

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

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It has been shown that many ligands dramatically affect the electrochemical oxidation of Cr(II). Pecsok and Lingane (1) have investigated the polarographic behavior of Cr(II) in the presence of KCl, KSCN, CaCl₂, Me₄NBr, and several carboxylic acids. Large changes in apparent half-wave potential and in the degree of irreversibility of the oxidation were found by changing the nature of the supporting electrolyte solution.

Kemula and Rakowska (2), who studied the reduction of various Cr(III) species using cyclic voltammetry, showed that CrCl²⁺ is formed when Cr(II) is oxidized at a hanging mercury drop electrode in chloride solution.

Aikens and Ross (3) have studied the rates of oxidation of Cr(II) at mercury electrodes in the presence of fluoride, chloride, and iodide. They found that the rate of Cr(II) oxidation is proportional to the concentration of chloride over a fifty-fold change in chloride concentration, and that at a fixed potential, the accelerating effect of the halides decreases in the order (I⁻) > (Cl⁻) > (F⁻), the effect of fluoride being very small. They point out that the tendency for specific adsorption of halides also decreases in this order, while the stability of the Cr(II) complexes probably increases markedly in the same order.

Cr(III) is sufficiently inert to chloride substitution that the reaction $\text{Cr}^{3+} + \text{Cl}^- \rightarrow \text{CrCl}^{2+}$ may be ignored as a source of the complex CrCl²⁺. Therefore if the product of electro-oxidation of Cr(II) in chloride solutions is CrCl²⁺ the transition state must contain chloride. This in turn implies that the reaction mechanism is halide-bridged electron transfer (or halide atom transfer). Jones and Anson (4) have carried out exhaustive controlled potential electrolyses of Cr(II) solutions at a stirred mercury pool electrode in the presence of chloride. They found that when the initial chloride to Cr(II) ratio is less than or equal to one, no free chloride is found in the product solution, and when the initial chloride to Cr(II) ratio is greater than one the amount of chloride found is equal to the initial excess of chloride over Cr(II). This proves that the ligand-bridge mechanism obtains in that case.

We have studied this reaction further using chronopotentiometry to show that the formation of CrCl²⁺ in the oxidation of Cr(II) is quantitative when microcoulomb quantities of Cr(II) are oxidized as well as in mass electrolysis, to see if there is reactant adsorption, and to see if the reacting species is CrCl⁺.

The ratio of forward to reverse transition times was found to be three for oxidation of Cr(II) in solution containing excess chloride followed by reduction of generated CrCl²⁺. This demonstrates that CrCl²⁺ is the sole product of the oxidation.

Constancy of the chronopotentiometric constant with change in current density placed an upper limit of $1 \mu\text{C}/\text{cm}^2$ on the amount of reactant adsorbed on the electrode.

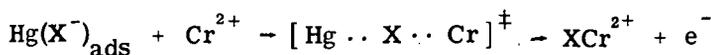
A lower limit of $500 \text{ sec}^{-\frac{1}{2}}$ was found for the quantity $k_f(k_f+k_b)^{\frac{1}{2}}/k_b$, where these constants are the forward and back pseudo-first-order rate constants for the reaction $\text{Cr}^{2+} + \text{Cl}^- = \text{CrCl}^+$ in 0.5 F chloride solution. The spectroscopic measurements of Pecsok and Bjerrum (5) place an upper limit of 5×10^{-4} l/mole on the equilibrium constant for this reaction. Combination of these two quantities places a lower limit of 10^{12} sec^{-1} on the quantity $k_f + k_b$. This limit is sufficiently high that it rules out prior complex formation as an important feature of the mechanism.

The effect of bromide on the oxidation of Cr(II) is qualitatively similar to that of chloride. Polarographic measurements of the rate of reduction of CrBr^{2+} and the rate of oxidation of Cr(II) in the presence of bromide show that the standard potential for the reaction $\text{Cr}^{2+} + \text{Br}^- = \text{CrBr}^{2+} + e^-$ is -0.500 v. vs. SCE and the pseudo-first-order standard rate constant is $1.85 \times 10^{-3} \text{ cm/sec}$. The apparent transfer coefficient obtained from the anodic reaction in the region -0.500 to -0.300 v. vs. SCE is 0.21 and that obtained from the cathodic reaction in the region -0.500 to -0.600 v. vs. SCE is 0.48. These values are uncorrected for double layer. The corresponding values for the reaction $\text{Cr}^{2+} = \text{Cr}^{3+} + e^-$ obtained from both the anodic and cathodic reactions are $0.74 \times 10^{-5} \text{ cm/sec}$ and 0.63. The standard potential is -0.650 v. vs. SCE.

Using these rate parameters one can show that the bromide-independent and bromide-dependent oxidations should proceed at roughly comparable rates over a wide range of potential and bromide concentration. Because of the potential dependence of the relative current efficiencies for the two reactions, a controlled potential technique, double potential step chronocoulometry (6), was chosen to study the reaction. An equation was derived which gives the coulombic yields for the two reaction pathways as a function of the kinetic parameters and experimental conditions (7). Calculations showed that under conditions where the oxidation of Cr(II) is diffusion controlled the product should be almost entirely CrBr^{2+} . This result was confirmed by double potential step chronocoulometric data.

The oxidation of Cr(II) in the presence of iodide is more difficult to study because the reaction occurs at potentials near that for depolarization of mercury. Cyclic voltammetry at slow sweep rates in solutions with constant iodide concentration and varying amounts of Cr(II) demonstrated that the product of Cr(II) oxidation is CrI^{2+} . Exhaustive electrolysis at -0.192 v. vs. SCE of Cr(II) solutions containing chloride and iodide were carried out to determine the product distribution between CrCl^{2+} and CrI^{2+} . The results obtained were in good agreement with values calculated from the rates of the competing reactions.

We conclude from these investigations that the oxidation of Cr(II) at mercury electrodes in the presence of chloride, bromide, or iodide proceeds via the mechanism



This mechanism undoubtedly also obtains for many other ligands which are adsorbed on mercury and for many other transition metal ions.

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