Autoxidation Reactions Catalyzed by Iron(III) and Iron(IV) Dithiolate Complexes[1]

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Abstract: Kinetic studies are reported on the autoxidation of triphenylphosphine catalyzed by $Fe(mnt)_2^-$ and $Fe(mnt)_3^{2-}$ where mnt^{2-} is *cis*-1,2-dicyanoethylene-1,2-dithiolate. Both iron complexes are excellent catalysts of triphenylphosphine autoxidation, but 1 mol of the iron(IV) complex catalyzes the oxidation of approximately 15 mol of triphenylphosphine compared to about 10 mol of triphenylphosphine for the iron(III) complex. The rate of oxygen uptake in the presence of either complex was found to be proportional to the concentration of both triphenylphosphine and the iron complex but independent of oxygen pressure. However, the $Fe(mnt)_3^{2-}$-catalyzed rate of oxygen uptake is 15 times the $Fe(mnt)_2^-$-catalyzed rate at 25° in acetonitrile. No evidence was obtained for the formation of molecular oxygen complexes. Less extensive studies of the catalyzed autoxidation of cumene and of triphenylarsine are described. The mechanisms of the autoxidation reactions are discussed.

Epstein, *et al.*,[2] recently attempted to prepare crystals of a five-coordinate adduct of triphenylphosphine with the bis[1,2-di(trifluoromethyl)-1,2-dithioethylene]iron(III) anion, $[(Fe(S_2C_2(CF_3)_2)_2]^-$, by evaporating an equimolar mixture of reactants. Instead of the desired product, the only compound isolated by them was a triphenylphosphine oxide adduct of the iron(III) anion. It was suggested by these workers that the reaction appeared to be another example of "the activation of molecular oxygen by a metal complex" since the atmosphere was the only source of oxygen in their system. The adducts of triphenylphosphine and triphenylarsine with the dicyano analog,[3] $[Fe(mnt)_2]^-$, of the trifluoromethyl complex also undergo similar oxidations at room temperature.[4] McCleverty and coworkers[5] have suggested that the cyanide, azide, and cyanate adducts of the latter iron(III) complex also oxidize in the presence of air to form a nitrosyl adduct.

These dithiolate complexes are evidently powerful autoxidation catalysts, for triphenylphosphine normally autoxidizes only at elevated temperatures even in the presence of radical initiators such as azoisobutyronitrile.[6] Other catalysts of similar activity include several complexes which catalyze autoxidation through the formation of stable oxygen adducts with the metal center.[7] This observation, as well as the unusual chemical and physical properties of dithiolate complexes,[8] suggested that oxygen adducts might also be important in dithiolate autoxidation. We have therefore investigated the mechanism of some of these autoxidation reactions, in particular the triphenylphosphine oxidation, in an attempt to obtain evidence for molecular oxygen complexes either as stable species or as reactive intermediates in these systems.

In the course of this work it was discovered that the tris-dithiolate complex, $[Fe(mnt)_3]^{2-}$, was an even more effective autoxidation catalyst than the corresponding bis complex. We have therefore also examined some reactions of this complex. Some qualitative observations consistent with our findings have recently been independently reported by Balch.[4]

Experimental Section

Materials. The preparation and purification of the materials used in this work have been described elsewhere.[9] All of the reactant solutions were prepared immediately prior to use.

Procedure. Oxygen consumption experiments were performed with a simple constant-pressure device consisting of a reaction vessel thermostated at 25.0 ± 0.1° and equipped with a magnetic stirrer. This vessel was connected to a flexible U tube containing mercury which allowed the pressure to be kept constant in the reaction vessel and enabled the volume change at constant pressure in the reaction vessel to be directly determined. These volume changes were corrected for the presence of acetonitrile vapor. In most experiments the reaction vessel was a 50-ml flask with a sidearm sealed by a silicone puncture seal. This arrangement permitted the introduction of reactant solutions without opening the system to the atmosphere. The apparatus was usually equilibrated with all of the reactants except triphenylphosphine which was introduced through the puncture seal after equilibration. In the experiments with oxygen, the system was first purged by bubbling oxygen through the solution for 15 min and then allowed to equilibrate before initiation of the reaction by the introduction of triphenylphosphine. It was also possible to mix all of the reactants, including triphenylphosphine, immediately degas the system by freeze, pump, thaw cycles, and then to initiate reaction by bubbling with oxygen or air for 2 min.

Another reaction vessel was used in instances where equilibration of the reactants in the presence of solid was required. The solid was placed in a bent sidearm which was attached by a ground glass joint to the reaction vessel. After equilibration the sidearm could be rotated allowing the solid to fall into the reactant solution. This technique was used in the attempt to detect oxygen adducts directly as well as in testing the effect of $FeCl_2$ and Na_2mnt on the reaction rate.

Kinetics and equilibria of reactions 2 and 3 were studied by the technique reported previously.[9]

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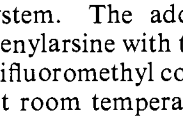
[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] I. Bernal, E. F. Epstein, and A. L. Balch, *Chem. Commun.*, 136 (1970).

[3] mnt^{2-} = maleonitriledithiolate



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[8] J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).

[9] J. K. Yandell and N. Sutin, *Inorg. Chem.*, 11, 448 (1972).

Product Analysis. Triphenylphosphine oxide was separated from the other reaction products by ion exchange on a Dowex 1-X2 column that had previously been washed with acetonitrile. In addition to triphenylphosphine oxide, another product, dithiin,[10] was not absorbed on the column. However, since the triphenylphosphine oxide was always present in much greater concentration, the dithiin did not interfere with the spectrophotometric determination of the oxide which has an absorbance maximum at 265 nm.[11] Because the molar absorptivity of triphenylphosphine is five times higher than that of the oxide at 265 nm, the spectrophotometric method is sensitive to small concentrations of triphenylphosphine.

Results

Where not specifically mentioned, the results refer to solutions in acetonitrile at 25°.

A. Reactions of $Fe(mnt)_2^-$. 1. Oxygen Independent Reactions. Bis(*cis*-1,2,dicyano-1,2-dithioethylene)iron(III), $Fe(mnt)_2^-$, is known to be a dimer in the solid state,[12] but in pyridine and other σ-bonding solvents it forms monomeric five-coordinate solvent adducts.[5] It is thought that the compound remains dimeric in weakly coordinating solvents such as dichloromethane and dichloroethane while spectral[5] and conductometric[13] data lead to the conclusion that $Fe(mnt)_2^-$ is monomeric in acetonitrile and acetone.

Addition of triphenylphosphine, triphenylarsine, or their oxides to solutions of $Fe(mnt)_2^-$ causes instantaneous color changes associated with the formation of five-coordinate adducts (eq 1). The equilibrium

$$Fe(mnt)_2^- + X \rightleftharpoons XFe(mnt)_2^- \qquad (1)$$

constants for this rapid, reversible reaction are 9.6×10^2 ($X = Ph_3P$), 5.6×10^2 (Ph_3PO), 3.8×10^5 (Ph_3AsO), and less than 5 M^{-1} (Ph_3As).[9] Complexes, which are presumably six coordinate, are formed with bidentate bases such as 1,10-phenanthroline. The stability constants of these complexes are greater than the stability constants of the complexes with monodentate bases.

After the initial rapid color change associated with the formation of the adducts, there are no further spectral changes after 40 hr in solutions containing triphenylarsine oxide or in rigorously degassed solutions containing triphenylphosphine. Small spectral changes are observed in solutions of $Fe(mnt)_2^-$ alone in the same time period. In the presence of air and high concentrations of cyanide, azide, chloride, or 1,10-phenanthroline (but not triphenylarsine oxide), $Fe(mnt)_2^-$ solutions undergo slow irreversible color changes (2–3 days) but in the absence of air these changes occur to a lesser extent. These changes may be interpreted as a slow partial displacement of mnt^{2-} from the metal, which in the presence of air goes to completion due to the irreversible oxidation of the free mnt^{2-}. Whatever the mechanism of such reactions, it is apparent the mnt^{2-} is only very slowly displaced from $Fe(mnt)_2^-$.

$Fe(mnt)_2^-$ also undergoes facile redox reactions. Polarographic studies have shown that $Fe(mnt)_2^-$ can be reduced in two reversible one-electron steps and oxidized in a single one-electron step with a half-wave potential in acetonitrile of -0.40 V relative to a calomel electrode.[8] It is expected from this value, based on the rules of thumb established by Davison and Holm,[14] that $Fe(mnt)_2^-$ will not be reduced by weak reducing agents. This was confirmed by the absence of any spectral changes on the addition of *p*-phenylenediamine or diphenylamine to $Fe(mnt)_2^-$ solutions. The rules of Davison and Holm also predict that the reduced species $Fe(mnt)_2^{2-}$ should be readily oxidized by molecular oxygen. This prediction is supported by the observation that degassed mixtures of Fe(II) and mnt^{2-} undergo rapid (10^{-2} sec) spectral changes when mixed with oxygen-saturated solutions.

Rapid decolorization (from brown-black to pale yellow) of solutions of $Fe(mnt)_2^-$ by *p*-quinone and tetrabromoethane also suggests that the complex may be readily oxidized by these oxidants.

2. $Fe(mnt)_2^-$-Catalyzed Autoxidation of Triphenylphosphine. Stoichiometry. In the presence of oxygen, mixtures of triphenylphosphine and $Fe(mnt)_2^-$ slowly change color. If the initial triphenylphosphine concentration is less than twice the $Fe(mnt)_2^-$ concentration the color change is qualitatively, but not quantitatively, consistent with the conversion of $Ph_3PFe(mnt)_2^-$ to $Ph_3POFe(mnt)_2^-$. Thus when sufficient triphenylarsine oxide was added at the end of the oxidation to completely complex the $Fe(mnt)_2^-$, it was found that the spectra in the visible region did not correspond exactly to that expected on the basis of the initial concentration of $Fe(mnt)_2^-$ indicating that some decomposition of the $Fe(mnt)_2^-$ had occurred. At higher triphenylphosphine to $Fe(mnt)_2^-$ ratios, extensive decomposition of the complex occurred, and the equilibrium spectra were very different from the spectra of the corresponding mixture of triphenylphosphine oxide and $Fe(mnt)_2^-$. *Determination of the triphenylphosphine oxide formed showed that at least 95% of the triphenylphosphine was converted to the oxide even when the initial concentration of triphenylphosphine was ten times the initial concentration of* $Fe(mnt)_2^-$.

The spectra of the ion-exchange eluate obtained from oxidized solutions with high initial triphenylphosphine to $Fe(mnt)_2^-$ concentration ratios also exhibited weak maxima at 310 and 327 nm. Oxidation of Na_2mnt by hydrogen peroxide in acetonitrile produced a species with an identical spectrum, which was reported by Simmons, *et al.*,[10] to be dithiin. Ultraviolet spectra of solutions of much higher total concentration but containing a large excess of triphenylphosphine indicated the presence of another species, which was tentatively identified as *trans,trans*-$Na_2(mnt)_2$ by comparison with the spectrum reported by Simmons, *et al.*

All of the above results were obtained in acetonitrile, but spectral changes were observed in acetone, dichloromethane, 1,2-dichloroethane, and 1-dichlorobenzene which suggest that triphenylphosphine converts to the oxide in these solvents as well. Analysis confirmed that triphenylphosphine oxide is quantitatively formed in dichloromethane and dichloroethane.

Experiments with the oxygen consumption apparatus showed that more oxygen was consumed during the reaction in acetonitrile than was necessary for complete oxidation of the triphenylphosphine. The amount of oxygen taken up depended on the experimental con-

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[10] H. E. Simmons, D. C. Blomstrom, R. D. Vest, J. R. Roland, and T. L. Cairns, *J. Amer. Chem. Soc.*, **84**, 4746 (1962).

[11] H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

[12] W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967).

[13] A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968).

[14] A. Davison and R. H. Holm, *Inorg. Syn.*, **10**, 8 (1967).

ditions; in air the solutions took up 1.1–1.4 g-atoms of oxygen per mol of triphenylphosphine, but in pure oxygen 1.4–1.7 g-atoms of oxygen were taken up per mol of triphenylphosphine. The ratio of oxygen consumed to triphenylphosphine oxidized also increased as the concentration of $Fe(mnt)_2^-$ increased, both in air and oxygen. Some typical results are given in Table I.

Table I. Rate of Oxygen Uptake by Triphenylphosphine Catalyzed by $Fe(mnt)_2^-$ in Acetonitrile at 25°

$10^4[Fe(mnt)_2^-]$,[a] M	$10^4[Ph_3P]$,[a] M	$10^7 R_{max}$,[b] M sec^{-1}	$10^4 R_{max}/[Fe(mnt)_2^-]$, sec^{-1}	$\Delta[O]/[Ph_3P]$[c]
		In Oxygen		
4.46	31.1	1.0	2.2	1.59
8.96	31.6	4.1	4.6	1.62
8.96	31.6	3.9	4.4	1.60
12.0	31.3	5.6	4.7	1.60
17.6[d]	31.3	8.5	4.9	
36.9	31.1	17	4.6	1.87
73.9	31.1	29	3.9	1.80
17.8	8.19	3.2	1.8	1.87
17.8	15.6	7.8	4.4	1.75
17.6[d]	31.3	8.5	4.9	
17.8	64.5	14.4	8.1	1.53
17.8	129	18.8	10.6	1.30
15.4[e]	31.2	3.7	2.4	1.85
19.5[e]	31.2	4.1	2.1	1.85
		In Air		
8.96	31.6	1.8	2.0	1.32
10.7	31.7	4.1	3.9	1.35
17.6[d]	31.7	7.6	4.3	
18.5	31.2	7.5	4.1	1.45
36.9	31.1	17	4.6	1.49
73.9	31.1	21	2.9	1.50

[a] Initial concentrations. [b] Maximum rate of oxygen uptake. [c] Gram atoms of oxygen consumed per mole of Ph_3P. [d] Runs in which the air-free reactants had stood for 2 hr before admitting oxygen. [e] In 1,2-dichloroethane.

No oxygen was taken up by solutions of triphenylphosphine in 3 days at 25°, nor was any oxygen taken up by $Fe(mnt)_2^-$ solutions in the same period. It was also found that no oxygen was absorbed when solid $Fe(mnt)_2^-$ was dissolved in acetonitrile either at 25 or −35°. Similarly, no oxygen absorption (or evolution) was observed when $Fe(mnt)_2^-$ was dissolved in solutions of triphenylphosphine. From these experiments an upper limit was calculated for the stability constant of possible oxygen adducts with $Fe(mnt)_2^-$ (or $Ph_3PFe(mnt)_2^-$), $K_{stab} = [O_2Fe(mnt)_2^-]/[Fe(mnt)_2^-][O_2] < 0.1$, where $[O_2]$ is the pressure of oxygen in atmospheres in equilibrium with the solution. No oxygen was evolved from an oxygen-saturated $Fe(mnt)_2^-$ solution when a large excess of triphenylarsine oxide was added. Such an evolution is expected if a significant concentration of an oxygen adduct had been present in the solution.

The electron spin resonance spectra of solutions of $Fe(mnt)_2^-$ alone and in the presence of an excess of either triphenylphosphine or triphenylarsine or their oxides were investigated at room temperature and at 77°K. No signal was detected with any of the bases except triphenylphosphine and then only at 77°K. At complex concentrations greater than 10^{-3} M a single isotropic line with a half-width of 50 G was observed at $g = 2.045$. At lower $Fe(mnt)_2^-$ concentrations the esr spectra exhibited some fine structure (Figure 1B) which increased with decreasing concentration but was not affected by the presence of oxygen. In ethanol, the esr spectra of solutions of phosphine and $Fe(mnt)_2^-$ were not concentration dependent and exhibited considerable fine structure (Figure 1A). The spectrum may be synthesized by the superimposition of two identical anisotropic powder spectra separated by 22 G. We therefore assign this spectrum to a single species with anisotropic g values and an isotropic hyperfine splitting of 22 G. This species must be the adduct $Ph_3PFe(mnt)_2^-$, the hyperfine splitting arising from the phosphorus nucleus ($I = {}^1/_2$). g values obtained by this analysis are $g_1 = 2.075$, $g_2 = 2.041$, and $g_3 = 2.013$. The mean g value, 2.043 ± 0.005, is in satisfactory agreement with the isotropic value of 2.046 reported by McCleverty, *et al.*[5]

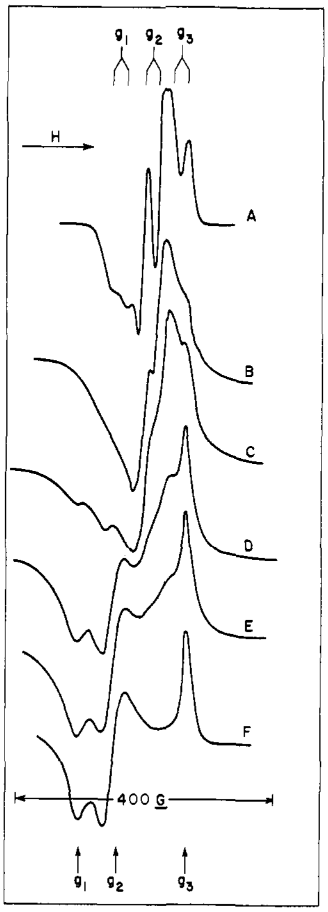

Figure 1. Electron spin resonance spectra of frozen reactant solutions at 77°K: A, $[Fe(mnt)_2^-] = 10^{-3}$ M, $[Ph_3P] = 10^{-2}$ M in methanol; B, $[Fe(mnt)_2^-] = 10^{-4}$ M, $[Ph_3P] = 10^{-2}$ M in acetonitrile; C, $[Fe(mnt)_3^{2-}] = 10^{-4}$ M, $[Ph_3P] = 5 \times 10^{-2}$ M in acetonitrile; D, $[Fe(mnt)_3^{2-}] = 10^{-4}$ M, $[Ph_3P] = 1 \times 10^{-2}$ M in acetonitrile; E, $[Fe(mnt)_3^{2-}] = 10^{-4}$ M, $[Ph_3P] = 4 \times 10^{-3}$ M in acetonitrile; F, $[Fe(mnt)_3^{2-}] = 10^{-4}$ M, $[Ph_3P] = 2 \times 10^{-2}$ M in acetonitrile. Approximately 2 min had elapsed between the mixing and freezing of the solutions in the case of systems C, D, and E. Spectrum F was taken after the solution had stood for 3 hr at room temperature.

Kinetics. As shown in Figure 2, the rate of oxygen consumption by solutions containing only $Fe(mnt)_2^-$ and triphenylphosphine initially increases with time then decreases in an approximately first-order manner. In order to obtain comparative rate data, the maximum rate of oxygen uptake was calculated from the maximum slope of the oxygen uptake curves such as

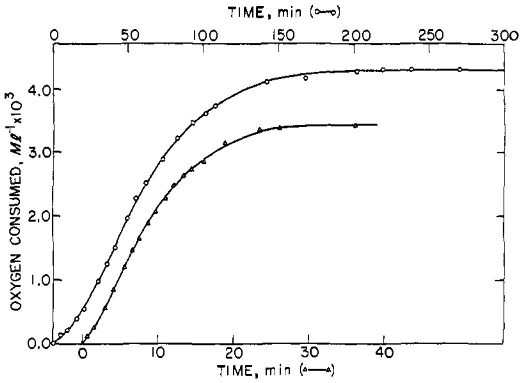

Figure 2. Gram atoms of oxygen consumed as a function of time in acetonitrile at 25°. Circles, $[Fe(mnt)_2^-] = 1.85 \times 10^{-3}$ M, $[Ph_3P] = 3.12 \times 10^{-3}$ M, reaction in air; triangles, $[Fe(mnt)_3^{2-}] = 4.29 \times 10^{-4}$ M, $[Ph_3P] = 3.15 \times 10^{-3}$ M, reaction in oxygen.

Figure 2. The results obtained in this way indicate that the maximum rate is proportional to the initial $Fe(mnt)_2^-$ concentration (Table I), but is almost independent of the oxygen pressure. An alternative method of treatment of the kinetic data—plotting log (oxygen consumed at $t = \infty$ *minus* oxygen consumed at time t) against time t and taking the slope of this plot at long times—yielded results which support the conclusions deduced from the maximum rate. The maximum rate data seem to indicate a somewhat less than first-order dependence on the initial phosphine concentration, but the slopes of the semilog plots were consistent with a first-order dependence.

Solutions of triphenylphosphine and $Fe(mnt)_2^-$ that were degassed immediately after mixing and then allowed to stand at 25° for 2 hr before bubbling oxygen through the solution to start the reaction still exhibited the usual induction periods although the reaction rate increased a little. Solutions of $Fe(mnt)_2^-$ and triphenylphosphine in 1,2-dichloroethane also consumed oxygen with a reaction profile similar to those obtained in acetonitrile, but the rate of the reaction was significantly slower (Table I).

A number of runs were performed to test the effect of small quantities (in amounts equal to 10% of the $Fe(mnt)_2^-$ concentration) of various compounds on the reaction profile. The oxidants iodine, tetrabromoethane, and ferric chloride had little effect on the maximum rate of oxygen consumption, but they removed the induction period so that the semilog plots were linear for at least the first two half-times. When an excess of any of these oxidants was added to $Fe(mnt)_2^-$ solutions, rapid color changes occurred, probably as a result of oxidation of the ligand and destruction of the complex.

The mild reductants diphenylamine and phenylenediamine had little effect on either the reaction rate or the induction period. Neither of these amines interact directly with $Fe(mnt)_2^-$ as evidenced by the lack of any change in the visible absorption spectrum of $Fe(mnt)_2^-$ on addition of either compound. The addition of ferrous chloride also had little or no effect on either the rate of reaction or the induction period. By contrast, addition of a small amount of Na_2mnt just before the addition of triphenylphosphine to the reaction mixture increased the rate of oxygen consumption and removed the induction period. (Complete conversion of triphenylphosphine to its oxide was demonstrated spectrophotometrically.) *trans,trans*-$Na_2(mnt)_2$ had a similar effect on the reaction rate, but *cis,cis*-$Na_2(mnt)_2$ was an even more effective autoxidation catalyst. It will be shown later that $Fe(mnt)_3^{2-}$ is an intermediate in the latter reaction.

In order to test the effect of blocking the vacant or labile sites on the $Fe(mnt)_2^-$ complex ion, two compounds that are known to form adducts with $Fe(mnt)_2^-$ were added to the reaction mixture. Addition of a large excess of triphenylarsine oxide so that the ratio $[Ph_3AsOFe(mnt)_2^-]/[Fe(mnt)_2^-] = 3.5 \times 10^3$, thus effectively blocking the labile fifth position, reduced the rate of oxygen uptake by a factor of 30. Excess 1,10-phenanthroline was even more effective in quenching the reaction. (In the presence of the highest phenanthroline concentration purple solids were observed in the reaction mixture after 2 days.) When the added phenanthroline concentration was approximately half the initial $Fe(mnt)_2^-$ concentration, the maximum rate of oxygen uptake was consistent with the expectation that since half the $Fe(mnt)_2^-$ was not complexed the reaction rate would be half that found in the absence of phenanthroline.

Mixtures of *cis,cis*- or *trans,trans*-$Na_2(mnt)_2$ and triphenylphosphine in acetonitrile only very slowly consume oxygen in the absence of $Fe(mnt)_2^-$. (If it is assumed that 1 mol of dimer reacts with 1 mol of oxygen, half times for the reaction were calculated to be greater than 50 hr.) Balch has reported the isolation of some triphenylphosphine oxides and triphenylphosphine sulfides from mixtures of $(mnt)_2^{2-}$ and phosphine after several days.[4]

3. $Fe(mnt)_2^-$-Catalyzed Autoxidation of Triphenylarsine. Solutions of triphenylarsine and $Fe(mnt)_2^-$ in acetonitrile take up oxygen slowly with the formation of triphenylarsine oxide. As in the triphenylphosphine autoxidation, the spectra of the product solutions were a little different from the spectra of $Fe(mnt)_2^-$-triphenylarsine oxide solutions of equal concentration. We again attribute these differences to some oxidative decomposition of the iron complex. The rate of oxygen consumption by triphenylarsine solutions was slow ($t_{1/2}$ = 10–50 hr), but the first-order rate plots were linear over more than two half-times. In contrast to the triphenylphosphine autoxidation no evidence of an induction period was found. However, the reaction rate was still only slightly dependent on the oxygen concentration, since the half-time for reaction was found to be only slightly less in oxygen than in air. (For $[Fe(mnt)_2^-] = 1.93 \times 10^{-2}$ M, $[Ph_3As] = 3.3 \times 10^{-2}$ M, $t_{1/2}$ = 42 hr in air and 36 hr in oxygen.)

B. Reactions of $Fe(mnt)_3^{2-}$. 1. Oxygen-Independent Reactions. $Fe(mnt)_3^{2-}$ is a six-coordinate complex of iron(IV) with an antiprismatic arrangement of the sulfur atoms about the metal.[15] Bases react with $Fe(mnt)_3^{2-}$ forming *cis,cis*-$(mnt)_2^{2-}$, a dimer of the oxidized ligand.[9]

$$2Fe(mnt)_3^{2-} + 2X \rightleftharpoons 2XFe(mnt)_2^- + (mnt)_2^{2-} \qquad (2)$$

Equilibrium constants for this reaction have been reported previously[9] for the monomeric bases triphenylarsine oxide, triphenylphosphine oxide, and pyridine. The ratio K_1^2/K_2, where K_1 and K_2 are the equilibrium

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(15) A. Sequeira and I. Bernal, to be submitted for publication.

constants for reaction 1 and 2, respectively, was found to be constant for all three bases. This result is not unexpected since this ratio is equal to K_3, the equilibrium constant for reaction 3. This reaction is rapid (half-

$$2\text{Fe(mnt)}_2^{-} + (\text{mnt})_2^{2-} \rightleftharpoons 2\text{Fe(mnt)}_3^{2-} \qquad (3)$$

times less than 30 sec at $[\text{Fe(mnt)}_2^-] = [(\text{mnt})_2^{2-}] = 3 \times 10^{-5}$ M). It was also shown that the rate of disappearance of Fe(mnt)_3^{2-} in the presence of triphenylarsine oxide was nearly proportional to both the complex concentration and the arsine oxide concentration.

It was anticipated that in the absence of air triphenylphosphine would react with Fe(mnt)_3^{2-} according to reaction 2. When these compounds were mixed, the absorbance at the absorption maximum of the iron(IV) complex (806 nm) did indeed rapidly decrease as expected from reaction 2. However, calculation of the equilibrium constant for this reaction from the Fe(mnt)_3^{2-} remaining at equilibrium yielded values in the range 7×10^{-2} to 2×10^{-1} M^{-1}, whereas a value of $(1.2 \pm 0.5) \times 10^{-2}$ M^{-1} was anticipated from the ratio K_1^2/K_3. It was discovered that the reason for this discrepancy was a further reaction between $(\text{mnt})_2^{2-}$ and triphenylphosphine. (This reaction is discussed later.) A brief study of the rate of reaction 2 with triphenylphosphine in the absence of air showed that the rate was first order in $[\text{Fe(mnt)}_3^{2-}]$, as was found for the same reaction with triphenylarsine oxide.[9]

In the presence of air or oxygen, a rapid decrease in absorbance at 806 nm was also observed when phosphine was added to solutions of the complex, but although the initial rate was the same as in degassed solutions more Fe(mnt)_3^{2-} was decomposed. This rapid decrease in absorbance, which was approximately first order (half-times 10–60 sec), was followed by a slower decrease that (at high phosphine concentrations) resulted in the complete disappearance of the Fe(mnt)_3^{2-} absorption maximum. As this slower decrease made it difficult to obtain "infinite time" values for the fast reaction, only initial rates of reaction were determined. The results of these studies are summarized in Table II. The initial rate is nearly proportional to the iron(IV) concentration and is independent of the oxygen pressure. The initial rate is also dependent on, but not proportional to, the initial triphenylphosphine concentration. These results are consistent with the expectation, based on kinetic studies of reaction 2 with Ph_3AsO, that the rate of the forward reaction is proportional to both the triphenylphosphine and Fe(mnt)_3^{2-} concentrations.

2. Esr Spectra. No esr signal was detected at 77°K in frozen solutions of either Fe(mnt)_3^{2-} on triphenylphosphine separately, but esr absorption was observed when these solutions were mixed at room temperature and then frozen. In the absence of air the observed resonance was similar to the spectrum observed for mixtures of triphenylphosphine and Fe(mnt)_2^- (Figure 1B) and is therefore assigned to the adduct $\text{Ph}_3\text{PFe(mnt)}_2^-$. In air or oxygen, however, a more complex spectrum was recorded. The shape of this spectrum was dependent on the ratio of the concentrations of triphenylphosphine and the complex (Figure 1C, D, E) and on the time allowed for the compounds to react at room temperature before freezing. It was apparent that the signal was a composite of two resonances, only one of which was dependent on the phosphine concentration. The phosphine-dependent signal is assigned to $\text{Ph}_3\text{PFe(mnt)}_2^-$ formed by reaction 2. The phosphine-independent signal, although developing slightly more slowly than the $\text{Ph}_3\text{PFe(mnt)}_2^-$ resonance, is evident even at short times (10 sec) and persists for many hours at room temperature. If sufficient time is allowed for all the phosphine to be converted to phosphine oxide only the phosphine-independent signal remains (Figure 1F). This spectrum is identical with the one obtained when the iron(III) complex, Fe(mnt)_3^{3-}, is exposed to oxygen. We have not been able to assign this spectrum to a definite species; however, it may be confidently assigned to a low-spin iron(III) complex probably involving ligands formed by the oxidation of the mnt^{2-} by oxygen. Addition of Ph_3AsO or $(\text{mnt})_2^{2-}$ to solutions containing Fe(mnt)_3^{2-} and phosphine results in the loss of all esr signals, indicating that the species responsible for the esr spectrum are labile.

Table II. Initial Rate of the Reaction of Triphenylphosphine with Fe(mnt)_3^{2-} in Acetonitrile at 25°

$10^4[\text{Fe(mnt)}_3^{2-}]$,[a] M	$10^4[\text{Ph}_3\text{P}]$,[a] M	$10^7 R_0$,[b] M sec^{-1}	$R_0/[\text{Fe(mnt)}_3^{2-}] \times [\text{Ph}_3\text{P}]$, M^{-1} sec^{-1}
	In Air		
0.303	31.5	2.6	2.7
2.03	31.9	24	3.7
4.00	32.4	47	3.6
6.00	32.4	73	3.8
0.303	31.5	2.6	2.7
0.303	76	4.8	2.1
0.303	122	7.0	1.9
3.94	15.4	25	4.1
4.00	32.4	47	3.6
4.00	36.0	49	3.4
4.00	73.6	82	2.8
	In Oxygen		
4.00	32.4	46	3.6
4.00	36.0	51	3.5
4.00	73.6	87	2.9

[a] Initial concentrations. [b] Initial rate.

3. Fe(mnt)_3^{2-}-Catalyzed Autoxidation of Triphenylphosphine. Stoichiometry. At all the catalyst concentrations studied except the lowest reported in Table III, the amount of oxygen taken up suggests that the triphenylphosphine was completely oxidized to phosphine oxide. This was confirmed by spectrophotometric determination of the phosphine oxide. The oxidation is therefore truly catalytic since 1 mol of the complex catalyzes the oxidation of about 15 mol of triphenylphosphine in pure oxygen and about 20 mol in air.

At the lowest catalyst concentrations reported in Table III oxidation of triphenylphosphine is not complete before all the Fe(mnt)_3^{2-} is destroyed. (Further oxidation, but at a much slower rate, does occur as Fe(mnt)_2^- is still present in solution.) As noted in the previous section, when solutions of triphenylphosphine and Fe(mnt)_3^{2-} are mixed in air or oxygen the rapid oxygen-independent reaction (reaction 2) is followed by a slower reaction that does not occur in the absence of oxygen and which results in the complete disappearance of Fe(mnt)_3^{2-} at sufficiently high phosphine concentrations. One possible reaction leading to the

Table III. Rate of Oxygen Uptake by Triphenylphosphine Catalyzed by $Fe(mnt)_3^{2-}$ in Acetonitrile at 25°

$10^4[Fe(mnt)_3^{2-}]$,[a] M	$10^4[Ph_3P]$,[a] M	$10^4[(mnt)_2^{2-}]$,[a] M	10^7R_{max},[b] M sec^{-1}	$R_{max}/[Fe(mnt)_3^{2-}][Ph_3P]$, M^{-1} sec^{-1}	$\Delta[O]/[Ph_3P]$[c]
		In Oxygen			
1.10	31.5		7.3	2.1	0.50
1.88	31.4		12	2.1	1.00
2.18	31.4		16	2.3	1.12
2.28	31.4		15	2.1	1.15
2.33	31.4		17	2.3	1.15
4.29	31.3		27	2.1	1.15
4.29	31.5		32	2.3	1.11
10.8	31.4		71	2.1	1.14
1.01	31.4	1.13	14	4.3	1.05
1.01	31.4	9.10	15	4.6	1.05
2.23	31.4	1.13	32	4.5	1.19
4.26	31.9	2.62	68	5.0	1.05
5.35	15.8		20	2.3	1.06
5.21	61.6		71	2.2	1.10
10.8	31.4		71	2.1	1.14
10.4	61.6		117	1.8	1.09
		In Air			
1.10	31.5		5.4	1.5	0.70
1.88	31.4		9.8	1.7	1.08
2.26	31.3		10.7	1.5	0.97
2.33	31.4		13	1.8	1.01
4.29	31.3		23	1.7	1.05
5.31	31.4		34	2.0	1.04
10.8	31.3		56	1.7	1.04

[a] Initial concentrations. [b] Maximum rate of oxygen uptake. [c] Gram atoms of oxygen consumed per mole of Ph_3P.

destruction of $Fe(mnt)_3^{2-}$ is the oxidation of the ligand to dithiin; however, no dithiin was detected even in solutions where the complex had been completely destroyed. (The sensitivity of the detection method puts an upper limit of 3% on the oxidation of the ligand to dithiin.) Another possibility is the formation of $Ph_3POFe(mnt)_2^-$ through reaction 2, but the equilibrium constant with X = Ph_3PO is too low[9] to account for the complete destruction of $Fe(mnt)_3^{2-}$ under the experimental conditions. More oxygen is consumed than is required for stoichiometric oxidation of the phosphine to phosphine oxide (Table III). This indicates the formation of another oxidation product. Possibly, as suggested on the basis of the esr evidence, the ligand's sulfur atoms are oxidized (mnt^{2-} alone is in part oxidized by oxygen presumably to a similar product.)

Kinetics. As was found in the $Fe(mnt)_2^-$-catalyzed system, the time dependence of the rate of oxygen consumption was not consistent with any simple kinetic behavior. At the higher $Fe(mnt)_3^{2-}$ concentrations in Table III, the rate increased with time initially (Figure 2), but at the lowest concentrations no induction period was apparent. The maximum rates of oxygen consumption reported in Table III were determined from plots such as Figure 2. From Table III it is evident that the maximum rate is proportional to both the catalyst and the phosphine concentrations, but almost independent of the oxygen concentration. The final portion of the reaction profile could be fitted to a semilog plot (log $[(O_2 \text{ consumed})_t - (O_2 \text{ consumed})_\infty]$ *vs.* time t) indicating first-order behavior. The relative slopes of these plots were consistent with the reaction order established on the basis of maximum rates.

Included in Table III are some data on the effect of adding *cis,cis*-$(mnt)_2^{2-}$ to the reaction mixture. The major effect of adding this dimer was to increase the maximum rate of oxygen uptake by almost a factor of 2. Associated with this effect was a decrease in the induction period, that is, a reduction in the extent of deviation from first-order behavior. (The run with $[(mnt)_2^{2-}] = 9.1 \times 10^{-4}$ M obeyed excellent first-order kinetics over three half-times. A value of 6.7 sec^{-1} for the pseudo-first-order rate constant was calculated from the slope of this semilog plot.) Adding $(mnt)_2^{2-}$ also increased the amount of triphenylphosphine oxidized at the lowest $Fe(mnt)_3^{2-}$ concentrations, presumably because the complex is regenerated by reaction 3 (or the reverse of reaction 2). Addition of 1,10-phenanthroline to the reaction mixture completely quenched oxygen uptake (no oxygen uptake in 20 hr).

Comparison of the data in Tables II and III demonstrates that the initial rate of the reaction of $Fe(mnt)_3^{2-}$ with triphenylphosphine is within a factor of 2 of the maximum rate of oxygen consumption under the same conditions.

C. Autoxidation of Na_2mnt. Solutions of Na_2mnt take up oxygen to the extent of 1 to 2 atoms of oxygen per molecule of Na_2mnt. The absorption spectrum of the reaction product (λ_{max} 365 nm) is different from either of the anticipated oxidation products, $(mnt)_2^{2-}$ (λ_{max} 390, 255 nm) or dithiin (λ_{max} 328, 312 nm). All the product was absorbed on an anion-exchange column indicating that the product was negatively charged. We tentatively suggest therefore that the major product is a salt of either a sulfonic or a sulfinic acid.

The rate of oxygen uptake by solutions of Na_2mnt is slow ($t_{1/2}$ = 70 min for solutions 5×10^{-3} M in Na_2mnt). Triphenylphosphine or triphenylarsine (3×10^{-3} M) did not alter the rate of oxygen uptake by solutions of Na_2mnt, although over long periods (20 hr) some triphenylphosphine oxide was found in the reaction mixture.

D. Autoxidation of $Fe(mnt)_3^{3-}$. Thoroughly degassed solutions of Fe(mnt)$_2^-$ (concentration about 9×10^{-4} M) containing a slight excess of Na$_2$mnt exhibit optical absorption maxima not present in the spectra of either reactant (660 (ϵ 1800), 1030 nm (ϵ 1300)) which we attribute to Fe(mnt)$_3^{3-}$, in disagreement with a previous report[5] of a maximum at 800 nm (ϵ 2000). In the absence of air no change in this spectrum was observed over several hours, but when the solutions were exposed to oxygen the maximum at 1030 nm disappeared and the peak at 670 nm rapidly shifted (in a few minutes) to longer wavelengths eventually reaching 805 nm. This maximum, which corresponds to the maximum of Fe(mnt)$_3^{2-}$, then more slowly decayed. Calculation using the known molar absorptivity of Fe(mnt)$_3^{2-}$ suggests that its maximum concentration is less than two-thirds of that expected for complete conversion of the iron(III) to the iron(IV) complex.

A strong esr signal is displayed by frozen degassed solutions (77°K) of Fe(mnt)$_2^-$ with excess mnt^{2-}. The line shape of the spectrum is characteristic of a randomly oriented $S = {}^1/_2$ species with three principal g values, $g_1 = 2.22$, $g_2 = 2.087$, and $g_3 = 1.985$, in reasonable agreement with the solid-state spectrum at 4°K ($g_1 = 2.225$, $g_2 = 2.114$, and $g_3 = 1.985$) reported by Gibson and Cotton.[16] No other resonances were detected in the range $g = 1$ to $g = 6$. On exposure to air at room temperature this signal rapidly disappears ($t_{1/2} \sim 15$ sec) and is replaced by another resonance which is identical with the spectrum observed in oxygen-saturated solutions of Fe(mnt)$_3^{2-}$ and triphenylphosphine (Figure 1F).

Double integration of the first-derivative spectra indicates that the product responsible for the spectrum obtained on oxidation of Fe(mnt)$_3^{3-}$ was formed at only one-tenth of the initial concentration of Fe(mnt)$_3^{3-}$. This observation is in accord with the previous result based on optical absorption studies, namely that the major oxidation product is Fe(mnt)$_3^{2-}$ (which does not give an esr signal).

E. Reaction of FeCl$_3$ with (mnt)$_2^{2-}$. Iron(III) (as FeCl$_3$) rapidly oxidizes Na$_2$(mnt)$_2$ to dithiin

$$\mathrm{Fe}^{3+} + 2(\mathrm{mnt})_2{}^{2-} \longrightarrow \mathrm{Fe(mnt)}_2{}^{-} + \text{dithiin} + 2\mathrm{S}$$

The visible absorption spectrum of mixtures of FeCl$_3$ and Na$_2$(mnt)$_2$ is identical with the spectrum of Fe(mnt)$_2^-$, and the presence of dithiin was established by its characteristic ultraviolet spectrum, after separation from the Fe(mnt)$_2^-$ by ion exchange.

F. Reaction of N$_3^-$, Cl$^-$, and CN$^-$ with Fe(mnt)$_2^-$. Rapid spectral changes presumably associated with the formation of five-coordinate adducts were observed on addition of these anions to Fe(mnt)$_2^-$ in methanol. Oxygen was consumed by these solutions over several days with concurrent bleaching of the solutions. In contrast to McCleverty, *et al.*,[5] we were unable to detect any esr signals in these systems. The amount of oxygen taken up and the color changes were consistent with irreversible autoxidation of mnt^{2-}.

G. Reaction of Triphenylphosphine with (mnt)$_2^{2-}$. The spectra of *cis,cis*-(mnt)$_2^{2-}$ solutions have an absorption maximum at 390 nm. On standing, the spectrum of dilute solutions (10^{-5} M) of this salt changes, decreasing in absorbance at 390 nm and increasing around 430 nm. These spectral changes, which were attributed by Simmons, *et al.*,[10] to isomerization of the cis,cis salt to the trans,trans salt, occurred much more slowly at higher concentrations (>10^{-4} M).

In the presence of triphenylphosphine changes were again observed in the spectrum of *cis,cis*-(mnt)$_2^{2-}$ at low concentrations (10^{-5} M), but in this case the absorption maximum shifted from 390 to 375 nm with little change in maximum absorbance. Again at higher concentrations of (mnt)$_2^{2-}$ this spectral change either did not occur or occurred at a very slow rate. The change in absorption spectrum was not affected by degassing the solutions. The well known reaction of triphenylphosphine with disulfides[17] to form thiols and triphenylphosphine sulfide or triphenylphosphine oxide suggests a possible explanation for these spectral changes. Spectrophotometric determination of the triphenylphosphine after the reaction was apparently complete showed, however, that neither triphenylphosphine sulfide nor triphenylphosphine oxide was formed to an appreciable extent.

H. Catalyzed Autoxidation of Cumene. Preliminary experiments indicate that both Fe(mnt)$_2^-$ and Fe(mnt)$_3^{2-}$ are excellent catalysts for the autoxidation of cumene, in contrast to the reported behavior of other metal dithiolate complexes.[18] Mixtures of cumene and acetonitrile (80% cumene) rapidly take up oxygen on the addition of either Fe(mnt)$_2^-$ or Fe(mnt)$_3^{2-}$. No induction period was observed and the initial rate of oxygen consumption was identical for the two complexes (2.9×10^{-6} mol l.$^{-1}$ sec^{-1} for solutions containing [Fe(mnt)$_2^-$] = 8.4×10^{-4} M and [Fe(mnt)$_3^{2-}$] = 4.3×10^{-4}). However, at lower cumene concentrations (7.0×10^{-3} M in acetonitrile) Fe(mnt)$_3^{2-}$ (7.1×10^{-4} M) catalyzes a very slow autoxidation reaction with a half-time of approximately 100 hr, whereas no oxygen consumption was observed with Fe(mnt)$_2^-$ (1.86×10^{-3} M) in 250 hr. Both complexes were rapidly decolorized in pure cumene (<1 min).

Discussion

The iron(III)- and iron(IV)-catalyzed oxidations of triphenylphosphine show similar kinetic behavior. The maximum rate of oxygen uptake in both systems is proportional to the initial concentrations of both the complex and the triphenylphosphine, but is nearly independent of the oxygen pressure. The independence of the reaction rate on the oxygen pressure is inconsistent with simple mechanisms involving direct reaction of the complexes with molecular oxygen, for such mechanisms predict that the rate of oxygen uptake be proportional to oxygen pressure (unless the reaction between the complex and oxygen is rapid and complete, which was independently shown not to be the case). There is therefore no direct evidence in either system for the formation of molecular oxygen complexes. Similarly, the direct interaction of oxygen with triphenylphosphine would lead to an oxygen pressure dependent reaction.

Because about 10–20 phosphine molecules can be oxidized for every iron complex ion present initially, the species that interacts with oxygen must be regenerated in the reaction scheme. This limitation on the mech-

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(18) C. Copping and N. Uri, *Discuss. Faraday Soc.*, **46**, 202 (1968).

anism excludes from consideration numerous possible reaction schemes that involve irreversible processes.

The iron(IV)-catalyzed reaction will be discussed first since it is more amenable to analysis. The similarity of the initial rate of disappearance of $Fe(mnt)_3{}^{2-}$ in the presence of triphenylphosphine (Table II) and the maximum rate of oxygen uptake under the same conditions (Table III) strongly suggests that these reactions are coupled. In addition, the rate of the forward reaction of $Fe(mnt)_3{}^{2-}$ with triphenylphosphine (reaction 2) and the rate of oxygen uptake are both proportional to the concentrations of the complex and of triphenylphosphine. Several reaction schemes can be devised which are consistent with these observations. In the simplest scheme molecular oxygen reacts with a half-bonded intermediate formed in reaction 2 ($Ph_3PFe(mnt)_3{}^{2-}$). Reactions 4, 5, and 6 then describe a feasible mechanism for the autoxidation reaction.

$$Fe(mnt)_3{}^{2-} + Ph_3P \xrightarrow{k_1} Ph_3PFe(mnt)_3{}^{2-} \qquad (4)$$

$$2Ph_3PFe(mnt)_3{}^{2-} + O_2 \longrightarrow 2Ph_3POFe(mnt)_2{}^{-} + (mnt)_2{}^{2-} \qquad (5)$$

$$(mnt)_2{}^{2-} + 2Ph_3POFe(mnt)_2{}^{-} \longrightarrow 2Ph_3PO + 2Fe(mnt)_3{}^{2-} \qquad (6)$$

If reaction 4 is the rate-controlling step, then the rate of oxygen uptake ($d[O]/dt$) is equal to $k_1[Fe(mnt)_3{}^{2-}]\cdot[Ph_3P]$. This is also the rate of the reaction of the iron(IV) complex with triphenylphosphine in the absence of oxygen if reaction 4 is assumed to be rate controlling in both instances.

$$Ph_3P + Fe(mnt)_3{}^{2-} \longrightarrow Ph_3PFe(mnt)_3{}^{2-} \qquad (4)$$

$$Ph_3PFe(mnt)_3{}^{2-} \longrightarrow Ph_3PFe(mnt)_2{}^{-} + mnt^{-} \qquad (7)$$

$$mnt^{-} + mnt^{-} \longrightarrow (mnt)_2{}^{2-} \qquad (8)$$

This mechanism is not unique and does not, as it stands, account for the induction period. We are unable to provide a satisfactory explanation for the induction period at this time, except perhaps by ascribing it to the presence of an inhibiting impurity. A further reaction is also necessary to account for the ultimate destruction of the iron complex. We propose that this reaction is the oxidation of the ligand by oxygen. This not only results in the destruction of $Fe(mnt)_3{}^{2-}$ but explains the excess oxygen taken up over the amount required for complete oxidation of the phosphine. It also satisfactorily accounts for the presence of the oxygen-dependent species that was detected by esr. Further interpretation of the mechanism of the autoxidation reaction requires a knowledge of the mechanisms of the individual steps, such as the phosphine substitution reaction. We are reluctant to speculate further about the autoxidation mechanism in the absence of this information.

The iron(III)-catalyzed rate of autoxidation is approximately 15 times slower than the rate of the iron(IV)-catalyzed reaction at the same concentrations. A possible mechanism for the $Fe(mnt)_2{}^{-}$-catalyzed reaction is therefore the slow formation of $(mnt)_2{}^{2-}$ (or $Fe(mnt)_3{}^{2-}$) in the induction period, which then catalyzes the reaction through the mechanism of the $Fe(mnt)_3{}^{2-}$-catalyzed reaction. About 10% of the $Fe(mnt)_2{}^{-}$ must be converted to $Fe(mnt)_3{}^{2-}$ in order to obtain the observed rate of oxygen uptake. Removal of the induction period by reductants and oxidants that react with $Fe(mnt)_2{}^{-}$ may then be rationalized by postulating that these reagents form $(mnt)_2{}^{2-}$ in reacting with the complex. This mechanism also suggests an explanation of the apparent catalytic inactivity of the analogous cobalt(III) complex ($Co(mnt)_2{}^{-}$),[4] namely, the cobalt complex does not undergo the equivalent reactions that convert $Fe(mnt)_2{}^{-}$ to the catalytically active $Fe(mnt)_3{}^{2-}$.

The catalysis of cumene oxidation by the iron dithiolate complexes is in contrast with a previous report that dithiolate complexes of cobalt, nickel, platinum, and palladium do not catalyze the autoxidation of methyl cumate,[18] even though these complexes strongly catalyze peroxide decomposition. Since the cumene used in the present work was not purified, it undoubtedly contained some cumene peroxide, so a probable mechanism involves peroxide decomposition into radicals. Speculation on the catalyst for this decomposition would be premature since the species present in solution are unknown.

Regardless of the detailed mechanisms of the reactions, these studies show that the iron complexes are powerful catalysts for the autoxidation of triphenylphosphine. This catalytic activity is probably a consequence of the lability of the complexes, combined with the existence of several oxidation states related by reversible one-electron transfer reactions. On this basis other transition metal dithiolate complexes might also be expected to be good redox catalysts, and indeed Dance and Cline[19] have recently reported that $Co(mnt)_2{}^{-}$ is also an excellent catalyst for the oxidation of thiols.

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