J. Am. Chem. Soc. 1986, 108, 3352–3358

Electrochemical Oxidation of [Dibenzo-18-crown-6-K][$Cr(CO)_5F$] and $Cr(CO)_6$: Characterization of [$Cr(CO)_6$]$^+$ and Its Substitution Reactions with Fluoride and Trifluoroacetate

R. N. Bagchi,[1] A. M. Bond,*[1] R. Colton,[2] D. L. Luscombe,[1] and J. E. Moir[1]

Contribution from the Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds, 3217 Victoria, Australia, and the Department of Inorganic Chemistry, University of Melbourne, Parkville, 3052 Victoria, Australia. *Received August 13, 1985*

Abstract: Electrochemical oxidation of the carbonyl fluoride complex [dibenzo-18-crown-6-K][$Cr(CO)_5F$] has been studied in dichloromethane, acetone, and acetonitrile to establish whether electrochemical synthesis of relatively rare higher oxidation state carbonyl fluoride complexes may be achieved. Thermodynamically, $Cr(CO)_5F$ is more stable than $Cr(CO)_5X$ (X = Cl, Br, I) but kinetically more reactive. At −70 °C, the formally chromium I complex $Cr(CO)_5F$ is moderately stable on the synthetic time scale in dichloromethane, while the formally chromium(II) species [$Cr(CO)_5F$]$^+$ can be observed on the electrochemical time scale at the same temperature. ESR data indicate that $Cr(CO)_5F$ decomposes to the very reactive 17-electron species [$Cr(CO)_6$]$^+$ which is only moderately stable in dichloromethane at −70 °C. [$Cr(CO)_6$]$^+$ can also be identified as a product of controlled potential electrolysis of $Cr(CO)_6$ in dichloromethane at −80 °C by a well-defined ESR spectrum consisting of a strong line from the ^{52}Cr ($I = 0$) nucleus and four weaker lines from the less abundant ^{53}Cr nucleus ($I = {}^3/_2$). The data contrast to some literature reports suggesting that $Cr(CO)_6$ cannot be oxidized in dichloromethane prior to the solvent limit and to data in acetonitrile where a broad ESR signal with a comparatively low g value has been reported. Oxidation of $Cr(CO)_6$ in the presence of fluoride does not lead to formation of $Cr(CO)_5F$ or [$Cr(CO)_5F$]$^+$. Instead, evidence for formation of a bridged complex of the kind $Cr_2(CO)_{10}(\mu\text{-}F)$ has been obtained. A reinvestigation of oxidation of $Cr(CO)_6$ in the presence of trifluoroacetate demonstrates that the previously noted report of irreversibility cannot be explained by ligand substitution and concomitant slow electron transfer. Rather, the reversible one-electron oxidation step is transformed into a chemically irreversible two-electron oxidation process involving complete loss of carbon monoxide. On the basis of the above data, prospects for electrochemical methods of synthesis of the relatively rare carbonyl fluoride complexes are discussed and successfully applied to the synthesis of $Mo(CO)_2(dpe)_2F$ by electrochemical oxidation of *cis*-$Mo(CO)_2(dpe)_2$ in the presence of fluoride (dpe = 1,2-bis(diphenylphosphino)ethane).

The chemistry of complexes where halide (chloride, bromide, and iodide) and carbonyl ligands are both bonded to a transition metal has been studied extensively as perusal of ref 3–12 would indicate. In contrast, comparatively few carbonyl fluorides are known. Indeed, early review articles implied they may not exist.[13] However, work in the last 10 years has proved that carbonyl fluoride complexes can be synthesized.[14–19] Thus, $Mo(CO)_4F_2$, $W(CO)_4F_2$, $Re(CO)_5F$, etc., are well-documented, but examples in the literature are still relatively few.

Although the electrochemistry of the group 6B pentacarbonyl halide anions [$M(CO)_5X$]$^-$ (M = Cr, Mo, W; X = Cl, Br, I) has been previously examined,[20,21] studies on analogous carbonyl fluorides have not been reported. Oxidation of [$Cr(CO)_5F$]$^-$ will be considered in this paper. Fluoride, being an electronegative element (σ-donor), favors the formation of high oxidation state complexes. Carbon monoxide (π-acceptor), by comparison, favors formation of low oxidation state complexes. In view of this substantially differing preference for high and low oxidation states, electrochemical studies could be expected to enhance the understanding of the stability and/or reactivity of carbonyl fluorides.

To study the influence of fluoride as a ligand when oxidizing [$Cr(CO)_5F$]$^-$, it turned out that the electrochemistry of the parent carbonyl $Cr(CO)_6$ needed to be reinvestigated. While formation of [$Cr(CO)_6$]$^+$ seems well-substantiated in solvents such as acetonitrile,[22,23] in dichloromethane some workers have claimed that no oxidation step is observed prior to the solvent limit[24] whereas an oxidation process complicated by surface phenomena has been described in another report.[25] Molten salt media[26] also provide stabilization of [$Cr(CO)_6$]$^+$. Interestingly, the ESR spectrum of [$Cr(CO)_6$]$^+$ is reported to be very broad, with a low g value,[22] in contrast to the relatively sharp signals observed with some of the well-characterized 17-electron substituted chromium carbonyl complexes. [$Cr(CO)_6$]$^+$ is of course expected to be highly reactive and is known to be prone to disproportionation.[22,23] Kochi et al.[27] have also observed that electrochemical oxidation of $Cr(CO)_6$ in acetonitrile leads to a substitution labile product. Intuitively, [$Cr(CO)_6$]$^+$ is expected to be more stable in a noncoordinating solvent, so that simple, well-defined electrochemistry reported in acetonitrile contrasted with the reported complex or absence of

---

(1) Deakin University.

(2) University of Melbourne.

(3) Abel, E. W.; Butler, I. S.; Reid, I. G. *J. Chem. Soc.* **1963**, 2068.

(4) Bennett, M. A.; Clark, R. J. H. *J. Chem. Soc.* **1964**, 5560.

(5) King, R. B. *Inorg. Chem.* **1964**, *3*, 1039.

(6) Murdoch, H. D. *J. Organomet. Chem.* **1965**, *4*, 119.

(7) Fischer, E. O.; Ofele, K. *Chem. Ber.* **1960**, *93*, 1156.

(8) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *Chem. Ind.* **1960**, 442.

(9) Paddock, N. L.; Ranganathan, T. N.; Wingfield, J. N. *J. Chem. Soc., Dalton Trans.* **1972**, 1578.

(10) Calhoun, H. P.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1974**, 377.

(11) Murdoch, H. D.; Henzi, R. *J. Organomet. Chem.* **1966**, *5*, 166.

(12) Wilkinson, G., Ed. *Comprehensive Organometallic Chemistry*; Pergammon Press: Oxford, 1982; Vol. 3.

(13) Abel, E. W.; Stone, F. G. A. *Q. Rev., Chem. Soc.* **1970**, *24*, 498.

(14) Kemmitt, R. D. W.; Peacock, R. D.; Wilson, I. L. *Chem. Commun.* **1968**, 772.

(15) Cihonski, J. L.; Levenson, R. A. *Inorg. Chem.* **1975**, *14*, 1717.

(16) Marshall, C. J.; Peacock, R. D.; Russell, D. R.; Wilson, I. L. *Chem. Commun.* **1970**, 1643.

(17) O'Donnell, T. A.; Phillips, K. A. *Inorg. Chem.* **1970**, *9*, 2611.

(18) Douglas, W.; Ruff, J. K. *J. Organomet. Chem.* **1974**, *65*, 65.

(19) O'Donnell, T. A.; Phillips, K. A.; Waugh, A. B. *Inorg. Chem.* **1973**, *12*, 1435.

(20) Bond, A. M.; Bowden, J. A.; Colton, R. *Inorg. Chem.* **1974**, *13*, 602.

(21) Bond, A. M.; Colton, R. *Inorg. Chem.* **1976**, *15*, 446.

(22) Pickett C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879.

(23) Seurat, A.; Lemoine, P.; Gross, M. *Electrochim. Acta* **1980**, *25*, 675.

(24) Cook, R. L.; Morse, J. G. *Inorg. Chem.* **1984**, *23*, 2332.

(25) Bond, A. M.; Carr, S. W.; Colton, R.; Kelly, D. P. *Inorg. Chem.* **1983**, *22*, 989.

(26) Sahami, S.; Osteryoung, R. A. *Electrochim. Acta* **1985**, *30*, 143.

(27) Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790.

0002-7863/86/1508-3352$01.50/0

processes in the noncoordinating solvent, dichloromethane, is surprising.

In addition to investigating possible anomalies in the literature it was felt that if fluoride is present, in situ, during the course of oxidative electrolysis of a carbonyl compound in a noncoordinating solvent that the possibility of possible replacement of carbon monoxide by fluoride ion exists. Kochi et al.[27] have already presented data in acetonitrile for oxidation of $Cr(CO)_6$ in the presence of anionic ligands such as trifluoroacetate. The irreversible electrochemistry observed in the presence of trifluoroacetate was explained by these authors in terms of slow electron transfer accompanying substitution of $[Cr(CO)_6]^+$ but it is not clear why the rate of electron transfer should be affected. Fluoride may be expected to act in an analogous fashion to trifluoroacetate, with respect to substitution. The mechanism of any substitution and variation of rate of electron transfer for both fluoride and trifluoroacetate has therefore been examined in addition to undertaking further investigations on the properties of the $[Cr(CO)_6]^{+/0}$ redox couple.

Fluoride, unlike chloride, bromide, and iodide, is not readily oxidized to the corresponding halogen. Consequently, application of the relatively positive potentials required to oxidize $Cr(CO)_6$ (1.46V vs SCE in acetonitrile[22]) will not give rise to simultaneous oxidation of $Cr(CO)_6$ and the fluoride ligand. Electrochemical oxidation of carbonyl compounds is therefore suggested to provide a systematic approach to synthesis of carbonyl fluoride complexes. An example of this synthetic route is presented with respect to electrochemical synthesis of $Mo(CO)_2(dpe)_2F$ (dpe = 1,2-bis(diphenylphosphino)ethane) since chromium carbonyl fluoride complexes formed via oxidation of $Cr(CO)_6$ in the presence of fluoride were too reactive to isolate.

Experimental Section

Reagents. Dibenzo-18-crown-6 (EGA-CHEMIE), tetraethylammonium fluoride (Fluka AG), chromium hexacarbonyl (Pressure Chemical Co), lithium trifluoroacetate (Alfa Products), and lithium acetate (BDH) and other compounds were used as supplied by the manufacturer except for drying under vacuum.

Tetraethylammonium perchlorate and tetra-*n*-butylammonium perchlorate (G. Frederick Smith Chemical Co.) were dried, in vacuo, at 60 °C for 4 h prior to use.

Solvents. All solvents were of either Analytical or HPLC grade and were used as supplied except for drying with standard procedures.[28]

Synthesis. All preparations were carried out under a nitrogen atmosphere in a Labconco 50004 Controlled Atmosphere Glovebox. All solvents were degassed with nitrogen prior to use.

(i) [Dibenzo-18-crown-6-K][$Cr(CO)_5X$] (X = F, Cl, Br, I). The method of preparation was based on that of Cihonski and Levenson.[15]

Chromium hexacarbonyl (1.7 mmol), dibenzo-18-crown-6 (2.7 mmol), and the potassium halide salt (3.4 mmol) in 40 mL of tetrahydrofuran and 40 mL of dichloromethane were irradiated with a Phillips HPK 125W mercury lamp for 4 h. The resulting yellow-orange solution was cooled on dry ice for 30 min and then quickly filtered. To the filtrate was added petroleum ether (bp 40–60 °C) to precipitate the crude product. Typical yields were of the order of 30–40% following recrystallization from dichloromethane/petroleum ether. All compounds synthesized were stored under nitrogen, in the dark at 0 °C.

(ii) $Mo(CO)_2(dpe)_2$ was prepared according to the literature method.[29]

Instrumentation. (a) Electrochemical. (i) General. All electrochemical experiments were performed in a Labconco Controlled Atmosphere Glovebox under nitrogen.

(ii) Cyclic and Rotating Disc Electrode Voltammetry. Cyclic voltammograms were recorded on a Bioanalytical Systems Inc. BAS CV-27 Cyclic Voltammograph. Working electrodes used were BAS platinum (Pt), gold (Au), and glassy carbon (GC) electrodes. A platinum wire auxiliary electrode was used in all experiments, and the reference Ag/AgCl (saturated LiCl in ethanol) was separated from the test solution by a salt bridge containing the same solvent and supporting electrolyte. A metrohm Rotating Disc Electrode Assembly (628-10) was used with Metrohm Electrodes for all rotating disc electrode voltammetry. Supporting electrolytes used were 0.1 M tetraethylammonium perchlorate in acetone and acetonitrile and 0.1 M tetra-*n*-butylammonium perchlorate in dichloromethane at 20 °C. At the lower temperatures of −70 °C saturated solutions of electrolyte were used.

Oxidation of a 1×10^{-3} M ferrocene solution in the appropriate solvent was used as a calibration standard throughout the course of this work.

(iii) Coulometry and Controlled Potential Electrolysis. Controlled potential electrolysis experiments were undertaken with a Princeton Applied Research PAR 173 Potentiostat/Galvanostat fitted with a PAR 179 digital coulometer. A platinum gauze basket was used as the working electrode, together with a platinum gauze auxiliary electrode separated from the test solution by a salt bridge containing the same solvent/supporting electrolyte as the test solution. The reference electrode used was the same as for the voltammetry.

(b) Electron Spin Resonance. Electron spin resonance data were obtained by using an X-band reflection type spectrometer employing 100 kHz modulation.[30] The oxidized 17-electron carbonyl compounds were generated in situ, using the PAR 173 Potentiostat/Galvanostat and electrochemical cell consisting of platinum working, platinum auxiliary and Ag/AgCl reference electrodes.[31]

(c) Infrared Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer in the range 2500–1700 cm^{-1} with use of NaCl cells. All spectra were recorded in degassed chloroform and calibrated against the polystyrene 1602-cm^{-1} peak. For the $[Cr(CO)_5X]^-$ complexes, infrared spectra were consistent with literature values.[15]

Results and Discussion

(a) General. As described in the Experimental Section, all of the complexes were isolated as yellow diamagnetic solids which were stable in air for short periods of time. The solution stability showed a general trend I > Br > Cl > F and dichloromethane > acetone > acetonitrile. The stability of $[Cr(CO)_5F]^-$ in dichloromethane and acetone was found to be markedly increased at lower temperatures, and much of the experimental data were obtained at −70 °C rather than at ambient temperatures.

(b) Electrochemistry of Dibenzo-18-crown-6. The compounds of interest in this study contain a crown ether in the cation. In acetonitrile on platinum electrodes, dibenzo-18-crown-6 exhibits an irreversible oxidation process involving strong adsorption at a potential of about +1.5 V vs. Ag/AgCl. Upon repeated scans the electrode response is found to become inhibited. Le Berre et al.[32] have previously reported that the oxidation of dibenzo-18-crown-6 leads to the formation of a polymeric film on the electrode surface. The responses on gold and glassy carbon electrodes occur at a similar potential to that on platinum but very somewhat in detail.

Fortunately, the oxidation of the crown ether occurs at very positive potentials (+1.4 V vs. Ag/AgCl) in all solvents and does not interfere with the electrochemistry of [dibenzo-18-crown-6-K][$Cr(CO)_5X$] (X = F, Cl, Br, I).

(c) Electrochemistry of [Dibenzo-18-crown-6-K][$Cr(CO)_5F$]. Two well-defined one-electron oxidation processes are observed under conditions of cyclic and rotating disk voltammetry (Figure 1) for [dibenzo-18-crown-6-K][$Cr(CO)_5F$]. The first process remains chemically reversible under all conditions (Table I) and data are essentially independent of electrode material (Pt, Au, glassy carbon) and solvent (dichloromethane, acetone, acetonitrile). This process can be defined as

$$[Cr(CO)_5F]^- \rightleftharpoons Cr(CO)_5F + e^- \qquad (1)$$

Deliberate addition of fluoride does not alter the electrochemical response nor does the deliberate addition of carbon monoxide. Results are essentially independent of concentration, except for evidence of ohmic (*iR*) drop at higher concentrations.

The second process is chemically irreversible at room temperature (Table I). However, at −70 °C the second oxidation process is also a chemically reversible one-electron step in both

---

(28) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergammon Press: Oxford, 1966.

(29) (a) Chatt, J.; Watson, H. R. *J. Chem. Soc.* **1961**, 4980. (b) Zingales, F.; Canziani, F. *Gazz. Chim. Ital.* **1962**, *92*, 343.

(30) Anderson, J. E.; Bagchi, R. N.; Bond, A. M.; Greenhill, H. B.; Henderson, T. L. E.; Walter, F. L. *Am. Lab.* (*Fairfield, Conn.*) **1981**, *13* (2), 21.

(31) Bagchi, R. N.; Bond, A. M.; Brain, G.; Colton, R.; Henderson, T. L. E.; Kevekordes, J. E. *Organometallics* **1984**, *3*, 4.

(32) Le Berre, V.; Carlier, R.; Tallec, A.; Simonet, J. *J. Electroanal. Chem.* **1982**, *143*, 425.

Table I. Cyclic Voltammetric Data[a] for Oxidation of 5×10^{-4} M [Dibenzo-18-crown-6-K][$Cr(CO)_5X$] (X = F, Cl, Br, I) at a Scan Rate of 200 mV s^{-1}

			first oxidation process			second oxidation process		
complex	electrode	solvent	$(E_p^{ox})_1$ (V)	$(E_p^{red})_1$ (V)	$(E^{r}_{1/2})_1$ (V)	$(E_p^{ox})_2$ (V)	$(E_p^{red})_2$ (V)	$(E^{r}_{1/2})_2$ (V)
$[Cr(CO)_5F]^-$	Pt	DCM	0.50	0.44	0.47	1.11	1.01[b]	1.06[b]
		Ac	0.60	0.53	0.57	1.06	0.97[b]	1.02[b]
		MeCN	0.54	0.47	0.50	1.03	*c*	*c*
	Au	DCM	0.51	0.42	0.47	1.12	*c*	*c*
		Ac	0.62	0.53	0.58	1.08	*c*	*c*
		MeCN	0.55	0.46	0.51	1.03	*c*	*c*
	G.C.	DCM	0.51	0.44	0.47	1.10	*c*	*c*
		MeCN	0.55	0.47	0.51	1.04	*c*	*c*
$[Cr(CO)_5Cl]^-$	Pt	DCM	0.51	0.42	0.47	1.10	0.99[b]	1.05
		Ac	0.63	0.55	0.59	1.08	1.00[b]	1.04
		MeCN	0.56	0.48	0.52	1.05	*c*	*c*
	Au	DCM	0.50	0.42	0.46	1.10	*c*	*c*
		Ac	0.64	0.57	0.61	1.10	*c*	*c*
		MeCN	0.56	0.46	0.51	1.13	*c*	*c*
	G.C.	DCM	0.52	0.43	0.48	1.10	*c*	*c*
		Ac	0.63	0.55	0.59	1.11	*c*	*c*
		MeCN	0.57	0.46	0.52	1.03	*c*	*c*
$[Cr(CO)_5Br]^-$	Pt	DCM	0.54	0.44	0.49	1.18	1.07[b]	1.13
		Ac	0.67	0.56	0.61	1.08	1.00[b]	1.04
		MeCN	0.60	0.52	0.56	1.09	*c*	*c*
	Au	DCM	0.54	0.44	0.49	1.18	*c*	*c*
		Ac	0.64	0.57	0.61	1.10	*c*	*c*
		MeCN	0.59	0.51	0.55	1.10	*c*	*c*
	G.C.	DCM	0.54	0.43	0.49	1.18	*c*	*c*
		Ac	0.64	0.56	0.60	1.10	*c*	*c*
		MeCN	0.59	0.52	0.56	1.10	*c*	*c*
$[Cr(CO)_5I]^-$	Pt	DCM	0.55	0.45	0.50	1.22	1.10[b]	1.16
		Ac	0.71	0.64	0.68	1.16	1.08[b]	1.12
		MeCN	0.62	0.54	0.58	1.15	*c*	*c*
	Au	DCM	0.56	0.47	0.51	1.18	*c*	*c*
		Ac	0.66	0.60	0.63	1.09	*c*	*c*
		MeCN	0.63	0.56	0.59	1.16	*c*	*c*
	G.C.	DCM	0.55	0.46	0.50	1.18	*c*	*c*
		Ac	0.67	0.60	0.63	1.09	*c*	*c*
		MeCN	0.63	0.56	0.59	1.16	*c*	*c*

[a] All potentials V vs. Ag/AgCl. $E^{r}_{1/2}$ for oxidation of 10^{-3}M ferrocene = 0.49 V (DCM), 0.61 V (Ac), 0.54 V (MeCN). [b] Data obtained at −78 °C. All other data obtained at 20 °C. [c] Chemically irreversible process with no reduction peak on reverse scan at stated temperature and scan rate. DCM dichloromethane, Ac = acetone, MeCN = acetonitrile, G.C. = glassy carbon. Electrode $(E_p^{ox})_n$ = peak oxidation potential for process n (n = 1, 2) $(E_p^{red})_n$ = peak reduction potential for process n (n = 1, 2).

acetone and dichloromethane. Thus the second process at low temperature is

$$Cr(CO)_5F \rightarrow Cr(CO)_5F^+ + e^- \quad (2)$$

At room temperature in dichloromethane, the second step is essentially independent of both fluoride and carbon monoxide concentration. In acetonitrile, however, the second process is modified by the addition of the carbon monoxide. The appearance of a shoulder on the second wave is probably due to a solvent-substituted species being formed. This would not be expected for dichloromethane as the coordinating ability of this solvent is very poor.

Controlled potential electrolysis at potentials more positive than the second oxidation wave is consistent with a two-electron oxidation in dichloromethane, acetone, or acetonitrile and no evidence for coordinated carbon monoxide could be found after the electrolysis. The room-temperature data at positive potentials can be explained by the overall process

$$[Cr(CO)_5F]^- \rightarrow Cr^{2+} + F^- + 5CO + 2e^- \quad (3)$$

Chemical oxidation with $NOPF_6$ in dichloromethane at −70 °C yields a yellow solution of $Cr(CO)_5F$. In situ monitoring of this reaction via rotating disc voltammetry (Figure 1) confirms the formation of the neutral chromium(I) species. The instability in solution was evidenced by a change from yellow to colorless after a few minutes. $[Cr(CO)_5F]^-$ is reformed after decomposition and a gas, assumed to be carbon monoxide, is evolved. At ambient temperatures, no electrochemical or infrared evidence could be obtained for formation of a carbonyl fluoride. Coulometric data at potentials in the limiting current region of the first wave are consistent with a two-electron oxidation. This fact and low-temperature data suggest that disproportionation occurs on longer time scales.

$$2Cr(CO)_5F \rightarrow [Cr(CO)_5F]^- + Cr^{2+} + 5CO + F^- \quad (4)$$

Electrochemical data for the complexes $[(CH_3CH_2)_4N][Cr(CO)_5X]^-$ (X = Cl, Br, I) have been reported.[20,21] The overall behavior of the fluoride is very similar to that of the other halides, except that the fluoride complex is far more reactive.

(d) Electrochemistry of [Dibenzo-18-crown-6-K][$Cr(CO)_5X$] (X = Cl, Br, I). Table I also summarizes the electrochemical data for the oxidation of the crown ether complexes of $[Cr(CO)_5X]^-$ (X = Cl, Br, I). The ease of oxidation shows a trend with the order of $(E^{r}_{1/2})_1$ being

$$[Cr(CO)_5F]^- > [Cr(CO)_5Cl]^- > [Cr(CO)_5Br]^- > [Cr(CO)_5I]^-$$

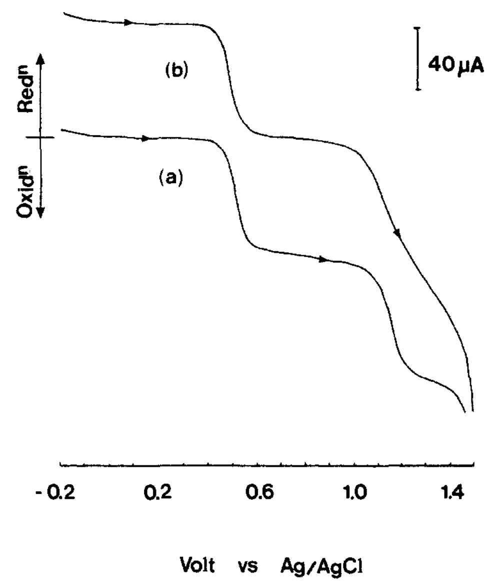

Figure 1. Rotating disc voltammograms of 10^{-3} M [dibenzo-18-crown-6-K][Cr(CO)$_5$F] in dichloromethane (saturated Bu$_4$NClO$_4$) on a glassy carbon electrode: (a) before oxidation with NOPF$_6$; (b) after oxidation with NOPF$_6$. Scan rate of 20 mV/s; temperature -70 °C; rotation rate 2000 rpm.

as would be expected from simple electronegativity arguments. Alternatively, this may be interpreted as a correlation between the donor/acceptor nature of the halide ligands and the oxidation potentials. The ligands in this type of substituted carbonyl complex may affect the highest occupied molecular orbital (HOMO) of the complexes in two ways:[24] (i) the energy of the π-type HOMO may be modified indirectly by the Lewis base σ-donation of the ligand, or (ii) if the ligand has vacant orbitals capable of participating in π-back bonding, then a lowering of the HOMO energy would result. Hence a net corresponding increase in the oxidation potential would be observed.

The halide ions have filled p-orbitals. However, except for the fluoride ion they have empty d-orbitals. Fluoride, an exclusive σ-donor, with no available d-orbitals for back-donation, would therefore be expected to have the least positive oxidation potential, as is observed. The decreasing ability for σ donation and availability of empty d-orbitals for back-donation accounts for the trend observed for Cl^-, Br^-, and I^-.

In summary, thermodynamically, Cr(CO)$_5$F is more stable than the other halides in the sense that less energy is required for its formation via oxidation. However, kinetically, it is the most reactive.

(e) **Electron Spin Resonance.** The neutral chromium(I) species Cr(CO)$_5$F is considered to be a 17-electron paramagnetic species that may generate an ESR signal, although none was reported for the related Cr(CO)$_5$I species.[33] If coupling occurs with fluorine ($I = {}^1/_2$) a doublet may be observed.

In situ electrolysis of [Cr(CO)$_5$F]$^-$ in dichloromethane at -80 °C occurs slowly and generated two single line signals of unequal intensity with g values of 1.982 and 1.969, rather than the expected doublet. This indicates that they arise from two different paramagnetic species. Both of these signals vanish at increased temperature. Coupling may not be observed because of (i) rapid electron exchange of Cr(CO)$_5$F with [Cr(CO)$_5$F]$^-$ as is the case with the mer-[Cr(CO)$_3$P$_3$]$^{+/0}$ system (P = phosphorus ligand)[34] and because (ii) the coupling constant is too small, or for other reasons.

The one-electron oxidation to produce Cr(CO)$_5$F described in eq 1 is obviously not the only reaction occurring, as it is necessary to account for the second ESR signal. Oxidation of Cr(CO)$_6$ generates the 17-electron species [Cr(CO)$_6$]$^+$. In situ electrolysis in dichloromethane at -80 °C generated the signal shown in Figure 2. This signal also disappears as the temperature is raised to 0 °C. Chromium exists as two isotopes, ^{52}Cr ($I = 0$) and ^{53}Cr ($I = {}^3/_2$). Hence the central intense signal at $g = 1.982$ can be attributed to ^{52}Cr and the four satellite features to ^{53}Cr. The spectrum is characterized by a small line width, indicating isotropic g-value which is consistent with octahedral symmetry. The coupling constant, A_{Cr}, is 2.16 mT at -80 °C. The differing intensities are due to the natural abundances of ^{52}Cr:^{53}Cr. viz. 90.45%:9.55%. The signal assigned to [^{52}Cr(CO)$_6$]$^+$ corresponds, within experimental error, to one of the signals obtained in the electrolysis of [Cr(CO)$_5$F]$^-$. Therefore, the peak of $g = 1.969$ can be assigned to Cr(CO)$_5$F. Consequently, on the time scale of preparative electrolysis the oxidation mechanism must account for the generation of [Cr(CO)$_6$]$^+$ as a product.

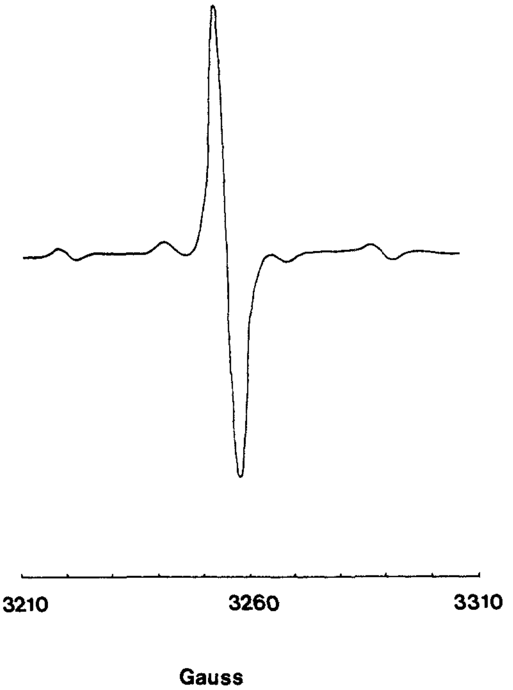

Figure 2. ESR spectra obtained from in situ electrolysis of Cr(CO)$_6$ in dichloromethane (saturated Bu$_4$NClO$_4$) at -80 °C.

A reaction scheme of the kind

$$[Cr(CO)_5F]^- \rightarrow Cr(CO)_5F + e^- \qquad (5a)$$

$$2[Cr(CO)_5F] \rightarrow [Cr(CO)_5F]^+ + [Cr(CO)_5F]^- \qquad (5b)$$

$$[Cr(CO)_5F]^+ \rightarrow Cr^{2+} + F^- + 5CO \qquad (5c)$$

$$Cr(CO)_5F + CO \rightarrow [Cr(CO)_6]^+ + F^- \qquad (5d)$$

is consistent with all of the available data, including the chemical oxidation with NOPF$_6$, which is considerably more rapid than the controlled potential electrolysis experiments. Pickett and Pletcher[22] reported an ESR spectra for [Cr(CO)$_6$]$^+$ in acetonitrile. The signal they obtained was extremely broad ($\simeq$1000 mT) in contrast to the very sharp (0.5 mT) signal obtained in dichloromethane. Also they did not observe any chromium coupling, and the g value of 1.842 differs considerably from the value of 1.989 obtained in this study. Comparison with data reported for other chromium (I) complexes as summarized in ref 35 indicates that the g and A_{Cr} values obtained in dichloromethane for [Cr(CO)$_6$]$^+$ are as expected. For example, the complex [Cr(C$_{10}$H$_8$)]$^+$ has a g value of 1.986 and A_{Cr} is 1.82 mT. Finally, deliberate addition of acetonitrile to a dichloromethane solution containing [Cr(CO)$_6$]$^+$ leads to rapid decay of the ESR spectrum and appearance of a broad signal as reported by Pickett and Pletcher. The broad

---

(33) Symons, M. C. R.; Bratt, S. W.; Wyatt, J. L. *J. Chem. Soc., Dalton Trans.* **1982**, 991.

(34) Bond, A. M.; Carr, S. W.; Colton, R. *Inorg. Chem.* **1984**, *23*, 2343.

(35) Lappert, M. F.; McCabe, R. W.; MacQuitty, J. J.; Pye, P. L.; Riley, P. I. *J. Chem. Soc.,Dalton Trans.* **1980**, 90.

Table II. Cyclic Voltammetric Data[a] for Oxidation of $Cr(CO)_6$ at 20 °C

				first oxidation process			second oxidation process
solvent	electrode	concn (M)	scan rate (mV s^{-1})	$(E_p^{ox})_1$ (V)	$(E_p^{red})_1$ (V)	$(E^r_{1/2})_1$ (V)	$(E_p^{ox})_2$[b] (V)
MeCN	Pt	5×10^{-3}	100	1.61	1.48	1.55	2.15
			200	1.59	1.42	1.50	2.24
			200	1.62	1.35	1.48	2.29
		5×10^{-4}	200	1.62	1.48	1.55	2.15
		1×10^{-4}	200	1.62	1.49	1.56	2.24
		1×10^{-4}	200	1.62	1.50	1.56	2.20
	G.C.	5×10^{-3}	200	1.62	1.49	1.55	2.04
		5×10^{-4}	200	1.62	1.50	1.56	2.01
		1×10^{-4}	200	1.61	1.50	1.56	2.01
		1×10^{-5}	200	1.61	1.52	1.56	2.02
	Au[c]	5×10^{-3}	200	1.66			2.12
DCM[d,e]	Pt	5×10^{-3}	200	1.86	1.44	1.65	
		5×10^{-4}	200	1.83	1.58	1.70	
		1×10^{-4}	200	1.84	1.56	1.70	
		1×10^{-5}	200	1.83	1.58	1.70	
	G.C.	5×10^{-3}	200	1.84	1.53	1.68	
		5×10^{-4}	200	1.83	1.52	1.68	
		1×10^{-4}	200	1.84	1.54	1.69	
		1×10^{-5}	200	1.84	1.52	1.68	

[a] All potentials V vs. Ag/AgCl. [b] Chemically irreversible process. [c] Complex behavior observed consistent with strong adsorption. [d] Wave shape not consistent with a simple diffusion controlled reversible oxidation process. Evidence for adsorption noted. [e] Second oxidation process is observed as a shoulder on solvent limit for oxidation in dichloromethane when high concentrations of $Cr(CO)_6$ are used. Other symbols as in Table I.

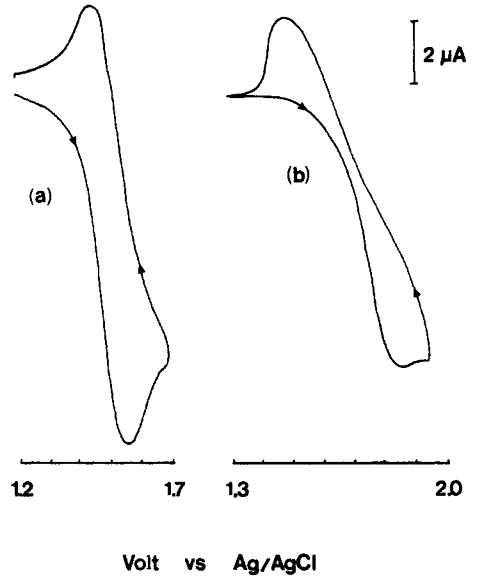

Figure 3. Cyclic voltammograms for oxidation of 10^{-3} M $Cr(CO)_6$ on a Pt electrode. First oxidation process shown only: (a) acetonitrile (0.1 M Et_4NClO_4); (b) dichloromethane (0.1 M Bu_4NClO_4). Scan rate 200 mV/s; temperature 20 °C.

signal is not believed to be due to $[Cr(CO)_6]^+$. More likely this is due to a complex formed by reaction of $[Cr(CO)_6]^+$ with acetonitrile such as $[Cr(CO)_5CH_3CN]^+$. The large line width is consistent with a large *g* anisotropy commonly associated with solution spectra of low symmetry.

(f) Electrochemistry of $Cr(CO)_6$. Results are summarized in Table II. In acetonitrile, two well-defined oxidation waves are observed on Pt electrodes in agreement with Pickett and Pletcher.[22] On Au, the response is characterized by significant adsorption. In dichloromethane, the first process at a platinum electrode appears complex and is also characterized by strong adsorption (Figure 3). The second oxidation process in dichloromethane is masked by the solvent oxidation. The observed electrochemistry in dichloromethane is in contrast to that of Cook and Moorse,[24] who could not observe a response in dichloromethane. However, provided dry solvents are used, the oxidation process is clearly observable, and ESR data at low temperatures (see previous discussion) support the formation of $[Cr(CO)_6]^+$.

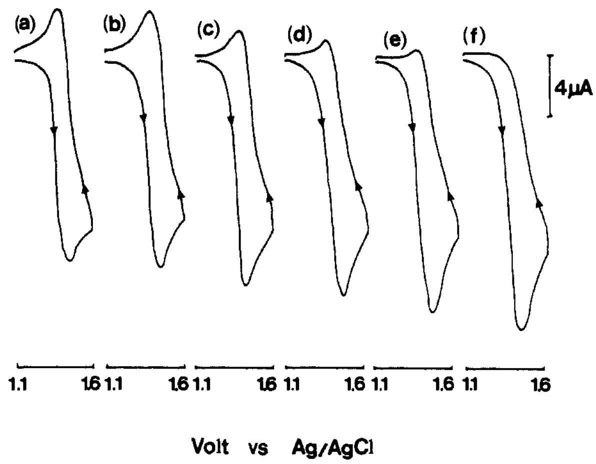

Figure 4. Cyclic voltammograms for the first oxidation wave of $Cr(CO)_6$ in acetonitrile (0.1 M Et_4NClO_4) at a platinum electrode, showing the effect of successive additions of LiTFA: (a) 10^{-3} M $Cr(CO)_6$; (b) 10^{-3} M $Cr(CO)_6$ + 1.0 mL of 10^{-2} M LiTFA; (c) 10^{-3} M $Cr(CO)_6$ + 2.0 mL of 10^{-2} M LiTFA; (d) 10^{-3} M $Cr(CO)_6$ + 3.0 mL of 10^{-2} M LiTFA; (e) 10^{-3} M $Cr(CO)_6$ + 4.0 mL of 10^{-2} M LiTFA; (f) 10^{-3} M $Cr(CO)_6$ + 5.0 mL of 10^{-2} M LiTFA. Scan rate 200 mV/s; temperature 20 °C; initial cell volume 10 mL.

The first oxidation step can be explained by the reaction

$$Cr(CO)_6 \rightarrow [Cr(CO)_6]^+ + e^- \tag{6}$$

Klinger and Kochi[27] have indicated that $[Cr(CO)_6]^+$ may be kinetically labile. In demonstrating this, they provided data for the first oxidation process in the presence of lithium trifluoroacetate (LiTFA) or lithium acetate (LiAc) and attributed the reaction to the sequence

$$Cr(CO)_6 \rightarrow [Cr(CO)_6]^+ + e^-$$

$$Cr(CO)_6^+ + TFA^- \rightarrow Cr(CO)_5(TFA) + CO \tag{7}$$

If a simple EC mechanism is operative with reversible charge transfer, then theoretically the oxidation process should show a small shift to less positive potentials on addition of TFA^-. Suprisingly Klinger and Kochi reported a large shift (200 mV) to more positive potentials, which they attributed to a decrease in

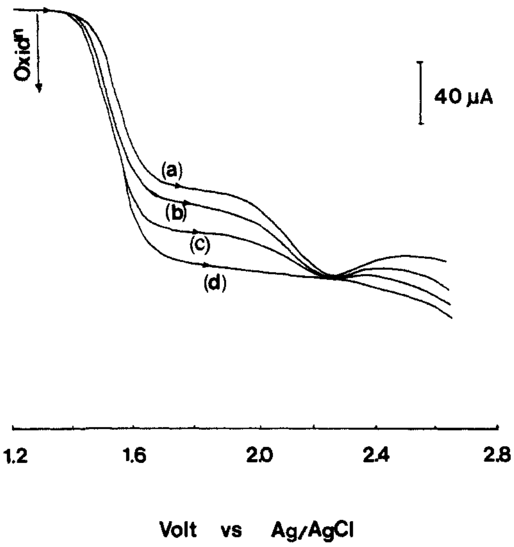

Figure 5. Rotating disc voltammograms for oxidation of Cr(CO)$_6$ in acetonitrile (0.1 M Et_4NClO_4) on a glassy carbon electrode: (a) 10^{-3} M Cr(CO)$_6$; (b) 10^{-3} M Cr(CO)$_6$ + 2.0 mL of 10^{-2} M LiTFA; (c) 10^{-3} M Cr(CO)$_6$ + 4.0 mL of 10^{-2} M LiTFA; (d) 10^{-3} M Cr(CO)$_6$ + 6.0 mL of 10^{-2} M LiTFA. Scan rate 10 mV/s; temperature 20 °C; rotation rate 2000 rpm; initial cell volume 10 mL.

the rate of electron transfer accompanying irreversibility. In view of this apparent anomaly, the work of Klinger and Kochi was repeated.

Figure 4 shows the effect of the addition of LiTFA on the first oxidation wave of Cr(CO)$_6$ in acetonitrile. Within experimental error (±20 mV), *no* potential shift was observed on addition to TFA$^-$. However, a significant increase in the height of the oxidation peak occurs, as does a decrease in the peak height of the reduction peak observed on reserve scans of the cyclic voltammogram. Data are more easily interpreted by rotating disc voltammetry (Figure 5). It can be seen that the limiting current of the first oxidation process is transformed from a one-electron to a two-electron process, concomitant with the disappearance of the second oxidation process.

This behavior can be explained if the substituted species Cr(CO)$_5$(TFA) is oxidized at less positive potentials than for oxidation of Cr(CO)$_6$. Since TFA$^-$ is an anionic ligand, as is F$^-$, this is possible since the process $Cr(CO)_5F \rightarrow [Cr(CO)_5F]^+ + e^-$ occur at less positive potentials than $Cr(CO)_6 \rightarrow Cr(CO)_6{}^+ + e^-$. Under this circumstance, the overall process can be described by eq 8 to 11.

$$Cr(CO)_6 \rightarrow Cr(CO)_6{}^+ + e^- \tag{8}$$

$$Cr(CO)_6{}^+ + TFA^- \rightarrow Cr(CO)_5(TFA) + CO \tag{9}$$

$$Cr(CO)_5(TFA) \rightarrow [Cr(CO)_5(TFA)]^+ + e^- \tag{10}$$

Then by analogy to eq 3

$$[Cr(CO)_5(TFA)]^+ \rightarrow Cr^{2+} + TFA^- + 5CO \tag{11}$$

Alternatively, Cr(CO)$_5$(TFA) may simply disproportionate as is the case with many 17-e complexes

$$2Cr(CO)_5\,TFA \rightarrow Cr(CO)_5\,TFA^- + Cr^{2+} + 5CO + TFA^- \tag{12}$$

This would also lead to an observed two-electron oxidation.

If fluoride is present in situ, instead of TFA$^-$, a similar substitution reaction may be expected to occur, although it should be noted from the ESR data that CO may replace F$^-$, rather than the reverse. Figure 6 shows successive additions of fluoride monitored by platinum rotating disc voltammetry in acetonitrile. A comparison of Figures 5 and 6 indicates that the reactions occurring for the fluoride are different from those for trifluoroacetate. In order to explain the significant decreases in the limiting current on addition of fluoride, some form of mechanism involving interaction between reactants and products must be operative. Possible examples would be

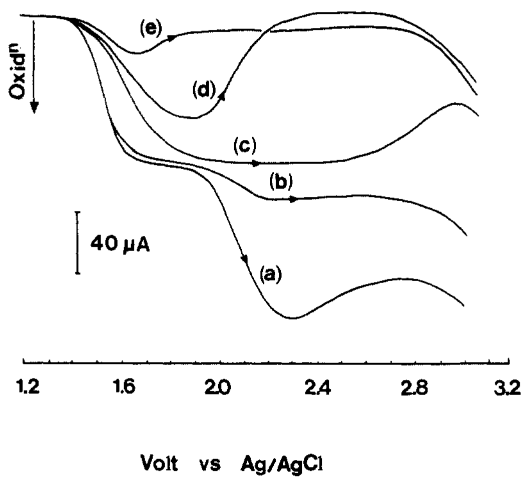

Figure 6. Rotating disc voltammograms for oxidation of Cr(CO)$_6$ in acetonitrile (0.1 M Et_4NClO_4) on a glassy carbon electrode in the presence of Et_4NF (TEAF): (a) 10^{-3} M Cr(CO)$_6$; (b) 10^{-3} M Cr(CO)$_6$ + 1.0 mL of 10^{-2} M TEAF; (c) 10^{-3} M Cr(CO)$_6$ + 2.0 mL of 10^{-2} M TEAF; (d) 10^{-3} M Cr(CO)$_6$ + 3.0 mL of 10^{-2} M TEAF; (e) 10^{-3} M Cr(CO)$_6$ + 4.0 mL of 10^{-2} M TEAF. Scan rate 10 mV/s; temperature 20 °C; rotation rate 2000 rpm; initial cell volume 10 mL.

$$Cr(CO)_6 \rightarrow [Cr(CO)_6]^+ + e^-$$

$$[Cr(CO)_6]^+ + F^- \rightleftharpoons Cr(CO)_5F + CO \tag{13}$$

$$Cr(CO)_5F \rightarrow [Cr(CO)_5F]^+ + e^- \tag{14}$$

$$[Cr(CO)_5F]^+ + 2Cr(CO)_6 + F^- \rightarrow [Cr_2(CO)_{10}(\mu\text{-}F)] + 2CO + Cr(CO)_5F \tag{15}$$

alternatively

$$[Cr(CO)_6]^+ + Cr(CO)_6 + F^- \rightarrow [Cr_2(CO)_{10}(\mu\text{-}F)] + 2CO \tag{16}$$

The dimeric species $Cr_2(CO)_{10}(\mu\text{-}F)$ postulated in eq 13 and 14 has not been reported. However, the Cl$^-$, Br$^-$, and I$^-$ analogues of the reduced form of this dimer,[36] $[Cr_2(CO)_{10}(\mu\text{-}X)]^-$, and the neutral iodide dimer $Cr_2(CO)_{10}(\mu\text{-}I)$ have been reported,[37-40] so this seems to be a likely product. Analogus bridged species have also been reported.[39-42] To ensure no reaction was occurring between chromium hexacarbonyl and fluoride before oxidation, the addition of fluoride to Cr(CO)$_6$ was monitored by infrared spectroscopy. No change was observed in the carbonyl region. The bridged fluoride complex is expected to be extremely reactive, and it is not surprising that it could not be isolated in the present work. However, this study has demonstrated the potential for synthesizing carbonyl fluoride complexes via electrochemical oxidation.

(g) Electrochemical Synthesis of Mo(CO)$_2$(dpe)$_2$F. The electrochemistry of [Cr(CO)$_5$F]$^-$ has shown that the previously unreported complexes Cr(CO)$_5$F and [Cr(CO)$_5$F]$^+$ are stable, at least on the electrochemical time scale at low temperatures.

Furthermore, electrochemical oxidation appears to offer prospects of making a wide range of carbonyl fluoride complexes. However, oxidation of molybdenum or tungsten carbonyl complexes in the presence of fluoride may be expected to lead to stable

---

(36) Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1821.

(37) Behrens, H.; Zilsperger, J. *Z. Naturforsch.* **1961**, *16* (B), 349.

(38) Chandler, T.; Kniek, G. R.; Greenway, A. M.; Enemark, J. H. *Cryst. Struct. Commun.* **1980**, *9*, 557.

(39) White, J. F.; Farona, M. F. *J. Organomet. Chem.* **1972**, *37*, 119.

(40) Kaim, W. *J. Organomet. Chem.* **1984**, *264*, 317.

(41) Huttner, G.; Borm, J.; Laszlo, Z. *J. Organomet. Chem.* **1984**, *263*, C33.

(42) Alper, H.; Damude, L. C. *Organometallics* **1982**, *1*, 579.

carbonyl fluoride complexes. Chemical oxidation of *cis*-Mo(CO)$_2$(dpe)$_2$ (dpe = 1,2-bis(diphenylphosphino)ethane) with NO$^+$PF$_6^-$ actually produces Mo(CO)$_2$(dpe)$_2$F.[43] Electrochemical oxidation of *cis*-Mo(CO)$_2$(dpe)$_2$ in CH$_2$Cl$_2$ occurs via two one-electron oxidation steps.[44] Controlled potential oxidative electrolysis in the presence of deliberately added fluoride, as might be expected, produces the stable seven-coordinate complex Mo(CO)$_2$(dpe)$_2$F (identified by infrared spectrum and comparison of other properties with an authentic sample) which has been well-characterized.[43] This example confirms our contention that electrochemical synthesis should provide a general route to preparation of carbonyl fluoride complexes.

Registry No. LiTFA, 2923-17-3; TFA$^-$, 14477-72-6; [B][Cr(CO)$_5$F] [B = dibenzo-18-crown-6-K], 101565-51-9; [B][Cr(CO)$_5$Cl] [B = dibenzo-18-crown-6-K], 101629-47-4; [B][Cr(CO)$_5$Br] [B = dibenzo-18-crown-6-K], 101565-52-0; [B][Cr(CO)$_5$I] [B = dibenzo-18-crown-6-K], 101565-53-1; Cr(CO)$_6$, 13007-92-6; Cr(CO)$_5$F, 101565-54-2; Cr(CO)$_5$F$^+$, 101565-55-3; Mo(CO)$_2$(dpe)$_2$F, 101565-56-4; *cis*-Mo(CO)$_2$(dpe)$_2$, 17523-42-1; F$^-$, 16984-48-8; Et$_4$NF, 665-46-3; Pt, 7440-06-4; Au, 7440-57-5; C, 7440-44-0.

---

(43) Snow, M. R.; Wimmer, F. L. *Aust. J. Chem.* **1976**, *29*, 2349.

(44) Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

Interaction Modes between Heavy Metal Ions and Water-Soluble Polymers. 1. Spectroscopic and Magnetic Reexamination of the Aqueous Solutions of Cupric Ions and Poly(vinyl alcohol)

Hiroshi Yokoi,* Satoshi Kawata, and Masamoto Iwaizumi

Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan. *Received September 16, 1985*

Abstract: The interaction mode between cupric ions and poly(vinyl alcohol) (PVA) in aqueous solutions has been reexamined in detail by EPR, NMR, magnetic susceptibility, and optical absorption techniques. Cupric ions exist as the olated polynuclear complex of Cu(OH)$_2$ solubilized by PVA at pH >6 and as ordinary hydrated ions at pH <6. This solubilization mechanism at pH >6 is of an inclusion type due to hydrophobic interaction, where Cu(OH)$_2$ is included by PVA chains with hydrophobic backbones toward the inside and with hydrophilic OH groups toward the outside of bulk water. This is a new interaction mode in the chemistry of polymer–metal complexes.

The polymer–metal complex has been the subject of increasing interest recently in the fields of catalytic reactions and metal ion separations,[1] in connection with biochemistry and environmental chemistry. Poly(vinyl alcohol) (PVA) is a simple synthetic water-soluble polymer. Aqueous solutions of cupric ions and PVA show a green coloration at pH >6,[2-4] with a remarkable decrease of viscosity.[5,6] This was interpreted by Kuhn et al. as a result of the formation of stable mononuclear copper(II) complexes with hydroxyl groups of PVA.[3] Curiously, the validity of this interpretation has not been questioned but generally accepted.[7] From the standpoint of coordination chemistry, it seems unlikely that alcoholic OH groups deprotonate at pH <7 to coordinate to cupric ions, even in the polymer domain, because the OH groups are generally assumed to have pK_a ~ 16.[8]

The purpose of this paper is to reinvestigate the aqueous solutions of cupric ions and PVA by spectroscopic and magnetic techniques and to report a new interaction mode between cupric ions and PVA, contradicting the above interpretation. This new interaction mode is very suggestive in considering the interaction between heavy metal ions and various natural macromolecules.

Experimental Section

Spectroscopic and Magnetic Measurements. A Varian E-4 EPR spectrometer (X-band) was used to measure EPR spectra of aqueous sample solutions at room temperature and of their frozen solutions at 77 K. All the EPR sample solutions contained 2.50 mM Cu^{2+}, 50 mM PVA (polymer residue concentration), and 0.10 M NaClO$_4$. The pH adjustment was done throughout this work without any buffer. A JEOL Model JNM-FT90Q FT NMR spectrometer was used in ^{1}H NMR studies and in magnetic susceptibility measurements by the Evans method at room temperature.[9] Aqueous solutions for ^{1}H NMR measurements contained 100 mM PVA and Cu^{2+} at various concentrations. In the application of the Evans method, 2% *tert*-butyl alcohol was used as an indicator. Visible and UV spectra were recorded at room temperature on a Shimadzu UV-240 spectrophotometer, using quartz 10- and 1-mm cells.

Chemicals. Hydrolyzed (100%) PVA with the average molecular weight 14 000 was purchased from Aldrich Chemical Co. The concentration of PVA was expressed in terms of the monomeric residues. All other reagents were of reagent grade or higher and were used without further purification.

Results and Discussion

EPR and Magnetic Susceptibility. Figure 1 shows EPR spectra both of an aqueous Cu^{2+}–PVA solution at pH 3.0 at room temperature and of its frozen solution at 77 K. These spectra were

---

(1) Pittman, C. U., Jr. In *Polymer-Supported Reaction in Organic Synthesis*; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980; Chapter 5. Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557. Skorobogaty, A.; Smith, T. D. *Coord. Chem. Rev.* **1984**, *53*, 55. Sahni, S. K.; Reedijk, J. *Coord. Chem. Rev.* **1984**, *59*, 1.

(2) Saito, S.; Okayama, H. *Kolloid Z. Z. Polymn.* **1954**, *139*, 150.

(3) Kuhn, W.; Toth, I. *Z. Naturforsch.* **1963**, *18A*, 112. Kuhn, W.; Toth, I.; Kuhn, H. J. *Makromol. Chem.* **1963**, *60*, 77.

(4) Gelfman, A. Ya.; Kvyatkovskaya, E. F.; Ruzan, R. G.; Skorobogatov, B. S. *Vysokomol. Soedin.* **1963**, *5*, 1534.

(5) Hojo, N.; Shirai, H.; Sakata, K.; Fukuda, M. *J. Chem. Soc., Jpn. Ind. Chem. Sect.* **1970**, *73*, 1862.

(6) Hojo, N.; Shirai, H.; Hayashi, S. *J. Polym. Sci.* **1974**, *C-47*, 299.

(7) Hojo, N.; Shirai, H. *J. Chem. Soc. Jpn.* **1972**, *96*, 1316.

(8) Riddick, J. A.; Bunger, W. B. In *Techniques of Chemistry*, 3rd ed.; Weissberger, A., Ed.; Wiley-Interscience: New York, 1970; Vol. 2, pp 146.

(9) Evans, D. F. *Proc. Chem. Soc.* **1958**, 115. Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Loliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.