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Kinetic and Equilibrium Studies of the Reactions of Iron(III) and Iron(IV) Dithiolate Complexes with Organic Bases¹

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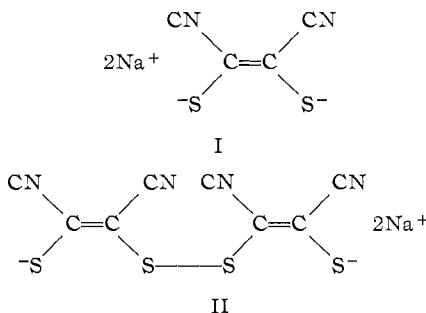
Equilibrium constants are reported for the formation of 1:1 complexes of bis(*cis*-1,2-dicyano-1,2-dithioethylene)iron(III), $\text{Fe}(\text{mnt})_2^-$, with triphenylarsine oxide, pyridine, triphenylphosphine, and triphenylphosphine oxide in acetonitrile at 25°. It is shown that these five-coordinate complexes and their six-coordinate analogs with the bidentate bases 2,2'-bipyridine, ethylenediamine, and the *cis*-1,2-dicyano-1,2-dithioethylene(2-) anion are labile. Substitution of the phenanthroline complex occurs more slowly. Equilibrium constants were determined for the reaction of the monodentate bases with tris(*cis*-1,2-dicyano-1,2-dithioethylene)iron(IV), $\text{Fe}(\text{mnt})_3^{2-}$, according to $2\text{Fe}(\text{mnt})_3^{2-} + 2\text{X} \rightleftharpoons 2\text{XFe}(\text{mnt})_2^- + (\text{mnt})_2^{2-}$ which involves formal reduction of the metal center. The rate of the reaction of $\text{Fe}(\text{mnt})_3^{2-}$ with triphenylarsine oxide was studied and found to be first order in both the complex and the triphenylarsine oxide concentrations with a second-order rate constant of $2.00 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°.

Introduction

From the extensive studies of dithiolate complexes of transition metal ions over the last decade,^{2,3} it has been concluded that the properties of these complexes are best rationalized by the use of molecular orbitals delocalized over the whole molecule rather than by localized molecular orbitals. This property, which manifests itself most strongly in the occurrence of series of oxidation states related by reversible one-electron steps, is shared by many biological metal catalysts such as the metal porphyrins. We have studied some substitution reactions of the formally iron(IV) complex tris(1,2-dicyano-1,2-dithioethylene)iron(IV), $\text{Fe}(\text{mnt})_3^{2-}$, with organic bases and the related reactions of bis(1,2-dicyano-1,2-dithioethylene)iron(III), $\text{Fe}(\text{mnt})_2^-$, with the same bases. The reactions of the iron(IV) complex are thought to be rate controlling in the efficient catalysis of the autoxidation of triphenylphosphine by this complex.^{3,4}

Experimental Section

Materials.—Tetraethylammoniumbis(1,2-dicyano-1,2-dithioethylene)iron(III), $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Fe}(\text{mnt})_2]$, was prepared from sodium *cis*-1,2-dicyanoethylene-1,2-dithiolate (Strem Chemicals), structure I, and iron(III) chloride by the method of Weiher,



Melby, and Benson.⁵ Elemental analysis was in accord with the empirical formula. Tetraethylammoniumtris(1,2-dicyano-1,2-dithioethylene)iron(IV), $[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{Fe}(\text{mnt})_3]$, was prepared by the method of Stiefel and coworkers.⁶ Triphenylarsine and tri-

phenylphosphine were recrystallized K & K Chemical and Eastman reagent chemicals, respectively. Eastman triphenylphosphine oxide and Mallinckrodt analytical reagent pyridine were used without further purification. Triphenylarsine oxide was prepared by oxidation of triphenylarsine with hydrogen peroxide according to Shriner and Wolf.⁷ Disodium *cis,cis*-bis(2-mercapto-1,2-dicyanovinyl) disulfide, $\text{Na}_2(\text{mnt})_2$ (shown in structure II), was prepared by oxidation of Na_2mnt with 1,1,2,2-tetrabromoethane in dimethoxyethane.⁸ Addition of methylene chloride to the filtrate precipitated a yellow solid which had an ultraviolet spectrum in ethanol similar to the spectrum of *cis,cis*- $\text{Na}_2(\text{mnt})_2$ published by Simmons, *et al.*⁸ This salt was found to be contaminated with sodium bromide and attempts to purify the salt were only partially successful. Pure tetraethylammonium salt was prepared by addition of a saturated aqueous tetraethylammonium bromide solution to a concentrated solution (10%) of the sodium salt in water. The yellow precipitate was collected and washed with small quantities of ice-cold water. According to Simmons, *et al.*, the *cis,cis* salt isomerizes to the *trans,trans* isomer in less than 2 hr, but 10^{-3} M solutions of the salt prepared in this work were stable over this time period, although more rapid spectral changes consistent with isomerization were observed in more dilute solutions (10^{-5} M).

Fisher Certified acetonitrile was refluxed over phosphorus pentoxide and then fractionally distilled. Dilute solutions (10^{-3} M) of $\text{Fe}(\text{mnt})_2^-$ in this solvent appeared to be stable for weeks, but more concentrated solutions deposited a fine brown precipitate on standing for more than 1 week. (Decomposition is commonly observed with this salt.³) Absorption spectra of freshly prepared solutions of $\text{Fe}(\text{mnt})_2^-$ in purified acetonitrile differed significantly from previously published data.⁹ In impure solvent, however, spectra similar to the reported spectrum were obtained although the results depended on the source of acetonitrile. Spectra of freshly prepared solutions of $\text{Fe}(\text{mnt})_3^{2-}$ were in quantitative agreement with the published spectrum,⁶ but some slow decomposition occurred over a period of days, particularly upon exposure to light.

Equilibrium and Kinetic Studies.—All of the reactions were studied in acetonitrile at 25° with freshly prepared solutions of the reactants.

Equilibrium constants for the formation of adducts of $\text{Fe}(\text{mnt})_2^-$ were determined spectrophotometrically at the wavelength of the absorbance maximum of $\text{Fe}(\text{mnt})_2^-$ (449 nm) and/or of the adduct. The spectra of the adducts had absorption maxima at 510 nm ($\epsilon 4.85 \times 10^3$) for Ph_3AsO , 443 nm ($\epsilon 9.3 \times 10^3$) and 480 nm ($\epsilon 4.8 \times 10^3$) for pyridine, 588 nm ($\epsilon 2.65 \times 10^3$) and 417 nm ($\epsilon 8.35 \times 10^3$) for Ph_3P , and 422 nm ($\epsilon 6.02 \times 10^3$) and 480 nm ($\epsilon 4.60 \times 10^3$) for Ph_3PO . Because of the small absorbance differences between $\text{Fe}(\text{mnt})_2^-$ and pyridine- $\text{Fe}(\text{mnt})_2^-$ mixtures, equilibrium constants for $\text{pyFe}(\text{mnt})_2^-$ were obtained by competition with $\text{Ph}_3\text{POFe}(\text{mnt})_2^-$. The equilibrium con-

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).

(3) A. L. Balch, *Inorg. Chem.*, **10**, 276 (1971).

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(7) R. L. Shriner and C. N. Wolf, *Org. Syn.*, **30**, 97 (1950).

(8) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Amer. Chem. Soc.*, **84**, 4746 (1962).

(9) J. A. McCleverty, N. M. Atherton, N. G. Connelly, and C. J. Winscom, *J. Chem. Soc. A*, 2242 (1969).

stants obtained directly were in agreement within experimental error with those determined by the competition method. All of the studies involving triphenylphosphine were performed in solvents that had been degassed by several freeze-pump-thaw cycles.

The spectral changes observed on addition of triphenylarsine to solutions of $\text{Fe}(\text{mnt})_2^-$ were quantitatively consistent with the presence of 1 part in 400 of triphenylarsine oxide. Consequently only an upper limit for the stability constant of $\text{Ph}_3\text{AsFe}(\text{mnt})_2^-$ was calculated. This was done by assuming that at either 449 or 510 nm the molar absorptivities of $\text{Fe}(\text{mnt})_2^-$ and its arsine adduct differed by at least 10%.

Esr spectra were obtained with a Varian V4500 X-band spectrometer; g values were determined relative to diphenylpicrylhydrazyl (DPPH).

Equilibrium constants for the reaction of $\text{Fe}(\text{mnt})_3^{2-}$ with the bases were calculated from the concentration of $\text{Fe}(\text{mnt})_3^{2-}$ present at equilibrium. This concentration was determined spectrophotometrically at the absorbance maximum of $\text{Fe}(\text{mnt})_3^{2-}$ (806 nm). At this wavelength the molar absorptivities of all of the other species in solution are less than 0.5% of the molar absorptivity of the iron(IV) complex.

The kinetics of the reaction between the iron(IV) complex and triphenylarsine oxide were generally studied by following the decrease in absorbance of the reaction mixture at 806 nm, although identical rates were obtained when the reaction was followed at 390 nm. Freshly prepared solutions containing all of the reactants except the iron(IV) complex were thermally equilibrated in a stirred 10-cm cell positioned in the cell compartment of a Cary 14 recording spectrometer. The reaction was initiated by the addition of a small volume of a freshly prepared solution of $\text{Fe}(\text{mnt})_3^{2-}$. Although solutions of $\text{Fe}(\text{mnt})_3^{2-}$ slowly change color (over a few days) in the absence of the added solutes, it was found that aged solutions followed kinetics identical with those of the fresh solutions.

Results

Bis(1,2-dicyano-1,2-dithioethylene)iron(III), $\text{Fe}(\text{mnt})_2^-$, is known to be dimeric in the solid state.¹⁰ It is thought that the complex remains dimeric in weakly coordinating solvents such as dichloromethane. Spectral and conductometric data indicate, however, that $\text{Fe}(\text{mnt})_2^-$ is monomeric in acetonitrile up to a concentration of at least $10^{-2} M$.¹¹ Good linear Beer-Lambert plots (at 449 nm) were found in this work over the concentration range 2×10^{-5} to $2 \times 10^{-3} M$ as expected for a completely dissociated complex. As the concentrations of $\text{Fe}(\text{mnt})_2^-$ used in this study are less than $10^{-3} M$, the concentration of dimer must be less than 1% of the total complex concentration in all of the reactant mixtures.

Addition of a variety of organic bases or inorganic ions to solutions of $\text{Fe}(\text{mnt})_2^-$ causes instantaneous color changes associated with the formation of monomeric five-coordinate adducts, many of which have been isolated and characterized.^{9,12} We have found that in acetonitrile these complexes are in rapid reversible equilibrium with free monomeric $\text{Fe}(\text{mnt})_2^-$



Representative values of K_1 , the equilibrium constant for reaction 1, are reported in Table I for the triphenylarsine oxide system, and average values for this compound and some other monodentate bases are presented in Table II.

Reaction of $\text{Fe}(\text{mnt})_2^-$ with triphenylarsine oxide or pyridine was complete in less than 5 sec even at the smallest concentrations needed to observe an absorbance change, allowing upper limits of 10^4 and $10^3 M^{-1}$

TABLE I
EQUILIBRIUM CONSTANT OF REACTION 1,
 $X = \text{Ph}_3\text{AsO}$, AT 25°

$10^4 \times$ initial concn, M		$10^{-2}K_1$, M^{-1}	$10^4 \times$ initial concn, M		$10^{-2}K_1$, M^{-1}
Ph_3AsO	$\text{Fe}(\text{mnt})_2^-$		Ph_3AsO	$\text{Fe}(\text{mnt})_2^-$	
1.44	1.57	3.66	2.26	1.98	4.17
1.68	1.57	3.94	2.26	1.98	3.18
2.12	1.98	3.99	2.40	1.98	4.07
2.12	1.98	3.47			Av 3.8 ± 0.3

TABLE II
SUMMARY OF EQUILIBRIUM CONSTANTS OF REACTIONS 1-3 AT 25°

Base	K_1 , M^{-1}	K_2 , M^{-1}	K_3 , M^{-1}
Ph_3AsO	$(3.8 \pm 1) \times 10^5$	$(1.6 \pm 0.2) \times 10^8$	9×10^7
Pyridine	$(5.2 \pm 1.5) \times 10^3$	$(3.1 \pm 1) \times 10^{-1}$	9×10^7
Ph_3PO	$(5.6 \pm 0.3) \times 10^2$	$(4.2 \pm 1) \times 10^{-3}$	7.4×10^7
Ph_3P	$(9.6 \pm 0.3) \times 10^2$	$(9 \pm 1) \times 10^{-3}$ ^a	...
Ph_3As	<5	$<2 \times 10^{-3}$...

^a This value was calculated from K_1^2/K_2 using the average of the K_2 values for the first three bases in this table. We were unable to determine a value of K_3 directly because of a reaction between triphenylphosphine and $(\text{mnt})_2^{2-}$.⁴

sec⁻¹, respectively, to be placed on the assumed second-order rate constants for these reactions. Displacement of one base by another was equally rapid.

Bidentate ligands, in particular 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy), have been reported⁹ to form low-spin six-coordinate complexes with $\text{Fe}(\text{mnt})_2^-$. Addition of these bases to solutions of $\text{Fe}(\text{mnt})_2^-$ causes rapid spectral changes presumably associated with complex formation, since the final spectra are identical with the spectra of solutions of the isolated complexes.¹² The phenanthroline complex is stable for at least several hours in the presence of a small excess of phenanthroline. However, a purple precipitate indicative of $\text{Fe}(\text{phen})_3^{3+}$ appears in 2 or 3 days in the presence of a large excess of phenanthroline. The bipyridine complex appeared to be stable for longer periods. Addition of phenanthroline to solutions of $\text{bipyFe}(\text{mnt})_2^-$ resulted in an immediate spectral change; the final spectrum being identical with the spectrum of $\text{phenFe}(\text{mnt})_2^-$. In solutions of $\text{phenFe}(\text{mnt})_2^-$ containing high concentrations of bipyridine spectral changes consistent with the formation of $\text{bipyFe}(\text{mnt})_2^-$ occurred with a half-time of about 10 min. Ethylenediamine (en) also produces rapid spectral changes when added to $\text{Fe}(\text{mnt})_2^-$. Although the complex $\text{enFe}(\text{mnt})_2^-$ has not been reported previously (only the perfluoro analog has been isolated⁹), it is reasonable to suppose that the spectral changes are associated with the formation of this complex. Again, addition of phenanthroline or bipyridine to $\text{enFe}(\text{mnt})_2^-$ solutions resulted in rapid spectral changes quantitatively consistent with the formation of $\text{phenFe}(\text{mnt})_2^-$ and $\text{bipyFe}(\text{mnt})_2^-$. Similarly $\text{enFe}(\text{mnt})_2^-$ is quantitatively formed by adding ethylenediamine to $\text{bipyFe}(\text{mnt})_2^-$.

In order to confirm these results we have investigated the electron spin resonance spectra of frozen solutions of $\text{Fe}(\text{mnt})_2^-$ with these bases at 77°K. $\text{Fe}(\text{mnt})_2^-$ alone does not give an esr spectrum but in the presence of the three bases, powder spectra characteristic of compounds with two principal g values were obtained and analyzed by the method of Kneubuhl.¹³ The spectra

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(12) E. F. Epstein and I. Bernal, *Chem. Commun.*, 136 (1970).

(13) F. K. Kneubuhl, *J. Chem. Phys.*, **33**, 1074 (1960).

of phenFe(mnt)₂²⁻ and bipyFe(mnt)₂²⁻ were identical with *g* values *g*₁ = *g*₂ = 2.120, *g*₃ = 2.003, and *g*_{av} = 2.081, in good agreement with the value of 2.083 determined by McCleverty, *et al.*⁹ The complex enFe(mnt)₂²⁻ displayed *g* values of *g*₁ = *g*₂ = 2.145, *g*₃ = 1.993, and *g*_{av} = 2.095. In accord with the results of the spectrophotometric studies, addition of an excess of phenanthroline or bipyridine to solutions of enFe(mnt)₂²⁻ followed by immediate freezing and observation of the esr spectrum showed that the ethylenediamine was substituted by the other two bases in less than 30 sec.

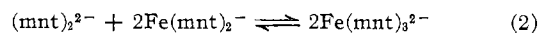
Semiquantitative studies indicated that the phenanthroline complex was more stable than either the bipyridine or the ethylenediamine complex and that all the bidentate ligands form much more stable complexes (*K* > 10⁶ M⁻¹) with Fe(mnt)₂²⁻ than do the monodentate bases.

Tris(*cis*-1,2-dicyano-1,2-dithioethylene)iron(III), Fe(mnt)₃³⁻, has an esr spectrum and a magnetic susceptibility consistent with its formulation as a monomeric, low-spin iron(III) complex.^{14,15} We have prepared this complex *in situ* by the addition of a small excess of Na₂mnt to Fe(mnt)₂²⁻ in thoroughly degassed acetonitrile. Although the esr spectrum of this solution at 77°K (*g*₁ = 2.22, *g*₂ = 2.087, *g*₃ = 1.985) is in substantial agreement with the solid-state spectrum previously reported¹⁴ (*g*₁ = 2.225, *g*₂ = 2.114, *g*₃ = 1.986), the absorption spectrum is totally different from the spectrum reported by McCleverty, *et al.*¹⁵ These workers observed an absorption maximum in the solution spectrum of 800 nm, but we found no evidence of a maximum at this wavelength; instead maxima were observed at 1030 nm (*ε* 1300) and 670 nm (*ε* 1700). Exposure of the solutions to atmospheric oxygen resulted in the rapid disappearance of these absorption bands and the formation of a new band with a maximum at 805 nm, suggesting that the spectrum reported by McCleverty and coworkers is the spectrum of air-oxidized Fe(mnt)₃³⁻. The major product of this oxidation is the iron(IV) complex Fe(mnt)₃²⁻.

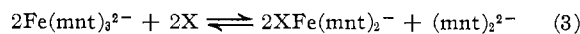
Apparently triphenylarsine oxide does not interact with Fe(mnt)₃³⁻ since a concentrated (0.1 M) solution of the oxide did not affect the absorption spectrum of Fe(mnt)₃³⁻, but addition of phenanthroline to a solution of this complex results in rapid (<1 min) spectral changes consistent with the formation of phenFe(mnt)₂²⁻. Fe(mnt)₃³⁻ is also formed by the addition of mnt²⁻ to Ph₃AsOFe(mnt)₂²⁻ (in 0.1 M Ph₃AsO).

X-Ray diffraction studies¹⁶ have shown that the iron(IV) complex Fe(mnt)₃²⁻, prepared by reaction of air-saturated solutions of Fe(mnt)₂²⁻ with Na₂mnt, is monomeric with the structure expected for a tris-bidentate octahedral complex. Solutions of this salt exhibit a broad absorption band in the near-infrared spectrum with a maximum at 806 nm (*ε* 3300 ± 30). Addition of a small excess of the *cis,cis* dimer of the oxidized dithiolate ligand ((mnt)₂²⁻) to Fe(mnt)₂²⁻ results in the rapid formation of an absorption band with a maximum at 806 nm (*ε* 3330 ± 50). This band may be reasonably assigned to Fe(mnt)₃²⁻ formed through the

reaction



The complex Fe(mnt)₃²⁻ reacts with organic bases (X) with the formation of the corresponding five-coordinate adducts of Fe(mnt)₂²⁻



where (mnt)₂²⁻ was found to be the *cis,cis* isomer.⁸ Absorption maxima characteristic of the adducts were formed on addition of triphenylarsine oxide, triphenylphosphine oxide, or pyridine to Fe(mnt)₃²⁻ solutions, concurrently with the disappearance of the absorbance maximum of the iron(IV) complex. Also, the difference between the absorption spectrum of a solution of Fe(mnt)₃²⁻ and an equimolar solution of Fe(mnt)₂²⁻, both containing an excess of triphenylarsine oxide or pyridine, was found to be quantitatively identical with the spectrum of independently prepared *cis,cis*-(mnt)₂²⁻. From difference spectra the molar absorptivity of (mnt)₂²⁻ formed through reaction 3 was found to be (2.71 ± 0.03) × 10⁴ when X = Ph₃AsO, in good agreement with the value of (2.75 ± 0.03) × 10⁴ determined directly from solutions of (mnt)₂²⁻ alone. Reaction 3 was also shown to be reversible by the formation of Fe(mnt)₃²⁻ when (mnt)₂²⁻ was added to solutions of XFe(mnt)₂⁻.

The equilibrium constant for reaction 3, *K*₃, for X = Ph₃AsO, was calculated for various initial mixtures of the reactants and products from the concentration of Fe(mnt)₃²⁻ present at equilibrium (determined spectrophotometrically at 806 nm). The results are listed in Table III. Average values of *K*₃, that were determined in the same way for the other bases, are reported in Table II. Since *K*₁²/*K*₃ is equal to *K*₂, the equilib-

TABLE III
EQUILIBRIUM CONSTANT OF REACTION 3,
X = Ph₃AsO, AT 25°

Fe(mnt) ₂ ²⁻	10 ⁴ × initial concn, M		Ph ₃ AsO	10 ⁻³ <i>K</i> ₃ , M ⁻¹
	Fe(mnt) ₃ ²⁻	(mnt) ₂ ²⁻		
29.6	...	3.00	80.6	1.74
29.6	...	6.00	80.6	1.66
29.6	...	12.0	80.6	1.88
29.6	3.05	...	80.6	1.85
29.6	4.27	...	80.6	1.50
29.6	6.10	...	80.6	1.38
...	5.77	3.80	34.4	1.63
...	8.08	3.80	34.4	1.32
...	11.5	3.80	34.4	1.60
...	17.3	3.80	34.4	1.60
				Av 1.61 ± 0.12

rium constant for reaction 2, this ratio should be independent of the base in reactions 1 and 3. The consistency of *K*₁²/*K*₃ (Table II) confirms the stoichiometry of reactions 1 and 3.

Kinetic Measurements.—With X = Ph₃AsO and in the absence of added products, reaction 3 proceeds practically to completion provided the triphenylarsine oxide concentration is present in sufficient excess to maintain first-order conditions. (At the lowest [Ph₃AsO] in Table IV, 94% of the initial Fe(mnt)₃²⁻ reacts to form Ph₃AsOFe(mnt)₂⁻.) Under these conditions good first-order plots were obtained for the disappearance of Fe(mnt)₃²⁻. These plots yielded the pseudo-first-order rate constants in Table IV. These rate constants are plotted against the triphenylarsine

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(15) J. A. McCleverty, J. Locke, E. J. Wharton, and M. Gerloch, *ibid.*, A, 816 (1968).

(16) A. Sequeira and I. Bernal, *J. Phys. Chem.*, in press.

TABLE IV
RATE CONSTANTS FOR REACTION 3,
X = Ph₃AsO, AT 25°

10 ⁵ × initial concn, M			10 ⁻³ k, sec ⁻¹	10 ⁵ × initial concn, M			10 ⁻³ k, sec ⁻¹
Fe-(mnt) ₂ ²⁻	Ph ₃ -AsO	(mnt) ₂ ²⁻		Fe-(mnt) ₂ ²⁻	Ph ₃ -AsO	(mnt) ₂ ²⁻	
3.03	149	...	3.85	3.03	1580	...	32.5
3.03	313	...	7.26	15.7	9330	...	210
3.03	616	...	13.25	2.70	408	24	10.5
3.01	777	...	15.7	3.03	575	24	13.5
3.03	930	...	19.7	3.03	920	24	21.0
3.02	1230	...	25.3				

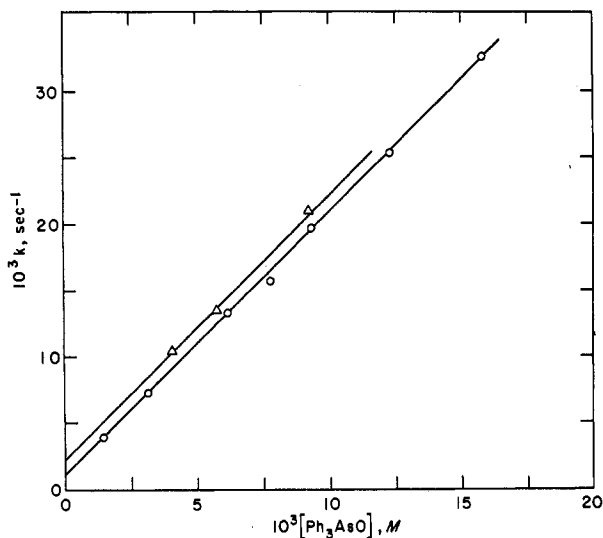


Figure 1.—Plot of k_{obsd} vs. the concentration of triphenylarsine oxide in acetonitrile at 25°. The solutions used to obtain the kinetic data shown in the upper curve contain $2.4 \times 10^{-3} M$ $(\text{mnt})_2^{2-}$.

oxide concentration in Figure 1. This plot shows that the kinetic data are consistent with the empirical rate equation

$$-\frac{d}{dt} [\text{Fe}(\text{mnt})_2^{2-}] = (k_a[\text{Ph}_3\text{AsO}] + k_b)([\text{Fe}(\text{mnt})_2^{2-}] - [\text{Fe}(\text{mnt})_2^{2-}]_{\text{eq}}) \quad (\text{I})$$

The constant k_b , which is the intercept in Figure 1, presumably arises from a small contribution to the observed rate constant from the reverse reaction. Consistent with this interpretation, addition of $(\text{mnt})_2^{2-}$ increased the magnitude of the intercept without affecting the slope of the plot of k_{obsd} vs. $[\text{Ph}_3\text{AsO}]$ (see Figure 1). The value of k_a calculated from the slope of these plots is $2.00 \pm 0.05 M^{-1} \text{sec}^{-1}$ at 25°. No significant deviation from eq 4 was observed even at much higher triphenylarsine oxide concentrations; a run at $[\text{Ph}_3\text{AsO}] = 0.093 M$ gave $k_a = 2.2 M^{-1} \text{sec}^{-1}$. The kinetic and thermodynamic parameters did not change when the runs were performed in the absence of air.

Possible radical intermediates in reaction 3 could not be detected by esr either in reacting solutions at room temperature or in frozen pellets prepared by freezing droplets of the reactant mixture in liquid nitrogen.

Discussion

The equilibrium data strongly support the validity of reactions 1–3; in particular the consistency of K_2 leaves little doubt that the stoichiometry of the reactions is correctly described. We find no evidence either

in the spectra or in the equilibrium studies for the formation of six-coordinate species with the monodentate bases, in contrast to the recent conclusion of De Vries, *et al.*,¹⁷ based on Mössbauer spectra at 77°K.

The values of K_1 decrease in the order $\text{Ph}_3\text{AsO} > \text{pyridine} > \text{Ph}_3\text{P} > \text{Ph}_3\text{PO} > \text{Ph}_3\text{As}$. This order is in general accord with the suggestion of Balch³ that iron(III) bis dithiolates behave as hard acids with respect to coordination in the fifth position, except that the stabilities of the phosphine and phosphine oxide adducts are in the wrong order. It is interesting to note in this context that the triphenylphosphine complex has a doublet ($S = 1/2$) ground state, whereas all the other adducts have quartet ($S = 3/2$) ground states. Caughey, *et al.*,¹⁸ have reported that (deuteroporphyrin IX dimethyl ester)iron(III) also behaves as a hard acid in its coordination with halide ions.

All of the five-coordinate adducts studied are labile with respect to formation and dissociation. This suggests, considering the variety of donor atoms, that this lability is a common feature of five-coordinate bis-dithiolate complexes of iron(III). A similar complex with a quartet ground state, monochlorobis(diethyl-dithiocarbamato)iron(III), is also reported to be labile.¹⁹

In contrast to the relatively weakly bonded, labile, apical ligands, the dithiolate ligands in the basal plane are inert to substitution to a degree comparable to "normal" low-spin iron(III) complexes. This may be attributed to the extraordinary stability achieved by electron delocalization over the π system of the ligand. The planar configuration of the two dithiolate ligands appears to be unessential for this stability for the dithiolate ligand is also inert to substitution in $\text{Fe}(\text{mnt})_2^{2-}$. The sulfur-bonded ligands are presumably not coplanar in the latter complex.

Since octahedral low-spin iron(III) complexes are usually inert to substitution, it is surprising to find that the complexes $\text{Fe}(\text{mnt})_3^{3-}$, $\text{enFe}(\text{mnt})_2^{2-}$, and $\text{bipyFe}(\text{mnt})_2^{2-}$ are labile in solution (complete substitution in less than 20 sec). The complex tris(diethyl-dithiocarbamato)iron(III) has also been reported to be labile¹⁹ and it was suggested that the lability is due to the presence of some high-spin complex in equilibrium with the low-spin form. This explanation may be applicable to $\text{Fe}(\text{mnt})_3^{3-}$ as magnetic susceptibility studies of this complex show deviations from Curie's law that may be related to the existence of a thermally accessible high-spin state.¹⁵ However, it is unlikely that the other complexes are also sufficiently close to a spin-state crossover to be able to rationalize their lability in this way. The formally cobalt(III) complex $\text{phenCo}(\text{mnt})_2^{2-}$ is also substitution labile²⁰ even though low-spin cobalt(III) complexes are usually inert to substitution. However, since the oxidation states in dithiolate complexes are ill defined (because of electron delocalization over the whole molecule), considerable caution is required in the comparisons of the reactions of dithiolate complexes with complexes containing metal ions in less ambiguous oxidation states.

Disregarding the formal oxidation states, reaction 3

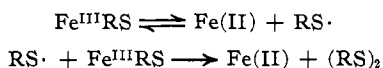
(17) J. L. K. F. De Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, **10**, 81 (1971).

(18) W. S. Caughey, H. Eberspaecher, W. H. Fuchsman, S. McCoy, and J. O. Alben, *Ann. N. Y. Acad. Sci.*, **155**, 722 (1969).

(19) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).

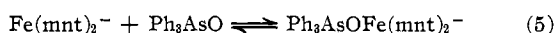
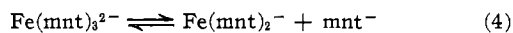
(20) D. G. DeWit, M. J. Hynes, and D. A. Sweigart, *ibid.*, **10**, 196 (1971).

and in particular reaction 2 are similar to the well-known reactions of iron(III) salts of thiols such as cysteine: $2\text{Fe}^{\text{III}}(\text{RS})_n^{3-n} \rightarrow 2\text{Fe}(\text{II}) + \text{RSSR}^{2-}$. Reactions 2 and 3 involve a similar change in the formal oxidation state of both metal and ligand. The thiol reactions,²¹ in contrast to reaction 3, obey second-order kinetics ($d[\text{Fe}(\text{II})]/dt = k[\text{Fe}(\text{III})]^2$) which is attributed to the initial formation of iron(III) dimers. Second-order kinetics would, however, also be expected from the reaction scheme

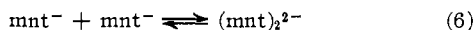


if the first reaction may be treated as a rapid preequilibrium. Since reaction 3 has been found to follow good first-order kinetics, mechanisms of the above type are not applicable to the dithiolate systems. In particular, initial dimerization either as the slow reaction in the mechanism or as a rapid preequilibrium is not consistent with first-order behavior.

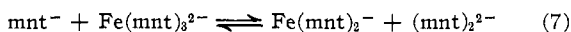
At first glance reactions 4–7 constitute a reasonable mechanism for reaction 3



and either



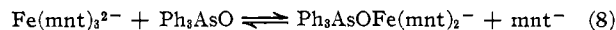
or



However, close analysis indicates that the first-order dependence on both $\text{Fe}(\text{mnt})_3^{2-}$ and Ph_3AsO concentra-

(21) D. L. Leussing and L. Newman, *J. Amer. Chem. Soc.*, **78**, 552 (1956).

tions is not realizable through this scheme. We consider the most plausible mechanism to involve direct attack of the nucleophiles on $\text{Fe}(\text{mnt})_3^{2-}$ or on a half-bonded intermediate (reaction 8). This reaction would



then be followed by either reaction 6 or 7 in a rapid second step. This mechanism is consistent with the observed first-order dependence on both $\text{Fe}(\text{mnt})_3^{2-}$ and Ph_3AsO concentrations provided that the reverse of reaction 8 can be ignored (*i.e.*, provided $k_6[\text{mnt}^-]^2 \gg k_{-8}[\text{Ph}_3\text{AsOFe}(\text{mnt})_2^-][\text{mnt}^-]$). In terms of this interpretation the value of k_a calculated from the slope of Figure 1 is the second-order rate constant for reaction 8. There are, of course, other possible reaction schemes consistent with the kinetic data. For example, a mechanism involving the elimination of mnt^{2-} from $\text{Fe}(\text{mnt})_3^{2-}$ in the first step is a possible alternative to the first reaction in the proposed mechanism, but we consider it less likely on thermodynamic grounds. We are unable at this time to assign a detailed mechanism to reaction 3 with any confidence.

Finally, another system in which iron in an oxidation state of 4 has been proposed is oxyhemoglobin.^{22,23} In terms of this oxidation state assignment the deoxygenation of oxyhemoglobin may be considered as a reductive elimination reaction in which ferroheme and molecular oxygen are formed. The deoxygenation reaction would then be analogous to reaction 3 for in each case a low-spin iron(IV) complex is postulated to undergo rapid reductive elimination.

(22) N. Sutin in "Oxidases and Related Redox Systems," T. E. King, H. S. Mason, and M. Morrison, Ed., Wiley, New York, N. Y., 1964, p 46.

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Metal Carbonyl-Trifluorophosphine Systems. XI. The Fluxional Cyclohexadienetricarbonyliron(0) System

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1,3-Cyclohexadieniron tricarbonyl reacts with phosphorus trifluoride to yield a series of compounds of the general type $\text{C}_6\text{H}_8\text{Fe}(\text{PF}_3)_x(\text{CO})_{3-x}$. The individual species are separable by glpc and are light yellow solids of moderately low volatility. Both infrared and fluorine nmr show that the mono- and diphosphines contain two distinct isomers although these isomers are not separable by glpc. These isomers appear to exist owing to the ability of the CO and PF_3 ligands to occupy either apical or basal sites in the square-based pyramidal structure.

Introduction

1,3-Cyclohexadieniron tricarbonyl, $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$, was first prepared by Hallam and Pauson¹ and found to be closely related to butadieniron tricarbonyl, $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$, prepared as part of the same investigation. Proton nmr clearly indicates a similarity between the two complexes.² X-Ray crystallographic data on the fluorine analog, $\text{C}_6\text{F}_8\text{Fe}(\text{CO})_3$, shows that the cyclo-

hexadiene and butadiene complexes are structurally related.³

Studies of phosphine substitution into $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$ and into other dieneiron tricarbonyls are few. However, the coordination chemistry of the $\text{C}_4\text{H}_6\text{Fe}(\text{PF}_3)_x(\text{CO})_{3-x}$ system ($x = 1, 2, 3$) has been investigated in depth. This study included carbonyl force constant calculations and variable-temperature fluorine nmr.⁴

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