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Ligand Bridging by Halide in the Electrochemical Oxidation of Chromium(II) at Mercury Electrodes

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A variety of electrochemical techniques was employed to investigate the mechanism of oxidation of chromium(II) at mercury electrodes in the presence of chloride, bromide, and iodide. The results show that halide catalyzes the reaction and leads to halide-containing Cr(III) products according to $X^- + Cr(II) \rightarrow CrX^{2+} + e^-$. In the case of chloride and bromide at least, the homogeneous complexation reaction to form CrX^+ does not precede the electrode reaction. A variety of data on the potential dependence of the reaction products strongly suggests that, when it is adsorbed on the electrode, halide can act as an electron bridge and facilitate the oxidation. We conclude that the halide-catalyzed pathway is best represented by the scheme

$$Hg + X^- \longrightarrow Hg(X^-)_{ads}$$

$$Hg(X^-)_{ads} + Cr^{2+} \longrightarrow [Hg\cdots X\cdots Cr]^{\ddagger} \longrightarrow XCr^{2+} + e^-$$

It has been shown that many ligands dramatically affect the rate of electrochemical oxidation of Cr(II). Pecsok and Lingane,[1] in their investigation of the polarographic oxidation of Cr(II) in the presence of KCl, KSCN, $CaCl_2$, $(CH_3)_4NBr$, and several carboxylic acids, observed large changes in half-wave potentials and in the degree of irreversibility of the oxidation as the composition of the supporting electrolyte solution was changed. Kemula and Rakowska,[2] who studied the reduction of various Cr(III) species using cyclic voltammetry, showed that $CrCl^{2+}$ can be formed when Cr(II) is oxidized at a hanging mercury drop electrode in chloride solution. Aikens and Ross[3] studied the rates of oxidation of Cr(II) at mercury electrodes in the presence of fluoride, chloride, and iodide and found that, at fixed potential, the rate of Cr(II) oxidation is proportional to the concentration of chloride over a 50-fold change in chloride concentration and the general accelerating effect of the halides decreases in the order $I^- > Cl^- > F^-$, the effect of fluoride being very small. They pointed out that the specific adsorption of halides on mercury follows this same order.

$Cr(H_2O)_6{}^{3+} \equiv Cr^{3+}$ is sufficiently inert to chloride substitution that it is easy to provide conditions where the reaction $Cr^{3+} + Cl^- \rightarrow CrCl^{2+}$ may be ignored as a source of the complex $CrCl^{2+}$. Under such conditions, if the product of electrooxidation of Cr(II) in chloride solutions is $CrCl^{2+}$, the transition state must have contained chloride. This in turn suggests that the reaction mechanism involves halide-bridged electron transfer (or halide atom transfer). Jones and Anson[4] carried out controlled-potential electrolyses of Cr(II) solutions at a stirred mercury pool electrode in the presence of chloride and found that when the initial ratio of chloride ion to Cr(II) is less than or equal to 1, no uncoordinated chloride is found in the product solution, while when the initial chloride to Cr(II) ratio is greater than 1, uncoordinated chloride equal to the initial excess of chloride over Cr(II) is found. This suggests that oxidation under these conditions occurs by a chloride bridge mechanism.

We have extended this study by investigating the electrochemical oxidation of Cr(II) in the presence of chloride, bromide, and iodide in order to obtain a more precise description of the ligand-bridging mechanism and to test its generality.

Experimental Details

Standard operational amplifier instrumentation was used to apply the desired voltage wave forms to the electrodes. The various electrochemical techniques employed included chronopotentiometry,[5] polarography, cyclic-sweep voltammetry, chronocoulometry,[6] and controlled-potential electrolysis. For the chronopotentiometric experiments a mercury drop electrode hanging from an amalgamated gold wire was used: the drop area was 0.0566 cm². Chronopotentiometric transition times were corrected for spherical diffusion when necessary.[7] A commercially available (Brinkman Instruments, Inc.) hanging mercury drop electrode with 0.0409-cm² area was used for the chronocoulometric and cyclic voltammetric experiments. The experimental details and the apparatus employed for controlled-potential electrolysis have been described before.[4]

The reference electrode was either a NaCl sce or a KCl sce isolated from the test solution with a salt bridge containing $NaNO_3$ or Na_2SO_4 solution. Potentials are reported *vs.* the KCl sce unless otherwise specified.

The cell was carefully designed to exclude oxygen. Gas outlet traps containing V(II) or Cr(II) solutions were used to prevent back-diffusion of oxygen into the cell. All solutions were deaerated with prepurified nitrogen which was passed through a V(II) washing tower, a tube containing copper turnings at 400°, and finally a water washing tower.

Cr(II) stock solutions were prepared electrolytically from chromium(III) perchlorate solutions by the method of Schaefer.[8]

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

[2] W. Kemula and E. Rakowska, *Roczniki Chem.*, **36**, 203 (1962).

[3] D. A. Aikens and J. W. Ross, Jr., *J. Phys. Chem.*, **65**, 1213 (1961).

[4] J. G. Jones and F. C. Anson, *Anal. Chem.*, **36**, 1137 (1964).

[5] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter VIII.

[6] F. C. Anson, *Anal. Chem.*, **38**, 54 (1966).

[7] J. G. Jones, Thesis, California Institute of Technology, Pasadena, Calif., 1967.

[8] W. P. Schaefer, Thesis, University of California at Los Angeles, Los Angeles, Calif., 1961.

Sodium perchlorate stock solutions were made by neutralization of 60% $HClO_4$, with filtered, saturated NaOH solution. NaCl was purified by precipitation with HCl gas. NaBr was purified by recrystallization from ethanol. All other chemicals were standard reagent grade and were used without further purification. The source of $CrBr_2^+$ was "chromic bromide" available from K & K Laboratories.

Except where otherwise specified, solutions were 0.100 F in $HClO_4$ and were adjusted to an ionic strength of 1.00 by addition of $NaClO_4$. The experiments were carried out at 27°.

Results and Discussion

Oxidation of Cr(II) in Chloride and Bromide Solutions.—We investigated the chronopotentiometric behavior of Cr(II) in chloride and bromide solutions with three objectives in mind: (1) to see if oxidation of Cr(II) produces $CrCl^{2+}$ and $CrBr^{2+}$ quantitatively under chronopotentiometric conditions, (2) to see if the adsorption of chloride and bromide induces substantial specific adsorption of Cr(II), and (3) to see if $CrCl^+$ or $CrBr^+$ is formed rapidly near the electrode just prior to electron transfer.

Formation of $CrCl^{2+}$.—The chronopotentiometric reduction of $CrCl^{2+}$ gives a well-defined wave that is separated from the reduction wave due to Cr^{3+} only under the special conditions of high $CrCl^{2+}$ concentrations and large current densities. Under these conditions, when the current direction is reversed following the chronopotentiometric oxidation of Cr(II), the ratio of the forward generation time [for Cr(II) oxidation] to the reverse transition time corresponding to the reduction of $CrCl^{2+}$ is near the theoretical value of 3.00 corresponding to quantitative formation of $CrCl^{2+}$ during the oxidation of Cr^{2+}. For instance, in 2 F $HClO_4$, 0.5 F NaCl, and 30 mF Cr(II) with a current density of 4.650 mA/cm², this ratio was 2.97 ± 0.07. The oxidation takes place at potentials more positive than −400 mV under these conditions.

Formation of $CrBr^{2+}$.—In contrast with the oxidation of Cr(II) in perchlorate or chloride media, in moderately concentrated bromide solutions the oxidation is nearly reversible. As a consequence, a double wave is seen for the oxidation in solutions containing an excess of Cr(II) over bromide. The new wave appears at potentials more cathodic than those corresponding to the usual Cr(II) oxidation wave. The transition time for this new wave is determined by the bromide concentration which demonstrates that bromide is consumed at the electrode surface by the oxidation of Cr(II) and suggests that, like chloride, it serves as a bridge for Cr(II) oxidation.

When Cr(II) is oxidized chronopotentiometrically at large current densities in the presence of large excesses of bromide ($\gtrsim 0.1$ F), only a single cathodic wave is observed when the current direction is reversed and the ratio of the anodic generation time to the cathodic transition time is 3.00, showing that $CrBr^{2+}$ is formed quantitatively. However, when the oxidation is carried out at low current densities or lower bromide concentrations, the ratio of the anodic generation time, t_f, to cathodic transition time, τ_c, is greater than 3. For example, in solutions 1.00 mF in NaBr and 1.80 mF in Cr(II) which, because of the smaller diffusion coefficient of Cr(II), provides equal fluxes of Cr(II) and bromide ions at the electrode, the ratio t_f/τ_c varies from 5.00 to 5.75.

Table I illustrates the kind of potential dependence of t_f/τ_c that is obtained with solutions containing 1.00 mF NaBr and 20 mF Cr(II). The generation time, t_f, was restricted to values less than the calculated transition time for bromide, but the potential assumed by the electrode during the anodic generation period was highly variable as can be seen from Table I. While these data cannot be analyzed exactly because of the complexity of the relation between potential and surface concentration of bromide, it is clear that more $CrBr^{2+}$ is formed, the more anodic the potential. The third column in Table I gives an approximate value for the percentage of the anodic current which resulted in $CrBr^{2+}$ formation in each case.

TABLE I

POTENTIAL DEPENDENCE OF $CrBr^{2+}$ FORMATION[a]

E, mV *vs.* sce	t_f/τ_c	Approx[b] coulombic efficiency for $CrBr^{2+}$ generation, %
−440	106	19
−420	31.2	35
−400	13.6	52
−380	9.58	61
−370	7.50	68
−360	6.45	73

[a] E is the potential assumed by the electrode during the oxidation of Cr(II) under chronopotentiometric conditions. It was constant to within 10 mV for at least the final two-thirds of the forward generation time. The current density was 177 μA/cm². The solution was 20 mF in Cr(II) and 1.00 mF in NaBr. [b] Calculated by assuming constant current efficiency for $CrBr^{2+}$ production during the anodic generation time, t_f. The current efficiency is equal to $2\{(\tau_c/t_f)/[1 + (\tau_c/t_f)]\}^{1/2}$.

The same type of behavior is not observed in the case of chloride simply because the same conditions cannot be achieved. The large current densities and high chloride concentrations that must be used to obtain well-formed waves for $CrCl^{2+}$ reduction are sufficient conditions to ensure that $CrCl^{2+}$ is formed quantitatively during the oxidation. This is undoubtedly due to the combined effects of high chloride concentration and large overpotential for the anodic reaction. At lower chloride concentrations or smaller current densities a mixture of $CrCl^{2+}$ and Cr^{3+} would be formed, but it would not be easy to assay electrochemically.

These results are summarized as follows. (1) At large chloride concentrations and high current densities, the product of Cr(II) oxidation in the presence of chloride is entirely $CrCl^{2+}$. (2) At sufficiently large bromide concentrations the product of Cr(II) oxidation in the presence of bromide is entirely $CrBr^{2+}$ but at lower bromide concentrations both $CrBr^{2+}$ and Cr^{3+} are formed even when there is a stoichiometric excess of bromide. (3) The fraction of the product appearing as $CrBr^{2+}$ when a mixture of $CrBr^{2+}$ and Cr^{3+} is formed

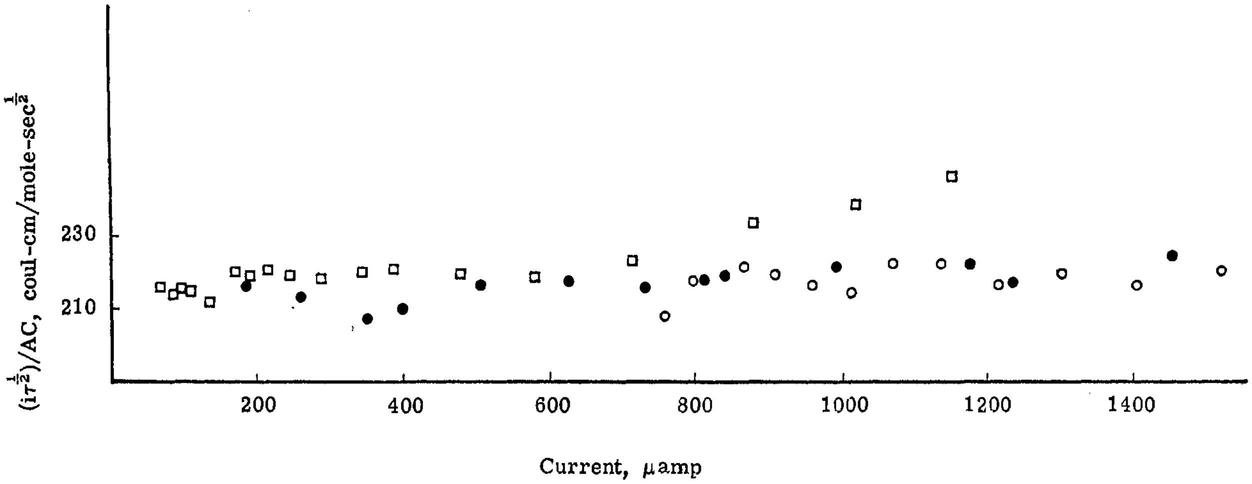

Figure 1.—Constancy of the chronopotentiometric constant as a function of current for Cr(II) oxidation in the presence of chloride and bromide: □, 4.0 mF Cr(II) in 0.1 F NaCl; ○, 2.9mF Cr(II) in 0.1 F NaCl; ●, 2.65 mF Cr(II) in 0.1 F NaBr. All solutions contained 0.1 F $HClO_4$ and $NaClO_4$ to adjust the ionic strength to 1.0.

is potential dependent and is greater at more anodic potentials.

We will return to the question of the product distribution when Cr(II) is oxidized in the presence of bromide, but first we present additional chronopotentiometric results that answer the question of whether a prior reaction is important in the mechanism.

Prior Complexation Reaction.—The fact that the $CrBr^{2+}$ fraction of the products formed from the oxidation of Cr(II) in bromide solutions shows a potential dependence (Table I) is already good evidence that the mechanism of $CrBr^{2+}$ formation does not involve the reaction

$$Cr^{2+} + Br^- \longrightarrow CrBr^+ \qquad (1)$$

proceeding in advance of the electrode reaction. Reaction 1 is a homogeneous complexation reaction which would proceed at a rate that is independent of the potential of the electrode. (A possible double-layer effect on the rate of this reaction would show a potential dependence of the opposite sign to that observed.) By contrast, the amount of bromide ion adsorbed on the surface of the mercury electrode shows a very strong potential dependence which parallels the increase in $CrBr^{2+}$ formation in Table I.[9]

Nevertheless, it has been argued that a reaction such as (1), rather than a ligand-bridging mechanism, could account for the observed electrode reaction products,[10] so it was important to demonstrate directly that this prior complexation step does not occur. Figure 1 shows the constancy of the chronopotentiometric constant, $i\tau^{1/2}/AC$, with current density for the oxidation of Cr(II) in chloride and bromide solutions. The chronopotentiometric constant decreases at current densities sufficiently high that a complexation reaction preceding the electrode reaction becomes rate limiting.[11] In the case of chloride, the observed constancy of $i\tau^{1/2}/AC$ shown in Figure 1 places a lower limit of about 500 sec$^{-1/2}$ on the quantity $k_f \cdot (k_f + k_b)^{1/2}/k_b$

$$k_f(k_f + k_b)^{1/2}/k_b > 500 \text{ sec}^{-1/2} \qquad (2)$$

where the rate constants are for the hypothetical reaction

$$Cr^{2+} + Cl^- \underset{k_b}{\overset{k'_f}{\rightleftharpoons}} CrCl^+ \qquad (3)$$

and k_f is a pseudo-first-order constant, $k_f = k'_f[Cl^-]$. From the data of Pecsok and Bjerrum,[12] the formation constant for $CrCl^+$, $K = k'_f/k_b$, is less than 5×10^{-3} M^{-1}. Therefore, in 0.1 F chloride solution

$$k_f/k_b < 5 \times 10^{-4} \qquad (4)$$

Combining the inequalities (2) and (4) we find

$$k_f + k_b > 10^{12} \text{ sec}^{-1} \qquad (5)$$

This limit is sufficiently extreme to rule out the formation of $CrCl^+$ in a reaction preceding the electrode reaction.

The data for bromide solutions are similar (Figure 1). While we do not have an estimate for the formation constant of $CrBr^+$, all available evidence indicates that $CrBr^+$ should be less stable than $CrCl^+$.[13] Therefore, kinetic effects due to prior complex formation should appear at lower current densities with bromide than with chloride. The absence of any decrease in the chronopotentiometric constant at high current densities argues that homogeneous formation of $CrBr^+$ prior to the electron-transfer step does not occur.

The absence of any *increase* in the chronopotentiometric constant at the highest currents rules out the

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[9] J. Lawrence, R. Parsons, and R. Payne, *J. Electroanal. Chem.*, **16**, 193 (1968).

[10] N. Sutin, *Electrochim. Acta*, **13**, 175 (1968).

[11] Reference 5, p 197 ff.

[12] R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1418 (1957).

[13] S. Arhland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

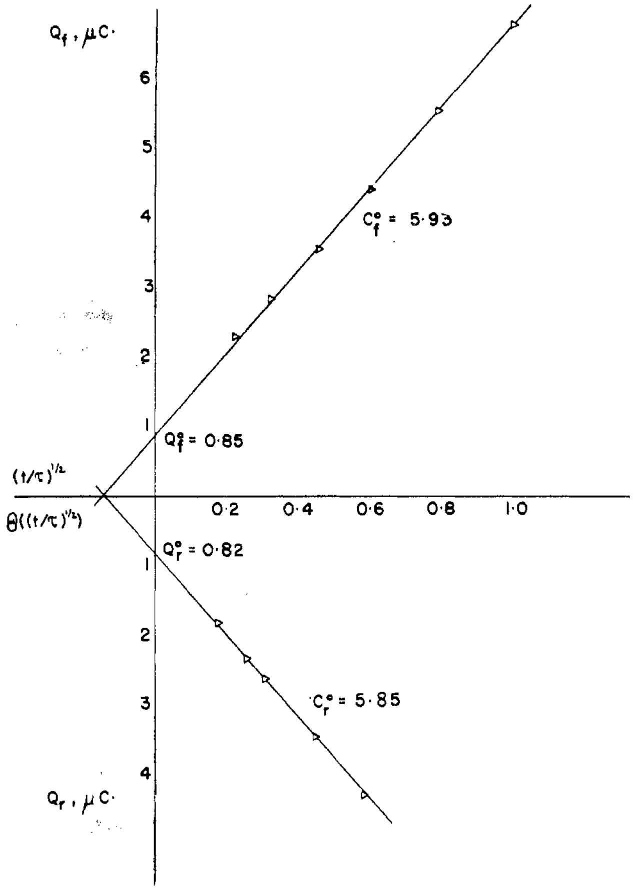

Figure 2.—Double-potential-step chronocoulometry with Cr(II) in bromide. The solution was 2.65 mF in Cr(II) and 0.878 F in NaBr. $E_1 = -0.250$ V *vs.* sce; $\tau = 38.5$ msec. The upper line corresponds to the oxidation of Cr^{2+} and the lower line to the reduction of the resulting $CrBr^{2+}$. For a detailed description of the chronocoulometric technique, consult ref 6.

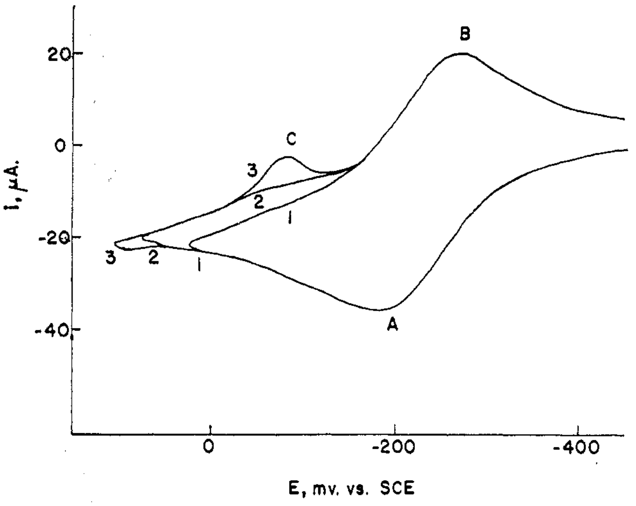

Figure 3.—Cyclic voltammetry of Cr(II) in iodide solution. The solution was 0.1 F in $HClO_4$ and 1.30 mF in NaI with the flux ratio $D_{Cr}^{1/2}[Cr(II)]/D_I^{1/2}[I^-] = 1.00$. The traces are numbered in the order of increasing extension into positive potentials. The feature C in trace 3 appears in solutions containing iodide alone. When the flux ratio is greater than 1.00, a second anodic peak appears at potentials anodic to A. Its position and height increase with increasing Cr(II) concentration. The potential scan rate was 134 mV/sec.

possibility that Cr^{2+} is adsorbed on the mercury electrode in these solutions. This is also evident from the chronocoulometric experiments to be described next.

The Product Distribution between Cr^{3+} and $CrBr^{2+}$.—The chronopotentiometric technique is not well suited to the study of potential-dependent processes, such as the potential-dependent formation of $CrBr^{2+}$. We therefore chose to study the oxidation of Cr(II) in bromide solutions using double-potential-step chronocoulometry,[6] a controlled-potential method that provides a rapid and convenient means of determining the amounts of product formed in diffusion-controlled electrochemical reactions.

The experiments were carried out in the following way. The potential of the mercury electrode in a solution of Cr(II) was initially fixed at −750 mV where no electrode reactions proceed. It was then stepped for a time τ to a potential E_1, at which the oxidation of Cr(II) is diffusion controlled, and then stepped back to −750 mV, where the reduction of $CrBr^{2+}$ is diffusion controlled but Cr^{3+} is not reduced. The total charge that had passed at any time was recorded and plotted *vs.* the square root of time.[6] Figure 2 shows a typical chronocoulometric result under conditions where $CrBr^{2+}$ is quantitatively formed in the oxidation. The equality of the two intercepts, Q_f° and Q_r°, indicates that the forward reaction $[Cr(II) \rightarrow Cr(III) + e^-]$ is diffusion controlled and that neither Cr(II) nor $CrBr^{2+}$ is adsorbed on the electrode. The slopes of the linear plots, C_f° and C_r°, are proportional to the concentrations of Cr(II) and $CrBr^{2+}$. Their equality indicates that $CrBr^{2+}$ is quantitatively formed from Cr(II) during the oxidation. Experiments over a wide range of bromide concentrations and initial potentials, E_1, gave the general result that at potentials more anodic than −300 mV and bromide concentrations higher than *ca.* 0.05 F, Cr(II) is oxidized quantitatively to $CrBr^{2+}$. A sample of the type of results obtained with low bromide concentrations is shown in Table II.

TABLE II

POTENTIAL DEPENDENCE OF THE FORMATION OF $CrBr^{2+}$ FROM CHRONOCOULOMETRIC OXIDATION OF Cr^{2+} IN 1.93 mF BROMIDE[a]

E_1, mV *vs.* sce	Apparent coulombic efficiency of $CrBr^{2+}$ formation, %	Cr(II) oxidation, diffusion-controlled
−300	81	No
−250	89	No
−200	99	Yes
−150	100	Yes
−100	100	Yes
−50	100	Yes

[a] The Cr^{2+} concentration was 1.5 mF. The duration of the forward step was about 40 msec.

These data confirm the chronopotentiometric evidence that the inclusion of bromide in the Cr(III) product is potential dependent, which strongly suggests that halide adsorption is essential to the mechanism. An attempt was made to rationalize the results of the potential-step experiments by calculating the amount of $CrBr^{2+}$ expected to be formed under various conditions assuming that Cr(II) is oxidized *via* two competing pathways

$$Cr^{2+} \longrightarrow Cr^{3+} + e^- \qquad (6)$$

and

$$Cr^{2+} + (Br^-)_{ads} \longrightarrow CrBr^{2+} + e^- \qquad (7)$$

The calculation requires accurate values of the heterogeneous rate constants and transfer coefficients for reactions 6 and 7. In addition, data on the double-layer structure in the bromide solutions are necessary to permit corrections of the measured kinetic parameters for the effects of the double layer.[14] We measured the necessary kinetic parameters and employed the double-layer data of Lawrence, Parsons, and Payne[9] to arrive at a complex equation from which the product distribution could in principle be calculated. Using this equation we were able to reproduce qualitatively the general features of the data in Table II. However, the calculated results are extremely sensitive to small changes in rate constants, transfer coefficients, and double-layer parameters, and the uncertainties in the kinetic and double-layer parameters were large enough to thwart a quantitative comparison of the calculated results with the experimental data.[15] Nevertheless, we were convinced that the data support our conclusion that under a wide variety of conditions of potential and bromide concentration reactions 6 and 7 compete and the product is a mixture of Cr^{3+} and $CrBr^{2+}$. Higher bromide concentrations and more anodic potentials favor formation of $CrBr^{2+}$. The oxidation mechanism for the bromide-assisted path is ligand-bridging as in the case of chloride.

Oxidation of Cr(II) in the Presence of Iodide.—The rate of aquation of CrI^{2+} is sufficiently large[16] that rapid techniques must be employed to measure the amount of CrI^{2+} formed in the electrochemical oxidation of Cr(II) in the presence of iodide. However, a fast potentiostatic technique such as double-potential-step chronocoulometry is not applicable because in iodide solutions Cr(II) oxidation and mercury oxidation are not well separated. This problem occurs at all iodide concentrations because, although lowering the iodide concentration moves the mercury oxidation to a more anodic potential, it also decreases the rate of Cr(II) oxidation so that a more anodic potential is required to assure diffusion control during the oxidation.

Figure 3 illustrates the cyclic voltammetric behavior of Cr(II) in dilute iodide solutions. The sweep was begun at −700 mV with the first half-cycle anodic. Peak A corresponds to the oxidation of Cr(II) by the iodide path and peak B is almost surely the reduction of CrI^{2+} formed during the anodic half-cycle. Peak B occurs at −262 mV and is absent in solutions containing Cr^{3+} and iodide. The separation between A and B is 75 mV.

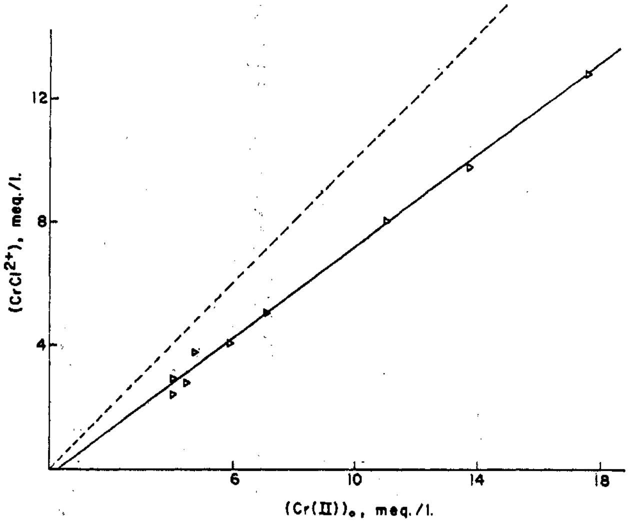

Figure 4.—The effect of iodide on the formation of $CrCl^{2+}$ in the controlled-potential oxidation of Cr(II). The initial concentrations were: sodium iodide, 2 m*F*; sodium chloride, 20 m*F*; chromium(II), 3.5–18 m*F*. All solutions contained 0.1 *F* $HClO_4$ and were adjusted to an ionic strength of 1.0 with $NaClO_4$.

Figure 3 corresponds to approximately equal concentrations of iodide and chromium(II). As the concentration of Cr(II) is increased at constant iodide concentration, peaks A and B do not change in height or position. This means that peak A is controlled by diffusion of iodide to the electrode in the presence of excess Cr(II). The similar behavior of peak B confirms the diagnosis that it corresponds to the reduction of the product formed at peak A (CrI^{2+}).

Controlled-Potential Oxidation of Chromium(II) in the Presence of Chloride–Iodide Mixtures.—The oxidation of Cr(II) in the presence of chloride–iodide mixtures presents the intriguing possibility that the product distribution might differ from that predicted by a simple parallel reaction scheme because iodide is adsorbed on mercury to a greater extent than is chloride. To investigate this possibility, large-scale electrolyses similar to those described in ref 4 were performed in solutions containing both iodide and chloride. Although none of the CrI^{2+} formed in these experiments survived long enough to be detected, the extent of its intermediacy could be determined from the amounts of Cr(II) that ended up as Cr^{3+} rather than $CrCl^{2+}$.

The oxidations were carried out at −192 mV. The product solutions were analyzed by titration with silver ion. The amount of uncoordinated chloride was determined from the silver ion required to go from the iodide end point to the chloride end point. The amount of $CrCl^{2+}$ formed was found from the difference between the titration value and the known total chloride present. In each experiment the initial chloride to iodide ratio was 10. At the prevailing chloride concentration and pH the induced formation of $CrCl^{2+}$ during the aquation of CrI^{2+} was negligible.[17]

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(14) P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers, New York, N. Y., 1965.

(15) Some details of these calculations are available in ref 7.

(16) J. H. Espenson, *Inorg. Chem.*, **3**, 968 (1964).

(17) M. Ardon, *ibid.*, **4**, 372 (1965).

The results are presented in Figure 4. The slope of the line defined by the experimental points is 0.75 mequiv of $CrCl^{2+}$/mequiv of Cr(II). The dotted line with a slope of 1.0 is obtained in the absence of iodide.[4] In the three experiments with the largest Cr(II) concentrations the difference between the amount of $CrCl^{2+}$ actually formed and the amount that would have been formed had no iodide been present is greater than the amount of iodide. This is possible because the time required for electrolysis (about 1 hr) is long compared with the lifetime of CrI^{2+}, so that iodide is being continuously regenerated and can take part repeatedly in the electrode reaction.

It is reasonable to expect that, of the total Cr(II) formed in these experiments, the fraction due to $CrCl^{2+}$ should be approximately equal to the ratio of the electrochemical rate of formation of $CrCl^{2+}$ to the sum of the rates for all possible electrochemical oxidation paths.

From Figure 2 of ref 3 we can extract the following rate constants for the oxidation of Cr(II) at −0.192 V *vs.* sce

$$\begin{aligned} k_1 &= 0.14 \times 10^{-2}\ \text{cm/sec} \\ (\text{Cl}^-)k_2 &= 2.73 \times 10^{-2}\ \text{cm/sec} \qquad (8) \\ (\text{I}^-)k_3 &= 6.40 \times 10^{-2}\ \text{cm/sec} \\ (\text{Cl}^-) = (\text{I}^-) &= 5 \times 10^{-6}\ \text{mol/cm}^3 \end{aligned}$$

Here k_1 is the rate constant in the absence of bridging ligands and $(Cl^-)k_2$ and $(I^-)k_3$ are the pseudo-first-order rate constants in the presence of chloride and iodide, respectively, for the ligand-bridged paths alone.

For the experiments of Figure 4 the value of the rate ratio, $(Cl^-)k_2/[(Cl^-)k_2 + (I^-)k_3 + k_1]$, was calculated for each initial Cr(II) concentration by assuming that the iodide concentration remained equal to its initial value and that the chloride concentration was equal to two-thirds of its final value plus one-third of its initial value (*i.e.*, approximately the average value of the chloride concentration during the electrolysis). The resulting ratios were approximately constant and equal to 0.74 ± 0.03. The agreement between this calculated ratio and the slope of the experimental line in Figure 4 confirms that the effect of iodide on the electrochemical oxidation of Cr(II) is qualitatively similar to the effects of chloride and bromide.

Conclusion

All of the evidence presented here supports the existence of a ligand-bridge mechanism for Cr(II) oxidation in chloride, bromide, or iodide solutions. Because of the substitution inertness of Cr^{3+}, formation of CrX^{2+} when Cr(II) is oxidized in these halide solutions implies that X is inserted into the coordination sphere of chromium prior to the electron transfer. The absence of kinetic effects due to prior complexation reactions between X^- and Cr^{2+} seems to rule out formation of CrX^+ in solution and leaves only the possibility that a bond is formed between X^- and Cr(II) in a fast step at the electrode surface. The potential dependence of the relative amounts of Cr^{3+} and $CrBr^{2+}$ formed on oxidation suggests that the potential-dependent adsorption of bromide is a controlling factor in the mechanism. The fact that this potential dependence can be rationalized by assuming the presence of two competing reactions supports our view of the mechanism.

We can summarize these conclusions by writing a detailed mechanism for the halide-catalyzed oxidation of Cr(II)

$$\text{Hg} + \text{X}^- \longrightarrow \text{Hg(X}^-)_{\text{ads}} \qquad (9)$$

$$\text{Hg(X}^-)_{\text{ads}} + \text{Cr}^{2+} \longrightarrow [\text{Hg}\cdots\text{X}\cdots\text{Cr}]^{\ddagger} \longrightarrow \text{XCr}^{2+} + \text{e}^-$$

Chloride, bromide, and iodide are extensively adsorbed on mercury at the potentials where oxidation of Cr(II) occurs.[18] The rate of adsorption is most probably diffusion controlled[19] so that a stoichiometrically sufficient quantity of halide (properly weighted by diffusion coefficients) in the bulk of the solution ensures the presence of adsorbed halide during the reaction.

In a very recent note[20] Watanabe and coworkers reported that in bromide media the polarographic half-wave potentials for $CrBr^{2+}$ reduction and Cr^{2+} oxidation coincide (demonstrating the reversibility of the electrode reaction under polarographic conditions) and show a dependence on the free bromide concentration which agrees with the Nernst equation. These results are in accord with the mechanism represented in reaction 9 (although they are insufficient to prove it) and correspond to the special case in which all of the steps in the reaction have had time to attain equilibrium.

There is ample evidence that the mechanism presented here is not an isolated one. We have already referred to the effects of other ligands on the rate of Cr(II) oxidation.[1] It is reasonable to expect that other anions which are strongly adsorbed and good ligands influence the rate by the same mechanism. Experiments to be reported later[21] in which thiocyanate is the bridging ligand afford additional strong evidence for this conclusion.

Acknowledgment.—This work was supported by the National Science Foundation.

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[18] D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947).

[19] Reference 14, p 118.

[20] I. Watanabe, E. Itabashi, and S. Ikeda, *Inorg. Chem.*, **7**, 1920 (1968).

[21] F. C. Anson, E. Passeron, and D. J. Barclay, experiments to be submitted for publication.