecific outer-sphere interactions of bromide ion and/or perchlorate ion with aquochromium(III) ion and bromochromium(III) ion may appear as a dependence of the composite $[Q_1(1 + Iq_{12})/(1 + Iq_{02})]$ upon the concentration of bromide ion. The dependence is approximately linear when log $[Q_1(1 + Iq_{12})/(1 + Iq_{02})]$ is plotted *vs.* the concentration of bromide ion (Figure 1). This figure resembles a Harned's rule plot for the activity coefficient of an electrolyte in a series of solutions of varying composition but constant ionic strength. The slope of the line $((\Delta Z^2)^{-1}\Delta \log [Q_1(1 + Iq_{12})/(1 + Iq_{02})]/\Delta[\mathrm{Br}^-])$ is ~0.03, which is not larger than values observed for the activity coefficients of electrolytes in solutions of constant ionic strength but varying composition.[24]

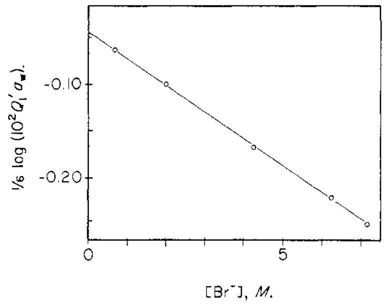

Figure 1.—The dependence of Q_1 upon solution composition [$I = 7.14$ *M* (perchloric acid + hydrobromic acid), 45°].

Kinetic Studies of the Formation of Bromochromium(III) Ion.—The data presented in Table II show that the reaction order with respect to bromide ion is less than first and that it decreases with increasing concentration of bromide ion. An empirical correlation of the bromide ion concentration dependence of the rate is

$$\frac{\mathrm{d}[\mathrm{CrBr}^{2+}]}{\mathrm{d}t} = \frac{\alpha[\mathrm{Br}^-]}{1 + \beta[\mathrm{Br}^-]}[\mathrm{Cr}^{3+}] \qquad (7)$$

as demonstrated by the linearity of a plot of (k') (which is equal to $[\mathrm{Cr}^{3+}]/(\mathrm{d}[\mathrm{CrBr}^{2+}]/\mathrm{d}t)$) *vs.* $1/[\mathrm{Br}^-]$ (see Figure 2). Values of the parameters α and β obtained from such plots follow (given as I (mol l.$^{-1}$), α (l. mol^{-1} sec^{-1}), β (l. mol^{-1})): 4.1, 9.9×10^{-8}, 0.51; 5.8, 2.57×10^{-7}, 0.40; 7.1, 9.8×10^{-7}, 0.54.

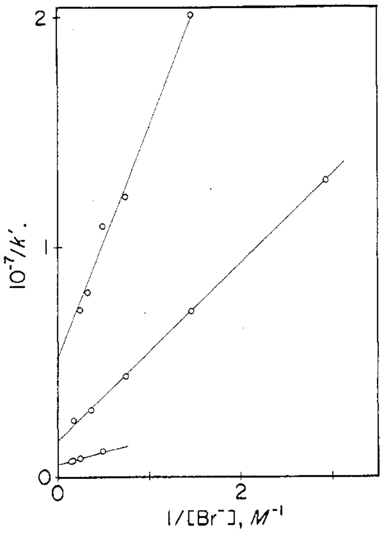

Figure 2.—The dependence of reaction rate upon the concentration of bromide ion (45°): upper line, $I = 4.1$ *M;* middle line, $I = 5.8$ *M;* lower line, $I = 7.1$ *M.*

If formation of bromochromium(III) ion in solutions containing hexaaquochromium(III) ion, bromide ion, perchlorate ion, and ion pairs of hexaaquochromium(III) ion with bromide ion or perchlorate ion occurred exclusively by a pathway with a transition state of composition $\{\mathrm{Cr(OH_2)_6}^{3+}\cdot\mathrm{Br}^-\}^{\ddagger}$, the rate law would be

$$\frac{\mathrm{d}[\mathrm{CrBr}^{2+}]}{\mathrm{d}t} = \frac{k(q_{01}/(1 + q_{02}I))[\mathrm{Br}^-][\mathrm{Cr}^{3+}]}{1 + \dfrac{q_{01} - q_{02}}{1 + q_{02}I}[\mathrm{Br}^-]} \qquad (8)$$

The coefficient of the concentration of bromide ion in the denominator is $(q_{01} - q_{02})/(1 + Iq_{02})$, a function identical with that obtained from the spectrophotometric study of ion pairing. However, the quantity (the coefficient of the concentration of bromide ion) in the empirical rate law is appreciably larger than q_0', the quantity evaluated in the spectrophotometric study.[25] At the ionic strengths in question the values of q_0' (an apparent association equilibrium quotient for the 1-1 ion-pairing reaction) presented in Table I are 0.21 ± 0.02 ($I = 4.1$ *M*), 0.15 ± 0.01 ($I = 5.8$ *M*), and 0.21 ± 0.02 ($I = 7.1$ *M*).

Discussion

Although this study characterizes quantitatively the inner-sphere interaction of chromium(III) and bromide ion, conversion of the data to an equilibrium quotient is rendered uncertain by the difficulties in characterization of the outer-sphere interactions. There is almost certainly an appreciable concentration

---

(24) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, pp 427–429.

(25) An alternate method for comparing the kinetic data and the spectrophotometric data is the following. If an ion pair $\mathrm{Cr(OH_2)_6}^{3+}\cdot\mathrm{Br}^-$ is responsible for the enhancement of light absorption in the zero-time spectrum and if the transition state for formation of inner-sphere bromochromium(III) ion has this same composition, a plot of log k *vs.* log $(\bar{a} - a_0)$ should be linear with slope unity. Such a correlation can be attempted since kinetic measurements were made at concentration and temperature conditions studied spectrophotometrically. The plots were linear, but the slope was not unity in any case. Values of the slope (at 45°), which did not depend upon the wavelength of the spectrophotometric study, are 0.753 ($I = 4.08$ *M*), 0.80 ($I = 5.8$ *M*), and 0.87 ($I = 7.2$ *M*). An advantage in this correlation of the two types of data is the absence of the intermediate stage of data treatment, the calculation of ion-pair equilibrium quotient values.

of outer-sphere species containing two associated anions, *e.g.*, $Cr(OH_2)_6^{3+} \cdot (Br^-)_2$. If $q_{01} = 0.24$ (an intermediate value chosen from Table I), the statistically expected value of the equilibrium quotient for stepwise association of a second bromide ion is 0.105.[26] Electrostatic repulsion may lower this, but even an equilibrium quotient of 0.05 would give a ratio $[Cr(OH_2)_6^{3+} \cdot (Br^-)_2]/[Cr(OH_2)_6^{3+} \cdot Br^-] = 0.2$ at 4 *M* bromide. The correct values of q_{01} are appreciably larger than the values tabulated in Table I for two reasons. If ion pairing by perchlorate occurs, the apparent equilibrium quotient q_0' is the composite $(q_{01} - q_{02})/(1 + Iq_{02})$, which must be smaller than q_{01}. In addition, correlation of spectrophotometric data in terms of 1–1 interaction gives too small a value of q_{01} if both 1–1 and 1–2 interactions are responsible for the enhanced light absorption.[27,28] The problems arising from approximate conformity of the system to the Kruh conditions[27,28] can be avoided by studying solutions in which the metal ion is in large excess.[29] This approach is, however, not practical for a system involving a polyvalent metal ion if the equilibrium quotient for association is small. (For instance if $q = 0.5$, a metal ion concentration of 2 *M* would be needed to convert half of the ionic ligand to the ion pair.)

The kinetic data for formation of bromochromium(III) ion are correlated with an equation (eq 8) consistent with the presence of the species $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_6^{3+} \cdot Br^-$, and $Cr(OH_2)_6^{3+} \cdot ClO_4^-$ and the transition state $\{Cr(OH_2)_6^{3+} \cdot Br^-\}^{\ddagger}$; the derived values of the parameter $(q_{01} - q_{02})/(1 + Iq_{02})$ do not agree, however, with the values obtained from spectral data. It is necessary, therefore, to draw one of the following conclusions. (a) Transition states and species other than those listed above play roles in the reaction mechanism and in enhancing the light absorption. (b) The ratio of the activity coefficients of the outer-sphere species $Cr(OH_2)_6^{3+} \cdot Br^-$ and the transition state of the same composition depends mildly upon the concentration of bromide ion in solutions of constant ionic strength. (c) The absorbancy indices of the several species show a mild dependence upon bromide ion concentration in solutions of constant ionic strength. These possibilities are not easily checked. The point has already been made that there may be present at appreciable concentrations outer-sphere species containing two associated bromide ions. Evidence that the aquation of iodochromium(III) ion occurs by an SN1 mechanism[30–32] suggests that the formation and aquation of monobromochromium(III) ion may occur in part by such a pathway. At the highest concentration of bromide ion studied, the pseudo-first-order rate constant for formation of bromochromium(III) ion at 45° is 1.47×10^{-6} sec^{-1}. The rate constant for ^{18}O exchange under these conditions (45°, $I = 7.1$ *M*) is estimated[33] to be 1.5×10^{-4} sec^{-1}. This inequality ($k' < k_{exch}$) neither rules out nor proves a contribution of an SN1 pathway to the reaction in which bromochromium(III) is formed.

Despite the relatively low stability of inner-sphere bromochromium(III) species, their inertness allows their characterization.[34] The inner-sphere association increases dramatically with an increase in electrolyte concentration. In part, this is due to the decrease in activity of water with increasing electrolyte concentration.[35] At 45°, Q_1' increases from 4.84×10^{-3} to 0.284 with an increase from 0.44 to 8.93 *M* hydrobromic acid. This ~60-fold increase is reduced to a ~17-fold increase if Q_1' is converted to Q_1 ($Q_1 = Q_1'a_w$) since the activity of water decreases by a factor of ~3.5 with this increase of electrolyte concentration. The increase in Q_1 with increase of electrolyte concentration is due primarily to a decrease in the apparent value of ΔH. This trend is the same as observed in the analogous chloride system.[16]

Values of equilibrium quotients for the two stepwise association reactions as a function of electrolyte concentration allow investigation of the validity of an assumption proposed by Bjerrum[36] for the activity coefficient factor for such ion association reactions in concentrated electrolyte solution. Bjerrum[36] assumed that the activity coefficient factors for successive reactions are independent of the value of ΔZ^2 for the reaction, *i.e.*

$$\frac{f_{MX_n{}^{3-n}}}{f_{MX_{n-1}{}^{4-n}} f_{X^-}} \simeq \frac{f_{MX_{n-1}{}^{4-n}}}{f_{MX_{n-2}{}^{5-n}} f_{X^-}}$$

If this assumption is correct, values of the equilibrium quotient for the reaction

$$Cr(OH_2)_6^{3+} + Cr(OH_2)_4Br_2^+ = 2Cr(OH_2)_5Br^{2+}$$

should be independent of electrolyte concentration even though $\Delta Z^2 = -2$. The data presented earlier, with the apparent value of Q_2' corrected for the assumed contribution from tribromochromium(III), lead to values of Q_1'/Q_2', the equilibrium quotient for the "scrambling" reaction, which vary with the concentration of bromide ions. The variation is approximately the same at each of the temperatures studied, being an increase by a factor of ~1.8 for an increase of the concentration of hydrobromic acid from 5 to 9 *M*.

If the isomeric dibromochromium(III) species are present in the statistically expected relative amounts, the statistically expected value of Q_1'/Q_2' is 2.4. The observed values range from ~2.5 to ~5.4.

---

[26] In this calculation, it is assumed that there are eight equivalent sites for outer-sphere association; these are the eight faces of the octahedron.

[27] R. J. Kruh, *J. Amer. Chem. Soc.*, **76**, 4865 (1954).

[28] C. F. Baes, *J. Phys. Chem.*, **60**, 878 (1956).

[29] J. K. Rowley and N. Sutin, *ibid.*, **74**, 2043 (1970).

[30] M. Ardon, *Inorg. Chem.*, **4**, 372 (1965).

[31] P. Moore, F. Basolo, and R. G. Pearson, *ibid.*, **5**, 223 (1966).

[32] S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, **92**, 1215 (1970).

[33] Extrapolated from the value obtained at 25° by J. P. Hunt and R. A. Plane, *ibid.*, **76**, 5960 (1954), using $\Delta H^{\ddagger} = 27$ kcal mol^{-1}.

[34] An even more extreme example of inertness allowing characterization of a very unstable complex ion is iodochromium(III) ion ($Q = [CrI^{2+}]/[Cr^{3+}][I^-] = 7 \times 10^{-5}$ at $I = 4.2$ *M* and 25°) studied by T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7**, 1915 (1968).

[35] H. Coll, R. V. Nauman, and P. W. West, *J. Amer. Chem. Soc.*, **81**, 1284 (1959).

[36] J. Bjerrum, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **22**, No. 18 (1946).