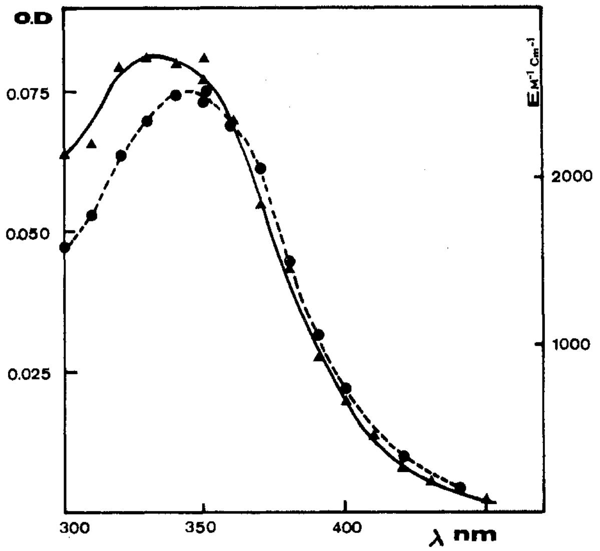

Figure 1. Absorption spectra of the complexes, measured 50 μsec after the pulse, with the solution composition of 1×10^{-2} *M* $CuSO_4$ and 1.0 *M* methanol (N_2O saturation and pH 3.65 ± 0.05): ●, 1×10^{-3} *M* maleic acid; ▲, 1×10^{-3} *M* fumaric acid.

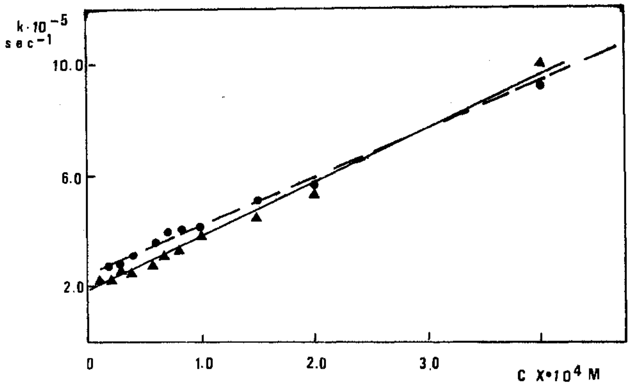

Figure 2. Dependence of the observed specific rates of reaction, *k*, on the unsaturated carboxylic acid concentration. Aqueous solutions containing 1×10^{-2} *M* $CuSO_4$ and 1.0 *M* methanol (pH 3.65 ± 0.05 and N_2O saturation) at 22 ± 2° were used: ●, fumaric acid; ▲, maleic acid.

Table I. Stability Constants of Copper(I) with Maleic and Fumaric Acids[a]

	Maleic acid		Fumaric acid	
[C], *M*	OD	$10^{-4}K_8, M^{-1}$	OD	$10^{-3}K_8, M^{-1}$
1.0×10^{-5}	0.0100	1.3	0.0089	10.0
2.0×10^{-5}	0.0200	1.5	0.0147	9.6
3.0×10^{-5}	0.0240	1.5	0.0200	9.5
4.0×10^{-5}	0.0306	1.4	0.0262	10.0
6.0×10^{-5}	0.0401	1.4	0.0333	9.5
7.0×10^{-5}			0.0345	8.5
8.0×10^{-5}	0.0438	1.3	0.0378	8.8
1.0×10^{-4}	0.0481	1.2	0.0414	8.3
1.5×10^{-4}	0.0543	1.2	0.0488	7.9
2.0×10^{-4}	0.0621	1.3	0.0567	7.9
4.0×10^{-4}	0.0677	0.9	0.0718	9.1
7.0×10^{-4}	0.0759	1.1	0.0783	8.5
	Av	1.3	Av	9.0

[a] All solutions were N_2O saturated and contained 1×10^{-2} *M* $CuSO_4$ and 1.0 *M* methanol at pH 3.65 ± 0.05; OD measurements were taken at 350 nm, 50 μsec after the end of the pulse. Accuracy of K_8 is ±20%. [C] is the concentration of the unsaturated carboxylic acid, at 22 ± 2° and $\mu = 0.04$.

at 350 nm. The results are summarized in Table I. [The calculation was carried out by assuming the value obtained for K_8 in the kinetic runs, and calculating the optical density for a solution in which 100% of the Cu(I) formed appears in the complex, OD_T, from K_8 and the measured OD in solutions for which $C = 7 \times 10^{-4}$ *M*, using the equation $OD_T = OD(1 + K_8C)/K_8C$. Using the value of OD_T K_8 was calculated for all other concentrations by applying the equation

$$K_8 = \frac{OD}{OD_T - OD}\frac{1}{C}$$

The average of these values of K_8 was used for a new calculation until a self-consistent value was obtained.] The average values for K_8 thus obtained, $(1.3 \pm 0.2) \times 10^4$ and $(9.0 \pm 2.0) \times 10^3$ M^{-1}, for maleic and fumaric acid, respectively, are in good agreement with those obtained from the kinetic study.

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Registry No. Copper(I) fumarate, 54964-69-1; copper(I) maleate, 55028-63-2.

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(9) The reviewers have requested the derivation of the rate law. The reaction studied can be summed up as

$$A + B \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} C$$

where $[C]_{t=0} = 0$, $[A]_{t=0} = A^0$, and $[B] >> A^0$. Therefore $d[C]/dt = -d[A]/dt = k_8[A][B] - k_{-8}[C] = k_8[A][B] - k_{-8}(A^0 - [A]) = (k_8[B] + k_{-8})[A] - k_{-8}A^0$. Integration of this equation yields $-\ln\{(k_8[B] + k_{-8})[A] - k_{-8}A^0\} = (k_8[B] + k_{-8})t +$ constant. If the equilibrium concentrations are A^∞ and C^∞, respectively, then $k_8A^\infty[B] = k_{-8}C^\infty = k_{-8}(A^0 - A^\infty)$; $k_{-8}A^0 = (k_8[B] + k_{-8})A^\infty$. Therefore $-\ln\{(k_8[B] + k_{-8})[A] - (k_8[B] + k_{-8})A^\infty\} = (k_8[B] + k_{-8})t +$ constant *or* $-\ln([A] - A^\infty) = (k_8[B] + k_{-8})t +$ constant. Thus the observed rate constant k equals $k_8[B] + k_{-8}$.

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Crown Ethers in Inorganic Chemistry. Preparation and Characterization of the Group 6 Pentacarbonyl Hydroxides and Fluorides

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Crown ethers have been employed recently in organic chemistry to dissolve inorganic salts in nonpolar media and to thereby promote reactions that would either occur only slowly or not at all.[2-5] As yet, we know of no reports of their use *as an aid* in the synthesis of transition metal complexes. Depending upon the ring size of the crown ether, different cationic species may be complexed with varying degrees of efficiency.[2,3] Also, increasing the size and number of organic moieties attached to the perimeter of the crown increases the solubility of the inorganic salt. For example, $KMnO_4$ has been dissolved in benzene by complexation with crown ethers.[6]

There are relatively few transition metal–carbonyl–hydroxide complexes known, among which are the species $[M_2(CO)_6(OH)_3]^{3-}$ (M = Mo, W)[7–9] and $[Re_2(CO)_6(OH)_3]^-$,[10] which presumably have three bridging hydroxo groups between the two metal atoms. The Mo and W complexes were synthesized by direct reaction of the parent hexacarbonyls with KOH. The Re analog was prepared by the reaction of KOH with the $Re(CO)_5X$ (X = Cl, Br, I) complexes. To date there have been no definitive reports of a pentacarbonyl hydroxide of either group 6 or group 7 metals (possible evidence for $Mn(CO)_5OH$ has been presented[11]). Their preparation would be desirable for comparison with the structurally related halide complexes and with the bridged species mentioned above. Additionally, group 6 pentacarbonyl complexes with oxygen donor ligands which can be isolated as discrete solids are relatively uncommon.[12]

The fluoro complexes $Re(CO)_5F$,[13] $Cr(CO)_5F^-$, and $W(CO)_5F^-$ [14] have recently been prepared. The Re derivative was obtained by fluoride exchange with $Re(CO)_5Cl$ and by direct reaction of XeF_2 with $Re_2(CO)_{10}$. The Cr and W complexes were obtained either by reaction of AgF with the $M_2(CO)_{10}{}^{2-}$ species or by irradiation of the hexacarbonyls in the presence of $[(C_6H_5)_3P]_2NF\cdot CH_2Cl_2$.

In this paper we report the use of the crown ethers dibenzo-18-crown-6 and 18-crown-6 to facilitate the preparation of the complex anions $M(CO)_5X^-$ (M = Cr, W; X = F, OH). We find that cations consisting of potassium ions complexed with crown ethers function as effective counterions for anionic carbonyl complexes. While this research was in progress, the synthesis of the $M(CO)_5F^-$ species and their infrared spectra in the carbonyl stretching region were reported.[14] We herein extend those vibrational studies to the metal–carbon and metal–fluorine stretching regions. Electronic spectral data are also reported.

Experimental Section

$Cr(CO)_6$, $W(CO)_6$, and tetraethylammonium fluoride were obtained commercially and used without further purification. Dibenzo-18-crown-6 was prepared by the method of Pedersen[15] and 18-crown-6 by the method of Gokel et al.[16] All preparative work was carried out in a nitrogen atmosphere. Solvents were deoxygenated by purging with nitrogen.

Infrared spectra were recorded in the range 600–200 cm^{-1} on a Beckman IR-12 spectrophotometer; polyethylene plates were used with the samples in a Nujol mull. For the range 2200–500 cm^{-1}, solution spectra in chloroform were recorded with a Digilab FTS-20 spectrophotometer using KBr cells. Solid-state Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer using the 514.5-nm line of a CRL 53G argon ion laser. Ultraviolet–visible spectra were recorded on a Cary 14 spectrophotometer.

[Dibenzo-18-crown-6-K][W(CO)$_5$OH]. $W(CO)_6$ (0.20 g), dibenzo-18-crown-6 (0.20 g), and KOH (0.20 g) in a 100-ml flask with 20 ml of CH_2Cl_2 were stirred together while irradiating with a Hanovia high-pressure quartz mercury vapor lamp at room temperature for 2 hr. After filtration, petroleum ether (bp 30–60°) was added to the yellow filtrate to produce a fluffy yellow precipitate which was recrystallized twice from ethanol–petroleum ether to rid the product of uncomplexed dibenzo-18-crown-6. At this point, either a reddish oil or a yellow solid was obtained, which upon recrystallization from CH_2Cl_2–petroleum ether gave a bright yellow powder. The yield was 52% based on dibenzo-18-crown-6. Anal. Calcd for $C_{25}H_{25}KO_{12}W$: C, 40.55; H, 3.40. Found: C, 41.30; H, 3.90. The preparation of the yellow chromium analog was similar with a yield of 20%.

[Dibenzo-18-crown-6-K][W(CO)$_5$F]. $W(CO)_6$ (0.30 g), dibenzo-18-crown-6 (0.20 g), and $KF\cdot 2H_2O$ (0.10 g) in a 100-ml Pyrex flask with 20 ml of tetrahydrofuran (THF) and 20 ml of CH_2Cl_2 were irradiated for 2 hr. The resulting yellow solution was cooled in Dry Ice for 0.5 hr and then quickly filtered. To the filtrate at room temperature petroleum ether (bp 30–60°) was added to produce a yellow precipitate which was recrystallized from CH_2Cl_2–petroleum ether. After recrystallization, the yield was 27% based on the dibenzo-18-crown-6. Anal. Calcd for $C_{25}FH_{24}KO_{11}W$: C, 40.44; H, 3.24; F, 2.56. Found: C, 39.31; H, 3.54; F, 2.24. The preparation of the yellow chromium analog was similar.

The above reaction was also carried out with 18-crown-6 to give a product containing the same anion as shown by comparison of infrared spectra. The 18-crown-6 is much less soluble than dibenzo-18-crown-6 in the THF–CH_2Cl_2 solutions and accordingly the yield was markedly lower. The complex itself is quite insoluble in common organic solvents; dissolution in nitromethane leads to rapid decomposition.

The hydroxo and fluoro derivatives of chromium were not subjected to chemical analysis because of the lower yields and lower stability relative to the tungsten complexes (decomposition was observed after 24 hr at room temperature).

Et$_4$N[W(CO)$_5$F]. $W(CO)_6$ (0.20 g), tetraethylammonium fluoride (0.12 g), and 25 ml of CH_2Cl_2 in a 100-ml Pyrex flask were treated as in the above reaction. The synthesis is extremely undependable and fails for no apparent reason. The best yield was ca. 7%. The yellow Cr analog was prepared in a similar fashion. An added disadvantage to the preparation is that the material often forms oils which can be converted to solids only with great difficulty (if at all). The $M(CO)_5F^-$ (M = Cr, W) anions were confirmed by infrared spectroscopy. Analytical data were not obtained because of the low yields.

Results and Discussion

Synthetic Studies. The procedures outlined provide simple and direct routes to two anionic derivatives of the group 6 metal hexacarbonyls. The hydroxo species represent the first examples of $[M(CO)_5OH]^-$ type complexes while the fluoro derivatives contain the same anions recently synthesized by Douglas and Ruff.[14] In both cases we found that the chromium analogs were less stable thermally than those of tungsten. More interesting than the actual complexes is the method of preparation and, more specifically, the cations employed.

Tetraalkylammonium ions are probably the counterions most frequently used to enhance the solubility of inorganic anions in organic media. While other counterions such as PPN ($(PPh_3)_2N^+$) have been used in certain instances,[14,17,18] the tetraalkylammonium cation remains the favorite of most workers. One advantage to the latter is that a considerable number of $(NR_4)X$ salts are readily available from commercial sources for a number of different R and X groups. However, this is not always the case; for $X^- = CN^-$ considerable effort and ingenuity were expended before a satisfactory procedure for the isolation of a $(NR_4)CN$ salt was attained using chromatographic techniques.[19] Cyanate salts are also now available using similar procedures.[20] In addition to the lack of certain tetraalkylammonium salts in the solid state (such as the hydroxo salt), another of their disadvantages in preparative procedures is the occasional occurrence of oils which are often not readily tractable. We suggest that the use of K-crown cations as illustrated here offers certain advantages over other counterions: (1) crown ethers themselves are now easily prepared in high yields from inexpensive starting materials,[2,15,16] (2) potassium salts of essentially all simple anions are readily available as anhydrous solids and thus there is no need to maintain a large collection of tetraalkylammonium salts, and (3) the occurrence of oils is infrequent and a simple recrystallization of any oil that is encountered gives a well-defined solid material (no oiling was reported by Pedersen in the preparation of crown compounds of simple anions[3]). The major point is that a cation, *in association with any anion desired*, is available by simply *mixing* the crown ether with the appropriate potassium salt of that anion. In line with the findings of Pedersen[2,3] the K-dibenzo-18-crown-6 complexes were more soluble than the K-18-crown-6 species; this solubility effect is apparently responsible for the differing yields of the complexes. The failure of tetrabutylammonium fluoride in

Table I. Infrared and Raman Spectra (cm^{-1}) of the Group 6B Pentacarbonyl Fluorides and Hydroxides

		ν(CO)				ν(M–F)	ν(M–C)		
		A_1^{eq}	B_1	E	A_1^{ax}	A_1	A_1^{ax}	A_1^{eq}	E
$Cr(CO)_5F^-$ [a]	Ir[c]	2057 w	1976 m	1923 s	1864 m				
	R[d]	2065 m	1973 s		1822 m	413 sh	510 m	392 s	
$W(CO)_5F^-$ [a]	Ir[c]	2062 w	1971 m	1922 s	1854 m	451 m			363 s
	R[d]	2072 m	1968 s	1918 w	1819 m		507 m	432 s	
$Cr(CO)_5OH^-$ [b]	Ir[c]	2050 w		1923 s	1878 sh				
$W(CO)_5OH^-$ [b]	Ir[c]	2064 w		1923 s	1902 sh				

[a] Cation is Et_4N^+. [b] Cation is [dibenzo-18-crown-6-K]$^+$. [c] $CHCl_3$ solvent for carbonyl region and Nujol mull if ν(M–F) and ν(M–C) are reported. [d] Solid state.

Table II. Electronic Spectra of the Group 6B Pentacarbonyl Fluorides and Hydroxides

	λ, nm	ε		λ, nm	ε
$Cr(CO)_5F^-$ [c]	433.8		$Cr(CO)_5OH^-$	388.6	1,070
(CH_2Cl_2)	258.5		(CH_2Cl_2)	284.0	9,420[a]
				277.6	10,900[a]
$W(CO)_5F^-$ [c,d]	457.1	575	$W(CO)_5OH^-$	469.8	380
(EtOH)	413.5	2,850	(EPA)[b]	416.0	2,260
	333.2	1,010		337.6	940
	302.1	1,650		281.1	7,180[a]
	284.8	2,140		274.0	8,700[a]
	247.0	15,540		248.3	39,800

[a] Band characteristic of cation. [b] EPA is a 5:5:2 mixture of ethyl ether, isopentane, and ethanol. [c] Cation is Et_4N^+. [d] Although no analysis was obtained for this Et_4N^+ complex, the ε's for the first two bands are within 5% of the values for the K-crown complex. This material was recrystallized to constant ε.

synthesizing the $M(CO)_5F^-$ anions was ascribed to a solubility problem by Ruff,[14] whereas Liotta has found that the use of crown ethers with KF enhances the reactivity of fluoride ion.[4] Pedersen has discussed the preparation and isolation of some simple K-crown salts,[2,3] but in the present work it was not found necessary to prepare these first.

Several disadvantages of K-crown cations should be noted: (1) for the more complicated crown ethers such as the dibenzo and dicyclohexyl derivatives the large number of atoms (26 nonhydrogen atoms for dibenzo-18-crown-6) would present a less favorable case for an X-ray structural characterization than would, say, a tetramethylammonium salt (five nonhydrogen atoms), (2) their spectral characteristics[2] are somewhat poorer than for R_4N^+, (3) ion pairing may be a potential problem (this requires further investigation), and (4) varying ratios of K^+ to crown ether in simple salts[3] may also be a problem with complex anions (no difficulty was encountered in this study). There are several aspects of the second point which require further comment. In all of the crown ethers mentioned the metal–carbonyl stretching region in the infrared region (ca. 2000 cm^{-1}) is transparent and thus carbonyl complexes may be easily characterized. Proton NMR spectra are simple for K-18-crown-6 salts. The ultraviolet spectra of 18-crown-6 and dicyclohexyl-18-crown-6 are such that K-crown complexes may be investigated in this spectral region; dibenzo-18-crown-6 has an absorption at ca. 275 nm which changes in shape slightly as a function of the anion.[2] In recording ultraviolet spectra and far-infrared spectra of the fluoro complexes it was necessary to use the tetraethylammonium salts to reduce spectral interference.

In order to utilize crown ethers more fully in inorganic syntheses of the type described here, it may be useful in some situations to have a simple and general method for exchanging the K-crown cations with tetraalkylammonium or other cations. Work in this direction is in progress.

Vibrational Studies. Infrared data in the carbonyl region for the chromium and tungsten pentacarbonyl hydroxides are presented in Table I. Interference from the K-crown counterion prohibited observation of the M–OH and M–C stretching regions. The spectra for both derivatives show the carbonyl stretching patterns and relative intensities expected for a $M(CO)_5L$ complex of C_{4v} symmetry. The A_1^{eq} and E modes are at essentially the same energy as in the pentacarbonyl halides and other monosubstituted group 6 metal carbonyl derivatives of type $M(CO)_5X^-$ where X is an anion. The A_1^{ax} mode is at higher energy than in the halides by ca. 40 cm^{-1} and is more in line with the derivatives for which X = CN^-,[17,21] NCS^-,[21] and NO_3.[22] An attempt to locate the B_1 mode by Raman spectroscopy was unsuccessful. The position of the A_1^{ax} mode for the fluoro complexes shifts drastically from the infrared spectra (in $CHCl_3$ solution) to the Raman spectra (solid state). This phenomenon may also be observed in a comparison of Raman[23] and infrared[24] data of related compounds wherein such shifts are observed for some bands while others remain unshifted.

In the infrared spectra of the fluoride derivatives in the carbonyl region four bands are observed (Table I), in agreement with the work of Douglas and Ruff.[14] The B_1 mode for $W(CO)_5F^-$ is at 1971 cm^{-1} and is fairly intense considering that it is infrared forbidden. The increased intensity may be caused by ion pairing between the $W(CO)_5F^-$ anion and the K-crown or tetraethylammonium cations which may distort the idealized C_{4v} symmetry. The same pattern of bands was seen in the $Cr(CO)_5F^-$ derivative. Solid-state Raman spectra in this region follow the same pattern observed for other group 6 pentacarbonyl halides.[23] Infrared data in the M–C and M–F stretching regions are also presented in Table I. No infrared bands were observed in the M–C region for $Cr(CO)_5F^-$; however, the bands may be intrinsically weak. The M–C stretches are assigned by correlating the observed frequencies with previously reported data for the other group 6 halides.[23]

Since the average W–X stretching frequencies are ca. 34 cm^{-1} lower in energy than the Re–X frequencies in the respective pentacarbonyls,[13,23] the position of the W–F A_1 mode may be estimated to lie at 441 cm^{-1} in light of the Re–F frequency being at 475 cm^{-1} in $Re(CO)_5F$.[13] The band at 451 cm^{-1} in $W(CO)_5F^-$ is thus attributed to the W–F stretching mode; it is not observed in the Raman spectrum because it is buried under the strong 432 cm^{-1} absorption. The generally observed (and expected) trend for M–X stretching frequencies is Cr–X > W–X. While this is indeed true for X = Br and I, the values for ν(Cr–Cl) and ν(W–Cl) are 257 and 258 cm^{-1}, respectively. In fact, the energy difference ν(Cr–X) – ν(W–X) decreases from a value of 22 cm^{-1} for X = I^- to –1 cm^{-1} for X = Cl^-. Thus, it is not totally unexpected to observe *the M–F stretch at lower frequency in the Cr (413 cm^{-1}) than in the W analog (415 cm^{-1})*. Both of these values lead to higher M–X stretching force constants than in the other $M(CO)_5X^-$ species.[23] A more extensive discussion of force constants would be unwarranted without a complete normal-coordinate analysis.

We note that it has not been possible to obtain Raman spectra of anions associated with K-crown cations, even when the tetraalkylammonium salts do give spectra. The explanation for this is not immediately obvious.

Electronic Spectral Studies. The ultraviolet and visible spectra of the complex anions are given in Table II. Spectra of the Cr derivatives were recorded in CH_2Cl_2 because of relatively limited solubility in most other solvents. No extinction coefficients were determined for the fluoro complex because of stability problems; this was not unexpected considering the relatively low stability of $Cr(CO)_5Cl^-$ in the same solvent. The higher stability of $Cr(CO)_5OH^-$ was surprising. $W(CO)_5F^-$ is reasonably stable in solution but follows the expected stability order I > Br > Cl > F. The spectra of the complexes (except for $Cr(CO)_5OH^-$) match the expected pattern in number of peaks and relative intensities.[25,26] We are unable to account for the fact that while the spectra of the $W(CO)_5X^-$ (X = halide, OH) complexes are all similar, the only band seen for $Cr(CO)_5OH^-$ is at much higher energy than in the $Cr(CO)_5X^-$ (X = halide) complexes. The limitation of the K-dibenzo-18-crown-6 cation in ultraviolet spectroscopy is illustrated by the hydroxo spectra.

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Registry No. [Dibenzo-18-crown-6-K]$[W(CO)_5OH]$, 54964-71-5; [dibenzo-18-crown-6-K]$[Cr(CO)_5OH]$, 55000-28-7; [dibenzo-18-crown-6-K]$[W(CO)_5F]$, 54964-72-6; dibenzo-18-crown-6, 14187-32-7; $Et_4N[W(CO)_5F]$, 54964-73-7; $Et_4N[Cr(CO)_5F]$, 54964-74-8.

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Reduction of μ-Superoxo-bis[pentaamminecobalt(III)] by Hexaammineruthenium(II) and a Correlation of Kinetic Data for Two Series of Redox Reactions

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The classification of electron-transfer reactions into either inner-sphere or outer-sphere categories is generally based upon the nature of primary reaction products,[1] including in some cases the identification of binuclear intermediates,[2] as well as information regarding the lability or inertness of metal ion reactants.[3] In addition there are now several examples in which the less restrictive criteria of linear free energy correlations[4] have been successful in providing a means of differentiating between mechanisms.[5-7] These correlations have hitherto been established for reactions involving two reductants, for example, Cr^{2+} and V^{2+}, with a common series of oxidants.[8,9]

Such correlations should also apply, but are less well established,[10] for the converse situation in which the reactions of two oxidant species with a common series of reductants are compared. Here we seek to test further this possibility and in doing so report data for the reduction of the μ-superoxo-bis[pentaamminecobalt(III)] complex by $Ru(NH_3)_6^{2+}$.

Experimental Section

Hexaammineruthenium(III) trichloride (Johnson Matthey Chemicals Ltd.) was purified as previously described[11] (λ_{max} 275.5 nm, ϵ 472 M^{-1} cm^{-1}) and reduced to hexaammineruthenium(II) (λ_{max} 275 nm, ϵ 640 M^{-1} cm^{-1}) using a Jones reductor column, containing amalgamated zinc shot (Hopkin and Williams, Analar grade), under argon gas.[12]

The μ-superoxo-bis[pentaamminecobalt(III)] complex was prepared by oxidation of μ-peroxo-bis[pentaamminecobalt(III)] chloride in situ using ammonium peroxodisulfate, $(NH_4)_2S_2O_8$.[13] The perchlorate salt was isolated and solutions ca. 0.01 *M* in 0.1 *M* $HClO_4$ were made up immediately (λ_{max} 670 nm, ϵ 890 M^{-1} cm^{-1}) and stored at −5° in a light-proof flask.

The stoichiometry of the reaction was shown to be 1:1 by treating freshly generated $Ru(NH_3)_6^{2+}$ with an excess of the μ-superoxo complex and measuring the absorbance change at 670 nm. The μ-peroxo complex which is formed is unstable in acid solution,[14] and when excess $Ru(NH_3)_6^{2+}$ is used, further reaction occurs with the oxygen released.[11] Absorbance changes corresponding to the reaction of the μ-superoxo complex and the subsequent decomposition of the μ-peroxo intermediate were monitored on a Durrum-Gibson stopped-flow spectrophotometer. Concentrations of $Ru(NH_3)_6^{2+}$ pertaining to each run were checked immediately following stopped-flow runs by addition to an excess of μ-superoxo complex and measuring the absorbance change at 670 nm.

Results and Discussion

The reaction was monitored at the 296-nm peak of the μ-superoxo complex, ϵ 2.45×10^4 M^{-1} cm^{-1}.[15] At this wavelength two stages were observed, the first of which is assigned to (1). The $Ru(NH_3)_6^{2+}$ was in at least eightfold

$$\begin{aligned}&Ru(NH_3)_6^{2+} + (NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5^{5+} \rightarrow\\&\quad Ru(NH_3)_6^{3+} + (NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5^{4+}\end{aligned} \quad (1)$$

excess and the ionic strength maintained at $I = 0.1$ *M* using $LiClO_4$–$HClO_4$. Plots of absorbance changes, log $(A_t - A_\infty)$, against time were linear to at least 80% completion and yielded first-order rate constants. A threefold variation of $[Ru(NH_3)_6^{2+}]$, which was the maximum it was possible to achieve, indicated a first-order dependence on reductant and a rate law (2). Values of *k* at temperatures 1.5–15° are given in Table I.

$$\text{rate} = k[Ru(NH_3)_6^{2+}][\mu\text{-}O_2^-] \quad (2)$$

The two stages were less well separated at the higher temperatures, and as confirmation of our procedure and in order to ensure that a correct A_∞ was being used, a full consecutive reaction treatment was carried out for a number of runs.[16] Rate constants in Table I are seen to be independent of $[H^+]$ in the range 0.01–0.10 *M*. The range of concentrations of H^+ and ClO_4^- as well as the range of temperatures over which reliable data could be obtained was restricted by the stability of $Ru(NH_3)_6^{2+}$.[17] Activation parameters, $\Delta H^\ddagger = 0.8 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = -25.8 \pm 1.8$ cal K^{-1} mol^{-1}, were obtained by a least-squares treatment (no weighting factor).

The second stage of reaction corresponds to the decomposition of the primary product, the μ-peroxo-bis[penta-