

sulfoxide-nitromethane mixtures. Scott, Weeks, Bracken, and King²⁰ have suggested hydrogen bonding between coordinated water molecules in $\text{Cr}(\text{OH}_2)_6^{3+}$ and Me_2SO to explain the stabilization of this complex relative to $\text{Cr}(\text{OH}_2)_5(\text{Me}_2\text{SO})^{3+}$. Johnson and King¹³ have proposed that the dominant factor governing the outer-sphere interactions is hydrogen bonding between $\text{Co}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ and Me_2SO . Glavaš and Reynolds²¹ have suggested a specific interaction between coordinated and free dimethylformamide (DMF) for $\text{Co}(\text{NH}_3)_5(\text{DMF})^{3+}$ in water-DMF mixed-solvent media to explain the dependence of the first-order aquation rate constant on the mole fraction of DMF.

An alternative explanation for the observed results is that the acetonitrile complex is preferentially completely solvated by water in the water-acetonitrile solvent systems and by Me_2SO in the Me_2SO -acetonitrile solvent systems. In case this were true, the data yield no information on the possible rotation of $\text{Co}(\text{NH}_3)_5^{3+}$ or the lack of it. However, complete preferential solvation by one solvent seems less likely than partial preferential solvation.

The ΔH^\ddagger values for both k_w and k_A in Table III do not show any significant trend with X_A ; the values for $X_A = 0.1$ are equal to those for $X_A = 0.9$ within the experimental error. The values of ΔS_A^\ddagger for k_A are also constant over the same solvent range. The ΔS_w^\ddagger values for k_w may show a slight trend from small positive to small negative values with increasing X_A , but the

trend is too small to have much significance. However, ΔS_A^\ddagger is positive relative to ΔS_w^\ddagger so that moving a water molecule from the first to the second coordination sphere in the reaction with acetonitrile seems to create more disorder than moving an acetonitrile molecule from first- to second-coordination-shell sites in the reaction with water. The ΔH_A^\ddagger values for acetonitrile replacing water are somewhat larger than the value ($26.6 \text{ kcal mol}^{-1}$)²² for water replacing water and also somewhat larger than the value ($25.4 \pm 1.3 \text{ kcal mol}^{-1}$)¹³ for Me_2SO replacing water. In mixed water-DMF media the ΔH^\ddagger value²¹ for DMF replacing water decreased slightly with increasing X_{DMF} , but at 0.1 mole fraction of DMF it was $29.4 \pm \text{kcal mol}^{-1}$ in good agreement with the present values of ΔH_A^\ddagger . The small differences in ΔH_A^\ddagger for water replacement could reflect differences in solvation energy changes in the different solvents when the leaving water molecule moves from a first- to a second-coordination-sphere site and when the entering solvent molecule (water, Me_2SO , DMF, or acetonitrile) is correctly positioned for entry to the vacated first-coordination-sphere site.

Acknowledgment. The authors wish to thank Professor Stephen Prager, University of Minnesota, for informative and stimulating discussion concerning aspects of absolute rate theory.

Registry No. $\text{Co}(\text{NH}_3)_5(\text{NCCH}_3)^{3+}$, 44819-13-8; $\text{Co}(\text{NH}_3)_5(\text{OH}_2)^{3+}$, 14403-82-8; $\text{Co}(\text{NH}_3)_5(\text{OSMe}_2)^{3+}$, 44915-85-7; NCCH_3 , 75-05-8; OSMe_2 , 67-68-5.

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Oxidation of Substituted Iron Carbonyl Complexes in Acetonitrile, Acetone, and Dichloromethane at Mercury and Platinum Electrodes

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The oxidative electrochemistry of the substituted iron carbonyl complexes $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$, where L is a monodentate tertiary phosphine, arsine, or stibine ligand, has been studied in acetone, dichloromethane, and acetonitrile at both Hg and Pt electrodes. At platinum electrodes, for $\text{L} = \text{AsPh}_3$ or SbPh_3 the initially generated 17-electron cations $[\text{Fe}(\text{CO})_4\text{L}]^+$ and $[\text{Fe}(\text{CO})_3\text{L}_2]^+$ are unstable in all solvents while with phosphorus ligands the species $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$ has some stability in dichloromethane. Reactions leading to decomposition are considered. In marked contrast, at mercury electrodes, the cations appear to be substantially more stable than at platinum, and chemically reversible behavior can be observed where the response is completely irreversible at platinum. The data are explained in terms of a chemically modified pathway at mercury electrodes giving rise to "mercury stabilized" cations.

Redox processes are often studied at mercury electrodes. However, organometallic carbonyl complexes are commonly involved in formation of mercury complexes³ and therefore the possibility of observing an interaction between mercury and the complex at the electrode surface is likely.^{4,5} In work from these laboratories concerning organometallic electrode processes, the apparently faster rate of electron transfer

(heterogeneous charge transfer) at mercury electrodes than at platinum or carbon electrodes has been noted.^{6,7} Furthermore, the occurrence of chemically modified behavior (homogeneous kinetics) at mercury electrodes for oxidation of molybdenum and tungsten complexes^{8,9} as well as for other systems⁷ has also been observed. The possibility that the above

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Table I. Analytical Data for $\text{Fe}(\text{CO})_5$ Derivatives

	% calcd			% found		
	C	H	P/As/ Sb	C	H	P/As/ Sb
$\text{Fe}(\text{CO})_4\text{PPh}_3$	61.4	3.5	7.2	61.5	3.6	6.8
$\text{Fe}(\text{CO})_4\text{AsPh}_3$	55.7	3.2	15.8	55.9	3.2	15.8
$\text{Fe}(\text{CO})_4\text{SbPh}_3$	50.7	2.9	23.3	51.2	3.1	23.0
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	70.5	4.6	9.3	68.1	4.5	9.7
$\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$	62.3	4.0	19.9	58.7	3.9	18.1
$\text{Fe}(\text{CO})_3(\text{SbPh}_3)_2$	58.7	3.9	17.9	58.7	3.9	18.1
$\text{Fe}(\text{CO})_3(\text{SbPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2^a$	55.4	3.6	28.8	55.0	3.9	28.3

^a This sample analyzed was crystalline, and thus the chances of occluded solvent being present in the crystal were much higher than for the other compounds, which were powders.

effects have arisen because of a formation of a mercury intermediate at the electrode surface would seem substantial and may be a relatively common phenomenon. Indeed, the presence of such interactions could readily lead to incorrect interpretation of data, if not accounted for. Such an example, that of iron carbonyl, is considered in the present investigation, where previously published data appear to be inconsistent.

The electrochemistry of iron carbonyl, $\text{Fe}(\text{CO})_5$, and substituted species has been examined on a number of occasions,¹⁰⁻¹⁷ and while it is clear that the compounds can be oxidized, some conflicting data appear in the literature. For example, electrochemical studies on $\text{Fe}(\text{CO})_5$ at platinum in a range of solvents indicate that $[\text{Fe}(\text{CO})_5]^+{}^{10-13}$ is a very reactive species. However, as part of a detailed study of trimeric iron carbonyl complexes, Bond et al.¹⁵ briefly described the electrochemistry of some $\text{Fe}(\text{CO})_{5-x}\text{L}_x$ complexes ($x = 0-2$; $\text{L} = \text{PPh}_3$, $\text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$ at mercury electrodes. In particular in acetone, oxidation processes having adsorption characteristics were noted at mercury electrodes, although the overall processes were attributed to reaction 1.



By contrast, no well-defined waves were observed at platinum electrodes. In dichloromethane, electrochemical oxidation of $\text{Fe}(\text{CO})_3\text{L}_2$ [$\text{L} = \text{PPh}_3$, PPh_2Me , $\text{P}(\text{OPh})_3$, $\text{P}(\text{NMe}_2)_3$] produced a chemically reversible couple at platinum electrodes under conditions of cyclic voltammetry.¹³ Chemical oxidation with AgPF_6 was reported to give a range of products including the cation $[\text{Fe}(\text{CO})_3\text{L}_2]^+$. Recently,¹⁷ a cation, $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$, was isolated from this reaction, but a silver intermediate is implicated in the reaction.

In view of the existence of incomplete literature reports on the oxidative processes of monomeric iron complexes of the type $\text{Fe}(\text{CO})_{5-x}\text{L}_x$ ($x = 1, 2$) but nevertheless an indicated mercury electrode and solvent dependence, a detailed examination of the series of complexes $\text{Fe}(\text{CO})_{5-x}\text{L}_x$, where $x = 1$ or 2 and $\text{L} = \text{PPh}_3$, AsPh_3 , or SbPh_3 , in acetone, dichloromethane, and acetonitrile at both Pt and Hg electrodes has been undertaken in an endeavor to assess whether mercury does modify the observed behavior. The techniques involved

Table II. Infrared and ^{13}C NMR Data for $\text{Fe}(\text{CO})_5$ Derivatives

compd	ν_{CO} in CH_2Cl_2 , cm^{-1}	chemical shift of carbonyl resonances in CD_2Cl_2 , ppm vs. Me_4Si
$\text{Fe}(\text{CO})_4\text{PPh}_3$	2040, 1963, 1935	214.0 ^a
$\text{Fe}(\text{CO})_4\text{AsPh}_3$	2040, 1966, 1937	213.9
$\text{Fe}(\text{CO})_4\text{SbPh}_3$	2036, 1960, 1931	213.4
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	1879	215.0 ^b
$\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$	1879	214.9
$\text{Fe}(\text{CO})_3(\text{SbPh}_3)_2$	1874	213.2

^a $J_{\text{P-C}} = 19 \text{ Hz}$. ^b $J_{\text{P-C}} = 29 \text{ Hz}$.

include dc cyclic voltammetry at both Pt and Hg electrodes, dc polarography at a dropping-mercury electrode (dme), controlled-potential electrolysis, and coulometry at both Pt and Hg electrodes.

Experimental Section

Analyses. Carbon, hydrogen, phosphorus, and arsenic analyses were performed by the Australian Microanalytical Service. Analytical results are given in Table I.

Chemicals. Commercial samples of $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$, and all ligands were used without further purification, except for $\text{Fe}_2(\text{CO})_9$, which was dried under vacuum for 10 min prior to use. All solvents were of analytical reagent grade purity.

Instrumentation. Infrared spectra were recorded on Unicam SP1200 and Perkin-Elmer 457 spectrophotometers and calibrated against polystyrene. ^{13}C NMR were recorded on a JEOL FX100 spectrometer. ESR spectra were taken on a Varian 450/15 spectrometer.

Polarograms and voltammograms were recorded on a PAR Model 170 electrochemistry system. For studies in dichloromethane, 0.07 M Et_4NClO_4 was used as the supporting electrolyte, while, for studies in acetone and acetonitrile, 0.1 M Et_4NClO_4 was used. A three-electrode system employing positive feedback circuitry was used on all occasions with platinum wire as the auxiliary electrode. The reference electrode was Ag/AgCl (saturated LiCl , acetone) in all cases and was separated from the test solution by a salt bridge containing the supporting electrolyte in the appropriate solvent. The working electrode was either a Pt wire or a dropping-mercury electrode. Solutions were degassed with nitrogen prior to recording polarograms or voltammograms. For voltammograms recorded at scan rates faster than 1 V per second, a Tektronix D13 storage oscilloscope was used to display the output, and the signal was recorded photographically. Otherwise data were displayed on an X-Y recorder. All experiments were run at $(20 \pm 2)^\circ\text{C}$ unless otherwise stated.

Coulometric experiments were performed at Hg pool and Pt gauze electrodes, with use of a PAR Model 173 potentiostat in conjunction with a Model 9600 coulometric cell system and a Model 179 digital coulometer. The auxiliary electrode (platinum gauze) was separated from the test solution by a porous Vycor sinter. The test solution was stirred and degassed with nitrogen throughout the experiment. Controlled-potential electrolysis experiments at platinum were performed at 1.00 V and at mercury at 0.8 V vs. Ag/AgCl . The supporting electrolyte was 0.2 M Bu_4NClO_4 .

Preparations. $\text{Fe}(\text{CO})_4\text{L}$. These complexes were prepared by stirring stoichiometric amounts of $\text{Fe}_2(\text{CO})_9$ and the appropriate ligands in THF (dried over molecular sieves) at room temperature, in a CO atmosphere for about 3 h. The solution was filtered and the solvent removed by evaporation under vacuum. In the case of $\text{Fe}(\text{CO})_4\text{PPh}_3$ and $\text{Fe}(\text{CO})_4\text{AsPh}_3$ the yellow crystals were purified by vacuum sublimation. The sublimate was $\text{Fe}(\text{CO})_4\text{L}$, and the residue contained $\text{Fe}(\text{CO})_3\text{L}_2$. $\text{Fe}(\text{CO})_4\text{SbPh}_3$ was purified by fractional crystallization from dichloromethane/hexane.

$\text{Fe}(\text{CO})_3\text{L}_2$. Stoichiometric amounts of $\text{Fe}_3(\text{CO})_{12}$ and the appropriate ligand were refluxed in THF for 30 min. The solutions were filtered, and the solvent was evaporated under vacuum. The yellow crystals were purified by recrystallization from dichloromethane/hexane and chromatography on a column of alumina with use of dichloromethane as eluant.

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Table III. Electrochemical Data for Oxidation of Approximately 10^{-3} M Solutions of $\text{Fe}(\text{CO})_5\text{-xL}_x$ in Acetone (0.1 M Et_4NClO_4) at 20°C^a

cyclic voltammetry (scan rate = 500 mV s ⁻¹)							
	Pt electrodes		Hg electrodes			<i>E</i> _{1/2} ^c	polarography (drop time = 0.5 s) <i>E</i> _{1/2}
	<i>E</i> _{ox}	<i>E</i> _{red}	<i>E</i> _{ox}	<i>E</i> _{red}			
Fe(CO) ₄ PPh ₃	~1.2 ^b	none	0.80	0.60	0.57 ^d	0.75	0.74 ^e
Fe(CO) ₄ AsPh ₃	~1.2 ^b	none	0.79	0.62	0.54 ^d	0.70	0.69 ^e
Fe(CO) ₄ SbPh ₃	~1.2 ^b	none	0.77	0.69	0.56 ^d	0.73	0.64 ^e
Fe(CO) ₃ (PPh ₃) ₂	0.71	0.55	0.62	0.54		0.58	0.54 ^{e,f}
Fe(CO) ₃ (AsPh ₃) ₂	0.78 ^b	none	0.48	0.39	0.27 ^d	0.45	0.55 ^{e,f}
Fe(CO) ₃ (SbPh ₃) ₂	0.79 ^b	none	0.56	0.45	0.35 ^d	0.49	0.58 ^{e,f}

^a All potentials V vs. Ag/AgCl. ^b Chemically irreversible waves, very drawn out and peak potential critically dependent on history of Pt electrode. Values quoted refer to first scan on well-cleaned electrode. ^c $E_{1/2}$ calculated from the reversible couple determined from fast scan rate work. ^d Appears at slow scan rates, absent at very fast scan rates. ^e Adsorption indicated, $E_{1/2}$ values very dependent on concentration and drop time. ^f Maxima present, prewave present, complicated polarograms at higher concentration.

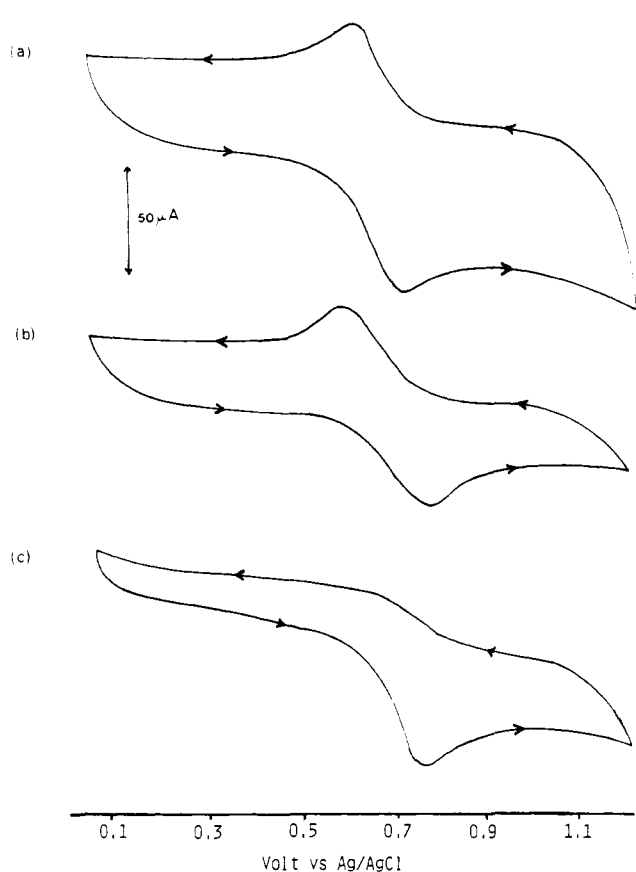


Figure 1. Cyclic voltammograms at 20°C of approximately 10^{-3} M $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ at Pt electrodes (scan rate = 500 mV s^{-1}) in (a) acetone, (b) dichloromethane, and (c) acetonitrile.

Analytical data (Table I) as well as IR and NMR spectroscopic measurements (Table II) were used to characterize the complexes. For all these derivatives, the compounds in the solid state were observed to darken perceptibly on standing for long periods of time. It was also noted that the compounds decomposed more rapidly in strong light. However, the decomposition could be prevented by storage of the samples under nitrogen in the dark. Solutions of the compounds in all solvents used were unstable to light and air and were observed to decompose even when protected from light.

Results and Discussion

Electrochemical Oxidation Studies. The oxidative electrochemical data for the iron carbonyl complexes are provided in Table III.

The oxidation of the $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ complex is discussed in detail first, as it exhibits the simplest behavior, and the results and conclusions drawn for this complex may be extended to provide explanations for the behavior of the complexes. Figure 1 shows dc cyclic voltammograms at Pt elec-

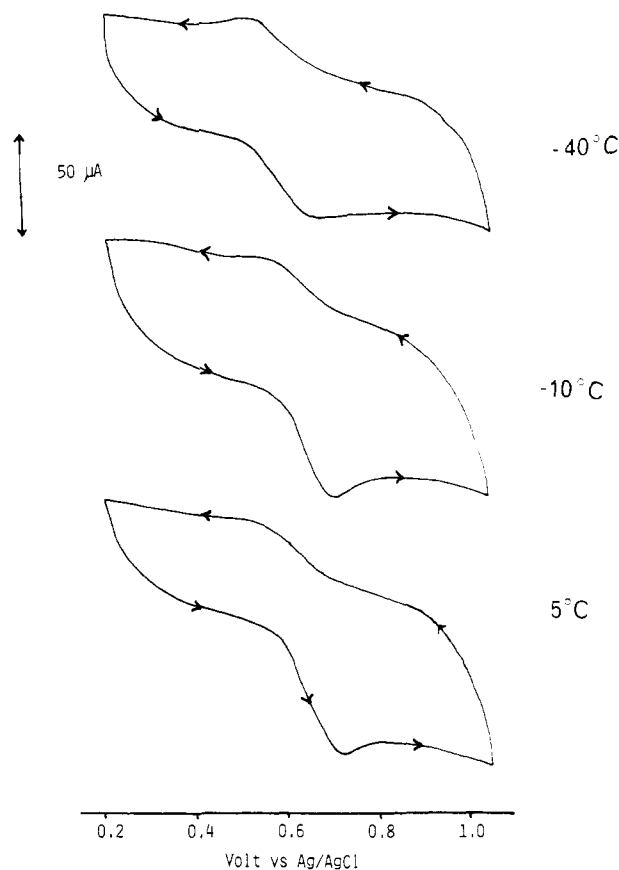


Figure 2. Cyclic voltammograms of approximately 10^{-3} M $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ at Pt electrodes in acetonitrile at low temperatures (scan rate = 500 mV s^{-1}).

trodes for $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ in acetone, dichloromethane, and acetonitrile at 20°C . All solutions were prepared and kept in the dark in order to minimize decomposition. The oxidative process to form the cation $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$ was found to be chemically reversible in acetone and dichloromethane but chemically irreversible in acetonitrile; i.e., on the reverse scan reduction of the cation could be observed in acetone and dichloromethane, but in acetonitrile no reduction peak was observed, indicating that a chemical process was occurring after oxidation to remove the cation from solution. Peak-to-peak separations from cyclic voltammograms indicated that the electron transfer step at platinum electrodes is quasi-reversible.

Figure 2 shows cyclic voltammograms of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ in acetonitrile at several low temperatures. It can be seen that at -40°C , the oxidative process can be considered to be chemically reversible. However, the electron-transfer step is relatively slow at the lower temperatures and departs con-

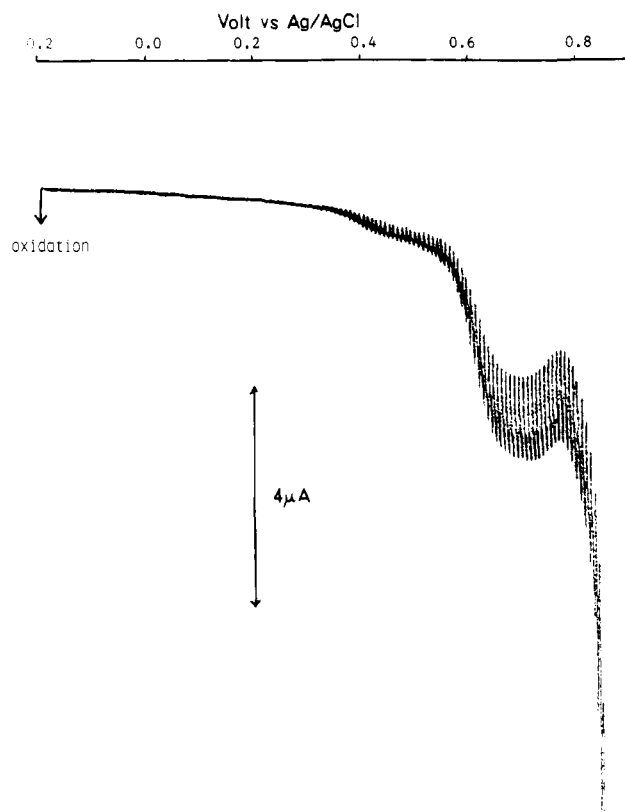
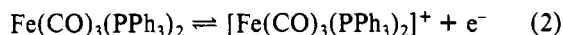


Figure 3. Polarogram at 20 °C of approximately 10^{-3} M $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ in acetone (0.1 M Et_4NClO_4) (0.5 s drop time).

siderably from Nernstian or reversible behavior. Thus, in acetone, dichloromethane, and acetonitrile (at low temperatures) the electrode process can be described by eq 2.

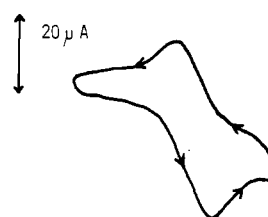
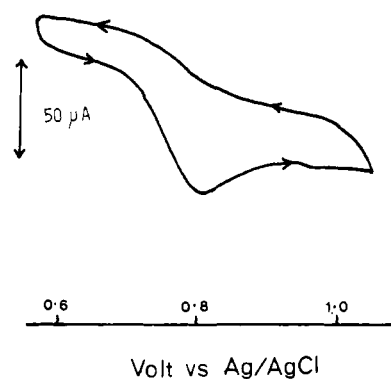


Electrochemical data provided were only obtained with carefully degassed and dried solvents, recrystallized supporting electrolytes, and fresh solutions. It was found that on standing significant deviations in the electrode response could be observed and that the response is critically dependent on solution conditions. Figure 3 shows the polarographic behavior of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ in acetone. The response is characterized by a prewave occurring 0.2 V before the main oxidation wave, a maximum, and significant concentration dependence of the half-wave potential. Under conditions of cyclic voltammetry at a mercury electrode, a chemically reversible response was obtained in acetone and dichloromethane, as was the case at a platinum electrode. Also, in acetonitrile the extremely interesting result of a chemically reversible response was observed, as shown in Figure 4, under conditions where totally irreversible chemical behavior was found at Pt. The response at Hg electrodes unlike that at Pt was virtually insensitive to the solution conditions.

All of the above results indicate that the presence of the mercury electrode causes significant stabilization of the cation. As mentioned previously, the prewaves observed were characteristic of adsorption, indicating some interaction between the mercury electrode and the carbonyl complex. Thus it is likely that a mercury-containing intermediate is forming at the surface of the electrode.

Controlled-potential electrolysis at Pt electrodes in acetone or acetonitrile produced a deep yellow solution. No evidence could be found for the $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$ cation, and coulometric data indicated the overall oxidation process was a two-electron process. A polarogram of the oxidized solution is identical with one obtained for a solution of PPh_3 twice as

Pt response



Hg response

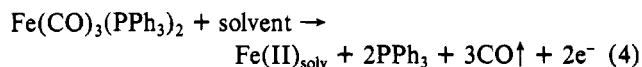
Figure 4. Cyclic voltammograms at 20 °C of approximately 10^{-3} M $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ in acetonitrile at Hg and Pt electrodes (scan rate = 500 mV s^{-1}).

concentrated as the initial solution and corresponds to the overall electrode process¹⁸

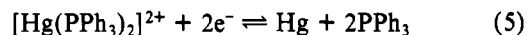


Thus PPh_3 is released as the oxidized species decomposes.

The overall reaction in acetone or acetonitrile, therefore, is consistent with eq 4.



At Hg electrodes in acetone or acetonitrile a four-electron oxidation resulted, and a dc polarogram of the final solution showed a reduction process corresponding to eq 5.



Thus at Hg electrodes, the PPh_3 liberated in the presence of mercury causes further oxidation as described by eq 3. No carbonyl-containing products were found on examination of the infrared spectrum of the oxidized solution regardless of solvent or type of electrode. Despite the "stabilization" of the cation at mercury electrodes, the overall process under the long time scale controlled potential electrolysis experiments is therefore effectively identical with that at platinum.

In dichloromethane, at platinum electrodes at -78°C , coulometry indicated that a one-electron oxidation occurred. ESR monitoring of the experiment produces the spectrum shown in Figure 5. This spectrum corresponds to that previously reported for $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$.¹³ At higher temperatures, a value of $n > 1$ was obtained under coulometric

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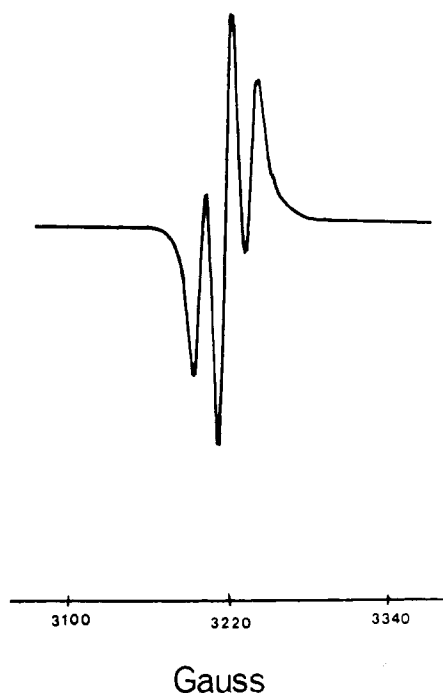


Figure 5. ESR spectrum of a solution of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ in dichloromethane after a controlled-potential electrolysis experiment.

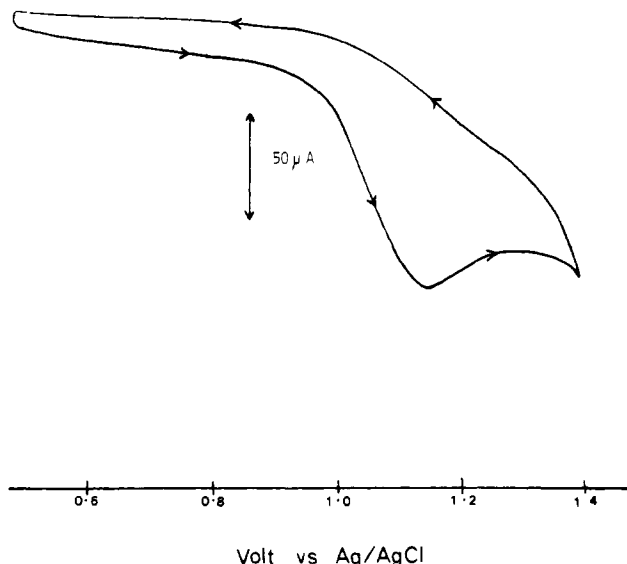


Figure 6. Cyclic voltammogram at 20 °C of approximately 2×10^{-3} M $\text{Fe}(\text{CO})_4\text{AsPh}_3$ in acetone (scan rate = 500 mV s^{-1}).

conditions and a yellow solution resulted rather than green as was the case at -78°C . Clearly, the cation is not completely stable at ambient temperatures although it can be observed in dichloromethane under conditions of controlled potential electrolysis, in contrast to acetonitrile and acetone.

The electrochemical oxidations of the other carbonyls studied $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$, $\text{Fe}(\text{CO})_3(\text{SbPh}_3)_2$, and $\text{Fe}(\text{CO})_4\text{L}$ where $\text{L} = \text{PPh}_3$, AsPh_3 , and SbPh_3 were very similar and data are summarized in Table III. Unlike the case for $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ the oxidation of these complexes in acetone, acetonitrile, and dichloromethane was irreversible at Pt under all conditions (even at low temperatures with fast scan rates), and the shape and position of the oxidation waves were critically dependent on the treatment of the Pt surface. Only with scrupulously clean electrodes and fresh, degassed solutions could a response similar to that shown in Figure 6 be obtained. However, after a few scans the wave broadened and shifted

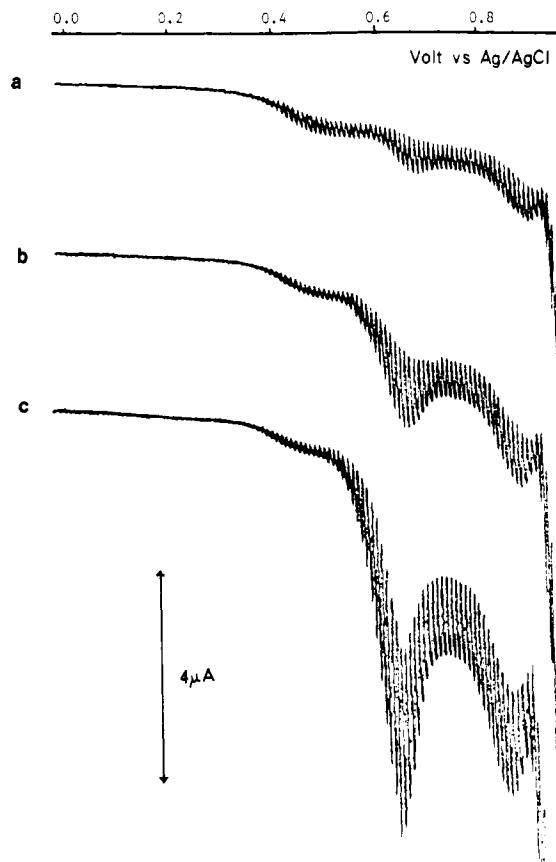


Figure 7. Polarograms at 20 °C of $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ in acetone (scan rate = 20 mV s^{-1} ; drop time = 0.5 s): (a) 3×10^{-4} M; (b) 7×10^{-4} M; (c) 10^{-3} M.

to more positive potentials, suggesting that decomposition products were coating the electrode surface causing ill-defined waves. These results show that the AsPh_3 - and SbPh_3 -substituted cations are far less stable than the PPh_3 analogue and that the disubstituted cations are more stable than the monosubstituted cations. Data obtained from controlled-potential electrolysis experiment on these complexes also failed to yield any evidence for stable cations.

Polarograms were characterized by substantial concentration dependence and adsorption effects, as shown in Figure 7.

Cyclic voltammetry at a dropping-mercury electrode gave a response which was chemically irreversible and frequently complicated at slow scan rates, but, as the scan rate increased, so did the chemical reversibility and at very high scan rates a single reversible wave is seen. This result further confirms the concept of the formation of a "mercury stabilized" cation being produced at mercury electrodes.

A clear trend is apparent for the series of complexes $\text{Fe}(\text{CO})_4\text{L}$. Figure 8 shows cyclic voltammograms at a dropping-mercury electrode for the three tetracarbonyls at a scan rate of 50 V s^{-1} over a range of 1.0 V. It can be seen that the stability of the "mercury stabilized" cation increases with decreasing atomic mass of the group 5 donor. Thus with more bulky ligands, steric interactions between the phenyl rings of the ligand, and the surface of the electrode may cause a destabilization of the adsorbed complex. At mercury electrodes, each of the PPh_3 , AsPh_3 , and SbPh_3 ($\text{Fe}(\text{CO})_4\text{L}$) complexes are oxidized at similar potentials, which is consistent with known data on complexes of these ligands when they exhibit reversible behavior at platinum electrodes.¹⁹ The

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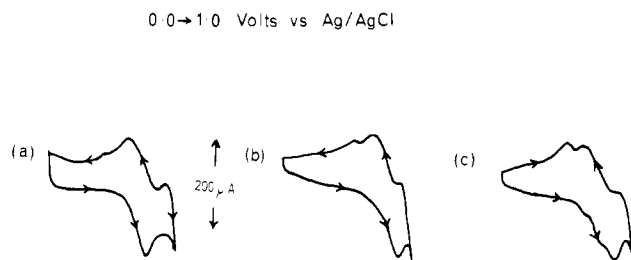


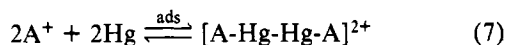
Figure 8. Cyclic voltammograms at a mercury electrode in acetone at scan rates of 50 V s^{-1} and at 20°C for (a) $\text{Fe}(\text{CO})_4\text{PPh}_3$, (b) $\text{Fe}(\text{CO})_4\text{AsPh}_3$, and (c) $\text{Fe}(\text{CO})_4\text{SbPh}_3$ (concentration approximately 10^{-3} M).

rather ligand-dependent result obtained at platinum is consistent with the nonthermodynamically significant response obtained at this electrode surface.

It is apparent that the oxidative electrochemistry of these iron carbonyl complexes is a complicated process which is dependent on a number of variables. The degree of reversibility with respect to the apparent formation of the cation is critically dependent on the nature and number of ligands, the type of electrode, the solvent, temperature, and scan rate. Nevertheless, some general trends are observed. The stability of the cation $[\text{Fe}(\text{CO})_{5-x}\text{L}_x]^+$ is greatest when $x = 2$, when L contains a phosphorus donor, and when the more reactive Hg electrode, lower temperatures, faster scan rates, and the noncoordinating solvent dichloromethane are used.

The Hg adsorption or complex formation appears to inhibit decomposition of the cation. Presumably Pt is unable to form similar complexes or adsorbed intermediates to those formed by Hg, and even on the electrochemical time scale, the use of Pt electrodes reveals the considerable instability which is really inherent in the cation. This feature of Hg stabilization may be very widespread in the oxidation of carbonyl complexes, as the degree of electrochemical reversibility often appears to be greater at Hg than at Pt as stated in the introduction. However, unlike the previous work, studies of very reactive 17-electron cations enables this feature to be seen unambiguously.

In the field of organometallic chemistry, complexes containing mercury in addition to another metal are extremely common.³ Furthermore, it is a frequent observation that organometallic complexes having an electronic configuration of 18 electrons exhibit considerable stability relative to isostructural species having 16, 17, 19, or other electronic configurations. Clearly, one way a 17-electron system A^+ can react to generate an 18-electron complex is to form an organometallic mercury complex at the electrode surface. For example, eq 6–8 would generate chemically reasonable species.



If such surface reactions occur, in preference to alternative decomposition pathways, an apparently (mercury) stabilized cation could be observed. Theories for reactions of these kind are extremely complex, although qualitative observations are consistent with some of those presented in the literature.^{4,20,21} Mercury–iron organometallic complexes of the type $\text{HgFe}(\text{CO})_4$ are well-known.^{22,23} X-ray crystallographic studies of

the isomorphous $\text{CdFe}(\text{CO})_4^{23}$ complex have shown that they are polymeric with roughly octahedral stereochemistry. With five-coordinate cations, $[\text{Fe}(\text{CO})_{5-x}\text{L}_x]^+$, mercury can easily occupy the sixth position to form a mercury complex (adsorption). Furthermore, oxidation of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ with mercury salts²⁴ is believed to produce stable intermediates containing mercury.

The influence of surface reactions has in other instances led to the observation of simplified electrode processes.²⁵ For example surface-active substances have been indicated as being able to inhibit disproportionation steps in inorganic reactions.^{25,26} Similarly, in the reduction of nitrophenol, the initial charge-transfer step involves formation of a radical anion which may undergo further reduction or disproportionation.^{25,27} The presence of surface-active alcohols makes the reduction proceed via a less complex path by inhibiting disproportionation. Thus, the presence of the anion radical is readily observed via a simple one-electron reduction. By contrast, in the absence of alcohol a four-electron reduction step is observed. For the oxidation of substituted iron carbonyl complexes, surface reactions involving mercury complex formation also appear to simplify the electrode process.

The instability of the cation is not unreasonable, as many other 17-electron systems have been shown to disproportionate or be attacked by electron donors so that the metal atom can attain the required 18-electron configuration as noted previously.^{8,9} Thus it is by its electron donor properties that Hg can stabilize the otherwise unstable 17-electron system. The effect of acetonitrile on the stability of cations has also been observed previously in other systems.⁹ This solvent can coordinate strongly to the metal atom.

Chemical Oxidation Studies. (i) **Oxidation with Silver Perchlorate.** In an attempt to substantiate proposed mechanistic pathways $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ was oxidized chemically in dichloromethane with use of silver perchlorate.

Although silver perchlorate is insoluble in dichloromethane, the pale yellow solution turned an intense green after only a few minutes upon agitation of the reaction mixture. This color has previously been reported to be the color of the species $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$.^{13,17} The infrared spectrum of the green solution showed a strong band at 2000 cm^{-1} , also consistent with the published report for the cation, and bands due to starting material. As the intensity of the infrared band at 2000 cm^{-1} dropped, bands characteristic of small amounts of $\text{Fe}(\text{CO})_4\text{PPh}_3$ appeared in the spectrum. No evidence for the presence of this complex was ever found after electrochemical oxidation, in either the infrared spectrum or the cyclic voltammogram of the oxidized solution. However, this is not surprising since at the potential of the controlled-potential electrolysis experiments, this complex would also be oxidized. The coulometric value of $n > 1$ is consistent with this observation.

(ii) **ESR Studies.** Chemical oxidation with AgClO_4 as described above generated a green solution which gave an intense ESR signal which was a well-defined 1:2:1 triplet and essentially the same as the signal generated from controlled-potential electrolysis experiments (Figure 5). The g value and splitting parameters were essentially the same as those provided in ref 13. The signal slowly decayed with time. The green color also faded, as noted previously, and disappearance of the

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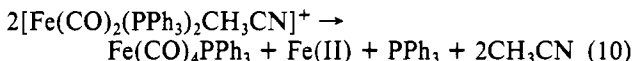
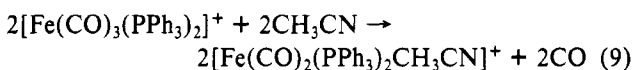
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ESR signal was consistent with infrared data, so it seems reasonable to conclude that the paramagnetic complex with a ν_{CO} of 2000 cm^{-1} is indeed the green cation $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$.

An ESR spectrum of a product of chemical oxidation has previously been reported,¹³ but no comment on instability of the product was made. More recent work¹⁷ indicates a silver complex is formed as an intermediate in this reaction. This complex in turn generates the cation with release of metallic silver, and ESR spectra of even AsPh_3 complexes can be observed via the silver-stabilized cation despite the observation of an irreversible electrochemical response. Thus, silver complexes analogous to those proposed for mercury in this work also provide stabilized intermediates, lending strong support to the hypotheses proposed in this work.

(iii) **Reaction with Acetonitrile.** After generation of green $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$ in dichloromethane via oxidation of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ with silver perchlorate, acetonitrile was added dropwise. Immediately the acetonitrile was added, rapid evolution of carbon monoxide was observed, the green color faded, and infrared monitoring demonstrated the formation of $\text{Fe}(\text{CO})_4\text{PPh}_3$. That is, the decomposition pathway for the cation appears to be catalyzed rapidly by acetonitrile. Presumably, a mechanism of the kind



accounts for the decomposition of $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$. Similar mechanisms can be proposed for all $\text{Fe}(\text{CO})_x\text{L}_{5-x}$ species. Thus, when adsorption or complex formation at the surface occurs at mercury electrodes, this inhibits attack of the cation by a coordinating solvent, giving rise to the observation of an apparently mercury-stabilized cation. In principle, any coordinating species including acetonitrile can contribute to the decomposition of the 17-electron cation, so that the rather nonreproducible behavior noted at platinum electrodes vs. the very reproducible response at mercury is probably explicable in terms of trace, but variable amounts of coordinating impurities present in the solvent/supporting electrolyte. Alternatively, trace levels of impurity on the platinum electrode could lead to nonreproducible behavior.

Registry No. $\text{Fe}(\text{CO})_4\text{PPh}_3$, 35679-07-3; $\text{Fe}(\text{CO})_4\text{AsPh}_3$, 35644-25-8; $\text{Fe}(\text{CO})_4\text{SbPh}_3$, 35917-16-9; $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, 21255-52-7; $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$, 20516-72-7; $\text{Fe}(\text{CO})_3(\text{SbPh}_3)_2$, 20516-73-8; $\text{Fe}_2(\text{CO})_9$, 15321-51-4; $\text{Fe}_3(\text{CO})_{12}$, 17685-52-8.

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Oxidation of Manganese(II) Phthalocyanine by Molecular Oxygen

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Manganese(II) phthalocyanine fails to react with oxygen when dissolved in rigorously purified, dry pyridine. Reaction does occur, however, in pure *N,N*-dimethylacetamide to yield a solution of an oxygen adduct. The reaction may be reversed slowly by degassing, more rapidly upon exposure to bright white light or upon addition of an electron donor in vacuo. Addition of certain electron donors, in oxygen, causes conversion to the known $\text{PcMn}^{\text{III}}\text{O}-\text{Mn}^{\text{III}}\text{Pc}$. This oxy-bridged species may be reconverted to the oxygen adduct by reaction with oxygen. The oxygen adduct may be isolated as a solid. Analysis, thermodynamic measurements, infrared (oxygen-18 isotopic substitution) and electronic spectra, magnetism ($S = 3/2$), and ESR appear consistent with the formulation $(\text{O}_2)\text{Mn}^{\text{III}}\text{Pc}$, a bound superoxide.

Introduction

Manganese(II) phthalocyanine when dissolved in pyridine was shown in 1959 to bind molecular oxygen reversibly,¹ to yield a product subsequently demonstrated² to be μ -oxo-bis-((pyridine)(phthalocyaninato)manganese(III)). Despite intensive effort³ many facets of this reaction remained to be explained. Until very recently this was the only manganese-containing system which appeared to bind molecular oxygen reversibly. Basolo, Hoffman, and co-workers⁴ have now shown that MnTPP (TPP = tetraphenylporphyrin) will bind oxygen reversibly but in a fashion which seems quite different from that of the phthalocyanine. There is evidence that salen,^{5a}

catechol,^{5b} sorbitol,^{5c} and some tertiary phosphine^{5d} manganese derivatives will form oxygen adducts. We might also include the rather esoteric $(\text{O}_2)\text{Mn}(\text{CO})_5$.⁶ Manganese is known to be intimately involved in the photooxidation of water during photosynthesis.⁷ Studies of the binding of molecular oxygen to manganese may provide insight into the mechanism by which water bound to manganese is oxidized to molecular oxygen—hence the importance of this area of research.⁸

In this paper we describe further details of the reaction in pyridine and extend the study to solutions in *N,N*-dimethylacetamide, a more attractive solvent for this reaction. Evidence

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