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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Notes

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

BY IWAO WATANABE, EIKI ITABASHI, AND SHIGERO IKEDA

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 mM $CrBr^{2+}$ 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
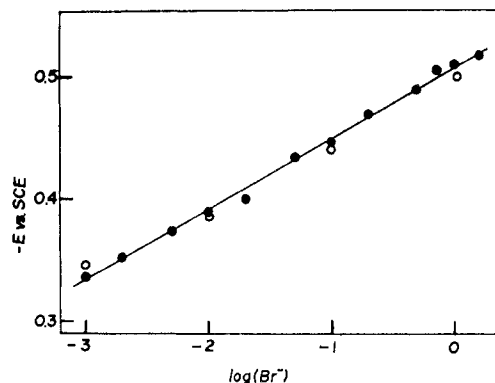

Figure 1.—Variation of the half-wave potential for 0.2 mM $CrBr^{2+}$ (●) and 0.2 mM Cr^{2+} (○) with log (Br$^-$) in HBr–HClO$_4$ ($\mu = 2.0$) solution.
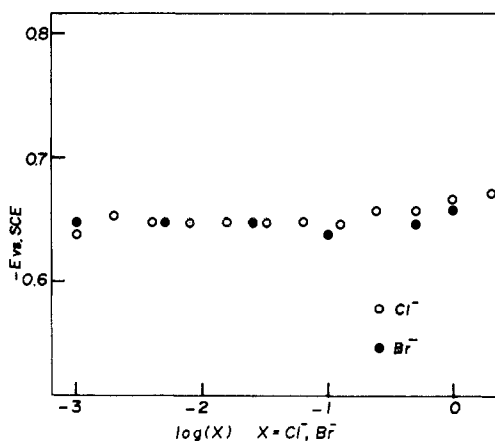

Figure 2.—Variation of the half-wave potential for 0.2 mM $CrCl^{2+}$ with log (Cl$^-$) (○) and log (Br$^-$) (●) in HX–HClO$_4$ ($\mu = 2.0$) solution.

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 $CrBr^{2+}$.

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.

(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).
(4) N. Tanaka, Y. Sato, and R. Tamamushi, *Rev. Polarog.* (Kyoto), **12**, 127 (1964).
(5) F. C. Anson and T.-L. Chang, *Inorg. Chem.*, **5**, 2092 (1966).

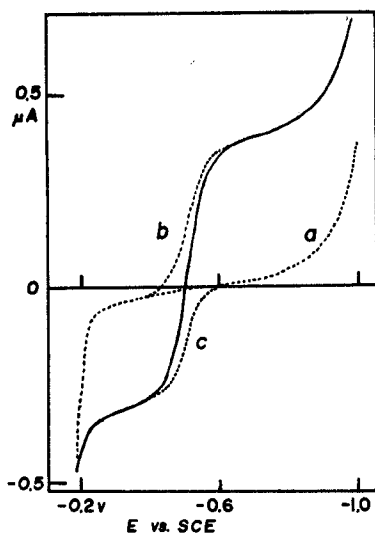(6) R. L. Pecsok and J. J. Lingane, *J. Am. Chem. Soc.*, **72**, 189 (1950).

Figure 3.—Current–potential curves for Cr^{2+} and $CrBr^{2+}$ in 2 M HBr: curve a, residual current; curve b, 0.2 mM $CrBr^{2+}$; curve c, 0.2 mM Cr^{2+}; solid line, 0.2 mM Cr^{2+} and 0.2 mM $CrBr^{2+}$.

Figure 3 shows an example of the polarograms when equal amounts of $CrBr^{2+}$ and Cr^{2+} are present. In considering these results we conclude that the reduction of $CrBr^{2+}$ at a dropping mercury electrode is reversible if bromide ion is present. Therefore the mechanism of the electrode reaction will be

$$(H_2O)_5CrBr^{2+} \rightleftharpoons (H_2O)_5-Cr-Br-Hg \text{ electrode}$$
$$\rightleftharpoons Cr^{2+} + Br^-$$
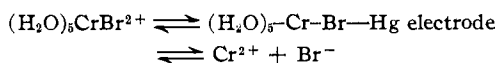
The most reasonable explanation of the electrode reaction seems to be that the halide ions act as bridging ligands in the case of the electron-transfer reaction between halogenochromium(III) complexes and Cr^{2+} [7,8] and that electrolytic oxidation of Cr^{2+} at the mercury pool electrode in the presence of halide ion produces the halogenopentaaquochromium(III) complex.[9]

One can therefore explain the dependence of the half-wave potential for $CrBr^{2+}$ on the concentration of bromide ion using the Nernst equation

$$E = E_0 - \frac{RT}{F} \ln \frac{(CrBr^+)}{(CrBr^{2+})} = E_0 - \frac{RT}{F} \ln \frac{(Cr^{2+})}{(CrBr^{2+})} K(Br^-)$$

where E_0 is the equilibrium potential for the $CrBr^+$–$CrBr^{2+}$ couple, and K is defined as

$$K = \frac{(CrBr^+)}{(Cr^{2+})(Br^-)}$$

At the half-wave potential, $(Cr^{2+}) = (CrBr^{2+})$ if $K \ll 1$, and

$$E_{1/2} = E_0 - \frac{RT}{F} \ln K - \frac{RT}{F} \ln (Br^-)$$

This equation is in accordance with the experimental result shown in Figure 1. Because the reduction potential for $CrCl^{2+}$ is far more negative than the oxidation potential for Cr^{2+} in bromide ion solution, the half-wave potential for $CrCl^{2+}$ observed did not vary with the concentration of bromide ions (Figure 2).

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In the further experiments, chloride ion also caused the negative shift of the half-wave potential for $CrBr^{2+}$; however, the reduction wave in chloride ion solution was not a reversible one. It is impossible at the reduction potential for $CrBr^{2+}$ to reduce the product of the reverse reaction

$$Cr^{2+} + Cl^- \xrightarrow{-e^-} CrCl^{2+}$$
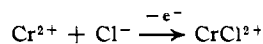
Experimental Section

Polarography.—All measurements were made in 2 M hydrogen ion solution with no maximum suppressor at 25.0 ± 0.1°. The polarograph used for all measurements was a Yanagimoto Model PA-102. The dropping mercury electrode had the following characteristics: $m = 1.628$ mg/sec, $t = 4.01$ sec/drop in 1 M perchloric acid at a potential of -0.6 V.

Materials.—[$CrBr_2(H_2O)_4$]Br·$2H_2O$ was obtained from Mitsuwa Chemical Co., Osaka, Japan, as $CrBr_3$·$6H_2O$ and was recrystallized twice from hydrobromic acid. A solution containing only bromopentaaquochromium(III) ion in perchloric acid was obtained by the use of a cation-exchange resin, Dowex 50W-X8, after the aquation of $CrBr_2^+$ to $CrBr^{2+}$. The procedure used for purification with the resin was quite similar to that described by Guthrie and King.[10] Chloropentaaquochromium(III) solution was prepared in the same way. Chromium(II) perchlorate solution was prepared by electrolytic reduction of chromium(III) perchlorate at a mercury pool electrode. Other reagents used were of Guaranteed Reagent grade.

Analyses.—Chromium content was determined spectrophotometrically as chromate ion after oxidation with peroxide in alkaline solution. Chloride and bromide ion were analyzed by amperometric titration with silver nitrate after neutralization of the solutions. Analyses of bromo- and chlorochromium(III) solutions gave ratios of Br:Cr = 1.01 and Cl:Cr = 0.998, respectively. Amperometric titration was also used to determine the content of chromium(II) with cerium(IV) standard solution.

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Tetraphenylarsonium Hydrogen Dihalide Hydrates[1]

BY KENNETH M. HARMON AND RALPH R. LAKE

We have found,[2] in contrast to an earlier report,[3] that the infrared spectrum of the hydrogen dibromide ion in a series of anhydrous tetraalkylammonium hydrogen dibromides is strongly affected by cation environment; similar observations have recently been independently reported by Evans and Lo.[4]

In continuing these studies we wished to examine the hydrogen dihalide salts of the large, delocalized tetraphenylarsonium cation. "Tetraphenylarsonium chloride hydrochloride" is a familiar compound; its prepara-

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(4) J. C. Evans and G. Y-S. Lo, *J. Phys. Chem.*, **71**, 3942 (1967).