A Chronopotentiometric Study of the Participation of Various Ligands in the Oxidation of Chromium(II)

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The effects of several ligands upon the electroöxidation of chromium(II) were studied by performing chronopotentiometry with current reversal on solutions of hexaquochromium(III) in a perchloric acid medium. The ligands investigated were fluoride, chloride, bromide, iodide, thiocyanate, sulfate, succinate, acetate, and oxalate. Of these, all but fluoride and succinate enhance the electrode reaction. Previous evidence that chloride, bromide, and iodide are included in the oxidation product was supported, and thiocyanate was found to participate in a similar manner.

It has been clearly established that chloride, bromide, and iodide enhance the rate at which chromium(II) is oxidized to chromium(III) at a mercury electrode.[1] Direct chemical analysis following the exhaustive controlled potential electrolysis of a solution initially containing both chromium(II) and excess chloride proves that the principal product of the reaction is chloropentaquochromium(III).[2] This evidence indicates that the species $(Cr\cdots X)^+$ adsorbed at the surface of the electrode is an intermediate in the oxidation. Presumably the reaction follows an analagous route when bromide or iodide are the ligands present. The bromo and iodo pentaquochromium(III) complexes dissociate at too rapid a rate, however, for their presence to be detected by direct product analysis.

The postulated intermediate of the form $(Cr\cdots X)^+$ adsorbed on mercury suggests that either of two possible mechanisms is operative. The chromium(II) complex CrX^+ may form in the bulk of the solution and diffuse up to the electrode to react. Alternately, hexaquochromium(II) could diffuse to the electrode surface where a previously adsorbed halide ion serves as a bridge for the electron transfer. Both mechanisms account for the rate enhancement since in either case the halide ion is available to serve as an electron bridge, and both similarly allow for the observed product.

A primary means of attacking the question of which of the two possible mechanisms is predominant has been the correlation of the effectiveness of a variety of ligands in enhancing the reaction with the degree to which they are specifically adsorbed on mercury and the stability of their chromium(II) complexes. Aikens and Ross[3] have reported that the effectiveness with which

the halides catalyze the reaction increases in the sequence fluoride, chloride, bromide, iodide. This is the same order in which they are increasingly adsorbed on mercury, while the best evidence indicates that the chromium(II) complexes become more stable in the reverse order.[4] Thus the halide evidence tends to support the adsorbed ligand hypothesis; it is certainly not by itself inconsistent, however, with the alternate complex formation interpretation.

To pursue this approach to the mechanism problem it is desirable to be able to determine the effectiveness with which a wide variety of ligands enhance the oxidation. Any information about the reaction products is also desirable. Pecsok and Lingane[5] have reported variations in the half-wave potential of chromium(II) anodic waves as a function of the ionic species present during polarographic studies. The comparison of these half-wave potential values is one method of determining the relative effectiveness with which different ligands participate in the oxidation. The more recent work of Kemula and Rakowska[6] shows that cyclic voltammetry can be similarly employed. It has the additional advantage that the products formed during the first cycle change the solution composition near the electrode and thus can be detected in subsequent cycles. For example, when cyclic voltammetry is performed on a solution of hexaquo chromium(III) in the presence of chloride, a peak is found in the second cathodic polarization at a potential less negative than the first cycle peak corresponding to the reduction of the hexaquo ion. This is explained as the reduction of the chloropentaquochromium(III) species formed during the first anodic polarization.

The application of chronopotentiometry with current reversal to the chromium(II) - chromium(III) system in these experiments takes advantage of much the same principles as Kemula and Rakowska's use of cyclic voltammetry. It has the great advantage over polarography that the experiments can be performed on stable, easily prepared solutions of hexaquochromium(III) instead of highly air-sensitive chromium(II) solutions. Also, as in cyclic voltammetry and unlike polarography, the products of the reaction can be observed by reversing the polarity of the working electrode during the electrolysis.

A chronopotentiogram of a solution containing hexaquochromium(III) and the ligand X^- is expected to appear as in Figure 1 if the oxidation of chromium(II) in the presence of X^- yields the product CrX^{++}, provided that this species is more easily reduced than the hexaquo ion.

Chronopotentiogram of Hexaquochromium(III) in the Presence of X^-

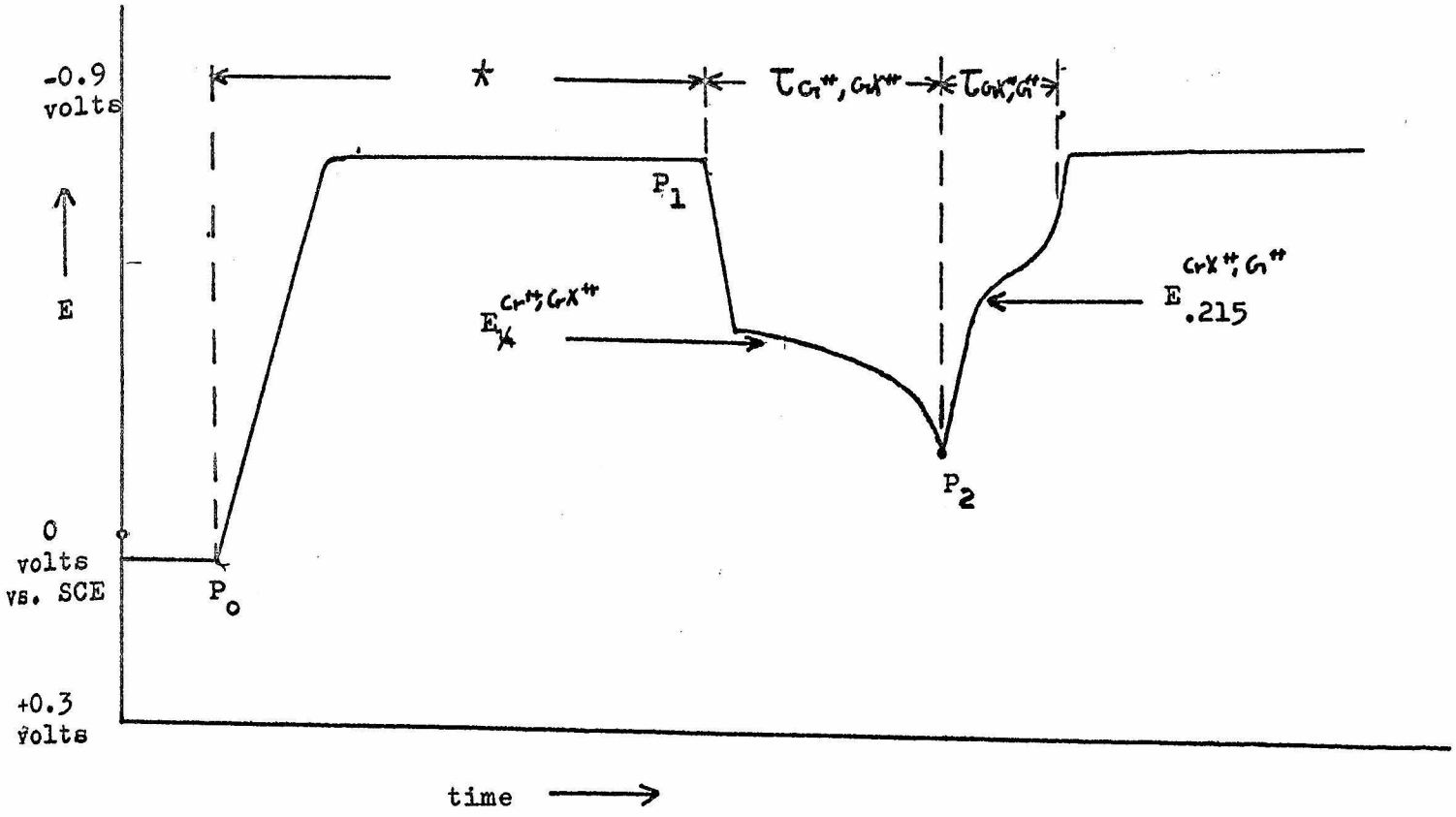

Figure 1. Current on cathodic at P_o. P_1 - First Current Reversal. P_2 - Second Current Reversal.

If the reduction of chromium(III) were 100% current efficient and $\tau^{Cr^{+++},Cr^{++}}$ where τ is the transition time for the bulk chromium(III) concentration, the relationship $t/\tau_{Cr^{+++},Cr^{++}}=3$ is predicted. In fact, however, it proved impossible to establish conditions under which this ratio had its theoretical value. $t/\tau_{Cr^{+++},Cr^{++}}$ was observed to be relatively independent of current density in the range investigated (500-1500 $\mu A/cm^2$) and fluctuated around a value of about four at a chromium(III) concentration of 20mM. This result is interpreted as implying a failure of the chromium(III) reduction reaction to proceed with 100% current efficiency, apparently due to the competitive reduction of hydrogen ion. The reduction of hexaquochromium(III) under the specified conditions gave a wave with $E_{1/4}$ = -0.85 volts vs. S.C.E. Competition from hydrogen ion reduction apparently was important even though the cathodic background was never less negative than -1.0 volts vs. S.C.E. in the solutions of pH = 2.6 These results are in keeping with the observations of previous investigators, and the 100% current efficient reduction of hexaquochromium(III) has never been reported.

The inability to obtain a 100% current efficient reaction during the first wave has two undesirable effects. First, the value of "t" cannot be used as an indication of the amount of chromium(II) generated and secondly it is not possible to indicate the position of the anodic wave by a theoretically meaningful potential. If the cathodic reaction were 100% current efficient and were allowed to proceed to its transition time before current reversal, the potential of the anodic wave at a time after reversal of $.215\,\tau_{Cr^{++};CrX^{++}}$ would provide a useful approximation of the formal potential of the chromium(III) - chromium (II) half cell. The serious lack of reversibility of the system impairs the usefulness of the approximation, but the failure to obtain a 100% current efficient cathodic wave derives it of all significance. ~~from the value of E in this case~~. Since it is important to be able to at least qualitatively compare the position of the anodic wave for different participating ligands, the value of $E_{1/4}^{Cr^{++};CrX^{++}}$ will be ~~was~~ used as a measure of the wave's position.

If the ligand X^- is present in excess of the chromium(II) concentration generated at the electrode surface and the oxidation during the anodic wave proceeds to a transition time entirely by the route

$$Cr^{++} + X^- \longrightarrow CrX^{++} + e^-$$

the value of $E_{.215}^{CrX^{++};Cr^{++}}$ is significant as a meaningful measure of the position of the cathodic wave which corresponds to the reduction of CrX^{++}. It is, of course, necessary for $\tau_{Cr^{++};CrX^{++}}$ to be the full transition time of the anodic wave for $E_{.215}^{CrX^{++};Cr^{++}} = E_f^{0\,CrX^{++};Cr^{++}}$. Since the couple CrX^{++},Cr^{++} is nearly reversible for X = Br^- and I^-, the assumptions underlying the relationship can be entirely satisfied if the current is reversed at the proper time.

As long as $\tau_{Cr^{++};CrX^{++}}$ does not exceed the anodic wave's transition time, the relationship $\tau_{Cr^{++};CrX^{++}}/\tau_{CrX^{++};Cr^{++}} = 3$ is predicted to hold provided that all the chromium(II) is oxidized by the route involving inclusion of X^-. In these experiments, the proximity of the values of $\tau_{Cr^{++};CrX^{++}}/\tau_{CrX^{++};Cr^{++}}$ to three was used as a qualitative measure of the current efficiency for the oxidation with inclusion. In the notation of Figure 1, the three experimental parameters measured were $E_{1/4}^{Cr^{++};CrX^{++}}$, $\tau_{Cr^{++};CrX^{++}}/\tau_{CrX^{++};Cr^{++}}$, and $E_{.215}^{CrX^{++};Cr^{++}}$. A comparison of these values for different participating ligands gives useful information about their relative effectiveness as participants in the reaction.

The hexaquo Cr(III) solution was prepared by the reduction with 30% H_2O_2 of .050F $Na_2Cr_2O_7$ in 0.5F $HClO_4$. Excess peroxide was decomposed by boiling for four hours with the solution in contact with a platinized platinum sheet. The aliquots used in the experiments, prepared by diluting this solution five times, were 20mM in Cr(III) and at pH 2.6. Solutions of all the ligands employed except succinate were made up by dissolving a weighed quantity of their sodium salts in a volumetric flask. The succinate solution was prepared from succinic acid. No standardizations were performed. Aliquots were transferred to the cell with a 1 ml pipet. Reagent grade chemicals and tap distilled water were used for all preparations.

A standard H-cell was employed. A Pt wire auxiliary electrode and an L&N STD 11-9931 S.C.E. reference were placed in one compartment in a 20mM $HClO_4$ solution. The KCl was replaced by NaCl in the S.C.E. to prevent precipitation of $KClO_4$ in the salt bridge of the electrode. The other compartment contained the hanging mercury drop electrode system designed after Shain and Kofler[7]. Each chamber of the cell was airtight and equipped so that dry nitrogen could be passed both through the solution and over its surface. The nitrogen outlet tubes were four feet long to minimize the diffusion of air into the cell through the outgoing N_2 system. All tubing was 5/16" Tygon. Nitrogen was vigorously bubbled through both chambers for fifteen minutes before each experiment and kept flowing over the solution surfaces throughout the trials. It was found that careful deaeration and maintenance of air free conditions was of primary importance to prevent the air-oxidation of the mercury electrode.

The mercury used was CIT "Special Hg." Drop diameters in the experiments were always about .16 cm with a corresponding surface area of .08cm^2. The sizes were determined with a precision of 1% by weighing a counted number of drops and calculating the surface area by approximating the drop shape as spherical.

The circuitry was routine. The constant current source was 135 volts supplied by three 45 volt Burgess B batteries in series. Most trials were performed at about 50μA. A C.P. Clare&Co. mercury wetted contact relay was used to minimize switching transients at the start of the electrolysis. A Moseley Autograf Model 135XY Recorder plotted the potential-time curves. Current was measured with a Triplett Electrical Instruments Co. Model 630-A meter.

Oxidation of Cr(II) in $HClO_4$

The chronopotentiometry of the chromium(II), chromium(III) couple was studied in a solution containing only hexaquochromium(III) ions in a non-complexing perchloric acid medium. In this study the characteristics of the electrode reactions with only the two hexaquo ions participating were established. Under these conditions the couple behaved as expected. Table I contains typical data from ten trials, five at each of two different current densities. As is the case in all the experiments the chromium(III) concentration is 20mM and the pH is 2.6. At that concentration a cathodic transition time of about twelve seconds is observed at a current density of 1020$\mu A/cm^2$.

I. Chronopotentiometry of $Cr(H_2O)_6^{+++}$ in $HClO_4$

Trial	Current Density(uA/cm^2)	Time Cathodic (sec.)	$t/\tau_{Cr^{++};Cr^{+++}}$	$E_{1/4}^{Cr^{++};Cr^{+++}}$ (v. vs.SCE)
1	1020	12.2	4.2	+.02
2	1020	12.4	4.0	-.04
3	1020	8.2	4.1	.00
4	1020	5.5	3.9	+.02
5	1020	5.5	3.8	+.02
6	510	6.1	4.1	+.02
7	510	6.2	3.9	-.04
8	510	15	4.3	-.02
9	510	15	4.3	-.06
10	510	30	5.4	+.03

mean $E_{1/4}$ = .00 volts vs. S.C.E.

The important result is that the anodic wave, representing the uncatalyzed oxidation of chromium(II), falls at zero volts vs. S.C.E. The data also indicate that the value is not particularly dependent upon current density. ~~in this range.~~ The ratios of the lengths of the cathodic waves to the anodic transition times support the conclusion that the reduction of chromium(III) is not 100% current efficient under the conditions of these experiments. When the duration of the cathodic polarization exceeds about fifteen seconds this ratio rapidly deteriorates from its best value of near four. The increased importance of spherical diffusion effects at long transition times is apparently responsible.

Participation of Chloride

If chloride is introduced into the solution, the anodic wave is shifted more negative by over three-tenths of a volt. Also, whereas in the absence of any ligands a second current reversal simply causes the potential to fall directly back to the value for the reduction of hexaquochromium(III), in chloride solutions such a reversal gives an observable wave at less negative potentials than those corresponding to the reduction of the hexaquo ion. This ~~is~~ is interpreted as being caused by the reduction of chloropentaquochromium(III) formed during the anodic wave and supports the conclusion that chloride is included in the product of the electrode reaction.

When chloride was present in a concentration that exceeded the concentration of the chromium(II) generated at the electrode surface, the anodic wave fell at $E_{1/4}$ = -0.36 volts vs. S.C.E. at a current density of 595 uA/cm^2. It was not possible to measure the transition time of the wave representing

the reduction of the chloropentaquo ion because it was located too close to the "background" wave for hexaquochromium(III) reduction. An approximate value for the $E_{.215}$ of this wave was -0.66 volts vs. S.C.E. Although the reduction of the hexaquo ion does not occur until -0.84 volts vs. S.C.E. under the electrolysis conditions, the chloro complex wave was still too indistinct to allow quantitative interpretation of the curves.

One effect which is relevant to the mechanism question was observed when a bulk chloride concentration was introduced which was significantly less than the concentration of chromium(II) generated at the electrode surface. If the catalyzed anodic wave were allowed to pass its transition time, the potential rose and leveled off giving another anodic wave at the potential for the oxidation of mercury to calomel. It is difficult to explain the existence of this wave which seems to imply the presence of significant free chloride at the electrode surface. All the chloride should have been consumed during the anodic chromium(II) wave being incorporated into the kinetically ~~kotically~~ stable chloropentaquochromium(III). ~~complex.~~ Although it is possible that this calomel wave is prolonged by the continued reaction of chromium(II) at the electrode, current reversal during the wave gives a transition time for the reduction of calomel which is nearly in a one-to-one ratio to that for the calomel's formation. This clearly implies that the mercury oxidation wave, which was often of a length that could account for the entire bulk chloride concentration, represents a significant reaction. It is possible that it is caused by the breakdown of the chloropentaquo complex yielding free chloride, but no other evidence for the dissociation of the complex under these conditions exists. As far as the experiments performed in this series are concerned, the observed calomel wave must be considered unexplained.

Participation of Bromide

The results of trials with bromide serving as the catalyzing ligand were similar to those obtained for chloride. With excess bromide present, the anodic wave was observed in an almost identical position, falling at -0.35 volts vs. S.C.E. The principal difference was that the hexaquo-chromium(II), bromopentaquochromium(III) couple behaved nearly reversibly with $E_{.215}$ for the bromo complex reduction wave being consistently observed at -0.36 volts vs. S.C.E. This behavior made the system ideal for studying the ratio $\tau_{Cr^{++},Cr^{X}}/\tau_{Cr^{X},Cr^{++}}$ and using this parameter as a qualitative measure

of the current efficiency for oxidation with inclusion.

The value of the ratio between the transition time of the anodic wave and that for the cathodic bromopentaquo complex reduction wave varied between 3.3 and 3.7. Most values fell at 3.4 or 3.5 provided only that excess bromide was present. The ratio seemed independent of the relative excess of bromide over chromium(II) and the potential at which the current was reversed. Qualitatively, the result is interpreted as implying a high, but not 100%, current efficiency for the oxidation with inclusion. Part of the deviation of the ratio from its theoretical value of exactly three may be accounted for by the spherical geometry of the electrode. However, this can be discounted as a major factor because ratios of exactly three were obtained with this apparatus on the oxidized mercury couple formed by performing anodic chronopotentiometry with current reversal on solutions of plain perchloric acid.

In the case of bromide, unlike chloride, it was possible to observe a double anodic wave if the bromide were present in concentrations significantly less than the chromium(II) concentration generated. The two waves ran together to a certain extent but were ~~distinctly~~ separable, differing in quarter-wave potentials by about 0.2 volts. As in the case of chloride, however, an effect entirely analagous to the unexplained calomel wave was observed. Even when chromium(II) was present in large excess over the bromide, a mercurous bromide wave could be observed after the transition time for chromium(II). Again, it was often of sufficient length to account for all the bromide present during the chromium(II) oxidation.

Because of the reversible character of the hexaquochromium(II) - bromopentaquochromium(III) couple and the clarity of the waves obtained, bromide offers the model system for studying the chronopotentiometry of catalyzed chromium(II) oxidation. Excellent waves of easily measured transition times were obtained in all cases. Numerical data were exceptionally reproducible, and minimal problems were encountered.

Participation of Iodide

Qualitatively, iodide had essentially the same effect on the chronopotentiometry of the system as bromide. The anodic wave fell at about -0.3 volts vs. S.C.E. and a second current reversal yielded a wave corresponding to the reduction of the iodopentaquochromium(III) complex. As was the case for bromide, the hexaquochromium(II) - iodopentaquochromium(III) couple behaved very reversibly. However, the data for iodide participation

were completely irreproducible. The values of transition times, transition time ratios, and the potentials at which waves occurred differed radically between trials carried out under apparently identical conditions.

An important systematic effect was in operation. The data of Table II illustrate the results obtained.

II. Chronopotentiometry of Iodide-Catalyzed Chromium(II) Oxidation

Trial	$E_{rev.}$ (v. vs.SCE)	$E_{1/4}^{Cr^{+3};CrI^{+2}}$	$E_{.215}^{CrI^{+2};Cr^{+3}}$	$\tau_{Cr^{+3};CrI^{+2}}/\tau_{CrI^{+2};Cr^{+3}}$
1	-0.82	-0.40	-*	∞
2	-0.82	-0.40	-	∞
3	-0.82	-0.36	-	∞
4	-0.86	-0.34	-	11.1
5	-0.88	-0.30	-	8.5
6	-0.90	-0.29	-	5.3
7	-0.90	-0.29	-	5.3
8	-0.93	-0.27	-0.25	4.2
9	-0.93	-0.28	-0.26	4.4
10	-0.94	-0.27	-0.24	4.0
11	-0.94	-0.26	-0.24	3.3

*Wave too short to allow measurement of $E_{.215}$.

All trials at 595 $\mu A/cm^2$

The $E_{rev.}$ column lists the potential at which the first current reversal was made during the initial cathodic wave. Clearly the potential of chromium(III) reduction was fluctuating over a range of over 0.1 volts, and apparently these variations influenced all subsequent behavior of a given trial. A strongly negative potential for the initial cathodic wave was invariably followed by an exceptionally positive position for the anodic wave. Finally, the ratio between the transition time for the anodic wave and that for the iodopentaquo complex reduction wave (an inverse measure of the current efficiency of the chromium(II) oxidation with inclusion) was smallest for strongly negative initial cathodic waves. Exactly the opposite relationship held for positively oriented chromium(III) reduction waves. The trials reported in Table II were performed in a random order unrelated to their positions on the chart. Also, the first current reversal was made long before a chromium(III) transition time so the value of $E_{rev.}$ is a good measure of the chromium(III) reduction potential throughout the first cathodic wave.

Not only is it difficult to explain the random fluctuations from trial to trial in this potential, but the impact of these variations is also unexpected. Apparently, the anodic waves which occur at the most positive potentials and are thus least catalyzed represent reactions of the highest current efficiency for chromium(II) oxidation with inclusion. It is reasonable

to speculate that these effects are associated with the strong adsorption of iodide onto mercury, but no explanation is offered.

Bromide-Chloride Mixtures

An experiment was performed with both bromide and chloride present in excess of the chromium(II) generated. Experiments of this type are of interest because chromium(II) is expected to form more stable complexes with chloride than bromide. On the other hand, bromide is more strongly adsorbed onto mercury than is chloride. Under conditions where all the chromium(II) can go by either the bromide or the chloride route, a strong preference for one or the other would supply evidence for either the adsorption mechanism or the complex formation mechanism depending on the favored route. Although the anodic chromium(II) wave falls in the same position for bromide catalysis as for chloride participation, behavior of the system on second reversal depends entirely on which route is used for the oxidation. Chloropentaquochromium(III) gives a cathodic wave at -0.66 volts vs. S.C.E. which is only barely separable from that of the hexaquo ion. The bromo complex, however, gives a clear cathodic wave at about -0.40 volts vs. S.C.E. In the trials with both ligands present the ratio between the transition time for the anodic wave and that for the bromo complex reduction, ranged from five to eight with most values falling consistently between six and seven. This departure from the ratio of 3.5 observed in solutions where excess bromide was the only ligand present indicates clearly that a significant percentage of the chromium(II) is oxidized by the chloride route when both ligands are present. A chloropentaquochromium(III) reduction wave was, in fact, directly observable although it mixed badly with background. No more quantitative an interpretation is possible, but it is at least certain that the oxidation proceeded by mixed paths. A similar experiment was attempted with a mixture of chloride and iodide present, but the unpredictable nature of the iodide catalysis made it difficult to tell which route was dominant.

Participation of Fluoride

With excess fluoride present during the anodic wave, a value of $E_{1/4}$ = +0.15 volts vs. S.C.E. was observed. This is 150 millivolts more positive than the value obtained in solutions with no ligands present. Clearly, under the experimental conditions, fluoride does not enhance the oxidation of chromium(II). Furthermore, the potential for hexaquochromium(III) reduction was at -1.1 volts vs. S.C.E. as compared with the usual cathodic wave position

of -0.85 volts vs. S.C.E. Although the reduction potential was at such strongly negative values, no interference from hydrogen evolution was observed. Qualitatively, the result can be interpreted as a large increase in the overpotential for both the anodic and cathodic reactions. No explanation of the mechanism can be offered.

One factor which must be considered in the interpretation of the data for fluoride, acetate, succinate, and oxalate is that the ions are all conjugate bases of weak acids and affect the hydrogen ion concentration of their solutions. In the case of dilute perchloric acid solutions of hexaquochromium(III), the problem is complicated by the acidic character of the hydrated chromium ions. The hydrogen ion concentration was not monitored in these experiments so the most meaningful statement that can be made about the pH is that it is at 2.6 or above for the solutions of these ions. Concentrations were sufficiently low that major changes in the pH should not have occurred.

Participation of Thiocyanate

The behavior of the system in the presence of excess thiocyanate indicated that the ligand strongly catalyzes the oxidation of chromium(II) and that at least two different products of the reaction involve included thiocyanate ions. The anodic wave was split into two distinct sections, one with a quarter-wave potential of -0.62 volts vs. S.C.E. and the other with a value of about -0.44 volts. On reversal at the transition time for the second segment of the anodic wave, a double cathodic wave resulted with values of $E_{.215}$ that corresponded exactly ~~with~~ to the anodic quarter-wave potentials. Apparently the oxidized forms of two reversible couples are formed during the anodic wave. Current reversal during the first section of the anodic wave gave a transition time ratio between the anodic and cathodic waves of four or five. The second couple could not be studied in the same way because the waves were not clearly defined enough to allow transition time measurements.

Effects of Acetate, Sulfate, Oxalate, and Succinate

Experiments with the ligands acetate, sulfate, and oxalate all gave similar results. Each anion caused the anodic wave to move to a catalyzed potential, but in no case was a second reversal wave observed corresponding to the reduction of an inclusion product. The anodic waves in the presence of excess sulfate and acetate were identical. Values for $E_{1/4}$ were -0.20 volts vs. S.C.E. in both cases, representing the significant catalytic potential shift 0.2 volts. The oxalate results were the most striking. An average

quarter-wave potential of -0.56 volts vs. S.C.E. was observed. This corresponds to a greater potential shift than that caused by any of the halides. Only thiocyanate, of the ligands studied, shifted the anodic wave to more negative potentials. Finally, the experiments in the presence of excess succinate gave an anodic wave with $E_{1/4}$ = -.03 volts vs. S.C.E. It was the single anion ~~found~~ studied that left the chromium(II) oxidation potential unchanged. At the pH of these experiments, succinate apparently does not participate in the electrode reaction.

The overall results of the experiments are summarized in Table III.

III. Summary of Experimental Results

Ligand	$E_{1/4}$ for Anodic Wave (volts vs. S.C.E.)	Behavior on Second Current Reversal
none	0.00	Direct Rise to $Cr(H_2O)_6^{+++}$ Reduction Potential
succinate	-0.03	" " " " " "
acetate	-0.20	" " " " " "
sulfate	-0.20	" " " " " "
oxalate	-0.56	" " " " " "
chloride	-0.36	An indistinct $CrCl^{++}$ wave at $E_{.215}$ = -0.66 volts vs. S.C.E.
bromide	-0.35	A clearly defined $CrBr^{++}$ wave at $E_{.215}$ = -0.36 volts vs. S.C.E. $i_{an.}/i_{ca.}$ = 3.5
iodide	-0.25 to -0.40	An Irreproducible CrI^{++} wave at $E_{.215}$ = -0.25 volts vs. S.C.E. $i_{an.}/i_{ca.}$ ranged from 3.3 to ∞.
fluoride	+0.15	Direct rise to exceptionally large $Cr(H_2O)_6^{+++}$ reduction potential of -1.1 volts vs. S.C.E.
thiocyanate	-0.62 and -0.44	A double wave corresponding to the reversible reduction of the products of the split anodic wave.

A wide variety of behavior was observed for the chromium(II) - chromium(III) couple depending on the ligands present during the experiment. The results can be considered as a meaningful survey of the effects of the anions on the oxidation reaction. The method used has the advantage of conveniently providing the kind of data presented in Table III for any given ligand. Its principal drawback is that the presence of a bulk hexaquochromium(III) concentration in the solution restricts the observation of oxidation products to chromium(III) complexes that are more easily reduced than the hexaquo

ion. This disadvantage could be eliminated by performing chronopotentiometry directly on chromium(II) solutions, but the experiments would be considerably less convenient to perform.

The most important results were the data for bromide, iodide, and thiocyanate. The evidence presented for the inclusion of bromide and iodide during the oxidation, although only semi-quantitative, is the most direct support available for the proposition. The discovery that thiocyanate is also included offers a new system for studying the oxidation mechanism, and the observation of a large catalytic effect by oxalate similarly opens up another new area of possible interest.

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