the greater σ-donor strength of DMCA is taken into account, the actual lowering must be considerably larger. This apparent steric effect then would be larger in the case of DMCA and acetonitrile than it is in the case of DMA and DMF although in the first case the increase in steric bulk takes place 1.4 Å further from the metal ion center. Consequently, it seems improbable to relate the smaller $Dq$ in DMCA to a steric effect and leaves less effective metal to ligand back-bonding as the most likely explanation.

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# Linear Free Energy Relationships for the Aquation of Acidopentaaquochromium(III) and Related Complexes. The "Stability Constant" of Iodopentaaquochromium(III) Ion

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For the reaction $Cr(H_2O)_6^{3+} + I^- = Cr(H_2O)_5I^{2+} + H_2O$, the equilibrium quotient $Q_I = [CrI^{2+}]/[Cr^{3+}][I^-]$ has the value $7.0 \times 10^{-5}\ M^{-1}$ at 25°, in a KI–HI medium of ionic strength 4.2 $M$ and $[H^+] = 0.26\ M$. The corresponding values of $\Delta H°$ and $\Delta S°$ are +7.6 kcal mol$^{-1}$ and +6.6 cal mol$^{-1}$ deg$^{-1}$, respectively. The dependence of $Q_I$ on acidity and ionic strength is analyzed. A linear relationship exists between the logarithms of the rate coefficients for aquation of $Cr(H_2O)_5X^{2+}$ and the negative logarithms of the corresponding equilibrium quotients $Q_X$; the slope is 0.56. The significance of this for the $(H_2O)_5CrX^{2+}$ and $(NH_3)_5CoX^{2+}$ systems is discussed.

Langford[1] has demonstrated that the free energy $\Delta F^*$ of activation for the aquation of acidopentaamminecobalt(III) ions is linearly related to the standard free energy change $\Delta F°$ for the over-all reaction

$$Co(NH_3)_5X^{2+} + H_2O \rightleftharpoons Co(NH_3)_5OH_2^{3+} + X^- \qquad (1)$$

The slope of the straight line is fully 1.0, which yields the useful information that, in the transition state of the aquation reaction, the role of the departing ligand X is strongly similar to its role in the product, *viz.*, that of a solvated ion. Langford[1] further argued, after Hammond,[2] that the incoming aqua ligand will be no more than very weakly bound in the transition state of the aquation reaction, since reactions such as (1) are not highly endothermic. Thus, *bond breaking* is the major characteristic of the aquation reaction. Basolo and Pearson[3] have shown that the same is true for the analogous reaction of the ions $Ir(NH_3)_5X^{2+}$; in this instance, the slope of the linear free energy plot is about 0.9.

The object of the present study was to collect sufficient data for the investigation of free energy relationships in the systems

$$Cr(H_2O)_6^{3+} + X^- \underset{k_0}{\overset{K_X}{\rightleftharpoons}} (H_2O)_5CrX^{2+} + H_2O \qquad (2)$$

where $k_0$ is the pseudo-first-order rate coefficient for the acid-independent aquation of the acidopentaaquochromium(III) ion (hereafter referred to as acidochromium(III), or $CrX^{2+}$) and $K_X$ is the thermodynamic formation quotient ("stability constant") of $CrX^{2+}$, defined as

$$K_X = \frac{a_{CrX^{2+}}a_{H_2O}}{a_{Cr^{3+}}a_{X^-}} = \frac{[CrX^{2+}]}{[Cr^{3+}][X^-]}a_{H_2O}\frac{y_{CrX^{2+}}}{y_{Cr^{3+}}y_{X^-}} \qquad (3)$$

in which $a_i$ represents the activity and $y_i$ the activity coefficient of species i. According to the ionic strength principle, it may be assumed that the activity coefficient quotient is constant at a given ionic strength $I = {}^1/_2\Sigma_i C_i Z_i^2$, and, since the water activity $a_{H_2O}$ is often not accurately known for the reaction conditions necessary to obtain satisfactory measurements of $[CrX^{2+}]$, we shall use in place of $K_X$ the quotient $Q_X$

$$Q_X = \frac{[CrX^{2+}]}{[Cr^{3+}][X^-]} = \frac{K_X y_{Cr^{3+}} y_{X^-}}{a_{H_2O} y_{CrX^{2+}}} \qquad (4)$$

While $k_0$ and $Q_X$ values are available in the literature for several simple anionic ligands $X^-$, equilibrium data for the system for which $X^- = I^-$ are conspicuously lacking, despite considerable current interest[4-6] in the behavior of the ion $CrI^{2+}$, and we now report our data on this system in connection with a linear free energy relationship between log $k_0$ and log $Q_X$ for reactions of the type (2).

## Experimental Section

**Materials.**—Baker Analyzed reagents were used throughout this work. All materials were checked for the absence of chloride ion. Chromium(III) perchlorate solutions were made by reduction of chromium(VI) oxide in aqueous perchloric acid with hydrogen peroxide. Dowex 50W-X8 ion-exchange resin (50–100 mesh, $H^+$ form) was prepared for use by flushing it with 3 $M$ hydrochloric acid until the eluate was completely transparent in

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[1] C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

[2] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 167.

[4] See, for example, ref 3, pp 201, 202.

[5] D. E. Pennington and A. Haim, *Inorg. Chem.*, **6**, 2138 (1967).

[6] A. Adin, J. Doyle, and A. G. Sykes, *J. Chem. Soc.*, *A*, 1504 (1967).

the region 220–300 mμ (5-cm cell); the resin was then washed with distilled water until no free acid nor chloride ion could be detected in the washings.

All spectrophotometric measurements were made using a Cary Model 15 spectrophotometer.

**Equilibration Experiments.**—Solutions of the desired Cr(III), $I^-$, and $H^+$ concentrations were prepared in a nitrogen-filled inert-atmosphere box by adding the appropriate weighed amounts of potassium iodide to ice-cold aliquots of deoxygenated solutions of hexaaquochromium(III) ion in aqueous perchloric acid, so that the perchlorate ion was precipitated essentially quantitatively, leaving iodide as the only anion in solution. The filtrate was heated in a closed, darkened, nitrogen-filled flask at about 70° for some 3 hr and then reequilibrated at the chosen reaction temperature (±0.05°) for a period of at least 10 half-lives of the aquation reaction.[7,8] An aliquot (usually 35 ml) of the equilibrated filtrate was diluted to 750 ml with deoxygenated water at 0°, and the solution was passed through Dowex 50W-X8 ($H^+$ form) resin (160 ml) contained in a 2.5-cm (inside diameter) jacketed column which was kept at 0° with circulating ice water. An atmosphere of $CO_2$ was maintained in the column throughout the experiment. The column was washed with cold, deoxygenated perchloric acid (0.1 *M*) until the eluate was free of iodide ion (as judged by its transparency in a 5-cm cell at 225 mμ, where aqueous iodide has an absorption maximum of ε 13,100).

Iodopentaaquochromium(III) ion was eluted in 50-ml fractions with 1.0–1.5 *M* perchloric acid, this being a good eluent for dipositive Cr(III) species on Dowex 50W-X8. The eluate was colorless, or at most very faintly green. The presence of $CrI^{2+}$ ion in these very dilute eluates could not be established directly, for, while chromium could be detected and estimated spectrophotometrically as $CrO_4^{2-}$ after oxidation with alkaline hydrogen peroxide, it proved to be impossible to demonstrate the presence of an equimolar amount of iodide by conventional analytical methods. However, the ultraviolet spectrum of a typical eluted fraction with $[H^+] = 1.242$ *M* showed a maximum at 260 mμ and shoulders at ~300 and ~215 mμ; for genuine iodopentaaquochromium(III) ion,[3] the same features appear at 260 (ε 5740), 306, and 210 mμ, respectively. On keeping the sample in the spectrophotometric cell compartment, thermostated at 25.00°, the absorbance at 260 mμ decreased according to a first-order rate law with a rate coefficient of $1.14 \times 10^{-5}$ sec$^{-1}$; at this temperature and acidity, authentic $CrI^{2+}$ aquates[3] with a rate coefficient of $1.12 \times 10^{-5}$ sec$^{-1}$. An isosbestic point at 237 mμ was maintained accurately throughout the spectral change; *i.e.*, a single reaction was being observed, this being the aquation of $(H_2O)_5CrI^{2+}$. The concomitant development of a well-defined maximum at 225 mμ, some 2.3 times as intense as the original maximum at 260 mμ, confirms that iodide ion (which has a maximum at 225 mμ (ε 13,100) in neutral water) is released by aquation of $CrI^{2+}$, in an equimolar amount. Such spectroscopic and kinetic checks on the identity of the eluted product were carried out from time to time on randomly selected samples in the course of these experiments.

It was therefore possible to determine the $CrI^{2+}$ concentration spectrophotometrically, by measuring the change of absorbance at 260 mμ when the sample had been kept for a period of at least 10 times the half-life of aquation of $CrI^{2+}$. As before, air was excluded, to prevent oxidation of iodide to iodine. Elution with 800 ml of 1.0–1.5 *M* $HClO_4$ was found to account for at least 99% of the $CrI^{2+}$; elution was very efficient, and the loss of $CrI^{2+}$ by aquation (at 0°) in the course of the slowest elutions could not have exceeded 1% of the total. However, in those experiments in which the yield of $CrI^{2+}$ was unusually low (*e.g.*, for $I < 2.0$ *M*), absorbance readings (5-cm cells) of individual fractions were of the order of 0.1 or less, so that the cumulative experimental error introduced a considerable uncertainty into the total $CrI^{2+}$ estimate; furthermore, the volumes of solution required in these cases were inconveniently large, and the working time was therefore too long for quantitative recovery of $CrI^{2+}$. Consequently, meaningful values of $Q_I$ could not be obtained at ionic strengths less than 2.0 *M*.

Table I

Values of $Q_I = [CrI^{2+}]/[Cr^{3+}][I^-]$ at $[H^+] = 0.260\ M^a$ and $I = 4.21\ M^b$

| Expt no. | Temp, °C | $[Cr^{3+}]$, *M* | $[I^-]$, *M* | $[K^+]$, *M* | $10^5Q_I$, $M^{-1}$ |
|---|---|---|---|---|---|
| 1 | 25.0 | 0.218 | 3.57 | 2.66 | 7.00 |
| 2 | 25.0 | 0.294 | 3.36 | 2.22 | 7.02 |
| 3 | 25.0 | 0.433 | 2.96 | 1.40 | 6.87 |
| 4 | 45.0 | 0.292 | 3.34 | 2.21 | 15.90 |
| 5 | 35.1 | 0.286 | 3.35 | 2.23 | 10.49 |
| 6 | 15.0 | 0.283 | 3.32 | 2.22 | 4.50 |

[a] Range ±0.003. [b] Range ±0.04.

The original equilibrated filtrates were analyzed for chromium content spectrophotometrically, following oxidation to $CrO_4^{2-}$ (ε 4820 at 372 mμ) with alkaline peroxide, and the iodide content was determined by Volhard's method. The hydrogen ion concentration was determined by a pH titration with sodium hydroxide solution, using a Beckman Model 1019 pH meter; the end point was obtained by Gran's method.[9] The potassium content was found by difference. The equilibrium quotients $Q_I = [CrI^{2+}]/[Cr^{3+}][I^-]$ for reaction 2 were calculated from the above data and are listed in Tables I and II.

The density of the equilibrated solution of expt 4 was found to be 1.3898 g ml$^{-1}$ at 23°; expt 2, 5, and 6 (at least) will be closely similar. It can be calculated that the stoichiometric concentration of "free" water will be about 46 *M* in this experiment, if $Cr^{3+}$ is present primarily as $Cr(H_2O)_6^{3-}$, and $H^+$ as $H_3O^+$; thus, water molecules outnumber other species by about 10 to 1 in these typical solutions.

## Results

Despite the exceedingly small yields of $CrI^{2+}$ (typically, only $^1/_{4000}$ part of the Cr(III) is present as $CrI^{2+}$) and the need to exclude oxygen rigorously at all stages of the experiments, remarkably consistent values of the equilibrium quotient $Q_I$ could be obtained at constant temperature and ionic strength (expt 1–3 of Table I have a standard deviation of about ±1% about the mean; however, expt 10 and 11 of Table II show that an error of ±3% or more is possible). In view of the considerable experimental effort required, data points were not in general duplicated, once the above fact had been established. It should be noted that, since the product $[Cr^{3+}][I^-]$ varied by a factor of over 1.6 in runs 1–3, without a significant variation in $Q_I$, it may be concluded that the extent of ion pairing is negligible for our present purposes.

It is rather surprising to find that the ionic strength principle appears to hold even at these high electrolyte concentrations and with the reactant ions themselves present as major solute species. Attempts were made to maintain constant ionic strength with perchlorate, in addition to iodide, but control experiments in which perchlorate was the only anion present showed that a chromium-containing species of apparent charge 2+ is released in the ion-exchange chromatographic procedure; separate experiments suggest that this may be the perchloratopentaaquochromium(III)

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(7) Reaction 2 (X = I) was found to be endothermic; thus, for example, for measurements at 25°, an excess of $CrI^{2+}$ was generated relatively rapidly by heating the solution to 70°, and the excess was aquated at 25° for 20 hr ($10t_{1/2}$) or more—see ref 8 for appropriate data.

(8) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

(9) F. J. C. Rossotti and H. Rossotti, *J. Chem. Educ.*, **42**, 375 (1965).

TABLE II

MEDIUM DEPENDENCE OF $Q_I$ AT 25.0°

| Expt no. | $[Cr^{3+}]$, $M$ | $[I^-]$, $M$ | $[K^+]$, $M$ | $[H^+]$, $M$ | $I$, $M$ | $10^5Q_I$, $M^{-1}$ |
|---|---|---|---|---|---|---|
| 7 | 0.0747 | 1.78 | 1.29 | 0.264 | 2.00 | 2.54 |
| 8 | 0.0968 | 2.31 | 1.76 | 0.261 | 2.60 | 3.84 |
| 9 | 0.317 | 2.23 | 1.01 | 0.260 | 3.18 | 5.00 |
| 1, 2, 3 | 0.22–0.43 | 0.36–0.30 | 2.7–1.4 | 0.259 | 4.24 | 6.96 |
| 10 | 0.505 | 4.08 | 2.31 | 0.261 | 5.60 | 10.63 |
| 11 | 0.531 | 4.05 | 2.21 | 0.250 | 5.64 | 9.99 |
| 12 | 0.300 | 3.32 | 1.44 | 0.987 | 4.22 | 8.14 |
| 13 | 0.286 | 3.40 | 2.02 | 0.518 | 4.26 | 7.84 |
| 14 | 0.286 | 3.49 | 2.46 | 0.167 | 4.34 | 6.84 |

TABLE III

KINETIC AND THERMODYNAMIC DATA FOR THE REACTIONS $Cr^{3+} + X^- \rightleftharpoons CrX^{2+}$ (AT 298.2°K)

| X | Log $Q_X$ | $I$, $M$ | $[H^+]$, $M$ | $\Delta H°$, kcal mol$^{-1}$ | $\Delta S°$, cal deg$^{-1}$ mol$^{-1}$ | 10 + log $k_0$[a] | Ref |
|---|---|---|---|---|---|---|---|
| F[b] | 4.33 | 0.5 | Various | 3.9 | 28 | 0.79 | *h, i* |
| Cl | −0.65 | 4.4 | 3.7 | 5.6 | 16 | 3.44 | *h, j* |
| | −0.96[c] | 1.0 | Various | 6.0 | | | *k* |
| Br | −2.65 | 2.0 | 0.5 | 5.1 | | 4.59 | *l, m* |
| I | −4.16[d] | 4.2 | 0.26 | 7.6[d] | 6.6[d] | 5.92 | *h* |
| | −5.0[d,e] | 1.0 | 0.26 | | | | |
| –NCS | 3.09 | 0 | Various | −2.1 | 6.9 | 1.96 | *n* |
| | 2.26[f] | 1.0 | 1.0 | | | | |
| $NO_3$ | −2.01[g] | 1.0 | 0.4 | 4.5[g] | 5.9[g] | 5.86 | *o, p* |

[a] $k_0$ is the rate coefficient for the aquation of $CrX^{2+}$ by the acid-independent pathway at ionic strength $I = 1.0$. [b] Data derived from those for $Cr^{3+} + HF \rightleftharpoons CrF^{2+} + H^+$ using data for $HF \rightleftharpoons H^+ + F^-$ from L. G. Sillén and A. E. Martell, "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964, p 257. [c] Extrapolated from measurements made at higher temperatures. [d] This work. [e] Extrapolated from the data at higher $I$. [f] Extrapolated from data at lower $I$ with a Debye–Hückel type of relationship from C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208, 1216 (1955). [g] Corrected for ion pairing. [h] See ref 8. [i] A. S. Wilson and H. Taube, *J. Am. Chem. Soc.*, **74**, 3509 (1952). [j] See ref 11. [k] C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967). [l] J. H. Espenson and E. L. King, *ibid.*, **64**, 380 (1960). [m] F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964). [n] See reference given in footnote *f* of this table. [o] M. Ardon and N. Sutin, *Inorg. Chem.*, **6**, 2268 (1967). [p] T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).

species postulated by Jones and Bjerrum,[10] and we are presently investigating this possibility further. In any event, this observation indicated that perchlorate ion should not be present in high concentrations in the reaction medium, since the presumably rather labile ion $CrClO_4^{2+}$ might have interfered with the method used to determine $CrI^{2+}$. As it happened, the low values of $Q_I$ dictated the use of maximum iodide concentrations in order to obtain satisfactory yields of $CrI^{2+}$, and it was actually advantageous to arrange the equilibration experiments so that iodide was the only anion present.

**The temperature dependence** of $Q_I$ at ionic strength $I = 4.2$ $M$, $[H^+] = 0.26$ $M$, is illustrated by runs 2, 4, 5, and 6 of Table I, and it will be seen that the reaction is appreciably endothermic (as might be expected in view of the naturally low affinity of the "soft" ligand $I^-$ for the "hard" acid $Cr^{3+}$). The thermodynamic parameters valid for 298.2°K are given in Table III, together with comparable data for similar reactions. A slight curvature of the plot of log $Q_I$ *vs.* $1/T$(°K) was apparent, consistent with $\Delta C_p° \sim +30$ cal deg$^{-1}$ mol$^{-1}$ as compared with +27 for the formation of $CrCl^{2+}$ [11] and +70 for $CrNCS^{2+}$;[12] however, the quality of the present data probably does not warrant such a detailed analysis.

**The hydrogen ion concentration dependence of** $Q_I$ at constant temperature and ionic strength is insignificant up to 0.26 $M$ (Table II, expt 1, 2, 3, 14), but $Q_I$ is seen to increase somewhat with increasing $[H^+]$ at higher acidities (runs 12 and 13). This effect is similar to that observed for the iron(III) chloride system[13] and probably owes its origin to the greater solvation requirements[14] of $H^+$ as compared to its substitute, $K^+$. Thus, at the higher electrolyte concentrations, the activity $a_{H_2O}$ of free water (which may be neither near unity nor yet constant—*vide infra*) may be significantly dependent upon the hydrogen ion concentration (if this is high) even at constant ionic strength, and so the quotient $Q_I$ of eq 4 will increase with increasing $[H^+]$ (*i.e.*, with decreasing $a_{H_2O}$) at constant temperture and ionic strength. We have therefore standardized our experiments at the convenient $[H^+] = 0.26$ $M$.

**The ionic strength dependence of** $Q_I$ at 25°, $[H^+] = 0.26$ $M$, over the range $I = 2.0$–$5.6$ $M$, is illustrated by runs 1–3 and 7–11 (see Table II). Since a value of $Q_I$ at $I = 1.0$ was desired for purposes of comparison with other $Q_X$, it was necessary to choose a representative (and, preferably, theoretically meaningful) mathematical function of $I$, to permit extrapolation beyond the

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

(11) H. S. Gates, Ph.D. Thesis, University of Wisconsin, 1956.

(12) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

(13) H. Coll, R. V. Nauman, and P. J. West, *J. Am. Chem. Soc.*, **81**, 1284 (1959).

(14) See, for example, the recent work of O. D. Bonner and G. B. Woolsey, *J. Phys. Chem.*, **72**, 899 (1968).

experimentally accessible region. We have attempted to adapt the Lietzke–Stoughton–Fuoss[15] "two-structure" equation for electrolyte activity coefficients as a guide in the choice of a representative equation. Since the volume fraction of solute may be estimated (from the density of the solution) to be as high as 0.14 at $I = 4.2$, we can calculate from the published data[15] that the Debye–Hückel structure may be ignored entirely, even at $I = 1.0\ M$. Activity coefficients $y$ of electrolytes may then be calculated from the "cell model" contribution alone

$$\ln y = BI^{1/3} + CI \qquad (5)$$

where $C$ is an adjustable parameter and $B$ can be calculated[15] from

$$-B = 0.54Z_1Z_2[2(\nu_1 + \nu_2)/(\nu_1 Z_1^2 + \nu_2 Z_2^2)]^{1/3} \qquad (6)$$

in which $Z_i$ is the charge of an ion i and $\nu_i$ is the number of ions i per "molecule." We assume that the activity coefficients $y_{Cr^{3+}}$, $y_{CrI^{2+}}$, and $y_{I^-}$ can be estimated as for 3:1, 2:1, and 1:1 electrolytes, so that $-B$ may be set at 1.42, 1.08, and 0.68, respectively, whence

$$\ln (y_{Cr^{3+}} y_{I^-} / y_{CrI^{2+}}) = -1.02I^{1/3} + I\Delta C \qquad (7)$$

Then, from eq 4, after converting to decadic logarithms and solving graphically for $K_I/a_{H_2O}$ and for $2.303\Delta C$, we obtained the equation

$$8 + \log Q_I = 0.78 + 2.35I^{1/3} - 0.17I \qquad (8)$$

which reproduces $Q_I$ values to within 2.5% on the average. The observed value of $\Delta C$ (0.074) seems reasonable.[15]

It has been tacitly assumed that $a_{H_2O}$ may be taken as being essentially constant throughout these experiments; however, activity data[16] for aqueous hydriodic acid solutions of comparable ionic strengths suggest that the activity of water in our solutions could vary from greater than 0.9 at $I = 2.0$ to less than 0.7 at $I = 5.6$. Nevertheless, we feel that these estimates of the variation of $a_{H_2O}$ are unduly pessimistic, since the major cationic species in our solutions is $K^+$, which will make much less demand upon solvent water for its own solvation than does $H^+$.[14] It might be mentioned here that $K_I$, in this context, is ***not*** to be identified with the value which $Q_I$ would have in practice at "infinite dilution," since on decreasing $I$ toward zero one would pass gradually into the Debye–Hückel region, in which $Q_I$ would rise again as $I$ diminished.

Equation 8 predicts the value of $Q_I$ to be $9.1 \times 10^{-6}\ M^{-1}$ at $I = 1.0\ M$, but, since the extrapolation used depends upon certain assumptions which may be erroneous, other arbitrarily chosen functions of $I$ were tested as bases for extrapolations. Most simple functions of $I$ do not give linear plots with $\log Q_I$,[17] but a good straight line is obtained when $\log Q_I$ is plotted against $\log I$, and the extrapolated value of $Q_I$ at $I = 1.0$ is then $1.08 \times 10^{-5}\ M^{-1}$. It is therefore felt that $Q_I$ can with confidence be set equal to $(1.0 \pm 0.1) \times 10^{-5}\ M^{-1}$ at unit ionic strength.

No attempt has been made to correct $Q_I$ values for possible ion-pair formation, since the data of expt 1–3 indicate that this is not an important factor.

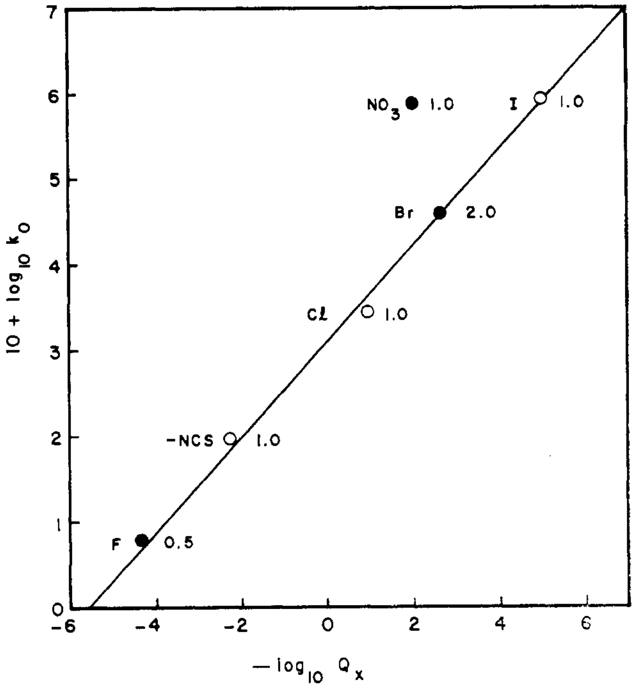

Figure 1.—Plot of log (rate coefficient) *vs.* log (equilibrium quotient) for the aquation of $(H_2O)_5CrX^{2+}$ ions. Filled circles represent actual experimental data; open circles represent values obtained by extrapolation (see text and Table III). Numerals to right of each data point are ionic strengths ($M$).

## Discussion

In seeking to establish a relationship between the free energy functions $\log k_0^{298.2}$ and $-\log Q_X^{298.2}$ (negative because $k_0$ refers to the *reverse* reaction in the sense of eq 2), it was necessary to choose some standard ionic strength at which the various data might be correlated. The literature values[18] of $Q_X$ for the type of reaction under consideration suggest that $Q_X$ is least ionic strength dependent in the region $I = 0.5$–$1.0$; furthermore, the available aquation rate data refer in every case to $I = 1.0\ M$, and $Q_X$ values were therefore extrapolated to $I = 1.0$ where necessary and possible, as outlined in Table III. It will be seen that no drastic revisions in $Q_X$ values were necessary.

The slope of the linear plot (Figure 1) of $\log k_0$ against $-\log Q_X$ (298.2°K, $I = 1.0\ M$) is 0.56, if the nitratochromium(III) data are ignored; the coefficient of correlation is 0.998 if $CrNO_3^{2+}$ is excluded, but falls to 0.947 if $CrNO_3^{2+}$ is given equal weight with the other $CrX^{2+}$, and so the nitrato complex appears to be anomalous in this context. Closely similar plots can be obtained for other temperatures, using the ap-

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[15] M. H. Lietzke, R. W. Stoughton, and R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S.*, **59**, 39 (1968).

[16] R. Haase, H. Naas, and H. Thumm, *Z. Physik. Chem.* (Frankfurt), **37**, 210 (1963).

[17] A fortuitously good straight line is obtained when $Q_I$ itself is plotted against $I$, but this is obviously a very unreliable basis for extrapolation.

[18] L. G. Sillén and A. E. Martell, "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

propriate enthalpies of reaction (Table III) and of activation (Table IV of ref 19) to extrapolate the data to the chosen temperature. Thus, log $k_0$ is linearly related to $-\log Q_X$ at 50° (if the nitrato complex is excluded) within the limits of accuracy of the extrapolations, and the slope of the line is 0.59. The linear free energy relationship is valid over a wide range of temperature because the differences in enthalpy of activation, $\Delta H_0^*$, between members of the series $(H_2O)_5CrX^{2+}$ are paralleled by corresponding differences in the standard enthalpy of reaction, $\Delta H°$. Thus, for the complexes $(H_2O)_5CrX^{2+}$ (where X is a ligand other than nitrato), we can deduce from Figure 1 that the transition state of the aquation reaction resembles the products $Cr(H_2O)_6^{3+}$ and $X^-(aq)$ to a moderate degree; one might say that the separation of $X^-$ is rather more than half (50–60%) completed in the transition state, since the slope is just over 0.5.

A similar conclusion was drawn[19] from the linear correlation of the entropy of activation $\Delta S_0^*$ for the aquation of $CrX^{2+}$ with the standard entropy $\bar{S}°_{cor}$ of the departed aqueous ligand $X^-$ (corrected for rotational entropy); the slope of this line was 0.53, very close to that of Figure 1. The entropy correlation suggests that solvation of the departing anion $X^-$ is a major driving force in these aquation reactions. However, $\Delta S_0^*$ for the aquation of $CrF^{2+}$ was apparently anomalously high, and it was suggested[8,19] that this could arise through relatively low electrostriction of solvent in the transition state if the separating species was HF rather than $F^-$; this is reasonable, since $CrF^{2+}$ differs from $CrX^{2+}$ (when $X^-$ is not appreciably basic) in that it can aquate by an acid-dependent pathway. This proposed modification of mechanism for $CrF^{2+}$ relative to other typical $CrX^{2+}$ is not necessarily inconsistent with the correlation of $CrF^{2+}$ as a "normal" species in Figure 1, since the free energy correlation simply tells us that for $CrF^{2+}$, as for other $CrX^{2+}$, the separation of X en route to the appropriate products is about 50–60% complete in the transition state. Baldwin, Chan, and Tobe[20] have suggested that, if electrostriction of solvent can be compared to the freezing of water, then it should contribute virtually nothing to the free energy $\Delta F^*$ of activation, since the free energy $\Delta F°$ of freezing of water is zero at 0° and would be negligibly small at 25°. Thus, for a series of related reactions, $\Delta F^*$ will be relatively insensitive to differences between members of the series in the extent of solvation of the transition state. Solvation effects will show up in $\Delta H^*$ and $T\Delta S^*$, and the solvation contributions to each of these factors will cancel. The aquation of $CrF^{2+}$ may be assisted by internal proton transfer (not necessarily complete) to F within the solvent shell, whereas for most $CrX^{2+}$ (where X is nonbasic) assistance may be provided through extensive solvation of $X^-$ as it departs, but the critical extent of Cr–X bond breaking is evidently essentially the same in all cases, and the nature of the assisting factors is not disclosed by a linear free energy relationship alone.

The failure of $CrNO_3^{2+}$ to correlate in the free energy relationship is embarrassing, since we have previously[19] considered the mechanism of aquation of this ion to be typical of $CrX^{2+}$ ($X^-$ being nonbasic) in seeking confirmation of the validity of the proposed $\Delta S_0^*$–$\bar{S}°_{cor}$ relationship. The closeness of the experimental value of $\Delta S_0^*$ for $CrNO_3^{2+}$ to that predicted on the basis of the entropy correlation was tacitly assumed to constitute confirmation that the mechanism of aquation of $CrNO_3^{2+}$ was indeed "normal," *i.e.*, that the separating species was $NO_3^-$. However, it may well be that this apparently successful prediction of $\Delta S_0^*$ was fortuitous and that $CrNO_3^{2+}$ aquates by a faster "abnormal" path and hence does not fit our proposed free energy relationship.[21] A possible alternative mechanism involves fission of the $CrO–NO_2$ bond, with separation of $NO_2^+$ in the rate-determining step.[23] The exchange of $O^{18}$ between nitrate ion and solvent water evidently involves O–N bond breaking in the protonated intermediate $[H_2O–NO_2]^+$, and the apparent activation enthalpy (21.5 kcal $mol^{-1}$)[24] for this reaction is very close to that for the aquation of $CrNO_3^{2+}$ (21.6 kcal $mol^{-1}$)[19,22] suggesting that $CrO–NO_2$ bond breaking may indeed be involved in the aquation reaction.[23] It may be noted, however, that both the fluoro and the nitrato complexes of the series $(NH_3)_5CoX^{2+}$ correlate well with their analogs in Langford's[1] free energy relationship.

The slope (0.56) of the free energy plot for the aquation of $CrX^{2+}$ is markedly different from those for $(NH_3)_5CoX^{2+}$ (= 1.0)[1] and $(NH_3)_5IrX^{2+}$ ($\sim$0.9).[3] This observation may help explain qualitatively why the measured activation enthalpies for aquation in the Cr and Co series are of comparable magnitude[25] ($\sim$24 kcal $mol^{-1}$) in spite of the substantial differences in the calculated crystal field activation energies[26] (2.0*Dq* or 9–10 kcal $mol^{-1}$ in the Cr series, as compared with 4.0*Dq* or 19–23 kcal $mol^{-1}$ in the Co series). Thus, the greater crystal-field contributions to the activation enthalpies in $Co(NH_3)_5X^{2+}$ are compensated by greater contributions from the enthalpies of hydration of the departing ligands $X^-$, since $X^-$ are evidently essentially fully separated and hydrated in the transition states of the Co series as against about half-separated and -hydrated in typical $CrX^{2+}$.

This argument can be pushed further to explain qualitatively why the activation enthalpies for the aquation of $CrX^{2+}$ fall in the order: X = F > NCS > Cl > Br > I > $NO_3$, while the corresponding sequence[25] for $(NH_3)_5CoX^{2+}$ is: X = NCS > $NO_3$ > (I?) >

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[19] T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).

[20] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

[21] The possibility that the value of $Q_{NO_3}$ reported by Ardon and Sutin[22] is in some way too high can be discounted; according to ref 19, the yields of $CrNO_3^{2+}$ obtained from molten $Cr(NO_3)_3 \cdot 9H_2O$ (effectively a 4.0 *F* solution) give independent (albeit rough) confirmation that these $Q_{NO_3}$ values are valid.

[22] M. Ardon and N. Sutin, *Inorg. Chem.*, **6**, 2268 (1967).

[23] We thank Professor E. L. King for drawing this to our attention.

[24] M. Anbar and S. Guttmann, *J. Am. Chem. Soc.*, **83**, 4741 (1961).

[25] See ref 3, p 164.

[26] See ref 3, p 145 ff.

Br > Cl > F. The enthalpies of hydration of the gaseous ions $X^-$ range from $-116$ to $-67$ kcal $mol^{-1}$ in the sequence:[27] $-\Delta H_h$ for $F^- \gg Cl^- > Br^- > NCS^- = NO_3^- > I^-$, and it may be that the sequence of activation enthalpies for the Co series reflects the relative hydration enthalpies of the heavily solvated departing ligands $X^-$, rather than the crystal field and bond strength factors which seem to be the dominant influence in the $CrX^{2+}$ series (in which it appears that solvation of $X^-$ in the transition state is rather less important).

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[27] V. P. Vasil'ev, E. K. Zolotarev, A. F. Kapustinskii, K. P. Mishchenko, E. A. Podgornaya, and K. B. Yatsimirskii, *Zh. Fiz. Khim.*, **34**, 1763 (1960).

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# Notes

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## Possible Bridging Ligand Effects of Bromide Ion in the Polarography of Bromopentaaquochromium(III) Complex

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Halogen ions are effective bridging ligands in the electron-transfer reaction between metal ions, and the presence of halide ion in the electrolyte solution influences the polarography of some metal ions.[1-5] In the polarography of $CrBr(H_2O)_5^{2+}$ in 2 *M* perchloric acid, we observed that the bromide ion added in the solution causes a negative shift of its half-wave potential. Figure 1 shows the half-wave potential plotted against the logarithm of bromide ion concentration giving a straight line with a slope of 58 mV. Such an effect of halide ion on polarography has not previously been reported.

The striking difference of the polarographic behavior of $CrBr^{2+}$ compared with that of $CrCl^{2+}$ is shown by comparing Figure 1 with Figure 2 which shows the half-wave potential for $CrCl^{2+}$ in various concentrations of halide ions. This comparison eliminates the possibility that the effect of bromide ion on the polarography of $CrBr^{2+}$ is due either to the change of double-layer potential[3,5] or to the change of the depolarizing complex such as the formation of electroinactive species.[4] It should be noted that $CrBr^{2+}$ is polarographically the most easily reducible chromium(III) complex in perchloric acid ever known, since the half-wave potential for 0.2 m*M* $CrBr^{2+}$ in 2 *M* perchloric acid is $-0.29$ V if the halide ion in the solution is completely removed. It has been reported by Pecsok and Lingane[6] that $Cr^{2+}$ ion can be oxidized at this potential. This means that the reverse reaction, Cr(II) → Cr(III), might take place at the reduction potential for $CrBr^{2+}$.

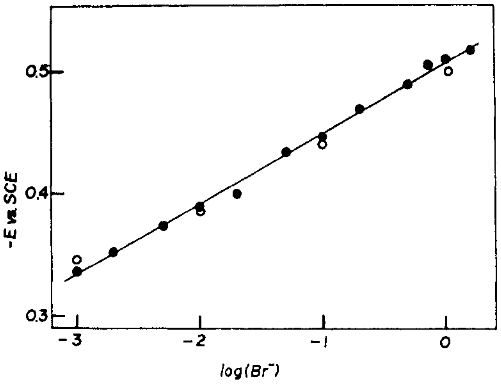

Figure 1.—Variation of the half-wave potential for 0.2 m*M* $CrBr^{2+}$ (●) and 0.2 m*M* $Cr^{2+}$ (○) with log $(Br^-)$ in $HBr-HClO_4$ ($\mu = 2.0$) solution.

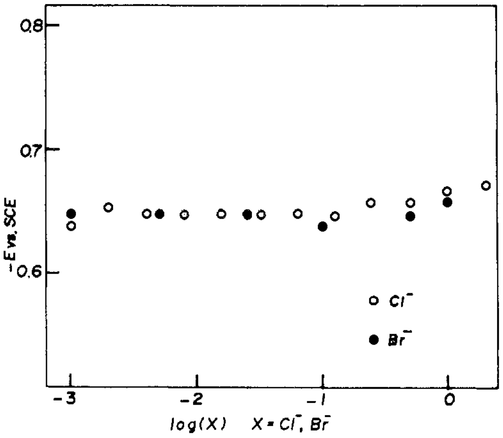

Figure 2.—Variation of the half-wave potential for 0.2 m*M* $CrCl^{2+}$ with log $(Cl^-)$ (○) and log $(Br^-)$ (●) in $HX-HClO_4$ ($\mu = 2.0$) solution.

The half-wave potentials for $Cr^{2+}$ ion are also shown in Figure 1. Each oxidation potential for $Cr^{2+}$ is quite the same as the reduction potential for $CrBr^{2+}$ when bromide ion is present in the solution.

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[1] R. Brdicka, *Collection Czech. Chem. Commun.*, **2**, 489, 545 (1930); **3**, 396 (1931).

[2] A. J. Engel, J. Lawson, and D. A. Aikens, *Anal. Chem.*, **37**, 203 (1965).

[3] K. Ogino and N. Tanaka, *Bull. Chem. Soc. Japan*, **40**, 1119 (1967).

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[5] F. C. Anson and T.-L. Chang, *Inorg. Chem.*, **5**, 2092 (1966).

[6] R. L. Pecsok and J. J. Lingane, *J. Am. Chem. Soc.*, **72**, 189 (1950).