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Low-Temperature Electrochemical Studies of Unstable Species. Pentacarbonylhalochromium(I) System

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Pentacarbonyliodochromium(I), $Cr(CO)_5I$, is unstable at room temperature in acetone solution, but it may be stabilized at low temperatures (−78°C). Its chemistry is dominated by two modes of reaction—oxidation of substrates and disproportionation. A detailed electrochemical study of these reactions has been undertaken, using especially the techniques of cyclic and normal-pulse voltammetry. The corresponding bromo and chloro complexes of chromium(I) have been shown to be considerably less stable than $Cr(CO)_5I$.

Introduction

In ESR, NMR, and other techniques of physical measurement, the use of low temperatures has been extensively exploited with great advantage. Electrochemistry, while now quite widely employed in investigations of inorganic complexes, has predominately been undertaken at ambient temperatures and has therefore been restricted to studies of complexes that are stable in solution at about 20°C. Furthermore, all of the low-temperature electrochemical studies reported so far have been based on the measurement and interpretation of current–potential curves of stable complexes rather than for monitoring concentrations of species that can only be studied at low temperatures. The ease and utility of undertaking low-temperature electrochemistry for investigation of kinetic phenomena associated with electrode processes is adequately demonstrated in the literature.[1–6] In the present work we wish to show how the properties of reactive and unstable complexes can be conveniently studied by low-temperature electrochemistry, particularly via the method of pulse voltammetry at platinum electrodes. At low temperatures, one of the inherent difficulties associated with electrochemical investigations is the ohmic *IR* drop. However, the sigmoidal-shaped-pulse voltammograms have a limiting-current region which is both linearly dependent on concentration for diffusion-controlled reactions and independent of uncompensated resistances. This combination of properties makes the technique eminently suitable for low-temperature electrochemistry as will be demonstrated in the present work on $Cr(CO)_5X$ complexes.

Pentacarbonyliodochromium(I) was first prepared by Behrens and Zizlsperger[7] by the stepwise oxidation of $[Cr_2(CO)_{10}]^{2-}$ with iodine first to $[Cr(CO)_5I]^-$ (yellow) and then to $Cr(CO)_5I$ (blue). In a recent electrochemical study[8] of the $[M(CO)_5X]^-$ series [M = Cr, Mo, W; X = Cl, Br, I] we showed that the couple $[Cr(CO)_5X]^-$–$Cr(CO)_5X$ was completely reversible on the electrochemical time scale for all of the halogens and suggested that the chloro and bromo derivatives analogous to $Cr(CO)_5I$ could be synthesized.

This present study shows that $Cr(CO)_5I$ is unstable at room temperature on the preparative time scale in acetone solution but that it is stable at −78°C in acetone solution. Electrochemical studies of its reactions at −78°C and its decomposition with increasing temperature are described. The corresponding bromo and chloro complexes are progressively even more unstable.

Experimental Section

Instrumentation. Electrochemical measurements were performed in acetone with a Princeton Applied Research Corp. Model 174 polarographic analyzer. The working and auxiliary electrodes were platinum disks and the reference electrode was Ag–AgCl (0.1 *M* LiCl; acetone) separated from the test solution via a salt bridge containing 0.1 *M* Et_4NClO_4. Low temperatures of −78°C were achieved by thermostating the electrochemical cell with an acetone–dry ice mixture. The supporting electrolyte was a saturated solution of Et_4NClO_4 and positive feedback circuitry was used to minimize the *IR* drop losses for all measurements. All solutions were degassed with argon prior to recording the voltammograms.

Preparations. $[Cr(CO)_5X]^-$ anions (X = Cl, Br, I) were prepared as their tetraethylammonium salts by the method of Abel et al.[9] $Cr(CO)_5I$ was prepared by the following procedure. $Et_4N[Cr(CO)_5I]$ (0.5 g) was dissolved in acetone (20 ml) and the solution was degassed using nitrogen and cooled to −78°C in an acetone–dry ice bath. A saturated solution of $KMnO_4$ in acetone–aqueous H_2SO_4 was prepared and this solution was added to the $[Cr(CO)_5I]^-$ solution. An intense deep blue color formed immediately. After a few minutes the vessel containing the solution was transferred to an ice bath and connected to a vacuum line. On pumping, the blue $Cr(CO)_5I$ and some acetone distilled over and were collected in a trap cooled in liquid nitrogen. The distillation was continued until the residue in the reaction flask turned red (due to the presence of excess $KMnO_4$). The trap which contained the distilled material was transferred to an acetone–dry ice bath and a beautiful blue solution of $Cr(CO)_5I$ was obtained as the solvent melted. This solution is air stable at −78°C.

$Cr(CO)_5Br$ and $Cr(CO)_5Cl$ are too unstable to be distilled (see text) so these compounds were prepared in situ by adding bromine and chlorine to $[Cr(CO)_5Br]^-$ and $[Cr(CO)_5Cl]^-$, respectively, at −78°C in acetone solution. $NO^+PF_6^-$ may also be used in these cases and this is probably the more convenient method.

Results and Discussion

(a) $Cr(CO)_5I$. Behrens and Zizlsperger[7] have shown that a variety of oxidants, including iodine, may be used to convert $[Cr(CO)_5I]^-$ to $Cr(CO)_5I$ and electrochemical evidence[8] suggested a fairly powerful oxidant was required. Although iodine was confirmed as being capable of oxidizing $[Cr(CO)_5I]^-$ in acetone or aqueous media, we preferred to avoid its use because of the possibility of iodine subliming with the product. In addition, later evidence (see below) showed that the reaction

$$[Cr(CO)_5I]^- + {}^1/_2I_2 \rightleftharpoons Cr(CO)_5I + I^-$$

is actually an equilibrium which further mitigates against the use of iodine. $KMnO_4$ and $NO^+PF_6^-$ were found to be excellent oxidants for $[Cr(CO)_5I]^-$; $KMnO_4$ was finally selected because of the possibility of volatile impurities from the $NO^+PF_6^-$ reaction.

Blue solutions of $Cr(CO)_5I$ in acetone were obtained as described in the Experimental Section. These solutions are stable at −78°C, but the compound decomposes rapidly as the solutions are warmed toward room temperature. Because of this instability $Cr(CO)_5I$ could not be isolated as a solid by this method of preparation so its identity was not established by conventional analysis, but it was identified unambiguously by its electrochemical behavior. Figure 1 is a cyclic voltammogram obtained with the blue solution at −78°C. Comparison with Figure 4 of ref 8 will show that the peak potentials are identical with that obtained by electrochemical oxidation of $[Cr(CO)_5I]^-$, thus confirming the identity of the compound as $Cr(CO)_5I$. This result depends upon the

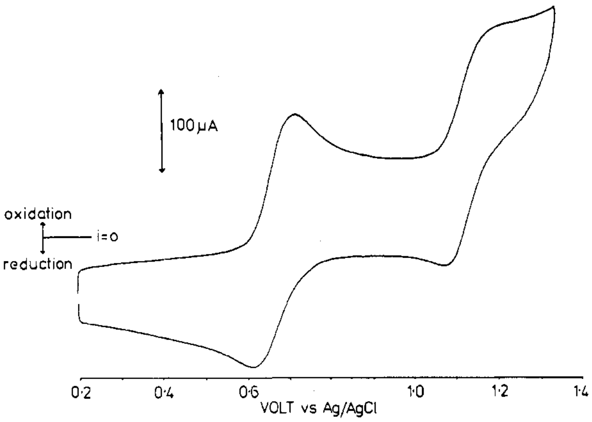

Figure 1. Cyclic voltammogram of a $Cr(CO)_5I$ solution in acetone at −78°C; scan rate 200 mV/sec.

demonstrated[8] reversibility at low temperatures of the reactions

$$[Cr(CO)_5I]^- \rightleftharpoons Cr(CO)_5I + e^-$$
$$Cr(CO)_5I \rightleftharpoons [Cr(CO)_5I]^+ + e^-$$

Attempts were made to substitute $Cr(CO)_5I$ with several tertiary phosphines and arsines including triphenylphosphine, bis(diphenylphosphino)methane, dpm, 1,2-bis(diphenylphosphino)ethane, dpe, and their arsenic analogues. In each case the blue solution of $Cr(CO)_5I$ at −78°C immediately turned yellow, and, after subsequent evaporation of the solvent, the resulting solid gave an infrared spectrum in the carbonyl region indicative of the formation of $[Cr(CO)_5I]^-$. In the case of triphenylphosphine it was shown that the solid also exhibited a very strong band at about 1100 cm^{-1}, attributed to a phosphorus–oxygen stretch, which suggests oxidation of the phosphine had occurred with subsequent coordination of PPh_3O. Infrared evidence suggested that the final product with excess triphenylphosphine was $Cr(CO)_5PPh_3$.[10]

The reaction with triphenylphosphine was then followed in detail by electrochemistry. A blue solution of $Cr(CO)_5I$ was prepared as described above and small aliquots from a very dilute solution of PPh_3 in acetone at −78°C were added. Figure 2 shows the pulse voltammograms at platinum electrodes observed as successive amounts of phosphine were added and the colors of the solutions are also noted. It is obvious that the wave heights remained unchanged (i.e., the total chromium concentrations are unchanged), but the color changed from blue ($Cr(CO)_5I$) to yellow ($[Cr(CO)_5I]^-$). The additional peak in the last voltammogram at about 0.5 V is due to excess PPh_3 in the solution. Thus the reaction between $Cr(CO)_5I$ and PPh_3 in acetone is a simple redox reaction giving $[Cr(CO)_5I]^-$ and PPh_3O.

As noted above, acetone solutions of $Cr(CO)_5I$ are unstable at temperatures approaching room temperature. On warming of such a solution from −78°C, the color changes progressively from blue, to dark green, to pale green, and finally to yellow. The infrared spectrum of this yellow solution suggested that it contained the $[Cr(CO)_5I]^-$ ion and this was confirmed by recooling the solution, adding further $KMnO_4$, and regenerating blue $Cr(CO)_5I$. However, as this cyclic process was repeated, it became obvious that steadily decreasing amounts of $Cr(CO)_5I$ and $[Cr(CO)_5I]^-$ were produced at each change, suggesting therefore that $Cr(CO)_5I$ disproportionates to $[Cr(CO)_5I]^-$ and some other product rather than being merely reduced to $[Cr(CO)_5I]^-$ on warming the solution (cf. PPh_3 reaction).

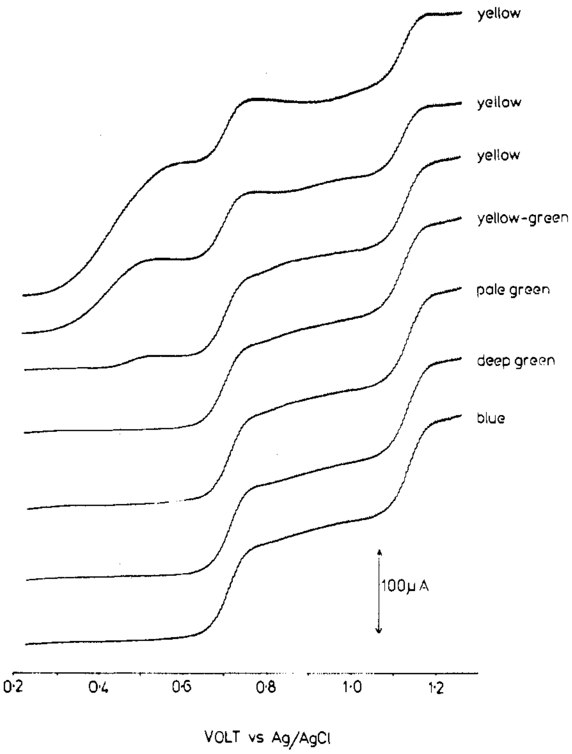

Figure 2. Pulse voltammogram of an initially blue solution of $Cr(CO)_5I$ in acetone at −78°C with successive additions of dilute PPh_3 solution.

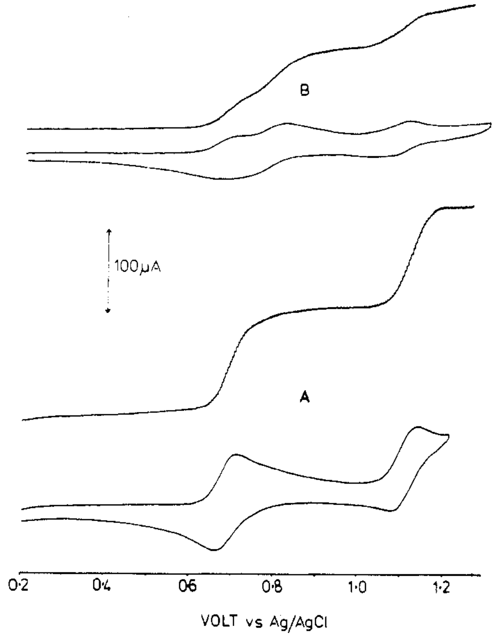

Figure 3. Pulse and cyclic voltammograms at −78°C of (A) the blue $Cr(CO)_5I$ solution and (B) the yellow solution of $[Cr(CO)_5I]^-$ formed by disproportionation of the original $Cr(CO)_5I$. Scan rate is 200 mV/sec for cyclic voltammetry and 1 mV/sec for normal-pulse voltammetry.

The reaction was then followed electrochemically. A blue solution of $Cr(CO)_5I$ was prepared as described above and its cyclic and pulse voltammograms were determined as shown in Figure 3A. The solution was then allowed to warm slowly, the color gradually changed from blue, to green, and to yellow as the temperature (measured using an alcohol thermometer) increased, and cyclic and pulsed voltammograms were recorded at approximately 5°C intervals. The solution was finally warmed to 35°C. It was apparent that the first wave in the cyclic voltammogram was gradually reduced in height but it was also distorted by a second wave appearing at about 0.77 V as the decomposition proceeded. The Cr(I)–Cr(II) wave (1.24 V) is not reversible at higher temperatures[8] and becomes very distorted. Thus in order to compare the electrochemical data before and after decomposition the fully decomposed solution was recooled to −78°C (to make the wave at 1.24 V reversible) and the voltammograms of the decomposed solution are shown in Figure 3B. It is difficult to make comparisons on the basis of the first wave because of the distortion due to the new feature at 0.77 V, but the second waves before and after decomposition are strictly comparable. Accurate measurement of the limiting current of the pulsed voltammograms shows a decrease in current *exactly* in the ratio 2:1. Thus it can be said that $\mathrm{Cr(CO)_5I}$ disproportionates in acetone solution according to the equation

$$2\mathrm{Cr(CO)_5I} \rightarrow [\mathrm{Cr(CO)_5I}]^- + \underset{\substack{\downarrow\\ \text{other products}}}{[\mathrm{Cr(CO)_5I}]^+}$$

The final chromium(II) species has not been identified. The solutions studied were dilute and after concentration by evaporation the only carbonyl-containing species detected by infrared spectroscopy was $[\mathrm{Cr(CO)_5I}]^-$. It is possible that the $[\mathrm{Cr(CO)_5I}]^+$ initially formed (and previously shown[8] to be unstable in acetone) reacts with the solvent to form $[\mathrm{Cr(solv)}_x]^{2+}$.

Solvent clearly plays an important role in the decomposition of $\mathrm{Cr(CO)_5I}$. We have prepared solutions of the compound in *n*-hexane which are reasonably stable at room temperature, but they immediately decomposed forming $[\mathrm{Cr(CO)_5I}]^-$ on pouring into acetone. Thermodynamic calculations based on previous data[8] show that the equilibrium for the disproportion reaction

$$2\mathrm{Cr(CO)_5I} \rightleftharpoons [\mathrm{Cr(CO)_5I}]^- + [\mathrm{Cr(CO)_5I}]^+$$

lies to the left, so the driving force for the disproportionation (if it occurs by this mechanism) is the instability of $[\mathrm{Cr(CO)_5I}]^+$ or its reaction with solvent, traces of moisture, etc.

The reaction between $\mathrm{Cr(CO)_5I}$ and $\mathrm{Et_4NI}$ in acetone at −78°C was also investigated in the hope of obtaining dihalo anions of the type $[\mathrm{Cr(CO)_4I_2}]^-$. However, this did not occur and instead the $\mathrm{Cr(CO)_5I}$ instantaneously oxidized the iodide to iodine as evidenced by the appearance of an additional wave attributable to iodine in the cyclic voltammogram. Intentional addition of iodine to the system confirmed the electrochemical assignment. Thus the reaction

$$[\mathrm{Cr(CO)_5I}]^- + {}^1\!/_2\mathrm{I_2} \rightleftharpoons \mathrm{Cr(CO)_5I} + \mathrm{I^-}$$

is a true equilibrium.

It is interesting to compare these results on $\mathrm{Cr(CO)_5I}$ with those obtained by other workers using similar systems. Pickett and Pletcher[11] have examined the electrochemical oxidation of $\mathrm{Cr(CO)_6}$ and showed the presence of the simple carbonyl cation $\mathrm{Cr(CO)_6^+}$ which is isoelectronic with $\mathrm{Cr(CO)_5I}$. The electrochemical behavior and thermal decomposition of $\mathrm{Cr(CO)_6^+}$ to $\mathrm{Cr(CO)_6}$ and a chromium(II) species are strictly analogous to the behavior of $\mathrm{Cr(CO)_5I}$.

Ruff[12] failed to observe oxidation of $[\mathrm{Cr(CO)_5I}]^-$ with iodine at 0°C. We believe this result is associated with the equilibrium nature of the $\mathrm{Cr(CO)_5I^-} + \mathrm{I_2} \rightleftarrows \mathrm{Cr(CO)_5I} + 2\mathrm{I^-}$ reaction and the fact that excess of iodine could be removed as the triiodide anion in this system.

(b) $\mathrm{Cr(CO)_5Br}$. Bromopentacarbonylchromium(I) is far less stable on the preparative time scale than its iodo analogue. Reaction of $[\mathrm{Cr(CO)_5Br}]^-$ with $\mathrm{Br_2}$ at −78°C did produce orange $\mathrm{Cr(CO)_5Br}$ which was identified by its electrochemical behavior[8]. However the compound could not be sublimed under the same conditions as used successfully for the iodo complex and the compound was not isolated. In situ monitoring of its reactions was therefore necessary. Oxidation of $[\mathrm{Cr(CO)_5Br}]^-$ with $\mathrm{NO^+PF_6^-}$ in acetone at −78°C also produced $\mathrm{Cr(CO)_5Br}$ and electrochemical monitoring of the decomposition pathway was possible. On allowing the $\mathrm{Cr(CO)_5Br}$ solution to warm up to about −40°C, complete decomposition of $\mathrm{Cr(CO)_5Br}$ occurred. When excess $\mathrm{NO^+PF_6^-}$ was present, complete elimination of $\mathrm{Cr(CO)_5Br}$ and $[\mathrm{Cr(CO)_5Br}]^-$ from the system occurred very rapidly due to the cyclic reaction

$$[\mathrm{Cr(CO)_5Br}]^- + \mathrm{NOPF_6} \rightarrow$$

$$\begin{tikzcd} \mathrm{Cr(CO)_5Br} \arrow[r, "\text{fast}"] & {[\mathrm{Cr(CO)_5Br}]^-} \arrow[l, bend left, "\mathrm{NOPF_6}"] & + & {[\mathrm{Cr(CO)_5Br}]^+} \arrow[d, "\text{(unstable)}"'] \\ & & & \text{products} \end{tikzcd}$$

Reactions with $\mathrm{Cr(CO)_5Br}$ are qualitatively the same as for the iodo complex, but its greater instability prohibited quantitative studies of the kind made with the iodo complex.

(c) $\mathrm{Cr(CO)_5Cl}$. The $\mathrm{Cr(CO)_5Cl}$ complex was found to be extremely unstable on the preparative time scale even at −78°C, and the disproportionation is too rapid to enable complete characterization of the species. Thus the reaction using $\mathrm{NOPF_6}$ and $[\mathrm{Cr(CO)_5Cl}]^-$ does not stop at the neutral chromium(I) species but proceeds directly to higher oxidation state species, presumably by a cyclic process similar to that described for the bromo analogue. A clear trend is therefore established in terms of stability: $\mathrm{Cr(CO)_5I} > \mathrm{Cr(CO)_5Br} > \mathrm{Cr(CO)_5Cl}$.

Conclusions

The present work has shown that the 17-electron species $\mathrm{Cr(CO)_5X}$ (X = Cl, Br, I) are both reactive and unstable in acetone. They readily oxidize ligands commonly used in carbonyl substitution reactions. The instability is associated with disproportionation to give the $[\mathrm{Cr(CO)_5X}]^-$ species and an oxidation state II species. The final product is not $[\mathrm{Cr(CO)_5X}]^+$. The instability trend with the iodo complex most stable and the chloro complex least stable parallels the stability trend also observed in the halocarbonyl anions $[\mathrm{Cr(CO)_5X}]^-$.

Finally it may be noted that the detailed investigation of the chromium system described here lends considerable support for the decomposition mechanism proposed[8] for the corresponding molybdenum and tungsten $\mathrm{M(CO)_5X}$ species which are so unstable that they cannot be seen even on the electrochemical time scale.

Registry No. $\mathrm{Cr(CO)_5I}$, 14911-59-2; $[\mathrm{Cr(CO)_5I}]^-$, 14911-71-8; $\mathrm{Cr(CO)_5Br}$, 14911-60-5; $[\mathrm{Cr(CO)_5Br}]^-$, 14911-72-9; $\mathrm{Cr(CO)_5Cl}$, 15226-15-0; $[\mathrm{Cr(CO)_5Cl}]^-$, 14911-56-9.

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