I. Autoxidation of Manganese(II) β-Diketonates

II. Synthesis of Dipivaloylmethane Chelates of Manganese(II)

Thesis by

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This thesis is dedicated to my wife, Michele, who has made the entire effort worthwhile.

ABSTRACT

Part I

The oxidation of several manganese(II) β-diketonates by molecular oxygen has been studied in benzene and ethanol with the goals of elucidating the mechanisms and understanding the influence of ligand structure on the reactivities of the chelates.

Autoxidation of bis(acetylacetonato)diaquomanganese(II) in benzene follows a two-term rate law which can be interpreted in terms of an uncatalyzed bimolecular reaction and an acetylacetone-catalyzed reaction of manganese(II) complex and oxygen. Excess acetylacetone inhibits autoxidation of the manganese(II) chelates in ethanol, suggesting that a key step is formation of a bond between metal and molecular oxygen. Kinetic studies in ethanol are complicated by autoxidation of β-diketone coordinated to the manganese(III) product and competition between manganese(II) and manganese(III) for available ligand.

The ligand bound to manganese(II) strongly influences the reactivity of the compound towards oxygen. A factor of 10^3 was observed between the rates of autoxidation of bis(ethylacetoacetato)-manganese(II) and bis(3-methylacetylacetonato)manganese(II). Results have been interpreted in terms of steric, resonance, and inductive effects.

Manganese β-diketonates catalyze the autoxidation of several organic cosubstrates. Catalytic behavior falls into three classes in which manganese is predominantly divalent, trivalent, or in between

the two extremes. Formation of a ternary complex of substrate, manganese, and oxygen is consistent with the limited data available.

Part II

Synthesis of bis(dipivaloylmethanato)manganese(II), $Mn(DPM)_2$, was attempted in aqueous acetone and methanol solution. A bis compound, $Mn(DPM)_2(H_2O)_2$, was prepared in aqueous acetone. The compound is octahedral, unlike the DPM chelates of other first-row transition metals, which suggests that steric factors alone do not control the geometry of these compounds. The product obtained from methanol solution contains bridging methoxy ligands and is probably a dimer, $[Mn(DPM)(OCH_3)]_2$.

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Part I

Autoxidation of Manganese(II) β-Diketonates

INTRODUCTION

Examples of the oxidation of metal complexes in homogeneous solution by molecular oxygen are found within all formal disciplines of chemistry. The study of these autoxidation* reactions has resulted in a clearer understanding of many important industrial and biological processes.[1-3]

The oxygen molecule, with two unpaired electrons, generally reacts readily with free radicals, a special class of which are paramagnetic metal ions. While the standard oxidation potential of the oxygen molecule is high, the reactions of this species are often slow

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E_0 = +1.23\,V \tag{1}$$

because the total reduction of oxygen takes place with initial production of $HO_2\cdot$ or H_2O_2 in steps less favorable thermodynamically than the overall process.

$$O_2 + H^+ + 1e^- \rightarrow HO_2\cdot \qquad E_0 = -0.32\,V \tag{2}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E_0 = +0.68\,V \tag{3}$$

Several general mechanisms for the autoxidation of metal ions have been proposed:[1,4]

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* *The term "autoxidation" in this context is a misnomer, but it* has been accepted to mean "spontaneous" oxidation by molecular oxygen at room temperature.

$$M^{n+} + H_2O \overset{K}{\rightleftharpoons} M(OH)^{(n-1)+} + H^+ \qquad (4)$$

$$M(OH)^{(n-1)+} + O_2 + H^+ \xrightarrow{k_1} M(OH)^{n+} + HO_2\cdot$$

$$M^{n+} + HO_2\cdot + H_2O \rightarrow M(OH)^{n+} + H_2O_2 \qquad (6)$$

$$M^{n+} + H_2O_2 \rightarrow M(OH)^{n+} + OH\cdot \qquad (7)$$

$$M^{n+} + OH\cdot \rightarrow M(OH)^{n+} \qquad (8)$$

Reactions (4)-(8) are known as the Haber-Weiss mechanism.[5] Kinetics of the oxidation of iron(II) in dilute acid solution,[6] vanadium(III),[7] and titanium(III)[8] are consistent with this mechanism. Cher and Davidson[9] suggested that first order behavior of the metal ion in the autoxidation of iron(II) in phosphate media could be explained by formation of an iron(IV) intermediate rather than $HO_2\cdot$. Chromium(II),[10, 11] plutonium(III),[12] iron(II) perchlorate,[13] and iron(II) sulfate,[14] and iron(II) chloride in methanol[15] react with molecular oxygen according to the rate law

$$-(d[M^{n+}]/dt) = k_2[M^{n+}]^2[O_2] \ . \qquad (10)$$

Proposed mechanisms involve formation of a binuclear intermediate followed by transfer of either one or two electrons. Reactions (11) and (12b) imply

$$Fe^{2+} + O_2 \rightleftharpoons Fe^{II}O_2^{\ 2+} \qquad (11)$$

$$Fe^{II}O_2^{2+} + Fe^{2+} \xrightarrow{k_2} Fe^{III}O_2^{+} + Fe^{3+} \qquad (12a)$$

$$\mathrm{Fe^{III}O_2{}^{+} + 2H^{+} \rightarrow Fe^{3+} + H_2O_2} \qquad (13a)$$

or

$$\mathrm{Fe^{II}O_2{}^{2+} + Fe^{2+} \rightleftharpoons (Fe^{II}O_2Fe^{II})^{4+} \xrightarrow{k_2} 2\,Fe^{IV}O^{2+}} \qquad (12b)$$

$$\mathrm{Fe^{IV}O^{2+} + Fe^{2+} \rightarrow 2\,Fe^{III}} \qquad (13b)$$

formation of complexes between metal ions and oxygen. Complexes of this type have been reported for a number of metal ions and several have been isolated.[1, 3, 16]

Two important questions must be answered before the reaction between a metal complex and molecular oxygen can be satisfactorily described: 1) Does the oxygen molecule enter the coordination sphere of the metal ion prior to electron transfer? 2) Does the reaction proceed by a one- or two-electron transfer?

Experimentally, it is a difficult task to answer both of these questions with certainty. An inner-sphere metal ion autoxidation can be established if 1) the formation constant for the metal - oxygen complex is large and its irreversible decomposition is slow,[17] 2) the oxidized metal complex is substitution inert and contains an oxygen atom from molecular oxygen,[10] or 3) the reaction is proportional to the oxygen concentration and the second power of the metal concentration. Conversely, an outer-sphere reaction can be identified if the oxidized species is substitution inert and contains no oxygen from the oxidant, or the rate of autoxidation is greater than the rate of ligand substitution of the metal complex. Two-electron transfer from metal ion to oxygen can be determined by 1) identifying the reaction product of $M^{(n+2)+}$ and M^{n+} and showing that it is not the expected one-electron oxidation product,[18] 2) oxidizing cosubstrate which is oxidized more slowly by the expected one electron reaction product,[15] or 3) isolating the two-electron oxidation product directly.

Even if these two questions can be answered successfully, the central problem of rationalizing rates and mechanisms with known properties of metal ions and molecular oxygen remains. There is a growing awareness that the theories of Haber, Weiss, and Uri[19] on metal ion autoxidation, which were based on analogies to one-electron metal ion oxidations with hydrogen peroxide, are not universally valid. Any successful approach must consider both the general theories of electron transfer and the chemical properties of the reactants. Recent reviews by Fallab[1] and Taube[4] are attempts to discuss the experimental results in this manner. The large number of variables associated with a metal complex-oxygen redox system, however, has forestalled presentation of a unified theory of metal complex autoxidation. Prediction of a given metal complex autoxidation mechanism can be made with little more confidence today than it could 30 years ago.

Mechanisms have been proposed for the autoxidation in solution of all first-row transition metal ions with variable valence except manganese. The hydrated manganese(II) ion is stable to oxidation by molecular oxygen in acid solution, but in basic solution or in the form of metal complexes, manganese(II) is readily autoxidized.[20] Nichols and Walton[21] proposed that autoxidation of $Mn(OH)_2$ in NH_4OH-NH_4Cl

buffer initially precipitated MnO_2 but did not state whether manganese(IV) was formed directly or by disproportionation of manganese(III). Gach[22] prepared tris(acetylacetonato)manganese(III) by air oxidation of the manganese(II) complex and Emmert[23] reported that bis(acetylacetonato)manganese(II) in methanol solution absorbed nine equivalents of oxygen.

Some of the most interesting and intriguing studies of the autoxidation of manganese complexes have been concerned with the essential participation of manganese in photosynthesis.[24] Gerretsen,[25] Kenten and Mann,[26] and Andrae[27] studied the oxidation of manganese(II) in the presence of oxygen and illuminated chloroplasts. Gerretsen[25] suggested that hydrogen peroxide was formed by the following process:

$$\mathrm{Mn}^{\mathrm{II}} + O_2 \rightarrow \mathrm{Mn}^{\mathrm{III}}(O_2^-) \xrightarrow{\overset{h\nu}{2e^-}} H_2O_2 + \mathrm{Mn}^{\mathrm{II}} \qquad (14)$$

Kenten and Mann[26] and Andrae[27] proposed that manganese(II) was oxidized by some intermediate in the system, not oxygen. Calvin, et al.,[28] extensively investigated the oxidation of manganese(II)-phthalocyanine complexes by molecular oxygen and studied the effect of light on the reactions. The stable oxidation product in weakly donating solvents was manganese(III); in good donor solvents, manganese(IV) was observed. The following general reaction scheme was presented.

$$2\,\mathrm{Mn}^{\mathrm{II}}(\mathrm{py})_2 \underset{h\nu}{\overset{\frac{1}{2}O_2+H_2O}{\rightleftharpoons}} 2\,\mathrm{Mn}^{\mathrm{III}}(\mathrm{OH})(\mathrm{py}) \underset{h\nu}{\overset{\overset{h\nu}{\frac{1}{2}O_2-H_2O}}{\rightleftharpoons}} \mathrm{Mn}^{\mathrm{IV}} = \mathrm{O} \qquad (15)$$

$$\mathrm{py} = \mathrm{pyridine}$$

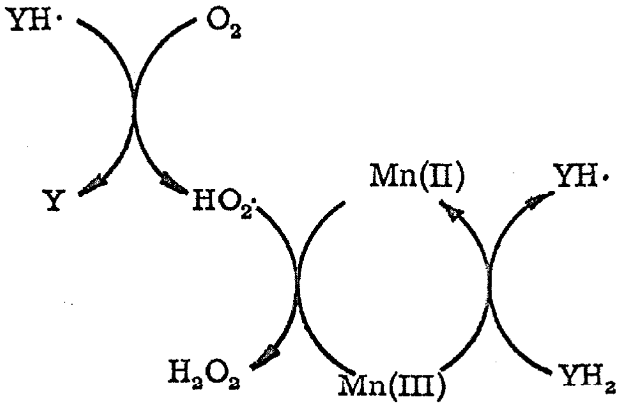
The role of manganese complexes as catalysts in autoxidation reactions has received much more attention than the autoxidation of manganese complexes themselves. Manganese salts are well known catalysts of free-radical autoxidations of organic molecules. Kagan and Lubarsky,[29] and Bawn, Hobin, and Raphael[30] studied the manganese acetate catalyzed oxidation of acetaldehyde. They concluded the trivalent metal ion oxidized the substrate to produce the chain initiating species and was regenerated mainly by reaction with hydroperoxide, not molecular oxygen.

$$\mathrm{RCHO} + \mathrm{Mn}^{\mathrm{III}} \rightarrow \mathrm{RCO}\cdot + \mathrm{Mn}^{\mathrm{II}} + \mathrm{H}^{+} \qquad (16)$$

$$\mathrm{RC(O)OOH} + \mathrm{Mn}^{\mathrm{II}} \rightarrow \mathrm{RC(O)O}\cdot + \mathrm{Mn}^{\mathrm{III}} + \mathrm{OH}^{-} \qquad (17)$$

Sym[31] reported the rate of the manganese catalyzed oxidation of hydroquinone was proportional to manganese(II) and oxygen concentrations, and inhibited by quinone. He suggested that the reactive species was a complex between metal and substrate. Manganese catalyzed autoxidation of 3, 5-di-*tert*-butyl pyrocatechol has been studied by Grinstead[32] who proposed that the key step was the oxidation of a metal-substrate complex to give semiquinone and manganese(III) followed by rapid reduction of the metal ion by the semiquinone to give *o*-quinone.

In the manganese catalyzed oxidations of dihydroxyfumaric acid[33] and 2, 3-diketo-gulonic acid[34] the metal ion acts in a redox cycle,



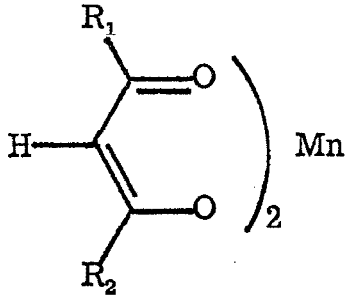
(18)

reacting with $HO_2\cdot$ to prevent its dismutation and produce manganese(III) to perpetuate the reaction chain. The oxidations probably occur in complexes between metal ion and substrate since free manganese(III) ions are unstable under the reaction conditions.

Brintzinger, Zell, and Ehrlenmeyer[35] proposed a mechanism for the autoxidation of several substituted hydrazines catalyzed by manganese(II) ions in phosphate and pyrophosphate buffers. The hydrazines are oxidized in aqueous solution at the same rate in the presence or absence of manganese(II) ions. In phosphate or pyrophosphate buffers, which form strong complexes with the metal, manganese is a catalyst for the oxidation. These complexes are also susceptible to air oxidation. The authors propose the rate determining step is a one-electron oxidation of manganese(II) followed by a rapid reduction of $O_2^{\overline{\cdot}}$ and manganese(III) by the hydrazine or hydrazine radical.

From the number and variety of reports in the literature, it is obvious that manganese complexes, operating in a redox cycle between the divalent state and a higher oxidation state, are able to catalyze the autoxidation of a variety of organic substances. Relatively few of these publications, however, reported experiments designed specifically to determine the mode of interaction of manganese complexes with oxygen.

The autoxidation of manganese(II) complexes with β-diketones in non-aqueous solvents was investigated to determine the mechanism of the reaction, and, specifically, whether chelation would enable oxidation states of manganese higher than three to participate in the reaction. The reactions were studied in non-aqueous solvents to minimize hydrolysis which leads to decomposition of oxidized manganese complexes. Earlier work in this laboratory indicated that structural changes in the alkyl groups about the chelate ring strongly affect the stability of the manganese(II) chelate towards air oxidation.[36]



19a $R_1 = R_2 = C(CH_3)_3$

19b $R_1 = R_2 = CH_3$

(19)

Compound 19a was reported to char immediately upon exposure to air,[36] while compound 19b could be prepared in air with no noticeable oxidation.[37] A quantitative measure of ligand effects on the autoxidation of manganese(II) complexes in solution was obtained by studying the oxidation by molecular oxygen of a series of bis(β-diketonato) manganese(II) complexes in benzene and ethanol.

Finally, the autoxidation reactions of the manganese complexes were studied in the presence of several organic cosubstrates to possibly intercept reactive intermediates, if they existed, and to ascertain the role of the manganese complexes in the induced oxidation of the cosubstrates.

RESULTS

Bis(acetylacetonato)diaquomanganese(II), $Mn(Acac)_2(H_2O)_2$, was an excellent substrate for use in these studies because it could be prepared, purified, and handled for reasonable periods of time in air without noticeable air oxidation. In solution it was oxidized at rates measurable by standard kinetic techniques. $Mn(Acac)_2(H_2O)_2$ was used instead of the anhydrous chelate for most of the kinetic runs because of its greater solubility in organic solvents.

Kinetic runs were conducted at 30±0.1°C unless stated otherwise in the various tables and figures. Reaction rates and rate constants have been corrected to 1 atm of oxygen. First order rate constants were calculated from the slopes of semi-logarithmic plots of absorbance of final product minus absorbance at time t *versus* time, $k_1 = 2.30 \log(A_\infty - A)/t$. Fractional rate orders were determined from slopes of log-log plots of initial rate *versus* initial concentration of reactant.

A. Autoxidation of Manganese(II) Complexes in Benzene Solution

1. Autoxidation of $Mn(Acac)_2(H_2O)_2$

$Mn(Acac)_2(H_2O)_2$ is oxidized quantitatively to tris(acetylacetonato)manganese(III), $Mn(Acac)_3$, in the presence of excess chelating agent. The spectrum of the reaction product is identical to the spectrum of $Mn(Acac)_3$ in benzene in the presence of excess ligand. Measurements of oxygen consumption and spectrophotometric analyses of manganese(III) products indicate the stoichiometry of the reaction is

$$4\,Mn(Acac)_2(H_2O)_2 + 4\,HAcac + O_2 \rightarrow 4\,Mn(Acac)_3 + 10\,H_2O. \tag{20}$$

$Mn(Acac)_3$ in benzene does not react further with oxygen and solutions are stable to decomposition for months.

In the presence of excess acetylacetone the reaction is first order in manganese(II) complex, oxygen, and excess ligand. Plots of $\log(A_\infty - A)$ versus time from spectrophotometric data obtained under pseudo-zero order conditions for oxygen are linear to at least four half-lives. Manganese(II) concentrations varied from 2.0×10^{-3} M to 1.0×10^{-2} M. The data in Table I indicate the first order dependence on oxygen pressure.

Table I

Rate Constants for Mn(III) Production in Benzene at Various Oxygen Pressures

Run	Mn(II) 10^3 M	HAcac M	P_{O_2} atm	k_1 10^2 sec^{-1}	(k_1) corr.* 10^2 atm^{-1}sec^{-1}
2-96	4.18	0.195	1.0	0.869	0.869
2-99	4.05	0.195	0.2	0.166	0.795
3-56	2.32	0.488	0.0384	0.227	5.90
–	2.3	0.488	0.2	1.23	5.90**

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* (k_1) corr. - First order rate constant corrected to 1 atm O_2.

** Figure 1.

The effect of excess ligand was studied at manganese(II) concentrations $2.3 \times 10^{-3}\,\underline{M}$ and $9.5 \times 10^{-3}\,\underline{M}$. The results (Fig. 1) show that the autoxidation of $Mn(Acac)_2(H_2O)_2$ is first order in free acetylacetone concentration. Both Fig. 1 and Fig. 2 indicate that at a given acetylacetone concentration, observed first order rate constants vary inversely with the initial concentration of $Mn(Acac)_2(H_2O)_2$.

The effect of water both in benzene solution and coordinated to the metal ion is shown in Table II.

Table II

Effects of Water on Autoxidation of $Mn(Acac)_2(H_2O)_2$

Run	Mn(II) $10^3\,\underline{M}$	HAcac $\underline{M}$	k_1 $10^2\,atm^{-1}\,sec^{-1}$
2-126	2.34	0.0975	0.987
3-12	2.44	0.0975	1.35
3-13	2.55	0.0975	1.83

The highest rate constant was observed for the autoxidation of the anhydrous chelate, $Mn(Acac)_2$, in benzene freshly distilled from sodium (Run 3-13). The lowest rate constant was for the autoxidation of $Mn(Acac)_2(H_2O)_2$ in benzene used for the kinetic studies (Run 2-126). Run 3-12, using $Mn(Acac)_2$ in water saturated benzene, gave a rate constant intermediate in value.

Tribenzylamine does not influence the autoxidation rate (Table

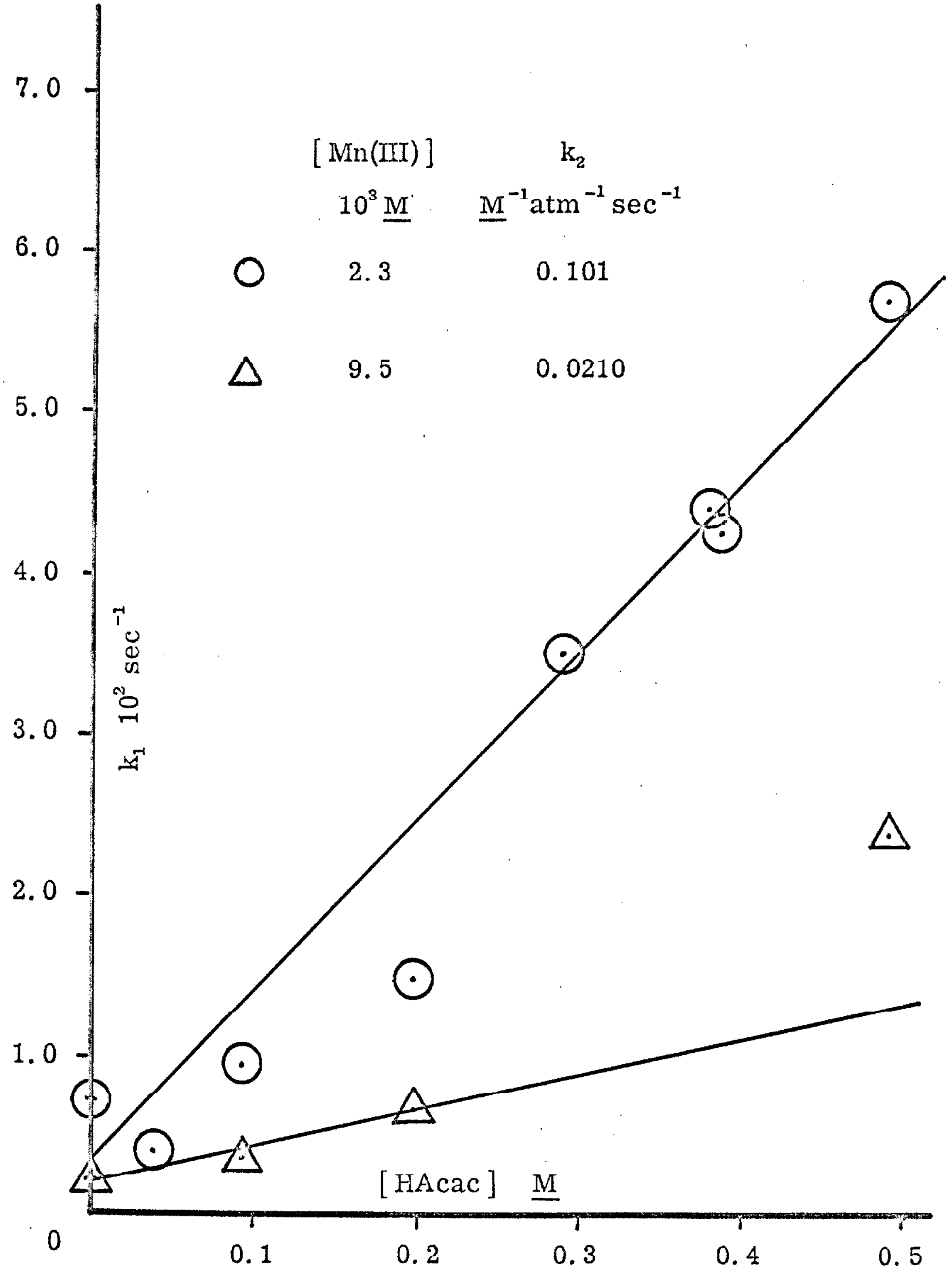

Fig. 1. Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Benzene First Order Rate Constant for Mn(III) Appearance vs. [HAcac] at constant [Mn(II)].

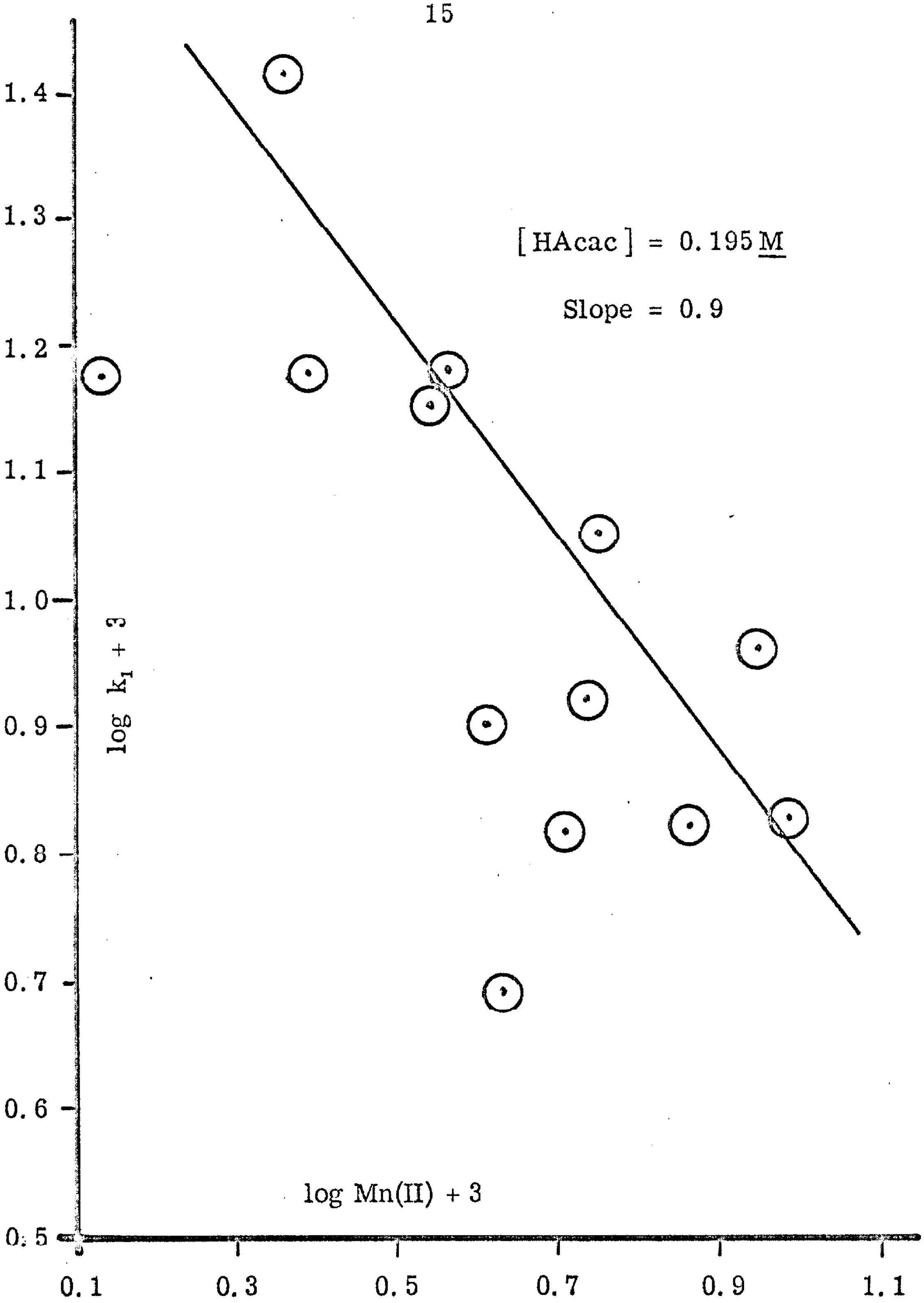

Fig. 2. Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Benzene First Order Rate Constant for Mn(III) Appearance vs. Initial [Mn(II)] at Constant [HAcac].

III). Pyridine and 2, 6-lutidine, however, inhibit the rate of manganese(III) production. Pyridine is a more effective inhibitor, on a molar basis, than 2, 6-lutidine. Furthermore, the observed first order rate constants vary inversely with increasing 2, 6-lutidine concentration.

Table III

Effect of Base on Autoxidation of $Mn(Acac)_2(H_2O)_2$

Run	Mn(II) $10^3 \underline{M}$	Base	$10^2 \underline{M}$	k_1* $10^2 atm^{-1} sec^{-1}$
2-62	4.16	pyridine	19.8	0.0101
2-63	4.66	2, 6-lutidine	8.78	0.430
2-112	2.31	—	—	2.61
2-116	2.27	($-CH_2)_3N$	4.09	2.44
2-118	4.50	2, 6-lutidine	19.7	0.152

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*HAcac = 0.195 $\underline{M}$

In the absence of excess chelating agent, the autoxidation of $Mn(Acac)_2(H_2O)_2$ exhibits marked deviation from first order kinetics as the concentration of product increases (Fig. 3). Rate constants for manganese(III) appearance, calculated from the first 40% of reaction. agree with the values obtained by extrapolating the data from Fig. 1 to zero free acetylacetone concentration. On the basis of the two runs conducted, the rate constants vary inversely with initial

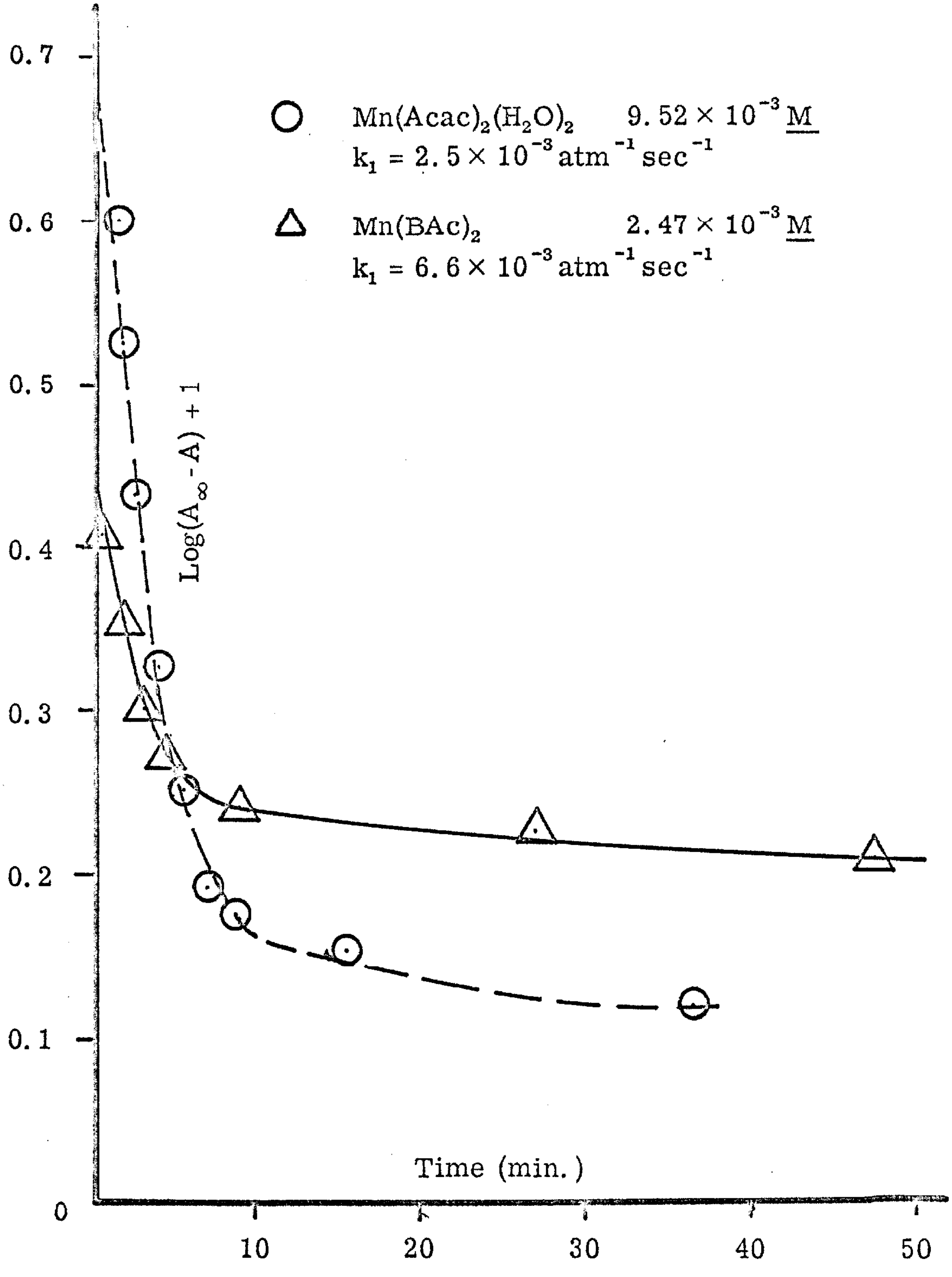

Fig. 3. Autoxidation of Mn(II) Complexes in Benzene with No Excess Diketone. Plot of log (A_∞-A) vs. Time.

$Mn(Acac)_2(H_2O)_2$ concentration ($[Mn(II)] = 6.36 \times 10^{-3}$ M, $k_1 = 3.82 \times 10^{-3}$ atm^{-1} sec^{-1}; $[Mn(II)] = 9.52 \times 10^{-3}$ M, $k_1 = 2.46 \times 10^{-3}$ atm^{-1} sec^{-1}). The spectrum of the product is similar to the spectrum of $Mn(Acac)_3$ in benzene (λmax = 1160 mμ, ϵ = 104 M^{-1} cm^{-1}), but the absorbance maximum has shifted to 1100 mμ (ϵ = 64 M^{-1} cm^{-1}).

Activation parameters for the autoxidation of 2.3×10^{-3} M $Mn(Acac)_2(H_2O)_2$ in benzene were calculated from data obtained at 15°, 30°, and 40° in the presence of excess acetylacetone. The results, shown in Table IV, are reported only to two figures because of the limited number of data and errors in extrapolation to zero acetylacetone concentration.

Table IV

Activation Parameters for Autoxidation of $Mn(Acac)_2(H_2O)_2$

Temp.	k_1* 10^2 atm^{-1} sec^{-1}	k_2** 10^2 M^{-1} atm^{-1} sec^{-1}
15°	0.10 ± .02	0.85
30°	0.29 ± .04	1.01 ± .03
40°	0.42	1.4
E_a	11 ± 1 kcal/mole	6.7 ± 0.7 kcal/mole
$\Delta S^{\ddagger}$	-34 ± 4 cal/°K mole	-45 cal/°K mole

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* HAcac independent path

** HAcac dependent path

The effect of the β-diketone ligand on the autoxidation of the manganese(II) complex is indicated in Table V. In all the cases studied, excess ligand accelerates the rate of reaction with molecular oxygen, but the effects are most pronounced with $Mn(Acac)_2(H_2O)_2$. Observed rate constants obtained at an initial manganese(II) concentration 3×10^{-3} M, extrapolated to zero free ligand concentration, vary by a factor of 10^3 in the order $Mn(Acac)_2(H_2O)_2$ (0.0028 $atm^{-1} sec^{-1}$) $<$ $Mn(BAc)_2$ (0.0066 $atm^{-1} sec^{-1}$) $<$ $Mn(PVA)_2$ (0.080 $atm^{-1} sec^{-1}$) $\ll$ $Mn(DPM)_2$ (2.8 ± 0.4 $atm^{-1} sec^{-1}$). The reason for the discrepancy in the data for $Mn(BAc)_2$ autoxidation (Runs 2-101, 141, 142, and Runs 2-143, 3-14, 17) is not understood. Autoxidation of $Mn(BAc)_2$ in the absence of added ligand follows a path similar to autoxidation of $Mn(Acac)_2(H_2O)_2$ in the absence of added ligand (Fig. 3). Less than 50% of the manganese(II) had been oxidized in two days, but when excess diketone was added, oxidation was complete within three hours. Rate constants for oxidation of <u>bis</u>(dipivaloylmethanato)manganese(II), $Mn(DPM)_2$, are semi-quantitative only, since, even at low oxygen pressure, the reactions were 90% complete within 2 minutes. Bis(trifluoroacetylacetonato)manganese(II) is not air oxidized in benzene solution.

Several potential organic cosubstrates were tested qualitatively to determine their influence on the autoxidation of $Mn(Acac)_2(H_2O)_2$ in benzene. Benzoin and substituted benzyl alcohols were studied in quantitative experiments (Table VI). Benzoin exhibits a small, accelerating effect on the reaction rate. Analyses of reaction products

Table V

Autoxidation of Mn(II) β-Diketone Complexes in Benzene

Run	Mn(II) 10^3 M	Ketone (ligand)	K M	k_1 $atm^{-1} sec^{-1}$
2-109	2.22	HAcac	0.376	0.0439
2-126	2.34	HAcac	0.0975	0.00988
2-97	2.91	HBAc	0.0288	0.0155
2-101	3.24	HBAc	0.0288	0.0150
2-141	3.47	HBAc	0.00947	0.0168
2-142	3.52	HBAc	0.0390	0.0178
2-143	2.47	HBAc	—	0.00655
3-14	3.54	HBAc	0.103	0.00948
3-17	3.67	HBAc	0.238	0.0135
3-59	2.62	HPVA	0.595	0.117
3-60	2.58	HPVA	0.0350	0.0825
3-61	2.66	HPVA	0.236	0.0938
3-62	10.31	HPVA	0.219	0.0712
3-64	3.62*	HDPM	0.0463	3.8
3-65	4.00*	HDPM	0.0207	3.2
3-66	3.44*	HDPM	0.0139	3.4

HAcac - acetylacetone
HBAc - benzoylacetone
HPVA - pivaloylacetone
HDPM - dipivaloylmethane

*[Mn(DPM)$_2$] calculated from absorbance of oxidized solution (ϵ_{1160} = 105 M^{-1} cm^{-1}).

Table VI

Effect of Cosubstrates on Autoxidation of $Mn(Acac)_2(H_2O)_2$

Run	$(Mn^{II})_0$ 10^3 M	C	$(C)_0$ 10^2 M	Po_2 atm	k_1* 10^2 atm^{-1} sec^{-1}
2-68	4.65	Benzoin	1.73	1.0	1.72
2-73	4.04	Benzoin	0.759	0.2	1.53
2-74	3.72	Benzoin	1.62	0.2	1.72
—	4.0	—	—	0.2	1.4 ‡
2-114	3.64	Benzyl alcohol	48.5	0.2	1.25 **
2-117	3.92	Benzyl alcohol	9.71	0.2	4.81 **
2-136	4.12	p-methoxy benzyl alcohol	44.3	0.2	0.585**
2-138	4.03	p-nitro benzyl alcohol	44.8	0.2	8.98 **

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*[HAcac] = 0.195 M

‡ Figure 2.

** (Initial rate) × 10^6 M sec^{-1}

show, however, that benzoin is not oxidized during the reaction.

Benzyl alcohol inhibits $Mn(Acac)_3$ production by a process inversely proportional to the alcohol concentration. Even though the concentration of alcohol is at least twenty-five times greater than the initial manganese(II) concentration, calculated rate constants decrease with time and the rate of manganese(III) appearance follows no simple rate law. Product analyses during the initial stages of the autoxidation indicate that benzaldehyde or benzoic acid are not produced. Furthermore, $Mn(Acac)_3$ does not rapidly oxidize benzyl alcohol in benzene solution. Inhibition is greatest for para-methoxybenzyl alcohol, and the least for para-nitrobenzyl alcohol. A plot of log initial rate of manganese(III) production versus σ_p is linear with slope +1.21.

Table VII indicates the qualitative effect of several classes of organic molecules on the appearance of manganese(III) during the autoxidation of $Mn(Acac)_2(H_2O)_2$. All results are relative to a blank of $Mn(Acac)_2(H_2O)_2$ in benzene. Alcohols appear to inhibit the reaction in the order tertiary > secondary > primary. Sterically hindered phenols and bases have no effect on the autoxidation. Aliphatic aldehydes completely inhibit manganese(III) appearance, but also react rapidly with $Mn(Acac)_3$.

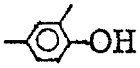
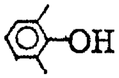
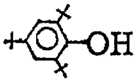
B. Autoxidation of Manganese Complexes in Alcohol Solution

1. Autoxidation of Manganese(II) Complexes in Ethanol

The autoxidation of $Mn(Acac)_2(H_2O)_2$ in ethanol, compared with the reaction in benzene, is a complex process. Total oxygen consumption is greater than the amount required for oxidation of the metal complex. Yet, manganese(II) is not quantitatively converted to manganese(III) except in a large excess of acetylacetone and strong base. At least three side reactions,

Table VII

Effect of Organic Reagents on Appearance of Manganese(III)

Cosubstrate	Effect	Cosubstrate	Effect
benzhydrol	none	salicylaldehyde	none
ethanol	–	benzaldehyde	–
isopropyl alcohol	–	isobutyraldehyde	– –
tert-butyl alcohol	–	propionaldehyde	– –
cyclohexanol	–	acetic acid	–
pinacol	–	acetylacetone	++
phenol	++	biacetyl	–
p-nitrophenol	+++	imidazole	–
	+	pyridine	–
	none	ethanolamine	–
	none	piperidine	–
catechol	++	tribenzylamine	none
hydroquinone	+++	aniline	+
cyclohexanone	none		

+ slightly accelerates

++ accelerates

+++ strongly accelerates

– inhibits

– – strongly inhibits

discussed in Subsection 4, interfere in the absence of these conditions to make a complete kinetic analysis of the data a formidable task.

Initial rate studies of oxygen consumption and manganese(III) appearance show that the autoxidation of $Mn(Acac)_2(H_2O)_2$ in ethanol is 3/2 order in manganese(II) complex (9×10^{-4} - 2×10^{-2} $\underline{M}$), first order in oxygen (0.2 and 1 atm), and approximately -0.23 order in excess acetylacetone (0.04 - 0.7 $\underline{M}$).

In the presence of free acetylacetone, the product of $Mn(Acac)_2(H_2O)_2$ autoxidation in ethanol is $Mn(Acac)_3$, since the spectrum of the product is identical to the spectrum of $Mn(Acac)_3$ in ethanol containing the neutral ligand (λ max = 1100 mμ, ϵ = 102 $\underline{M}^{-1}$ cm). The manganese(III) product in the absence of excess β-diketone is unknown, but may be a mixture of a bis(acetylacetonato)manganese(III) species, probably $Mn(Acac)_2(H_2O)(OH)$ or a dimer, $[Mn(Acac)_2(OH)]_2$, and $Mn(Acac)_3$. The spectrum of this product exhibits features similar to the spectra of both bis(acetylacetonato)-(diaquo)manganese(III) perchlorate and $Mn(Acac)_3$ in ethanol.

Figure 4 is a log-log plot of initial rate of manganese(III) appearance *versus* manganese(II) concentration in the presence and absence of excess acetylacetone. The scatter of the data for reaction in the absence of added diketone is due largely to the lack of precision with which the initial rate could be measured. Plots of manganese(III) produced or oxygen consumed *versus* time showed marked curvature after 2-3% of reaction. The experimental difficulty was eliminated when the autoxidation was conducted in excess acetylacetone; straight

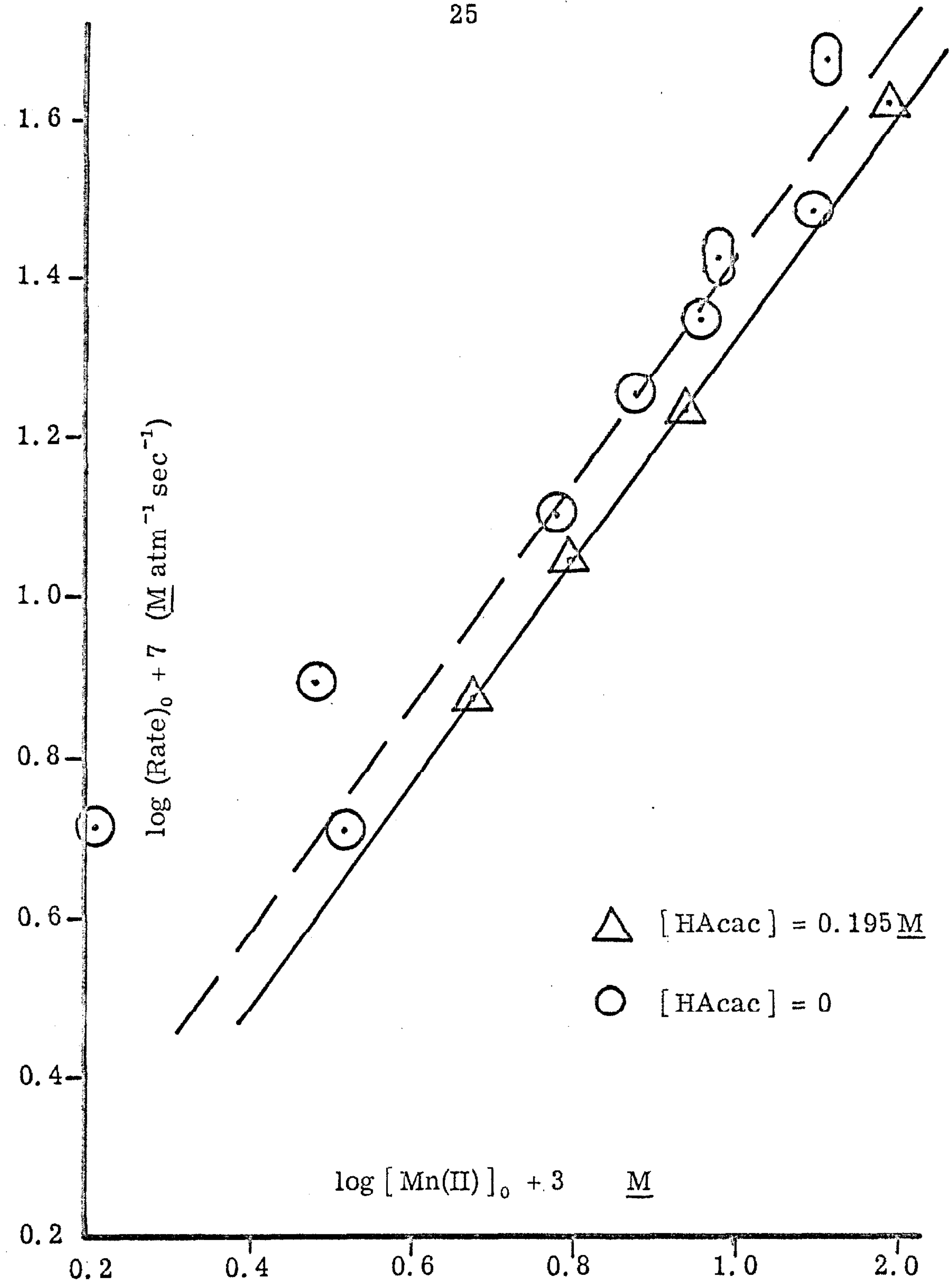


Fig. 4. Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Ethanol Initial Rate of Mn(III)) Appearance vs. $[Mn(II)]_0$ in Presence and Absence of Added Acetylacetone.

lines could be drawn through the initial 10-15% of these data.

Figure 5 is a plot of initial rate of $Mn(Acac)_2(H_2O)_2$ oxidation in the absence of excess ligand <u>versus</u> $[Mn(II)]^{3/2}$. The stoichiometry

$$\frac{d[Mn(III)]}{dt} = 4\left(-\frac{dO_2}{dt}\right) \tag{21}$$

was assumed and initial rates of oxygen consumption, measured under 1 atm of oxygen, were multiplied by 4. Data for manganese(III) appearance, obtained under 1 atm of air, were divided by 0.21 to correct them to 1 atm of oxygen. Both sets of data fall on the same straight line confirming a 4:1 stoichiometry, 3/2 order dependence on manganese(II), and first order dependence on oxygen for the initial reaction. In agreement with the observed stoichiometry, tests for formation of hydrogen peroxide were negative. Hydrogen peroxide, added to a solution of $Mn(Acac)_2(H_2O)_2$ in ethanol, rapidly oxidizes the complex to the trivalent state.

The effect of added acetylacetone, shown in Fig. 6, is unusual since excess ligand inhibits both the initial rates of manganese(III) appearance and oxygen consumption. The dependence of the rate on the manganese(II) concentration is about 1.6 order at 0.7 <u>M</u> acetylacetone concentration where the inhibition of added ligand has reached a maximum value.

A search for solvent oxidation products during the initial phase of the reaction in ethanol failed to detect acetaldehyde or acetic acid. Samples of reaction mixtures were injected into a gas-liquid

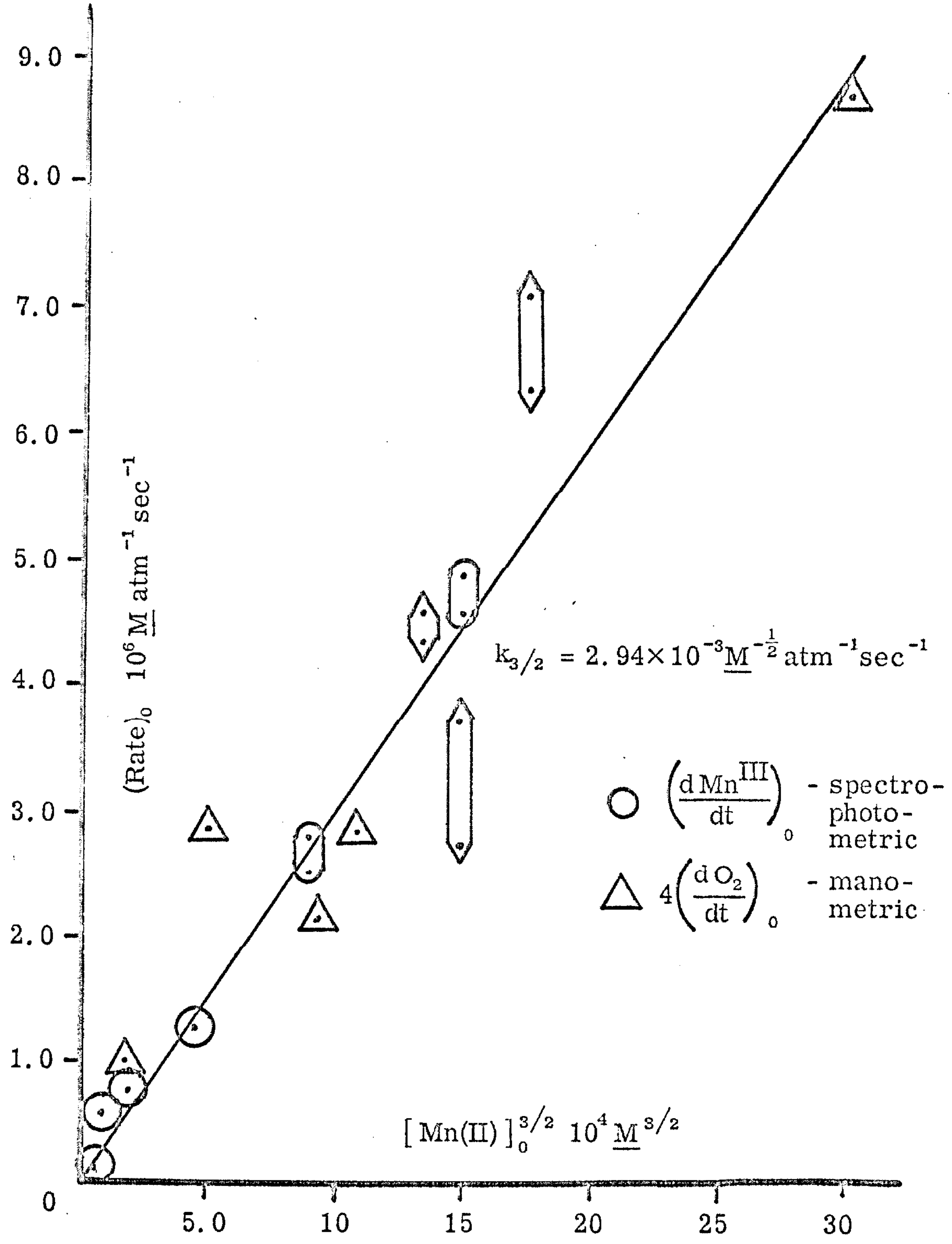


Fig. 5. Initial Rate of $Mn(Acac)_2(H_2O)_2$ Autoxidation in Ethanol vs. Initial $[Mn(II)]^{3/2}$.

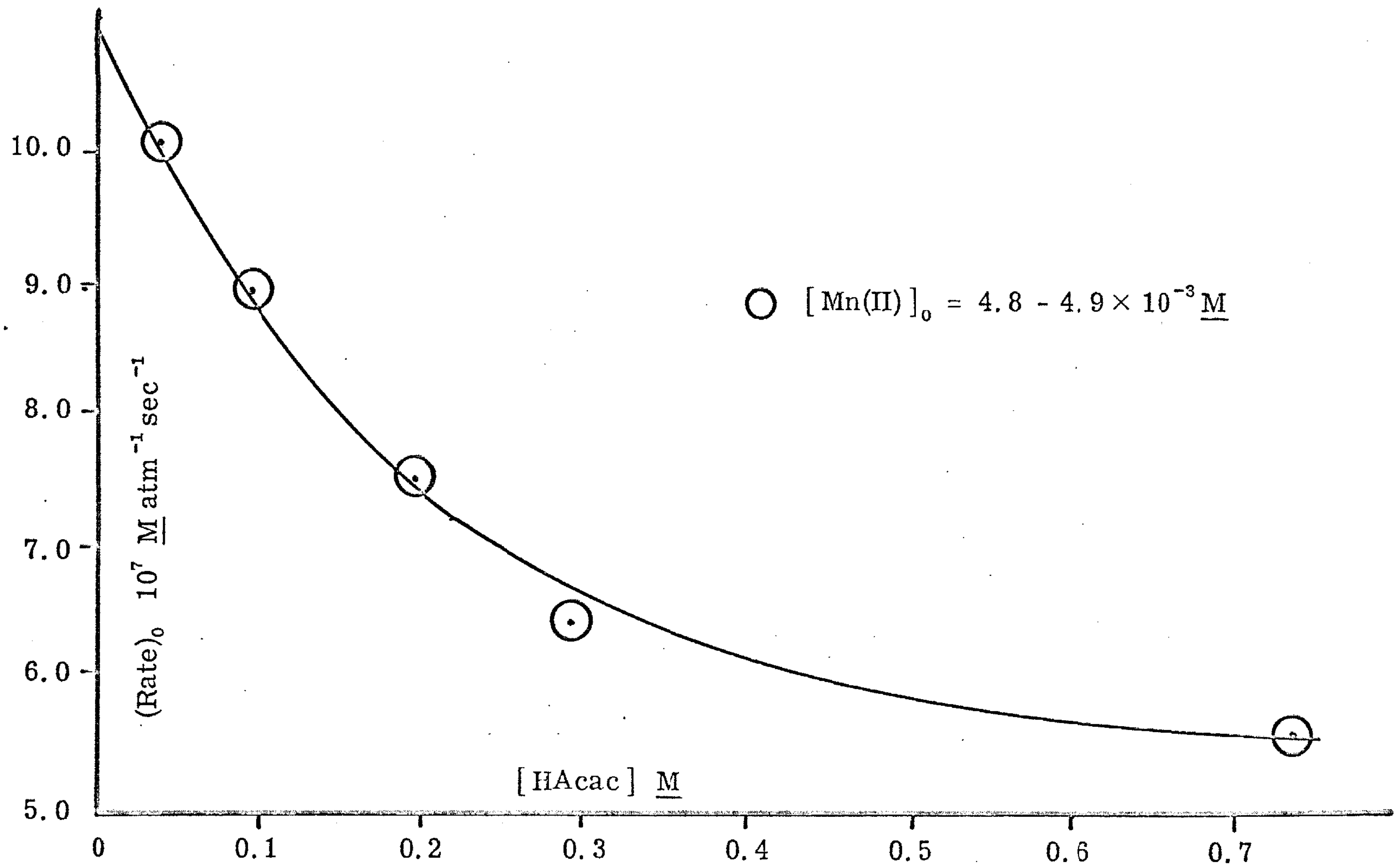


Fig. 6. Initial Rate of $Mn(Acac)_2(H_2O)_2$ Autoxidation in Ethanol vs. Acetylacetone Concentration at Constant $[Mn(II)]_0$.

chromatography column (5 foot column, 10% Carbowax 400 on teflon at 60° or 120°) with no success. Oxygen was passed through a series of bubblers containing ethanol solutions of 2, 4-dinitrophenylhydrazine (2, 4-DNP), $Mn(Acac)_2(H_2O)_2$, and, finally, 2, 4-DNP. Samples were withdrawn from the third bubbler and analyzed for aldehyde,[38] but none was detected.

Added $Mn(Acac)_3$ decreases the initial rate of $Mn(Acac)_2(H_2O)_2$ oxidation by molecular oxygen. Table VIII shows the magnitude of the effect in the presence of added acetylacetone.

Table VIII

Effect of Added $Mn(Acac)_3$ on Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Ethanol

Run	$[Mn(II)]_o$ 10^3 M	$[Mn(III)]_o$ 10^3 M	[HAcac] M	$(Rate)_o^*$ 10^6 M $atm^{-1} sec^{-1}$
2-94	8.14	7.19	0.195	1.05 ± .05
–	8.14	–	0.195	1.58 ‡
3-45	4.99	3.14	0.733	0.516
2-127	4.81	–	0.733	0.555

---

* Initial rate of Mn(III) production; $P_{O_2} = 1$

‡ Figure 4

Pyridine and 2, 6-lutidine, unlike their behavior in benzene solution, slightly accelerate the rate of autoxidation of $Mn(Acac)_2(H_2O)_2$ in ethanol. Piperidine, too, accelerates the initial rate of reaction, and, in the presence of 0.7 M acetylacetone, forces the reaction to follow overall first order kinetics, $k_1 = 1.67 \times 10^{-4}\ \mathrm{atm}^{-1}\ \mathrm{sec}^{-1}$ (Fig. 7). The initial rate of $Mn(Acac)_2(H_2O)_2$ oxidation in 0.7 M acetylacetone and a five-fold excess of piperidine over manganese concentration is still 3/2 order in manganese(II) (Table IX - Runs 3-46 and 3-82). Presence of a strong base alone is not sufficient to force the reaction to overall first order kinetics; without a large excess of acetylacetone, the oxidation deviates markedly from overall first order, following no simple kinetic rate law (Fig. 7). Piperidine is a more effective catalyst than 2, 6-lutidine. The accelerating effect of added base is reduced slightly as the concentration of base increases.

Activation parameters for the autoxidation of $Mn(Acac)_2(H_2O)_2$ in 0.2 M acetylacetone were calculated from initial rates at 15°, 30°, and 40° (Table X).

2. Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Isopropyl Alcohol and Methanol

The autoxidation of $Mn(Acac)_2(H_2O)_2$ was investigated briefly in isopropyl alcohol. The reaction in the presence of 0.2 M acetylacetone is 3/2 order in manganese(II). Analyses during the initial stages of the reaction indicate that acetone is not formed during the autoxidation of manganese(II) to manganese(III). At 1 atm of oxygen and 0.2 M acetylacetone, the rate constant for the initial production of $Mn(Acac)_3$ is $2.30 \times 10^{-3}\ \underline{M}^{-\frac{1}{2}}\ \mathrm{atm}^{-1}\ \mathrm{sec}^{-1}$. This value can be compared with the value for the oxidation of $Mn(Acac)_2(H_2O)_2$ in ethanol,

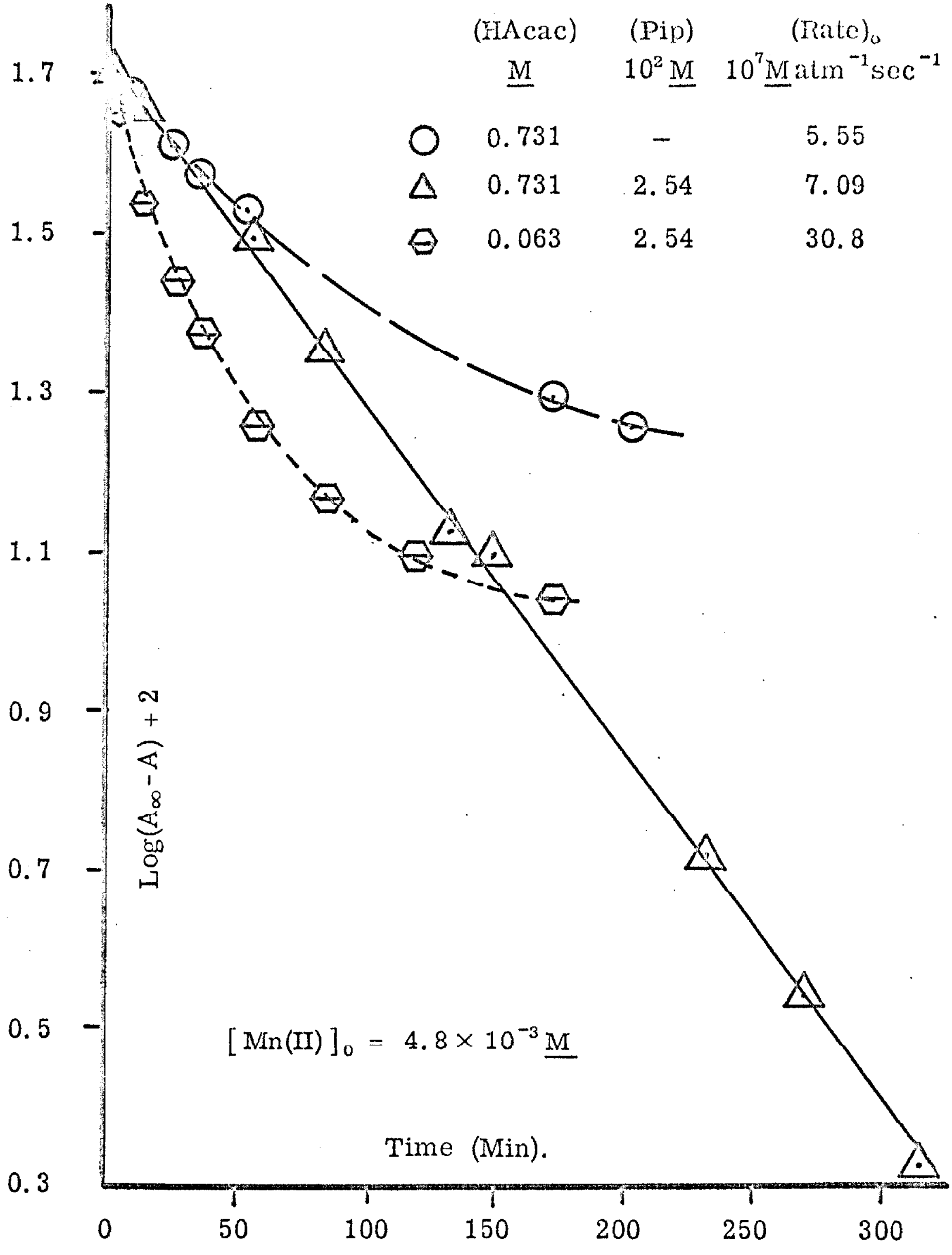


Fig. 7. Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Ethanol with Added Acetylacetone and Piperidine. Plot of $Log(A_\infty - A)$ *vs.* Time.

Table IX

Effect of Added Base on Autoxidation of $Mn(Acac)_2(H_2O)_2$ Ethanol

Run	$[Mn(II)]_0$ 10^3 M	Base*	$[B]_0$ 10^2 M	[HAcac] M	$(Rate)_0$** 10^6 M atm^{-1} sec^{-1}
1-86	10.30	–	–	–	1.32
1-170	10.13	pyr.	62.0	–	1.42
1-171	10.87	pyr.	2.06	–	1.68
2-56	6.28	lut.	8.78	0.195	1.13
3-42	6.63	pip.	0.662	0.195	1.72
–	6.28	–	–	0.195	1.09 ‡
3-43	5.10	pip.	0.509	0.733	4.05
3-46	5.01	pip.	2.54	0.733	0.707
3-68	5.07	pip.	2.54	0.0629	3.07
–	5.07	–	–	0.0629	0.967 ϕ
3-81	11.2	pip.	2.55	0.731	3.36
3-82	10.84	pip.	5.09	0.731	2.18

---

* pyr. = pyridine
lut. = 2, 6-lutidine
pip. = piperidine

** Initial rate of Mn(III) appearance; $P_{O_2} = 1$

‡ Figure 4

ϕ Figure 7

Table X

Activation Parameters for Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Ethanol

Temp. °C	$k_{3/2}$* 10^3 $M^{-\frac{1}{2}}$ atm^{-1} sec^{-1}	E_{act} kcal/mole	$\Delta S^{\ddagger}$ cal/°K mole
15°	0.895	10.8 ± 1.2	-35 ± 4
30°	2.00		
40°	3.72		

*Rate constant for Mn(III) appearance; [HAcac] = 0.195 M; P_{O_2} = 1 atm.

2.00×10^{-3} $M^{-\frac{1}{2}}$ atm^{-1} sec^{-1}.

$Mn(Acac)_2(H_2O)_2$ is oxidized more slowly in methanol than in ethanol or isopropyl alcohol. The rate constant based on manganese(III) production is 1.14×10^{-3} $M^{-\frac{1}{2}}$ atm^{-1} sec^{-1} in 0.082 M acetylacetone. In the absence of acetylacetone, the rate constant increases slightly to 1.20×10^{-3} $M^{-\frac{1}{2}}$ atm^{-1} sec^{-1}.

3. Autoxidation of Bis(β-diketonato)manganese(II) Complexes in Ethanol

Pronounced ligand effects on the rates of manganese(II) autoxidations are observed as the β-diketonate coordinated to the metal ion is varied. Figures 8a and 8b are log-log plots of initial rate of oxygen consumption *versus* manganese concentration at constant free ligand concentration. The complexes were prepared in the test

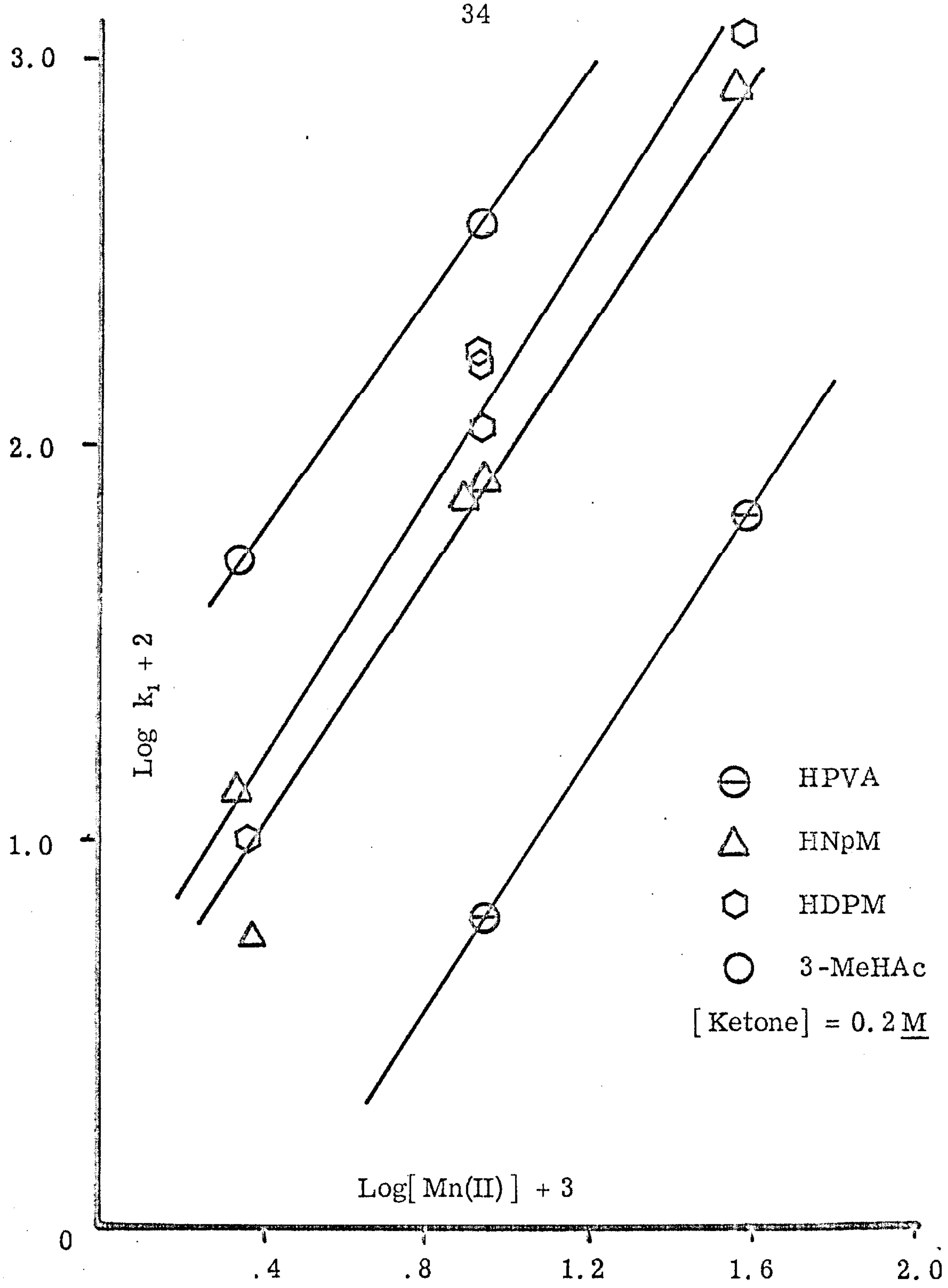


Fig. 8a. Autoxidation of Mn(II) β-Diketonate Complexes in Ethanol. Plot of Log First Order Rate Constant for O_2 Consumption vs. Log Initial [Mn(II)].

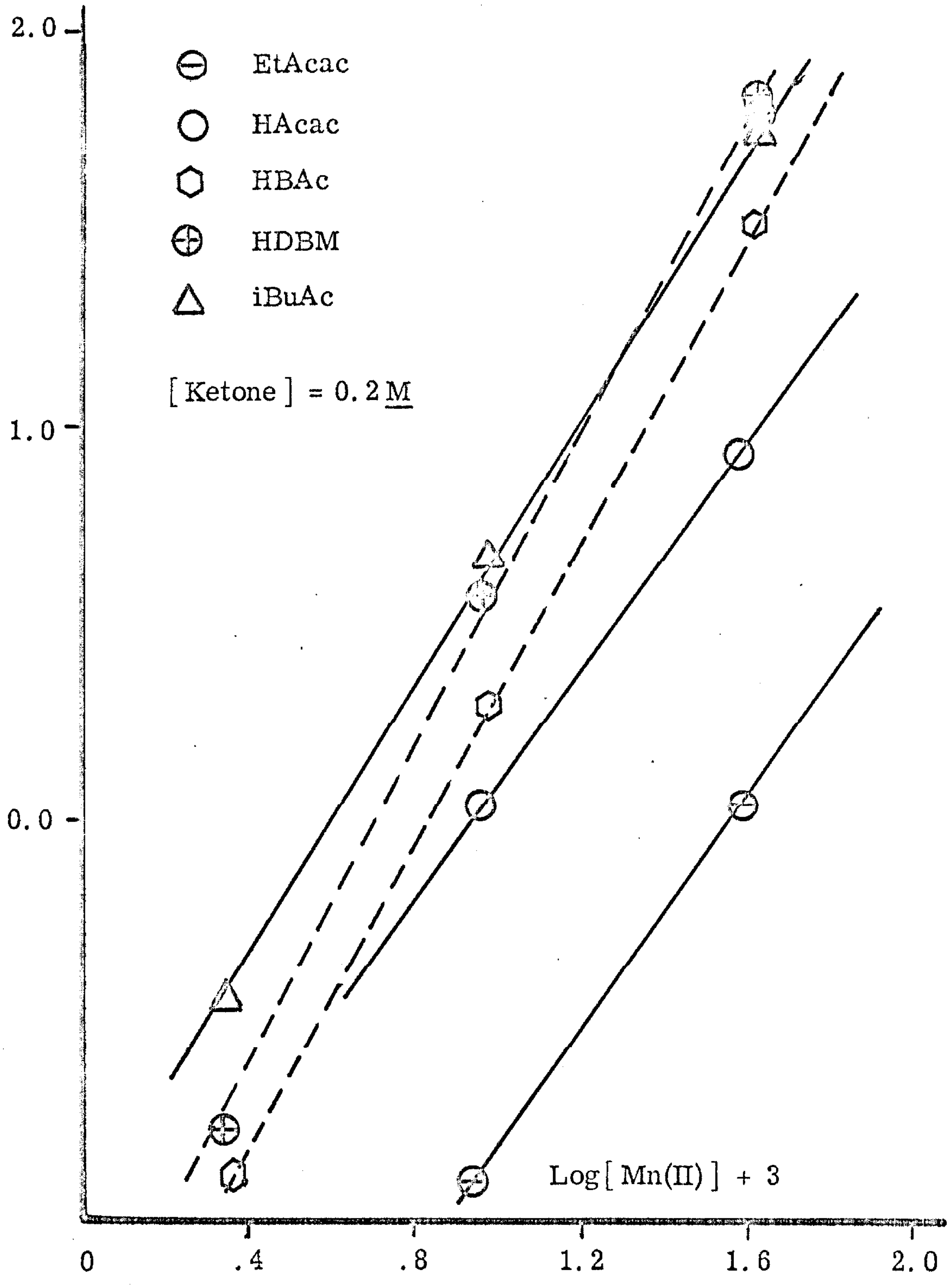


Fig. 8b. Autoxidation of Mn(II) β-Diketonate Complexes in Ethanol.

Key to Figs. 8a and 8b

HPVA	Pivaloylacetone
HNpM	Dineopentoylmethane
HDPM	Dipivaloylmethane
3-MeHAc	3-Methylacetylacetone
EtAcac	Ethylacetoacetate
HAcac	Acetylacetone
HBAc	Benzoylacetone
HDBM	Dibenzoylmethane
iBuAc	Isobutyrylacetone

chamber of the oxygen polarograph by neutralizing a solution of manganese(II) chloride and diketone, in excess of the 2:1 molar ratio needed to form a bis complex, with the required amount of base. Rate constants for autoxidation of $Mn(Acac)_2(H_2O)_2$ obtained by this method are greater than those obtained by manometric and spectrophotometric methods by a factor of three or four. This is fairly good agreement considering the difference in experimental procedure, the limited numbers of data, and the extrapolations involved.

The rates vary by a factor of 3×10^3 as the ligand changes from ethylacetoacetato to 3-methylacetylacetonato. Furthermore, bis(trifluoroacetylacetonato)manganese(II) and manganese(II) chloride are not autoxidized in ethanol solution. Figures 8a and 8b show that all but two of the manganese(II) chelates are autoxidized at a rate initially 3/2 order in manganese(II). The oxidations of bis(benzoylacetonato)manganese(II) and bis(dibenzoylmethanato)manganese(II) appear to be second order in manganese(II). A series of experiments was conducted in which excess ligand concentration was varied. The data were extrapolated to zero free ligand concentration to obtain the initial rate of autoxidation of the bis chelate. Rate constants for oxidation of a series of manganese(II) β-diketonato complexes are given in Table XI. The fourth column of Table XI indicates the dependence of the rate on the concentration of excess diketone. A rough correlation of the inhibitory effect of excess ketone with both size and coordinating ability of the ligand exists for the series acetylacetonato < isobutyrylacetonato < pivaloylacetonato.

Table XI

Autoxidation of Manganese(II) Chelates-Ligand Effects

Manganese(II) Chelate	Rate Constant*		
	$k_3/2$** $10^3\underline{M}^{-\frac{1}{2}}atm^{-1}sec^{-1}$	$k_3/2$‡ $10^3\underline{M}^{-\frac{1}{2}}atm^{-1}sec^{-1}$	m$^\phi$
Ethylacetoacetato	–	0.83	–
Acetylacetonato	14	6.0	-0.23
Benzoylacetonato	260‡‡	113‡‡	-0.30±.03
Dibenzoylmethanato	540±100‡‡	250‡‡	-0.30±0.1
Isobutyrylacetonato	66±15	29	-0.30±0.1
Pivaloylacetonato	160±20	44	-0.52±.07
Dineopentoylmethanato	1400	510	-0.37±.05
Dipivaloylmethanato	1300	1100	-0.1
3-Methylacetylacetonato	–	2200	–

---

* Rate constant for appearance of manganese(III); $[Mn(II)]_o = 8.5 \times 10^{-3}\underline{M}$

** Extrapolated to [Free Ligand] = 0

‡ [Free ligand] = 0.2 $\underline{M}$

‡‡ Second order rate constants, $10^3\underline{M}^{-1}sec^{-1}$

ϕ Dependence of rate on ketone concentration

The correlation breaks down with the dipivaloylmethanato chelate.

4. Autoxidation of Manganese(III) Complexes in Alcohol Solution

Oxygen consumption in the autoxidation of $Mn(Acac)_2(H_2O)_2$ is greater than required for oxidation of manganese(II) to manganese(III), and is due to ligand and solvent oxidation by the oxidized manganese species and molecular oxygen. Table XII illustrates the importance of these secondary reactions on the overall reaction.

Table XII

Excess O_2 Consumption in Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Ethanol [‡]

Run	$Mn(II)_0$ mmole	ΔO_2 mmole	t min	$Mn(III)_t$[*] mmole	xs O_2[**] mmole
1-82 [ϕ]	0.132	0.406	2,096		0.37
1-213	0.143	0.0202	78	0.062	0.0050
1-214	0.160	0.190	591	0.080	0.170
1-215	0.183	0.0914	318	0.11	0.063

[‡] No added acetylacetone; $P_{O_2} = 1$ atm.

[*] Total Mn(III) at time, t.

[**] xs $O_2 = \Delta O_2 - (\frac{1}{4})Mn(III)_t$.

[ϕ] $Mn(Acac)_2$ in methanol.

Analyses for acetylacetone at the end of the runs gave erratic results, but indicate the fraction of ligand remaining at the end of a run decreases with increasing reaction time. Aldehyde was identified qualitatively on the gas-liquid chromatograph.

Oxygen consumption by $Mn(Acac)_3$ in alcohol was observed with the oxygen polarograph and the manometric apparatus. Semilogarithmic plots of fraction oxygen unreacted *versus* time from polarographic experiments are linear to at least two half-lives, establishing the reaction as first order in oxygen. Plots of first order rate constant for oxygen consumption in several alcohols *versus* $Mn(Acac)_3$ concentration are linear (Table XIII). Manometric experiments, pseudo-zero order in oxygen, indicate that oxygen consumption is initially linear with time for the reaction of $Mn(Acac)_3$ with oxygen in methanol (Fig. 9). The pseudo-first order rate constant calculated from the data in Fig. 9, 7.61×10^{-5} atm^{-1} sec^{-1}, is in fair agreement with the value obtained by polarographic measurements, 15.5×10^{-5} atm^{-1} sec^{-1}. As the reaction proceeds, the rate of oxygen consumption

Table XIII

Oxygen Consumption by $Mn(Acac)_3$ in Alcohol

Alcohol	k_1* $10^5 atm^{-1} sec^{-1}$
Methanol	15.5
Ethanol	8.15
Propanol	3.59

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*Rate constant pseudo-zero order in oxygen; $P_{O_2} = 1$ atm.

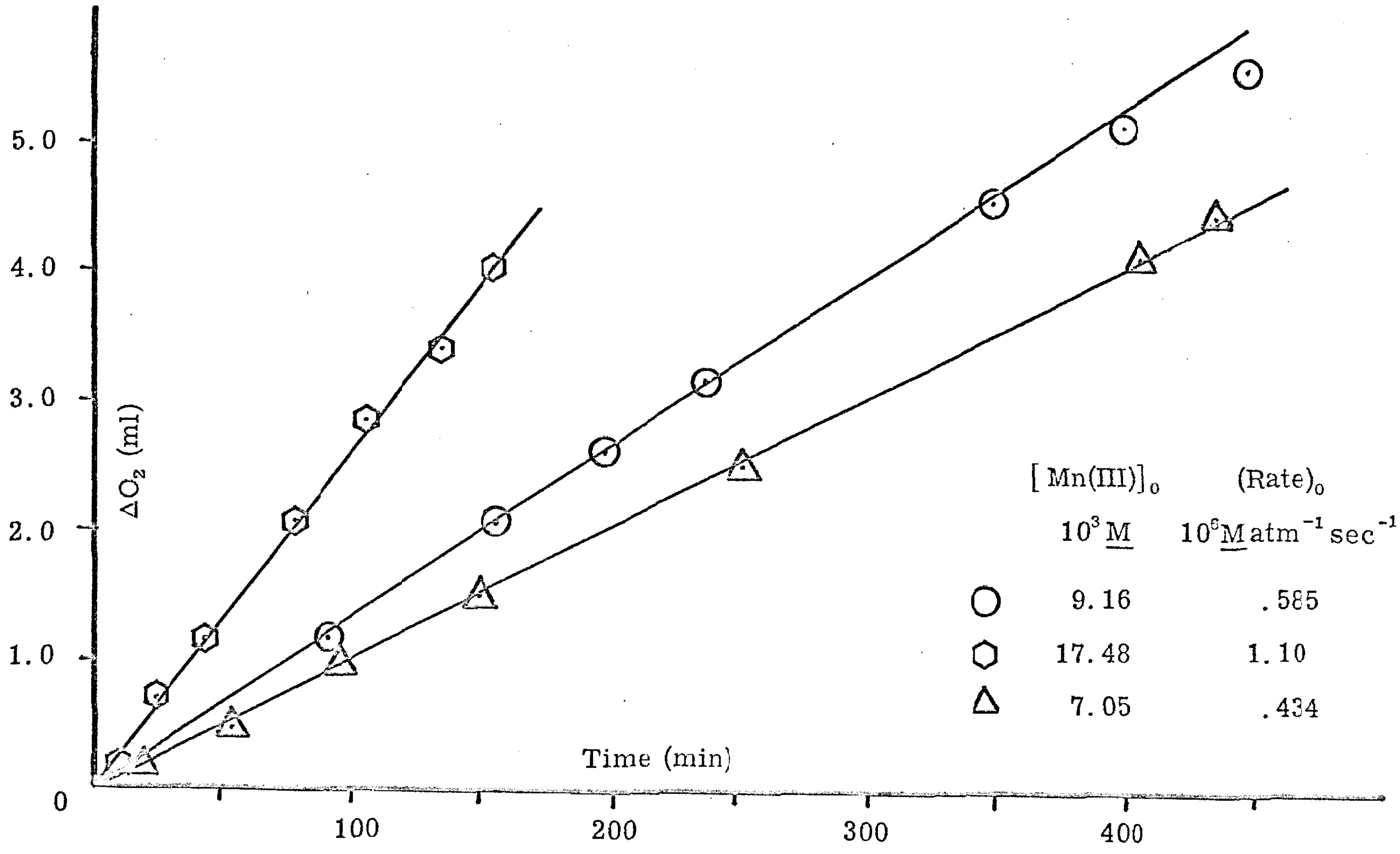


Fig. 9. Oxygen Consumption by Mn(Acac)$_3$ in Methanol. Plot of ΔO_2 vs. Time.

decreases and the color of the solution fades from deep brown to yellow-brown. This slow decomposition of the manganese(III) chelate was monitored spectrophotometrically at 1040 $m\mu$ in ethanol. Net $Mn(Acac)_3$ decomposition is first order in manganese(III) with a pseudo-first order rate constant for the process, 1.6×10^{-5} atm^{-1} sec^{-1}, assuming complete reduction to manganese(II). If the product of the reaction is $Mn^{III}(Acac)_2^+$ which decomposes much more slowly than $Mn(Acac)_3$, the rate constant for loss of one ligand is 4.4×10^{-5} sec^{-1}. These values can be compared with the pseudo-first order rate constant based on oxygen consumption for the reaction of $Mn(Acac)_3$ and oxygen in ethanol, 8.15×10^{-5} atm^{-1} sec^{-1}. Since neither the stoichiometry nor the immediate products of the decomposition reaction are known, a direct comparison of the two rate constants is not valid. Both results do point out, however, the importance of ligand oxidation in the reaction of $Mn(Acac)_3$ with oxygen in alcohol solution.

$Mn(Acac)_3$ in alcohol solution in the absence of oxygen undergoes a redox reaction which is much slower than the reaction in the presence of oxygen. Absorbance of degassed solutions sealed under vacuum and stored at 30° in the dark decreases to one-half their original value in 10-12 days. It is not known whether the reaction involves oxidation of ligand, solvent, or both.

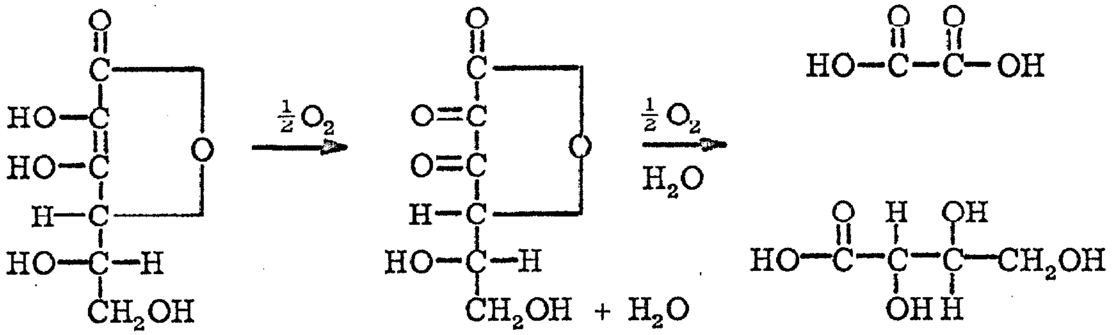
Added propionaldehyde has no effect on the rate of oxygen consumption in the reaction of $Mn(Acac)_3$ with oxygen in propanol. Acetylacetone inhibits the reaction of $Mn(Acac)_3$ with oxygen in methanol. A ten-fold excess of acetylacetone is sufficient to reduce the rate of oxygen consumption by a factor of five.

Oxygen consumption by tris(3-methylacetylacetonato)manganese(III) and tris(trifluoroacetylacetonato)manganese(III) were studied briefly. The apparent dependence of manganese(III) on the reaction rate for both chelates is approximately 1.7. Tris(3-methylacetylacetonato)manganese(III) is about three times as reactive towards oxygen as the second chelate.

C. Autoxidation of Manganese(II) Complexes in the Presence of Organic Cosubstrates

Cosubstrates were added to solutions of manganese(II) β-diketonate in methanol and their effect upon the rates of oxygen consumption and manganese(III) production was noted. The data may not be adequate to completely describe the mechanisms of the catalyzed oxidations but serve to indicate gross features of reactivity patterns. The cosubstrates have been divided into three classes based on their ability to affect manganese(III) production; Class I cosubstrates inhibit, Class II cosubstrates do not greatly affect, and Class III cosubstrates accelerate the appearance of manganese(III).

Class I cosubstrates studied are reducing agents, ascorbic acid, dehydroascorbic acid, and hydroquinone. In the induced oxidation of ascorbic acid by $Mn(Acac)_2(H_2O)_2$, manometric experiments under one atmosphere of oxygen are marked by a rapid consumption of oxygen (one mole oxygen per mole ascorbic acid) followed by a much slower rate of oxygen consumption and production of manganese(III). The catalyzed oxidations of both ascorbic acid and its oxidation product, dehydroascorbic acid, occur at similar, fast rates.



Induced autoxidation of ascorbic acid is 0.5 order in total manganese from 4×10^{-4} M to 9×10^{-3} M, whether initiated by $Mn(Acac)_2(H_2O)_2$ or $Mn(Acac)_3$, which is instantly reduced by the excess cosubstrate. Figure 10 is a plot of first order rate constant for oxygen consumption on the oxygen polarograph versus the square root of the manganese(II) concentration. The scatter in the data is probably due to trace acidic or basic impurities which would alter the fraction of ascorbate anion in solution. Ascorbic acid dependence is essentially zero from 5×10^{-3} M to 0.12 M, although first order rate constants for oxygen consumption increase at lower ascorbic acid concentrations because of competition from the more reactive dehydroascorbic acid produced in the oxidation.

Acetylacetone inhibits the induced autoxidation of ascorbic acid in methanol (Fig. 11). At acetylacetone and ascorbic acid concentrations, 0.084 M and 0.031 M respectively, the dependence of the

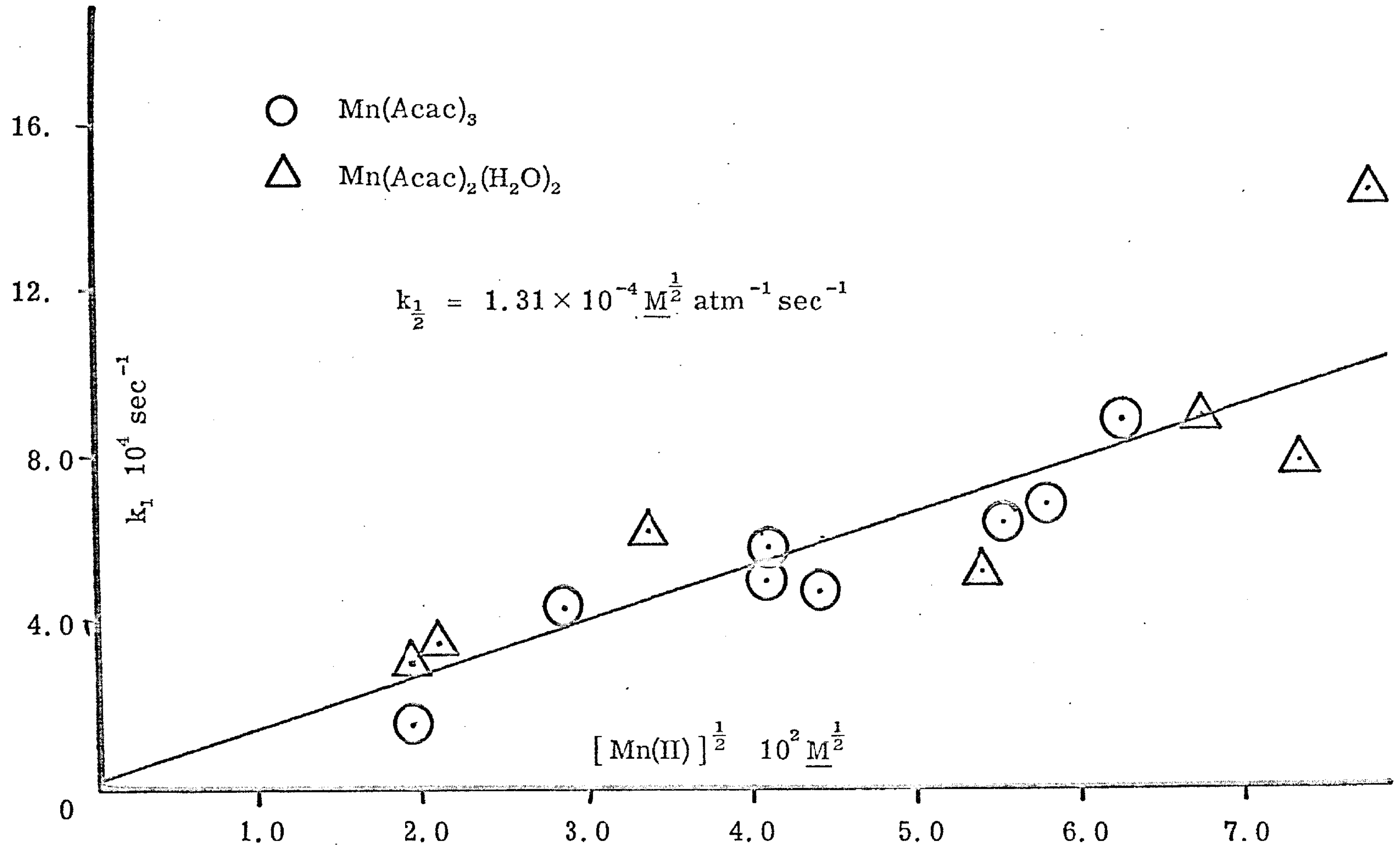


Fig. 10. Induced Autoxidation of Ascorbic Acid by Mn(Acac)$_2$
Plot of First Order Rate Constants for Oxygen Consumption <u>vs</u>. $[\text{Mn(II)}]^{\frac{1}{2}}$.

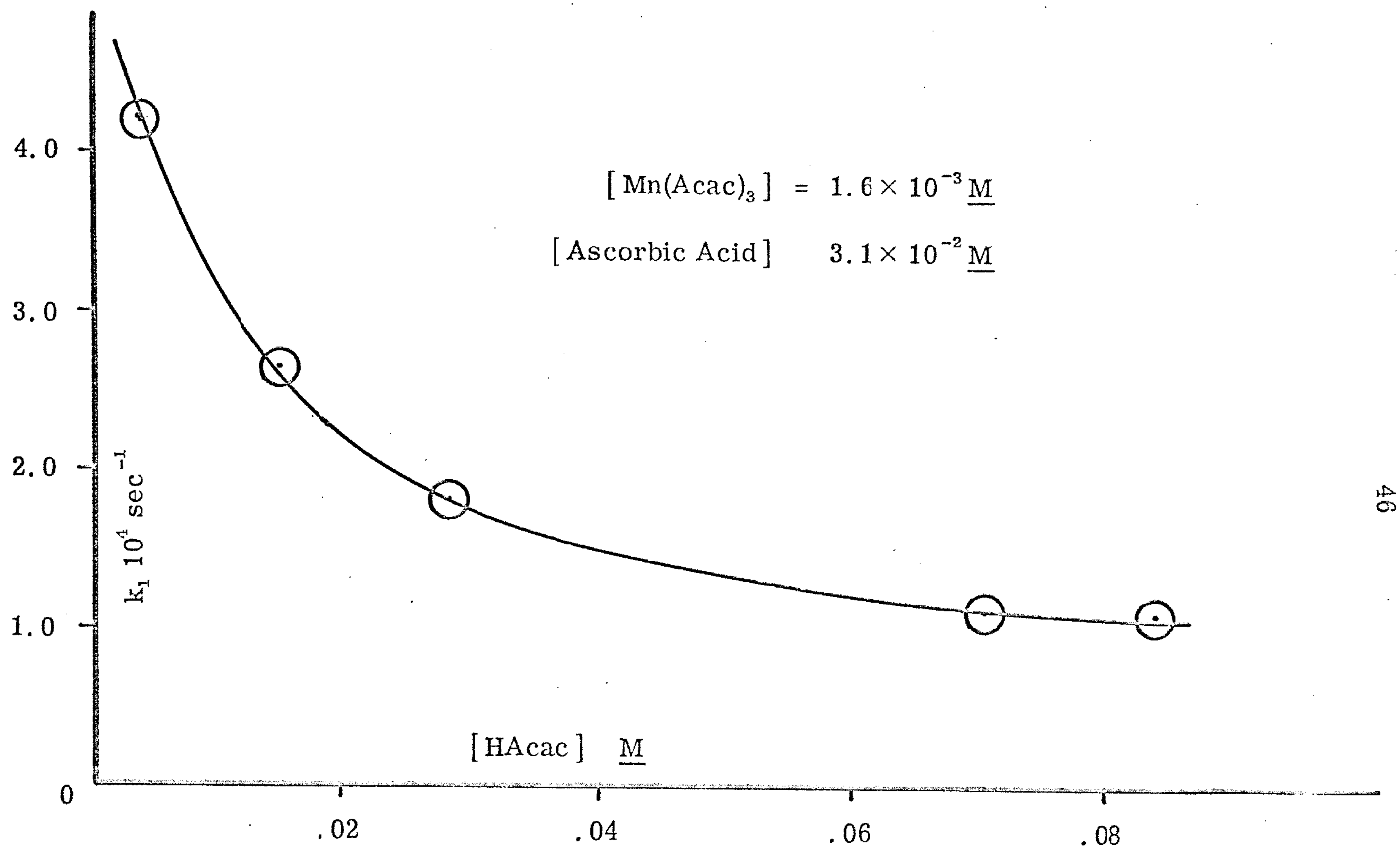


Fig. 11. Induced Autoxidation of Ascorbic Acid by Mn(Acac)$_3$. Plot of First Order Rate Constants for O_2 Consumption vs. [HAcac] at Constant [Mn(II)] and [Ascorbic Acid].

rate on the manganese(II) concentration is approximately 3/2, the same as it is in the autoxidation of $Mn(Acac)_2(H_2O)_2$ in the absence of ascorbic acid. Manganese(III) was not observed as a stable oxidation product. Under these conditions the pseudo-3/2 order rate constant based on oxygen consumption at one atmosphere of oxygen is $0.0132 \underline{M}^{-\frac{1}{2}} atm^{-1} sec^{-1}$. The corresponding rate constant for oxygen consumption by $Mn(Acac)_2(H_2O)_2$ in methanol at 0.084 M acetylacetone is $2.85 \times 10^{-4} \underline{M}^{-\frac{1}{2}} atm^{-1} sec^{-1}$, or about fifty times less than the rate constant for induced oxidation of ascorbic acid.

At a fixed concentration of $Mn(Acac)_2(H_2O)_2$ (0.0016 M) and acetylacetone (0.0140 M), the rate of the catalyzed oxidation of ascorbic acid varies with the concentration of cosubstrate. A four-fold increase in ascorbic acid concentration (0.032 M to 0.124 M) gives a 47% increase in the first order rate constant for oxygen consumption ($2.50 \times 10^{-4} sec^{-1}$ to $3.66 \times 10^{-4} sec^{-1}$).

The catalyzed oxidation of ascorbic acid by molecular oxygen was studied briefly in the presence of several other manganese complexes of β-diketones (Table XIV). First order rate constants for oxygen consumption did not depend on whether manganese(II) or manganese(III) initiated the reaction, in those cases studied.

Apparently no correlation exists between reactivity of the manganese(II) chelate towards oxygen and the catalytic effect of the chelate on the induced oxidation of ascorbic acid. Bis(ethylacetoacetato)manganese(II) is a better catalyst than bis(dipivaloylmethanato)manganese(II), although the latter complex is autoxidized over 10^3 faster in solution

Table XIV

Autoxidation of Ascorbic Acid by Manganese β-Diketonate Complexes in Methanol

Complex	m*	Rate Constant**	
		$k_{\frac{1}{2}}$	k_1
		$10^4 \underline{M}^{\frac{1}{2}} atm^{-1} sec^{-1}$	$10^3 atm^{-1} sec^{-1}$
HAcac	1/2	1.32 ± 0.13	–
HBAc	1/2	1.94 ± 0.12	–
HDBM	1/2	1.97	–
HPVA	1/2	2.59 ± 0.2	–
3-Me-HAc	1/2	3.57 ± 0.21	–
TFAcac	1	–	1.57 ± 0.15
HDPM	1	–	10.2 ± 0.3
EtAcac	1	–	26.8 ± 1.5

---

* Dependence of reaction rate on [Mn(II)].

** Based on oxygen consumption at 1 atm oxygen.

HAcac = acetylacetone
HBAc = benzoylacetone
HDBM = dibenzoylmethane
HPVA = pivaloylacetone
3-MeHAc = 3-methylacetylacetone
TFAcac = trifluoroacetylacetone
HDPM = dipivaloylmethane
EtAcac = ethylacetoacetate

than the former complex. Somewhat surprisingly, the rate dependence on manganese(II) is first order for bis(ethylacetoacetato)manganese(II), bis(trifluoroacetylacetonato)manganese(II), and bis(dipivaloylmethanato)manganese(II), while the kinetic order is 0.5 for the other β-diketonates studied.

Dehydroascorbic acid autoxidation is catalyzed by $Mn(Acac)_2(H_2O)_2$ in a reaction 0.5 order in manganese(II), first order in oxygen, and zero order in dehydroascorbic acid. The rate constant for oxidation of dehydroascorbic acid based on oxygen consumption at 1 atm of oxygen ($k_{\frac{1}{2}} = 6.60 \times 10^{-4}\,\underline{M}^{\frac{1}{2}}\,atm^{-1}\,sec^{-1}$) is about five times greater than the rate constant for oxidation of ascorbic acid ($k_{\frac{1}{2}} = 1.32 \times 10^{-4}$ $\underline{M}^{\frac{1}{2}}\,atm^{-1}\,sec^{-1}$) in methanol, catalyzed by $Mn(Acac)_2(H_2O)_2$.

Hydroquinone autoxidation is catalyzed by $Mn(Acac)_2(H_2O)_2$; the rate expression

$$\frac{d[O_2]}{dt} = k[Mn(II)]_T\,[O_2][Hq]^{0.06} \qquad (25)$$

is observed for manganese(II) concentrations $7 \times 10^{-3}\,\underline{M}$ - $4 \times 10^{-2}\,\underline{M}$ and hydroquinone concentrations $7 \times 10^{-3}\,\underline{M}$ - $8 \times 10^{-2}\,\underline{M}$. Rate constants for oxygen consumption in polarographic runs are first order to two half-lives. The reaction is probably zero order in hydroquinone concentration within experimental error. The value of k based on oxygen consumption at 1 atm of oxygen is 0.050 $atm^{-1}\,sec^{-1}$. A six-fold reduction in rate occurs when $Mn(Acac)_3$ is used initially instead of $Mn(Acac)_2(H_2O)_2$. Acetylacetone inhibits oxygen consumption in the catalyzed oxidation of hydroquinone. In the presence of 10^{-3} $\underline{M}$ $Mn(Acac)_2(H_2O)_2$, 0.07 $\underline{M}$ acetylacetone, and 0.037 $\underline{M}$ cosubstrate, the rate of oxygen consumption is reduced by a factor of 300.

Benzoin and hydrazobenzene do not appear to greatly affect the rate of production of manganese(III) in the autoxidation catalyzed by $Mn(Acac)_2(H_2O)_2$. With an initial concentration of $Mn(Acac)_2(H_2O)_2$ 8.28×10^{-3} $\underline{M}$ in ethanol, the initial rate of manganese(III) appearance is 7.75×10^{-6} $\underline{M}$ atm^{-1} sec^{-1} in the presence of 0.0337 $\underline{M}$ benzoin and 2.48×10^{-6} $\underline{M}$ atm^{-1} sec^{-1} in the absence of benzoin. Manganese(II) catalyzed autoxidation of benzoin is greater than 2.5 times faster than the manganese(III) catalyzed process. The initial rate of the reaction in the presence of both Class II cosubstrates can be described empirically as

$$\left(\frac{d[O_2]}{dt}\right)_0 = k_2[Mn(Acac)_2(H_2O)_2][\text{cosub.}]^{0.7}[O_2]\,. \qquad (23)$$

Plots of first order rate constant for oxygen consumption <u>versus</u> cosubstrate concentration at constant manganese(II) concentration are linear with a small, positive intercept with hydrazobenzene, indicating a slow, uncatalyzed autoxidation with this substrate. Second order rate constants based on oxygen absorption at 1 atm oxygen are 0.043 ± 0.01 $\underline{M}^{-1}$ atm^{-1} sec^{-1} with hydrazobenzene and $(6.8 \pm 0.4) \times 10^{-3}$ $\underline{M}^{-1}$ atm^{-1} sec^{-1} with benzoin.

Manganese(III) is rapidly produced from $Mn(Acac)_2(H_2O)_2$ in methanol in the presence of pyrocatechol or benzoquinone, and oxygen. The reaction of $Mn(Acac)_2(H_2O)_2$, catechol, and oxygen, monitored polarographically, occurs in two stages. The first reaction is a rapid oxygen consumption which is independent of the cosubstrate concentration but approximately equal to 0.5 of the manganese(II) concentration (Table XV). This process does not occur when $Mn(Acac)_3$ is the catalyst. A slower reaction described by the rate expression

$$\left(\frac{d[O_2]}{dt}\right)_0 = k[Mn]_T[O_2][Pc]^{\frac{1}{2}} \tag{24}$$

follows. Manganese and pyrocatechol concentrations were varied from 2.0×10^{-4} <u>M</u> to 8.0×10^{-3} <u>M</u>, and from 4.0×10^{-3} <u>M</u> to 1.3×10^{-1} <u>M</u>, respectively. First order rate constants for oxygen consumption do not depend on whether manganese(II) or manganese(III) is initially present. The reaction does require the β-diketonate ligand since manganese(II) chloride in methanol does not catalyze the oxidation. The value of the 3/2 order rate constant for manganese catalysis of pyrocatechol autoxidation based on oxygen consumption at 1 atm oxygen is $0.035 \pm 0.004\ \underline{M}^{\frac{1}{2}}\ atm^{-1}\ sec^{-1}$. With 10^{-3} <u>M</u> $Mn(Acac)_2(H_2O)_2$ and 0.037 <u>M</u> pyrocatechol, the rate of oxygen consumption is reduced by a factor of nine in the presence of 0.07 <u>M</u> acetylacetone.

Table XV

Mn(II) Catalyzed Autoxidation of Pyrocatechol

$[Mn(II)]_0$ 10^3 M	$[Pc]_0$ 10^2 M	$(\Delta O_2)^*$ 10^3 M	$(\Delta O_2)/[Mn(II)]_0$	k_1^{**} 10^3 sec^{-1}
0.984	3.59	0.525	0.53	0.804
2.22	3.59	1.05	0.47	1.58
2.03 ‡	3.50	0	0	1.55
1.03	12.9	0.641	0.62	1.43

---

* Initial rapid oxygen consumption; $[O_2]_0 = 1.92 \times 10^{-3}$ M.

** First order rate constant for oxygen consumption; O_2 polarograph.

‡ $Mn(Acac)_3$ used as catalyst.

Oxygen consumption by $Mn(Acac)_2(H_2O)_2$ and benzoquinone is initially first order in manganese(II) and oxygen and approximately zero order in substrate. The reaction proceeds at about one-third the rate of the $Mn(Acac)_2(H_2O)_2$ catalyzed oxidation of hydroquinone. The first order rate constant based on oxygen consumption is 0.019 atm^{-1} sec^{-1}. As the reaction proceeds, the rate of oxygen consumption deviates from first order toward apparently higher order. Replacing $Mn(Acac)_2(H_2O)_2$ with $Mn(Acac)_3$ reduced the rate of reaction by a factor of six.

SUMMARY OF RESULTS

A. Autoxidation of Manganese(II) Complexes in Benzene Solution

1. $Mn(Acac)_2(H_2O)_2$ autoxidation follows a two term rate law, $d[Mn(III)]/dt = 4(dO_2/dt) = (k_1' + k_1''[HAcac])[Mn(Acac)_2(H_2O)_2](P_{O_2})$, but k_1' and k_1'' vary inversely with initial manganese(II) concentration. At initial $Mn(Acac)_2(H_2O)_2$ concentration 2.3×10^{-3} M, $k_1' = .01$ sec^{-1} and $k_1'' = .106$ M^{-1} sec^{-1} at 30°. Activation parameters for k_1' are $Ea = 11 \pm 1$ kcal/mole and $\Delta S^{\ddagger} = -34 \pm 4$ cal/°K mole; for k_1'', $Ea = 6.7$ kcal/mole and $\Delta S^{\ddagger} = -45$ cal/°K mole.

2. Observed first order rate constants for $Mn(Acac)_2(H_2O)_2$ autoxidation increase as $[H_2O]$ in the system decreases.

3. Heterocyclic bases and alcohols inhibit manganese(III) production while certain phenols accelerate the reaction rate.

4. The relative rates of autoxidation of a series of manganese(II) β-diketone complexes vary in the order $Mn(Acac)_2(H_2O)_2$ (1) $<$ $Mn(BAc)_2$ (2.3) $<$ $Mn(PVA)_2$ (29) $\ll$ $Mn(DPM)_2$ (1000).

B. Autoxidation of Manganese(II) Complexes in Alcohol

1. The initial rate of $Mn(Acac)_2(H_2O)_2$ autoxidation in ethanol proceeds according to the rate expression $d[Mn(III)]/dt = 4(dO_2/dt) = k[Mn(Acac)_2(H_2O)_2]^{3/2}(P_{O_2})$ in the absence of added acetylacetone. The reaction is inhibited by excess ligand. The rate constant is $2.94 \times 10^{-3}\,\underline{M}^{-\frac{1}{2}}\,sec^{-1}$ at 30° in the absence of added ligand. In the presence of 0.2 $\underline{M}$ acetylacetone, $k = 2.00 \times 10^{-3}\,\underline{M}^{-1}\,atm^{-1}\,sec^{-1}$, $Ea = 10.8 \pm 1.2$ kcal/mole, and $\Delta S^{\ddagger} = -35 \pm 4$ cal/°Kmole.

2. Oxidation products of solvent or ligand were not detected during the initial stages of $Mn(Acac)_2(H_2O)_2$ autoxidation. Secondary reactions of the manganese(III) products with oxygen lead to oxidation of both solvent and ligand.

3. In the presence of strong base and 0.7 $\underline{M}$ neutral ligand, $Mn(Acac)_2(H_2O)_2$ autoxidation in ethanol is overall first order in manganese(II), $k_1 = 1.67 \times 10^{-4}\,atm^{-1}\,sec^{-1}$.

4. $Mn(Acac)_2(H_2O)_2$ is oxidized at approximately equal rates in ethanol and isopropyl alcohol but more slowly in methanol.

5. Varying the β-diketonate ligand bound to manganese(II) affects the rate of autoxidation. Rates vary by 3×10^3 as the ligand is changed from ethylacetoacetato to 3-methylacetylacetonato.

The reaction is 3/2 order in metal chelate for all cases studied except benzoylacetonato and dibenzoylmethanato (second order in metal complex).

C. Autoxidation of Manganese(II) Complexes in the Presence of Organic Cosubstrates

1. Three classes of cosubstrates have been found which distinctly affect the rates of both manganese(III) appearance and oxygen consumption.

2. Class I cosubstrates, ascorbic acid, dehydroascorbic acid, and hydroquinone inhibit manganese(III) production and accelerate oxygen consumption. The rate expression $d[O_2]/dt = k[Mn(II)]^n(P_{O_2})$ is observed, where n is 1/2 or 1 depending on the manganese(II) chelate and cosubstrate used.

3. Class II cosubstrates, benzoin and hydrazobenzene, are autoxidized according to the rate expression $d[O_2]/dt = k[Mn(Acac)_2(H_2O)_2][Cosub.](P_{O_2})$. Both oxygen consumption and manganese(III) production proceed at rates similar to the uncatalyzed $Mn(Acac)_2(H_2O)_2$ autoxidation.

4. With Class III cosubstrates, catechol and benzoquinone, the predominant manganese species is trivalent and

oxygen consumption is accelerated. Rate expressions $d[O_2]/dt = k[Mn(Acac)_2(H_2O)_2][Catechol]^{\frac{1}{2}}(P_{O_2})$ and $k[Mn(Acac)_2(H_2O)_2](P_{O_2})$ for benzoquinone are obtained.

5. Added β-diketone inhibits oxygen consumption in the catalyzed autoxidation of all three classes of cosubstrates studied.

DISCUSSION

The two most striking impressions obtained from this work are the magnitude of the ligand effect on the rates of autoxidation of manganese(II) complexes and the manner in which the solvent affects the course of the reaction. The pronounced ligand effects were expected; Hammond, Nonhebel, and Wu[36] reported that dipivaloylmethide chelates are air oxidized more readily than the acetylacetonates, and Fackler[39] stated that the stability of manganese(II) β-diketonates toward oxidation by molecular oxygen decreased roughly as the pKa of the β-diketone increased. Quite unexpected were the differences in rates and mechanisms for the autoxidation of manganese(II) complexes in benzene and alcohol solvents, although solvent effects in metal ion autoxidation have been reported before. Hammond and Wu[15] noted that the autoxidation of iron(II) chloride in methanol is second order in iron(II) and is more rapid than the autoxidation in aqueous solution which is first order with respect to iron(II).[40, 41]

Assignment of a unique mechanism for autoxidation of the manganese(II) complexes investigated in non-aqueous solvents is a difficult task. The requirements, outlined in the Introduction, for distinguishing between one- or two-electron transfer, and formation of a metal-oxygen complex rather than outer-sphere electron transfer are not met.

Manganese(II) and manganese(III) complexes are extremely labile to substitution in aqueous solution, and, although rates of ligand exchange would be reduced in less polar media, it is quite probable that the ligands bound to reactants and products observed in this study will be governed by thermodynamic considerations rather than kinetics. This is definitely true for manganese complexes in methanol,[42] where solvent exchange rates are greater than 10^5 sec^{-1}. Bimolecular ligand exchange processes in benzene are presumed to occur readily at room temperature. $Mn(Acac)_2(H_2O)_2$ and $Mn(Acac)_3$ broaden the nuclear magnetic resonance spectrum of uncoordinated acetylacetone (the same effect could result from dipole-dipole spin relaxation), benzoylacetone exchanges rapidly with the coordinated acetylacetonate of $Mn(Acac)_3$, and certain classes of organic molecules markedly affect the rate of $Mn(Acac)_2(H_2O)_2$ autoxidation.

Two methods, however, have been used in this work in attempts to determine the kinetically important species in solution. Reaction conditions were forced to maximize the concentration of a given species and the corresponding trend in reaction rate was recorded. Organic molecules potentially capable of intercepting intermediates in the autoxidation of manganese(II) to manganese(III) were added to the reaction solution, and, again, the effect was noted. The danger of this approach to detect reactive intermediates is that the cosubstrate might associate with the metal complex reactant and completely alter the reaction studied.

A. Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Benzene

The rate determining oxidation step involves one manganese(II) complex and one oxygen molecule. This kinetic result is consistent with both

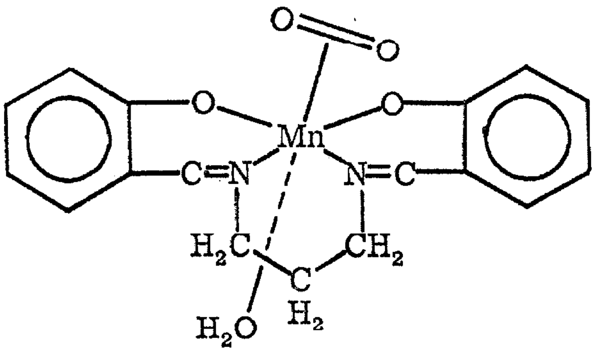
$$\mathrm{Mn(II)} + \mathrm{O_2} \longrightarrow \mathrm{Mn(III)} + \cdot\mathrm{O_2^-} \qquad (26)$$

and

$$\mathrm{Mn(II)} + \mathrm{O_2} \longrightarrow \mathrm{Mn(IV)} + \mathrm{O_2^{-2}} \qquad (27)$$

$$\mathrm{Mn(IV)} + \mathrm{Mn(II)} \xrightarrow{\text{fast}} 2\,\mathrm{Mn(III)} \qquad (28)$$

The data do not positively exclude any of the three possible oxidation paths, outer-sphere electron transfer, inner-sphere electron transfer, or hydrogen atom transfer. Oxidation of deuterium labeled $\mathrm{Mn(Acac)_2(H_2O)_2}$ might settle the question of hydrogen atom transfer, but these experiments were not performed. Formation of a metal-oxygen bond by a bimolecular displacement of coordinated water is a possibility. Johnson and Beveridge[43] reported that N, N-disalicylaldehyde-1, 3-propanediimine-manganese(II), 29, reversibly binds oxygen, nitrogen, and carbon monoxide in benzene.



(29)

Electron transfer could also conceivably occur through the orbitals of the ligands surrounding the metal ion center, either through the coordinated oxygen atoms or the ring of the β-diketone chelate. Oxygen is known to form charge-transfer complexes with aromatic compounds,[44] and may well form a similar complex with the "pseudo-aromatic" acetylacetonate.

Although the kinetic results do not eliminate any of the classes of mechanisms, study of the influence of excess ligand, water, and inhibitors provides further insight on the course of the reaction. For any given run, the observed data can be fitted to a first order rate law for manganese(III) production. However, variation of the concentration of acetylacetone shows that the first order constants, k_{obs}, are themselves complex; k_1' is a first order rate constant for manganese(III) appearance which is independent of ligand concentration, and k_1'', is a rate constant for a reaction path in which excess ligand participates.

$$k_{obs} = k_1' + k_1''[\mathrm{HAcac}]. \tag{30}$$

At a constant acetylacetone concentration, k_{obs} varies inversely with initial $Mn(Acac)_2(H_2O)_2$ concentration (Fig. 2). Thus the rate of $Mn(Acac)_2(H_2O)_2$ autoxidation in benzene fits first order kinetics in any given run, but the rate constants decrease with increasing initial concentration of metal complex. This suggests a pre-equilibrium reaction involving displacement of water from the coordination sphere of the metal ion since observed values of rate constants increase when the activity of water in the system is reduced by using the anhydrous chelate or benzene freshly distilled from sodium. Scatter in the data, most evident in Fig. 2, could be due to varying water activity as well as traces of acidic or basic impurities in the chelate or excess chelating agent. These effects would be magnified in a non-donor, non-solvating solvent like benzene.

For the acetylacetone-independent path, the pre-equilibrium step could be visualized as reversible formation of a metal-oxygen complex, equation 31. Formation of a five-coordinate species, equation 32, followed by the rate determining oxidation to manganese(III) is less

$$\mathrm{Mn(Acac)_2(H_2O)_2 + O_2 \rightleftharpoons Mn(Acac)_2(H_2O)(O_2) + H_2O} \quad (31)$$

$$\mathrm{Mn(Acac)_2(H_2O)_2 \rightleftharpoons Mn(Acac)_2(H_2O) + H_2O} \quad (32)$$

likely in a non-donor, non-solvating solvent like benzene, even though five-coordinate species, formed by addition of bases to $Mn(Acac)_2$, are known to exist in this solvent.[37]

The first order dependence on acetylacetone and the lack of evidence for oxidation products derived from the ligand imply that one molecule of acetylacetone is associated with the manganese(II) complex prior to the rate determining step.

$$\mathrm{Mn(Acac)_2(H_2O)_2 + HAcac \overset{K}{\rightleftharpoons} Mn(Acac)_2(HAcac)(H_2O) + H_2O} \quad (33)$$

or

$$\mathrm{Mn(Acac)_2(H_2O)_2 + HAcac \overset{K_1}{\rightleftharpoons} Mn(Acac)_2(HAcac)(H_2O)_2} \quad (34)$$

$$Mn(Acac)_2(HAcac)(H_2O)_2 + O_2 \overset{K_2}{\rightleftharpoons} Mn(Acac)_2(HAcac)(H_2O)(O_2) + H_2O \quad (35)$$

$$Mn(Acac)_2(H_2O)_2 + HAcac \rightleftharpoons Mn(Acac)_2(HAcac) + 2\,H_2O \quad (36)$$

Equation 33 would correspond to an equilibrium step prior to either an outer-sphere process or an irreversible bimolecular displacement of water by molecular oxygen. Equations 34 and 35 are one representation of some association of an acetylacetone molecule with the manganese(II) chelate with reversible formation of a metal-oxygen complex. The acetylacetone could be specifically solvated about the metal chelate, or, less likely, bound in a seven-coordinate complex. Equation 35 for the acetylacetone-dependent path is analogous to equation 31. Equation 36 implies loss of both coordinated water molecules with neutral acetylacetone functioning as a bidentate ligand.

The important feature of equations 31, 32, and 33-35 is that one water molecule is reversibly displaced from the coordination sphere of the metal ion prior to the rate determining step. The following argument pertains to equation 33 although analogous equations could be written for equations 31, 32, 34, and 35.

The two term rate expression for oxidation of the manganese(II) complex is

$$\begin{aligned} d[Mn(III)]/dt = {} & k_1'[Mn(Acac)_2(H_2O)_2]\,P_{O_2} \\ & + k_2[Mn(Acac)_2(HAcac)(H_2O)]\,P_{O_2} \end{aligned} \quad (37)$$

Since

$$[\mathrm{Mn(Acac)_2(HAcac)(H_2O)}] = \frac{K''[\mathrm{Mn(Acac)_2(H_2O)_2}][\mathrm{HAcac}]}{[\mathrm{H_2O}]} \qquad (38)$$

equation 37 becomes

$$d[\mathrm{Mn(III)}]/dt = [\mathrm{Mn(Acac)_2(H_2O)_2}]\left(P_{O_2}\right)\left(k_1' + \frac{k_2K''[\mathrm{HAcac}]}{[\mathrm{H_2O}]}\right) \qquad (39)$$

and

$$k_1'' = \frac{k_2\,K''}{[\mathrm{H_2O}]}\ . \qquad (40)$$

If equation 36 represents the pre-equilibrium step,

$$k_1'' = \frac{k_2\,K''}{[\mathrm{H_2O}]^2}\ . \qquad (41)$$

Equations 42-49 illustrate both possible cases, equations 40 and 41. The symbols A_2, A_2HA, HA, and T_A represent $\mathrm{Mn(Acac)_2(H_2O)_2}$, $\mathrm{Mn(Acac)_2(HAcac)(H_2O)}$ or $\mathrm{Mn(Acac)_2(HAcac)}$, HAcac and total chelate concentration, respectively.

$$A_2 + HA \overset{K}{\rightleftharpoons} A_2HA + H_2O \qquad (42)$$

$$T_A = A_2 + A_2HA \qquad (43)$$

$$K = \frac{(A_2HA)(H_2O)}{(A_2)(HA)} = \frac{(T_A - A_2)(H_2O)}{(A_2)(HA)} \qquad (44)$$

$$T_A = \frac{(A_2)[K(HA) + (H_2O)]}{(H_2O)} \qquad (45)$$

If $K(HA) \gg (H_2O)$,

$$T_A = \frac{K(A_2)(HA)}{(H_2O)} = (A_2HA) = (H_2O) \tag{46}$$

and, according to equation 40, as the total concentration of chelate increases, k_{obs} decreases. If $K(HA) \ll H_2O$,

$$T_A = A_2 . \tag{47}$$

Increasing total chelate concentration increases water concentration to the 1/2 power which is not in accord with the experimental results.

If both water molecules are displaced from $Mn(Acac)_2(H_2O)_2$ by the β-diketone, dependence of the observed rate constant on the total chelate concentration would be governed by the magnitude of the stepwise dissociation constants

$$K_1 = \frac{(A_2HA \cdot H_2O)(H_2O)}{(A_2)(HA)} \tag{48}$$

$$K_2 = \frac{(A_2HA)(H_2O)}{(A_2HA \cdot H_2O)} . \tag{49}$$

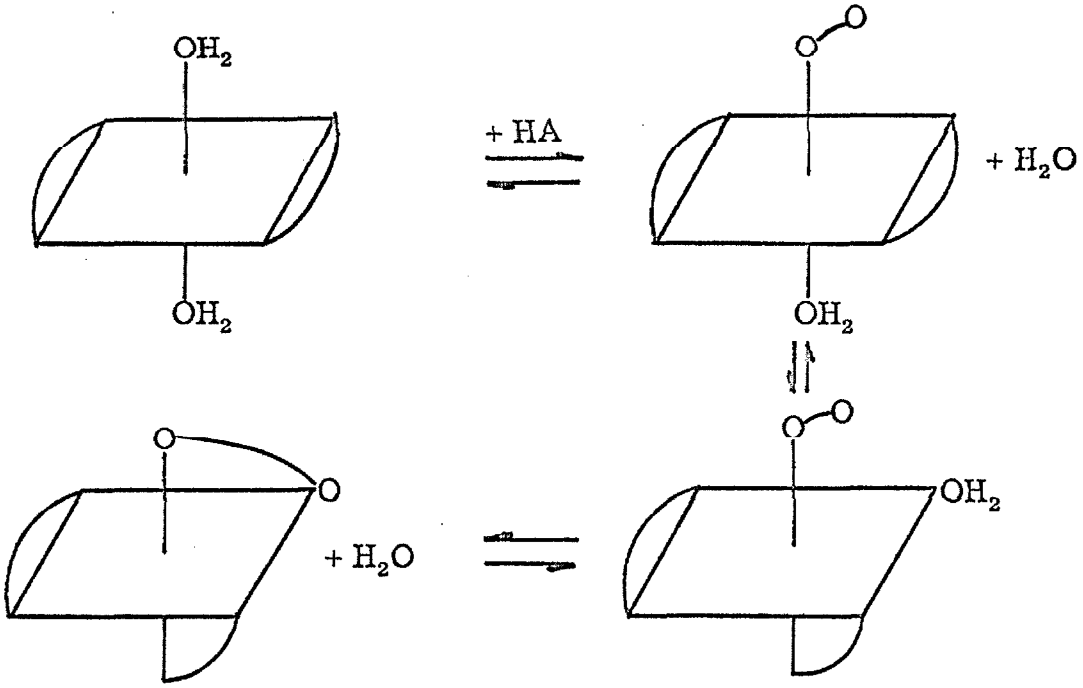
If K_1 is large, the concentration of water is proportional to the total chelate concentration, T_A, and, from equation 41, the observed rate constant would decrease with the square of T_A which is not observed. For small values of K_1 increasing T_A increases water concentration to the 1/2 power so that the observed rate constant varies inversely with T_A.

To summarize the above discussion, the experimentally observed inverse dependence of the rate constant on total chelate concentration is described by 1) displacement of one water molecule from $Mn(Acac)_2(H_2O)_2$ by a neutral acetylacetone molecule acting as a monodentate ligand ($K \gg 1$), or 2) replacement of both water molecules from the metal complex with the β-diketone acting as a bidentate ligand ($K_1 \ll 1$).

If the magnitude of K'' were known, it should be possible to decide whether the neutral ligand displaces one or two molecules of water. According to the data in Fig. 1, observed rate constants for autoxidation of 2.3×10^{-3} M $Mn(Acac)_2(H_2O)_2$ increase linearly to at least 0.5 M free ligand concentration. This suggests that K'' is small and equation 36 correctly describes the pre-equilibrium step prior to the rate-determining oxidation.

Neutral acetylacetone, functioning as a monodentate ligand, is probably not as good a donor as the smaller, more polar water molecule. Before the second donor atom of acetylacetone can coordinate to the metal, the complex must isomerize to bring the remaining water molecule, originally trans to the entering ligand, into the cis position. Once the molecule is in this configuration, the diketone should compete effectively with the water molecule for coordination to the central metal ion.

The rate accelerating effect of excess β-diketone and the lower activation energy of the ligand-dependent oxidation can be explained more readily if $Mn(Acac)_2(HAcac)$ is the reactive intermediate. This species differs from the structure of the final product only by a hydrogen atom, and one might expect the transition state for oxidation



(50)

of this species to be more stable than that for oxidation of $Mn(Acac)_2(H_2O)_2$. The energies of activation bear out this prediction; E_a for the ligand-dependent path is about 5 kcal/mole less than E_a for the acetylacetone-independent path.

The inhibitory effect of heterocyclic bases and substituted benzyl alcohols in the presence of excess acetylacetone affirms the proposition that before the electron transfer step, coordination of acetylacetone or molecular oxygen to manganese(II) occurs. Inhibition by base is governed by steric effects rather than base strength. The limited Hammett $\sigma\rho$ plot of the effect of para-substituted benzyl alcohols on the rate of $Mn(Acac)_2(H_2O)_2$ autoxidation shows that inhibition increases smoothly with an increase of the electron density on the hydroxyl oxygen which is also a measure of the donor strength of the alcohol. Thus, inhibition by both base and benzyl alcohol is due to ligand competition for coordination to the metal ion center.

In the absence of excess acetylacetone, the rate of $Mn(Acac)_2(H_2O)_2$ autoxidation deviates from first order as manganese(III) concentration increases. This phenomenon is probably due to a competition between manganese(II) and manganese(III) products for available ligand which decreases the concentration of autoxidizable manganese(II) complex. Equation 51 is only one of several possible formulations of

$$\begin{aligned} &Mn^{II}(Acac)_2(H_2O)_2 + Mn^{III}(Acac)_2(H_2O)(OH) \rightleftharpoons \\ &\qquad Mn^{III}(Acac)_3 + Mn^{II}(Acac)(H_2O)_3(OH) \end{aligned} \tag{51}$$

the ligand exchange reaction, since the manganese(III) product or distribution of products in solution is not known. The ultimate reduction product of oxygen must be hydroxide ion in equation 51 to maintain net charge balance. Hammond and Wu[15] observed a similar competition for ligand between metal ion reactants and products in their study of iron(II) chloride autoxidation in methanol.

As stated before, the kinetic evidence provides a limited number of facts from which several possible reaction schemes can be constructed. Thermodynamic data, if it were known, might further limit the number of choices.

It is possible to make a rough estimate of the oxidation half-cell potential for reaction 52 in water by combining the half-cell

$$Mn(Acac)_2 \longrightarrow Mn(Acac)_2^+ + 1\,e^- \qquad (52)$$

$Mn^{++}(aq)/Mn^{+++}(aq)$, -1.5 V, with the overall formation constant for $Mn(Acac)_2$, 1.8×10^7,[45] and the estimated overall formation constant for $Mn(Acac)_2^+$, 10^{13}.[45] E^0 for equation 52 is -1.0 V. Using an equation derived by Amis[46] relating E^0 with dielectric constant, D, where E^0,

$$E^0 = E_1^0 - \frac{6.03 \times 10^{23} Z_a Z_b e^2}{n D r} \qquad (53)$$

is the potential freed from charge effects, e, electronic charge, Z, ionic charge, n, number of electrons transferred, and r, the separation distance between ions, the potential increases about 0.6 volt in going from water to benzene (choosing r = 10 Å). Combining the half-cell potentials for the stepwise reduction of oxygen with the estimated potential for one-electron oxidation of $Mn(Acac)_2$, and correcting for the medium effect, free energies for the following reactions can be estimated, although rather crudely.

$$Mn(Acac)_2 + O_2 \rightarrow Mn(Acac)_2^+ + O_2^- \qquad \Delta F = +32\ \frac{\text{kcal}}{\text{mole}} \qquad (54)$$

$$Mn(Acac)_2 + H^+ + O_2 \rightarrow Mn(Acac)_2^+ + HO_2^- \qquad \Delta F = +20\ \frac{\text{kcal}}{\text{mole}} \qquad (55)$$

Estimating ΔF for a two-electron reaction which produces manganese(IV) would be more difficult.

$$Mn(Acac)_2 + H_2O + O_2 \rightarrow Mn(Acac)_2(O) + H_2O_2\ . \qquad (56)$$

Choosing the couple $Mn^{++}(aq)/MnO_2$, $E^0 = -1.26$ V, as the point of reference, chelation may increase the potential about +0.6 V.

Correction for the medium effect would amount to +0.3 V. ΔF for reaction 56 would be about -1 kcal/mole.

According to the Marcus theory of outer-sphere electron transfer,[47] the activation free energy, ΔF^*, is basically a function of the free energy of reaction, ΔF^0, work terms for bringing reactants together and separating products, W_r and W_p, radii of the reactants and distance between reactant centers, a_i and r, static dielectric constant, D, refractive index, η, and number of electrons transferred, n. For electron transfer between uncharged reactants to give charged

$$\Delta F^* = \frac{W_r + W_p}{2} + \frac{\lambda}{4} + \frac{\Delta F^0}{2} + \frac{(\Delta F^0 + W_p - W_r)^2}{4\lambda} \qquad (57)$$

$$\lambda = \left(\frac{1}{a_1} + \frac{1}{a_2} - \frac{1}{r}\right)\left(\frac{1}{\eta^2} - \frac{1}{D}\right)(ne)^2 \qquad (58)$$

$$W = N_{q_1 q_2} e^2/Dr \qquad (59)$$

products, reaction 54, W_r can be neglected. ΔF^* for this reaction, assuming $a_{MnA_2} = 5.5\text{Å}$, $a_{O_2} = 1.5\text{Å}$, and $r = 10\text{Å}$, is +4200 kcal/mole, a value not unexpected considering the unfavorable reaction free energy for a one electron change and the large work term for separation of oppositely charged products in non-polar benzene.

Estimates of ΔF^* for reactions 55 and 56 can not be made with the Marcus theory, although the values should be considerably less than that for an ionic mechanism. Therefore, by comparison with a theory for outer-sphere electron transfer, the autoxidation of $Mn(Acac)_2(H_2O)_2$ in benzene should proceed by hydrogen atom transfer or by formation of a metal-oxygen complex rather than by outer-sphere electron transfer. Furthermore, a two-electron oxidation, reaction 56, may be more favorable energetically than a one-electron oxidation, reaction 55.

On the basis of the kinetic evidence and the qualitative thermodynamic considerations, the most satisfactory mechanism (which still may not necessarily be the correct one) is presented below.

$$Mn(Acac)_2(H_2O)_2 + O_2 \overset{K'}{\rightleftharpoons} Mn(Acac)_2(H_2O)(O_2) + H_2O \qquad (60)$$

$$Mn(Acac)_2(H_2O)(O_2) \xrightarrow{K_1} \overset{IV}{Mn}(Acac)_2(O) + H_2O_2 \qquad (61)$$

$$\overset{IV}{Mn}(Acac)_2(O) + \overset{II}{Mn}(Acac)_2(H_2O)_2 \rightarrow 2\,Mn(III) \qquad (62)$$

$$Mn(III) + HAcac \rightarrow Mn(Acac)_3 + x\,H_2O \qquad (63)$$

A one-electron oxidation which produces $HO_2\cdot$ and manganese(III) directly can not be definitely ruled out, however.

In the absence of excess acetylacetone,

$$\overset{III}{Mn} + Mn(Acac)_2(H_2O)_2 \rightleftharpoons Mn(Acac)_3 + Mn(II) \qquad (64)$$

Mn(III) represents a manganese(III) species with two coordinated acetylacetones and Mn(II) indicates a singly chelated manganese(II) complex.

The oxidation path catalyzed by excess diketone is represented by equations 65-67.

$$Mn(Acac)_2(H_2O)_2 + HAcac \overset{K_1}{\rightleftharpoons} Mn(Acac)_2(HAcac)(H_2O) + H_2O \qquad (65)$$

$$Mn(Acac)_2(HAcac)(H_2O) \overset{K_2}{\rightleftharpoons} Mn(Acac)_2(HAcac) + H_2O \qquad (66)$$

$$Mn(Acac)_2(HAcac) + O_2 \xrightarrow{k_3} Mn(Acac)_3 + HO_2\cdot \qquad (67)$$

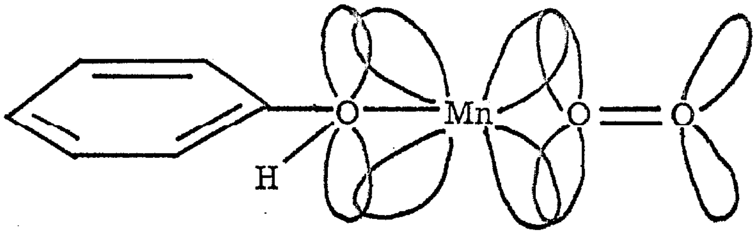
The oxidation of $Mn(Acac)_2(H_2O)_2$ by the ligand independent path is formulated as an inner-sphere reaction because this best explains the dependence of the observed rate constant on the manganese(II) concentration. The two-electron oxidation provides a path with more negative total free energy change than a one-electron oxidation.

An outer-sphere hydrogen transfer oxidation step is suggested for the ligand-dependent path based on arguments stated in previous paragraphs. A one-electron oxidation is proposed, free energy considerations notwithstanding, because $Mn(Acac)_3$ would be produced directly, and unlikely intermediates such as $Mn^{IV}(Acac)_2(HAcac)(O)$, $Mn^{IV}(Acac)_3^+$, or $Mn^{IV}(Acac)_3(OH)$ would not have to be introduced. The extent to which the transition state for the ligand-accelerated oxidation is stabilized relative to the ligand-independent route, is unknown, but it may be sufficient to overcome the unfavorable free energy change for one-electron reduction of oxygen.

The effect of added organic molecules on the autoxidation of $Mn(Acac)_2(H_2O)_2$, other than bases and alcohols, does not shed additional light on the reaction mechanism. The results of qualitative and quantitative experiments do warrant some comment, however.

Benzoin catalyzes the autoxidation, presumably by competing with the excess acetylacetone present in solution to form a complex with the metal substrate. It is not immediately clear, however, why benzoin is a catalyst for $Mn(Acac)_2(H_2O)_2$ autoxidation, though less effective in this respect than acetylacetone, whereas benzyl alcohol is an inhibitor. Both molecules are probably coordinated to the metal atom by an hydroxyl group and neither molecule is oxidized during the reaction. The difference may lie in the extent of π-bonding between ligand and metal. Both acetylacetone and benzoin have relatively low-energy vacant π-orbitals which stabilize the complex by accepting electron density from the metal. Fallab has stated that the presence of such polarizable, "soft", ligands enhances the ability of a complex to interact with the "soft" oxygen molecule.[1]

The surprising ability of phenols to accelerate the rate of manganese(III) appearance is undoubtedly due to formation of a complex with the metal chelate since phenols, substituted in both ortho positions do not noticeably accelerate the formation of $Mn(Acac)_3$. Phenols are good reducing agents and could donate an electron to molecular oxygen through the d-orbitals of the manganese atom. A mechanism of this



(68)

type has been identified by Fallab[1, 3] and observed for a number of metal catalyzed autoxidations. Alternatively, mechanisms based on hydrogen atom transfer can be proposed.

B. Autoxidation of $Mn(Acac)_2(H_2O)_2$ in Alcohol

Before attempting to discuss possible mechanisms for the autoxidation in alcohol, it is worthwhile to indicate briefly the manner in which the benzene and ethanol solvents affect the course of the reaction. Benzene is a non-donor, non-solvating solvent, while ethanol has fairly good solvating and donor properties. Thus ethanol, unlike benzene, would compete effectively with a number of potential ligands for coordination to the open positions of $Mn(Acac)_2$. In ethanol this compound exists predominantly as $Mn(Acac)_2(C_2H_5OH)_2$; in benzene, as $Mn(Acac)_2(H_2O)_2$. The effect of nitrogen bases on the autoxidation of $Mn(Acac)_2(H_2O)_2$ should be quite different in the two solvents. In benzene, nitrogen bases are good donors and inhibit the reaction by preventing the formation of a highly reactive manganese(II) species. Heterocyclic bases have little or no effect on the autoxidation in ethanol, and strongly basic amines accelerate the reaction.

The difference in solvating ability between benzene and ethanol has a profound effect on the autoxidation of $Mn(Acac)_2(H_2O)_2$. Formation of solvated charged species can occur in ethanol so that an outer-sphere electron transfer is a possibility. In addition, the oxidation potential of the couple, $Mn(Acac)_2/Mn(Acac)_2^+$, should be more negative in ethanol than in benzene because of solvation effects.[46]

1. Autoxidation of $Mn(Acac)_2(C_2H_5OH)_2$ in Ethanol.

Two very general classes of mechanisms are consistent with a rate expression in which the order in one or more reactants is not an integer. Both chain reactions and reactions with one or more reversible, pre-equilibrium steps often exhibit such a rate law.

A completely general chain mechanism which describes the observed initial reaction of $Mn(Acac)_2(H_2O)_2$ with oxygen in ethanol is

$$M + O_2 \overset{K_1}{\rightleftharpoons} MO_2 \tag{69}$$

$$M + HA \overset{K_2}{\rightleftharpoons} (M\text{-}HA) \tag{70}$$

$$M \xrightarrow{k_i} X \qquad \text{Initiation} \tag{71}$$

$$X + MO_2 \xrightarrow{k_p} X + Y \qquad \text{Propagation} \tag{72}$$

$$2X \xrightarrow{k_t} P \qquad \text{Termination} \tag{73}$$

$$(\text{Rate})_0 = \frac{K_1 k_p (k_i)^{1/2} (T_m)^{3/2} P_{O_2}}{\sqrt{2k_t}\,[1 + K_1(O_2) + K_2(HA)]^{3/2}} \tag{74}$$

According to equation 74, the initial rate is proportional to the 3/2 power of the total manganese(II) concentration, T_m, and the partial pressure of oxygen, if $[1 + K_2(HA)]$ is much larger than $K_1(O_2)$; the dependence of the rate on free ligand concentration is also correctly described if $K_2(HA)$ is less than one. Problems arise, however, when attempts are made to describe X and Y in terms of chemically meaningful intermediates. Furthermore, any chain mechanisms involving oxidation of solvent or ligand in the initial reaction can be ruled out immediately, unless kinetic chains were long, since the stoichiometry of the initial reaction is 4:1.

Two mechanisms containing one or more reversible steps appear to describe the data in a more nearly satisfactory manner.

Mechanism I

$$MnA_2 + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MnA_2(O_2) \qquad (75)$$

$$MnA_2(O_2) + MnA_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_2MnO_2MnA_2 \qquad (76)$$

$$A_2MnO_2MnA_2 \xrightarrow{k_3} 2\,A_2Mn^{IV}O \qquad (77)$$

$$A_2Mn^{IV}O + MnA_2 \longrightarrow 2\,Mn(III) \qquad (78)$$

$$MnA_2 + HA \overset{K_A}{\rightleftharpoons} MnA_2(HA) \qquad (79)$$

$$MnA_2 + MnA_2^{+} \overset{K_I}{\rightleftharpoons} MnA_3 + MnA^{+} \qquad (80)$$

Rate =

$$\frac{4\,K_1\,K_2\,k_3\,(T)^2\,(O_2)}{[1+K_A(HA)+K_I(Mn^{III})]\{[1+\frac{k_3}{k_{-2}}][1+K_A(HA)+K_I(Mn^{III})] + \frac{K_2k_3(T)}{k_{-1}}\}} \qquad (81)$$

$T \equiv$ total manganese(II) concentration

$MnA_2 \equiv Mn(Acac)_2(ROH)_2$

Two assumptions must be made for equations 75-80 to be considered a possible mechanism. The two terms within braces in equation 81 must be comparable in value over the range of manganese(II) concentrations studied, and both $K_A(HA)$ and $K_I(Mn^{III})$ must not be negligible compared to unity.

Mechanism II

$$MnA_2 \overset{K_1}{\rightleftharpoons} MnA^+ + A^- \tag{82}$$

$$MnA^+ + O_2 \overset{K_2}{\rightleftharpoons} MnA(O_2)^+ \tag{83}$$

$$MnA(O_2)^+ + MnA_2 \overset{k_3}{\rightarrow} \text{Products} \tag{84}$$

$$MnA^+ + HA \overset{K_A}{\rightleftharpoons} MnA(HA)^+ \tag{85}$$

$$MnA^+ + MnA_3 \overset{K_I}{\rightleftharpoons} MnA_2 + MnA_2^+ \tag{86}$$

$$\text{Rate} = \frac{K_1^{1/2} K_2 k_3 (MnA_2)^{3/2} (O_2)}{[1 + K_B(HA) + K_2(O_2) + K_I(MnA_3)/(MnA_2)]^{1/2}} \tag{87}$$

Equilibrium constants K_1 and K_2 in equations 82 and 83 must be small for the overall reaction to be 3/2 order in manganese(II). The value of K_1 is $10^{-3.07}$ at 30° in aqueous solution.[45] Therefore, the species (MnA_2) in the rate expression, equation 87, is nearly equal to the total manganese(II) concentration. The sum of $K_B(HA)$ and $K_I(MnA_3)/(MnA_2)$ must be greater than $K_2(O_2)$ and must not be small compared to unity. Equations 82-86 are not a unique representation of

Mechanism II. For example, equation 88 could replace equation 83, and equation 89 could be substituted for equation 85 without altering

$$MnA_2 + O_2 \overset{K_2'}{\rightleftharpoons} MnA_2(O_2) \quad (88)$$

$$MnA_2 + HA \overset{K_A'}{\rightleftharpoons} MnA_2(HA) \quad (89)$$

the form of the overall rate expression.

The two mechanisms proposed differ in two fundamental respects. The reactive manganese(II) species proposed in Mechanism I is $Mn(Acac)_2$, but in Mechanism II the important species is $Mn(Acac)^+$. The equation for inhibition by $Mn(Acac)_3$ in Mechanism I, equation 80, is the reverse of the reaction for $Mn(Acac)_3$ inhibition in Mechanism II. An estimate of the value of the equilibrium constant for the manganese(III) inhibition reaction, K_I, can be obtained from the values of the second formation constant of $Mn(Acac)_2$ and the third formation constant of $Mn(Acac)_3$, equation 90.[45]

$$MnA_2 + MnA_2^+ \overset{K_I}{\rightleftharpoons} MnA^+ + MnA_3 \quad (90)$$

The value of K_I is about 6 in aqueous solution. Since the formation constants used to obtain K_I were determined by two different people using two different methods, the error in this computed value could be significant. Thus it may not be possible to use a calculated estimate of K_I as a criterion to determine whether Mechanism I or Mechanism II properly describes the autoxidation of $Mn(Acac)_2(ROH)_2$ in alcohol.

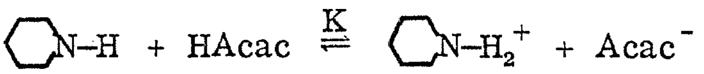
At least two other tests could be applied to differentiate between the two mechanisms. According to the rate expression for Mechanism I, the dependence of the initial rate on the total chelate concentration should approach second order as the concentration of excess ligand is increased. This trend has been observed, although it was not stated so explicitly in the results section. The experimental rate order in manganese(II) concentration was 1.35 ± 0.1 (HAcac = 0), 1.46 (HAcac = 0.2 M), and 1.62 (HAcac = 0.7 M). These differences were neglected when the results were compiled, and were ascribed, unconsciously, to deviation from a true 3/2 order reaction in metal chelate. The statement that the experimental dependence of the initial rate on the manganese(II) concentration increases with increasing ligand concentration must be made with some reserve until experiments at higher acetylacetone concentrations are conducted. Since $Mn(Acac)^+$ is the proposed reactive species in Mechanism II, initial rates of reaction should increase in the presence of acid. A few qualitative experiments were performed with added acetic acid, but the results are inconclusive since acetate is a potential ligand itself. Additional kinetic runs in the presence of a non-complexing acid are suggested.

Both mechanisms do have several important features in common. They account for inhibition by neutral ligand and manganese(III) products. Furthermore, inhibition of the initial rate by added manganese(III) should decrease as the concentration of neutral ligand increases; this was observed. Inhibition by neutral ligand is described in both mechanisms as a competition with oxygen for coordination to the metal ion. This is a reasonable assumption in view of the fact that acetylacetone accelerates the rate of $Mn(Acac)_2$-$(H_2O)_2$ autoxidation in benzene which is probably an outer-sphere process of some kind. The free energy change for the reaction $Mn(II) \rightarrow Mn(III) + e^-$ is more positive in alcohol than benzene, and it is conceivable that an inner-sphere process would be a more favorable reaction path in this solvent. Although there is no way of predicting beforehand that a change in mechanism should occur when the oxidation potential of a given couple changes, it is known that formation of a bond between oxidant and reductant facilitates electron transfer and reduces the energy of activation for the process.

Mechanisms similar to the one illustrated by equations 75 to 80 have been suggested for the autoxidation of other metal ions. Tanford et al.,[48] reported that the autoxidation of bis(glycylglycinato)cobalt(II) in basic aqueous solution is approximately 3/2 order in cobalt(II) and first order in oxygen. The proposed intermediate was an oxygen-bridged dimer which has been frequently observed in reactions of cobalt(II) complexes with oxygen. The deviation from second order was interpreted to indicate a sequence of reversible reactions before the rate determining step. Hammond and Wu[15] noticed in their study of the autoxidation of iron(II) chloride in methanol that the dependence of the rate on the iron(II) concentration was less than second order. Inhibition by iron(III) and the presence of more than one reactive iron(II) species was proposed to explain the kinetics.

2. Effect of Base on Autoxidation of $Mn(Acac)_2(C_2H_5OH)_2$ in Ethanol.

Piperidine accelerates the rate of $Mn(Acac)_2(C_2H_5OH)_2$ oxidation in the presence of excess acetylacetone. The phenomenon is probably due to formation of the tris(acetylacetonato)manganese(II) anion, $Mn(Acac)_3^-$, which might be expected to be more reactive than $Mn(Acac)_2(C_2H_5OH)_2$. The value of the equilibrium constant for reaction 91 is 280 in aqueous solution.



(91)

The third formation constant for the manganese(II)-acetylacetone complex is not known. Statistically, the ratio of the third stability constant to the second is 0.107,[49] and Schaefer observed a ratio of 0.551 for the vanadium(II)-acetylacetone complexes.[50] Therefore, a minimum value for the third stability constant of the manganese(II)-acetylacetone complex would be about 120. The rate acceleration is not due to coordination of manganese(II) and the amine since pyridine, which hardly affects the rate, and piperidine both form very weak complexes with metal ions.

A possible mechanism for the base-accelerated reaction is illustrated in equations 92-95.

$$Mn^{II}(Acac)_2(ROH)_2 + Acac^- \overset{K}{\rightleftharpoons} Mn^{II}(Acac)_3^- \qquad (92)$$

$$Mn^{II}(Acac)_3^- + O_2 \xrightarrow{k_1} Mn^{III}(Acac)_3 + O_2^{\overline{\cdot}} \qquad (93)$$

or

$$Mn(Acac)_3^- + H^+ + O_2 \xrightarrow{k_1'} Mn^{IV}(Acac)_3^+ + HO_2^- \qquad (94)$$

$$Mn^{IV}(Acac)_3^+ + Mn(Acac)_3^- \rightarrow 2\,Mn(Acac)_3 \qquad (95)$$

Intermediate reduction products of oxygen, $O_2^{\cdot-}$ and HO_2^-, are rapidly reduced by manganese(II).

This mechanism is consistent with the overall first order kinetics observed in the presence of a large excess of ligand (0.7 M). The initial rate varies with the ratio of piperidine concentration to manganese(II) chelate concentration, decreasing slightly as the ratio increases. Thus, the apparent dependence of the initial rate on the manganese(II) concentration with a five-fold excess of base, 3/2 on the basis of two runs, may be the result of more than one effect. The data are not sufficient to settle this point. At lower acetylacetone concentrations, deviation from first order kinetics is pronounced (Fig. 7). Quite possibly this is due to the autoxidation of ligand by the reaction of $Mn(Acac)_3$ and oxygen, which becomes important as the concentration of free ligand is reduced.

3. Solvent Effects on Autoxidation of $Mn(Acac)_2(ROH)_2$ in Alcohols.

Although very few data were obtained in alcohols other than ethanol, a distinct trend is observed. The rate constants increase as the dielectric constant of the alcohol decreases. This relationship is observed for a wide variety of reactions.[51] The observation is qualitative only, since the solvent probably would not effect the free energies of all of the reaction steps to the same degree. The donor strengths of these solvents vary slightly, further complicating attempts to correlate the data quantitatively.

C. Autoxidation of Mn(β-diketonate)$_2$ in Benzene and Ethanol

One of the original objectives of this research problem was to explain the large differences in reactivity between Mn(Acac)$_2$ and Mn(DPM)$_2$ towards oxygen. Generally, the oxidation potentials of metal complexes increase as the stability constants of the complexes increase. For a series of similar compounds, the rates of oxidation vary linearly with their oxidation potentials, and, hence, their stability constants. The proposal has been made, however, that sterically hindered compounds should be oxidized at rates greater than predicted by this correlation if oxidation leads to relief of strain.

The role of steric effects in determining the stability constants of β-diketone chelates has been studied by Guter and Hammond[52] and Martin and Martin.[53] Bulky groups on the β-diketone ring could reduce the stability constant of a chelate with a particular metal ion below an expected value by (1) disrupting planarity of the ring, (2) decreasing the distance between the coordinating oxygen atoms, (3) increasing the "F" strain,[54] the interference to approach of a second ligand by a coordinated ligand, and (4) increasing the hydrophobic character of the anionic ligand which would lead to charge distribution over a larger surface, reduced polarity, and, consequently, lower reactivity toward displacement of solvent molecules from the coordination shell of the metal ion.

Oxidation of sterically hindered chelates could be accelerated because of steric effects (1) and (2). Ionic radii of metals decrease as the oxidation state increases, so that steric strain from non-planarity of the chelate ring and close approach between coordinating oxygen atoms would be relieved. Bulky ligands could also disrupt the solvation about the metal-oxygen bonds which would reduce separation factors for stepwise stability constants, and give larger overall stability constants (more positive oxidation potentials) than expected on the basis of inductive effects.[52]

Several publications have appeared which attempt to discuss the electronic effects of varying the substituents on the β-diketone framework. Excellent correlations of certain physical measurements on a series of β-diketones or β-diketone chelates have been made with thermodynamic data. Lintvedt and Holtzclaw[55] obtained the nuclear magnetic resonance spectra for several β-diketones substituted with aliphatic and aromatic groups and showed that a linear relationship exists between the chemical shift of the enolic proton and the logarithm of the stability constants for complexes with several metal ions. Calmon and Maroni[56] determined the acidity constants for a series of aliphatic β-diketones and obtained linear relationships between the acidity constants of the keto and enol forms and the acidity constants of the corresponding substituted carboxylic acids. A similar correlation was obtained for the diketone acidity constants and Taft's σ^* constants.

For a series of manganese(II) chelates, the logarithms of the first order rate constants for manganese(III) appearance in benzene and the logarithms of the first order rate constants for oxygen consumption in ethanol were plotted against both the chemical shifts of the β-diketone enolic protons and Taft's σ^* constants (Figs. 12 and 13). The chemical shifts should be directly proportional to the oxidation potentials of the manganese(II) complexes, and the σ^* constants should be a function of the expected oxidation potentials in the absence of steric and resonance effects.

The most significant result is that the rate constants for autoxidation of $Mn(DPM)_2$ can be correlated with parameters which are proportional to the expected oxidation potential in the absence of steric effects.

In general, the correlation between the logarithms of the rate constants and σ^* values is better than the correlation with chemical shift data. Errors in determining the chemical shifts could account partly for the results in Fig. 12 since duplicate measurements of chemical shifts differed by as much as 0.25 ppm. Excluding the phenyl-substituted chelates for the moment, the rate constants in Fig. 12 are directly proportional to the chemical shifts within experimental error. Rates of autoxidation of the phenyl-substituted compounds in ethanol are lower than expected from the linear relationship of Fig. 12. The explanation of these results is not well understood, but may be due to the fact that the rates of oxidation of these chelates are more nearly second order in manganese(II) than 3/2 order observed for the other

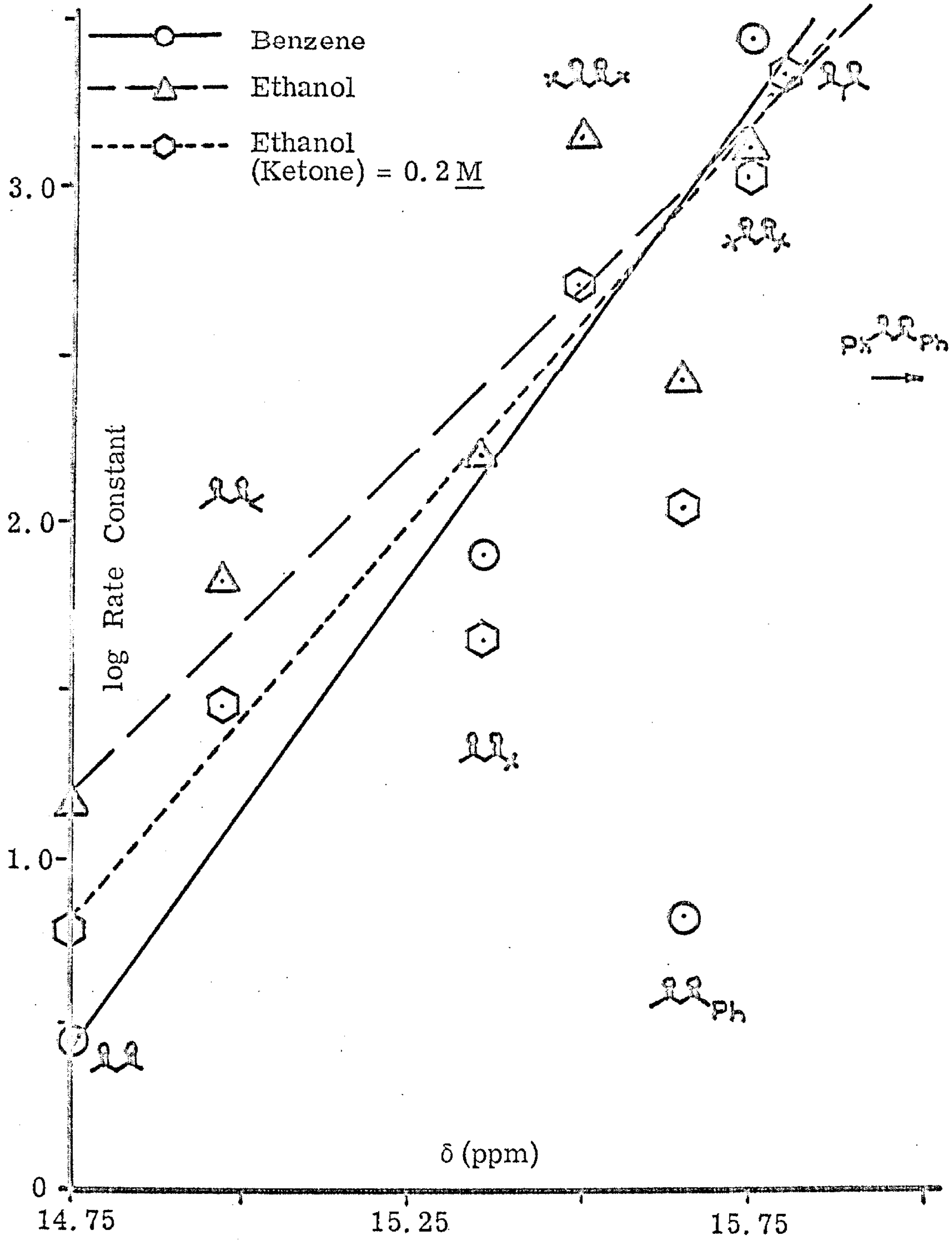


Fig. 12. Plot of log Rate Constant for Mn(III) Production vs Chemical Shift of β-diketone Enol Proton

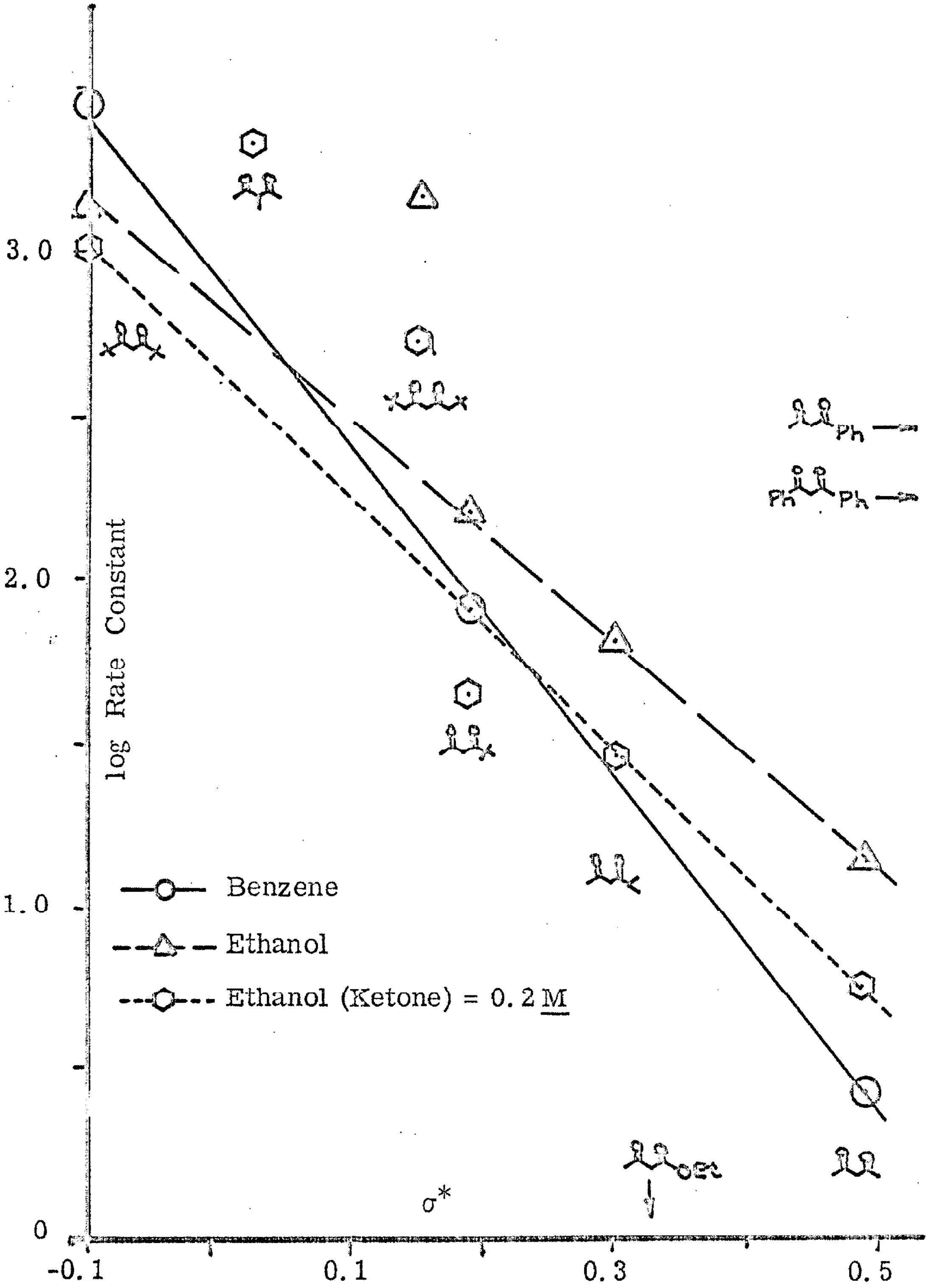


Fig. 13. Plot of log Rate Constant for Mn(III) Production *vs.* Taft's σ^* Constants

compounds. The chemical shift of the enolic proton could not be observed for ethylacetoacetate.

Differences between the logarithms of the observed rate constants for autoxidation of the 3-methylacetylacetonato and dineopentoylmethanato chelates and the values expected from the correlation with σ^*, Fig. 13, are probably outside of experimental error. A methyl group substituted on the central carbon atom of a β-diketone could disrupt the planarity of the ring and force the oxygen atoms closer together. These sources of strain would be relieved somewhat by oxidation of the compound to manganese(III). This explanation does not suffice for the dineopentoylmethanato compound. Although the aliphatic substituents are bulky, molecular models of this compound and $Mn(DPM)_2$ indicate that the terminal groups of both chelates interact with the methylene hydrogen and with one another to about the same extent. To minimize steric repulsion, however, the neopentyl groups must fold over the chelate ring, and may interfere with solvation of the oxygen atoms. The net effects of this interaction would be formation of a stronger metal-oxygen bond than expected, and, hence, a more positive oxidation potential.

Phenyl substituted manganese(II) chelates are oxidized at rates several orders of magnitude faster than predicted by the relationship with σ^*, Fig. 13. This confirms the suggestion of Guter and Hammond[52] and Lintvedt and Holtzclaw[57] that the net effect of a terminal phenyl group in a β-diketone chelate is to release electron density by resonance. Bis-(ethylacetoacetato)manganese(II) is oxidized at a lower rate than predicted by inductive effects since the ethoxy group disrupts the resonance of the chelate ring, reducing the stability of the chelate.[58]

D. Autoxidation of Manganese(III) β-diketone Chelates in Alcohol Solution

The reaction of manganese(III) β-diketonates with oxygen in alcohol solution complicates the kinetic analysis of the manganese(II) autoxidation. Oxidation of manganese(III) β-diketonates is an interesting reaction in its own right, especially since the reaction at 30° in ethanol and the reaction at 100° in diphenyl ether[59] proceed by apparently different mechanisms. Arnett, Freiser, and Mendelsohn[59] studied the autoxidation of $Mn(Acac)_3$ briefly at 100° in diphenyl ether and observed a dependence of the rate on the chelate concentration of 0.22.

In contrast, autoxidation of $Mn(Acac)_3$ in alcohol solution at 30° is first order in both manganese(III) concentration and oxygen pressure, and is inhibited by neutral acetylacetone. The limited experimental evidence can be interpreted by a mechanism in which a manganese(III) acetylacetonate species reacts directly with an oxygen molecule. Conceivably, the role of neutral acetylacetone is to inhibit this interaction, but the manner in which it acts is not clear. Reaction steps in which neutral ligand competes with oxygen for coordination to a partially dissociated manganese(III) species, equations 96-98, for example, are compatible with the data only if K_2 and K_4 are much

$$\mathrm{Mn(Acac)_3} \overset{K_1}{\rightleftharpoons} \mathrm{Mn(Acac)_2^+} + \mathrm{Acac^-} \qquad (96)$$

$$\mathrm{Mn(Acac)_2^+} + \mathrm{O_2} \overset{K_2}{\rightleftharpoons} \mathrm{Mn(Acac)_2(O_2)^+} \overset{k_3}{\rightarrow} \text{Products} \qquad (97)$$

$$\mathrm{Mn(Acac)_2^+} + \mathrm{HA} \overset{K_4}{\rightleftharpoons} \mathrm{Mn(Acac)_2(HA)} \qquad (98)$$

greater than unity. The first dissociation constant of $\mathrm{Mn(Acac)_3}$, K_1, is 1.4×10^{-4},[45] and, if K_2 and K_4 were also small, the rate of oxygen consumption would be proportional to the square root of the total manganese(III) concentration. Until estimates of these equilibrium constants are made, a mechanism similar to the one represented by equations 96-98 is speculative.

A second mechanism for the autoxidation of $\mathrm{Mn(Acac)_3}$ requires a rapid, reversible oxidation of ligand by manganese(III) within the chelate followed by the rate determining reaction with oxygen.

$$\mathrm{Mn(Acac)_3} \overset{K_1}{\rightleftharpoons} \overset{\mathrm{II}}{\mathrm{Mn}}\mathrm{(Acac)(\cdot Acac)} \qquad (99)$$

$$\mathrm{Mn(Acac)_2(\cdot Acac)} + \mathrm{O_2} \overset{k_2}{\rightarrow} \text{Products} \qquad (100)$$

The β-diketone radical must not react irreversibly with solvent or manganese(III) at an appreciable rate. Either process would have to be limited by the rate of $\mathrm{Mn(Acac)_3}$ decomposition in alcohol in the absence of oxygen which has a half life greater than a week. Despite the great stability of the β-diketone radical,[59] the restriction that it does not react further with manganese(III) may be unrealistic in view of the fact that manganese(III) rapidly oxidizes numerous free radicals.

A third mechanism can be written which does not involve dissociation of $Mn(Acac)_3$.

$$Mn(Acac)_3 + O_2 \overset{K_1}{\rightleftharpoons} Mn(Acac)_3(O_2) \tag{101}$$

$$Mn(Acac)_3(O_2) \xrightarrow{k_2} \text{Products} \tag{102}$$

$$Mn(Acac)_3 + HA \overset{K_3}{\rightleftharpoons} Mn(Acac)_3(HA) \tag{103}$$

Formation of a seven coordinate species between $Mn(Acac)_3$ and oxygen is, perhaps, the simplest explanation of the experimental evidence.

The autoxidation of $Mn(Acac)_3$ observed in this work can be contrasted with the destructive autoxidation of iron(III) β-diketonates,[60] $Mn(Acac)_3$ catalyzed polymerization of vinyl compounds,[61] and the oxidation of oxalate by manganese(III) in the presence of oxygen.[62, 63] Arnett and Mendelsohn[60] proposed that the first step of the destructive autoxidation of iron(III) β-diketonates in diphenyl ether at 100° was a reversible electron transfer from the ligand to iron(III), equation 104.

$$\overset{III}{Fe}(L)_3 \rightleftharpoons \overset{II}{Fe}(L)_2 + L\cdot \tag{104}$$

The reaction was 0.5 order in iron(III) chelate concentration and 0.24 order in oxygen pressure. Bamford and Lind[61] suggested a similar initiating step for the $Mn(Acac)_3$ catalyzed polymerization of vinyl monomers. The reaction scheme proposed by Launer,[62] modified by the results of Taube,[63] for the oxidation of oxalate by manganese(III) in the presence of oxygen in aqueous solution is shown below.

$$Mn^{III}(C_2O_4)_n^{3-2n} \xrightarrow{K_1} Mn^{II}(C_2O_4)_{n-1}^{2-2(n-1)} + C_2O_4^{\cdot -} \qquad (105)$$

$$C_2O_4^{\cdot -} + O_2 \rightarrow C_2O_6^{\cdot -} \qquad (106)$$

$$\begin{aligned} Mn^{II}(C_2O_4)_n^{2-2n} + C_2O_6^{\cdot -} + 2\,H^+ &\rightarrow \\ &Mn^{III}(C_2O_4)_n^{3-2n} + 2\,CO_2 + H_2O_2 \end{aligned} \qquad (107)$$

$$Mn^{III}(C_2O_4)_n^{3-2n} + C_2O_4^{\cdot -} \rightarrow Mn^{II}(C_2O_4)_n^{2-2n} + 2\,CO_2 \qquad (108)$$

Manganese(III) is generally a stronger oxidizing agent in aqueous solution than in non-aqueous solution, and will be readily reduced by a ligand which is a good reducing agent, such as oxalate. In this example, oxygen does not alter the initial rate of ligand oxidation which is first order in manganese(III). Obviously, the autoxidation of ligand bound to manganese(III) is strongly influenced by both the oxidation potential of the metal ion in a given solvent and the oxidation potential of the ligand.

The reactions of the 3-methylacetylacetonato and trifluoroacetylacetonato manganese(III) chelates with oxygen follow a different course from the autoxidation of $Mn(Acac)_3$. Both of these manganese(III) compounds are unstable with respect to decomposition in air in contrast to $Mn(Acac)_3$. The instability of tris(3-methylacetylacetonato)-

manganese(III) is probably due to strain in the planar ligand. Tris-(trifluoroacetylacetonato)manganese(III) is a better oxidizing agent than $Mn(Acac)_3$ and is probably readily solvolyzed. Conceivably, both compounds react by similar mechanisms, which, for the lack of sufficient data, cannot be specified.

E. Manganese Catalyzed Autoxidation of Organic Compounds in Alcohol Solution

Study of the autoxidation of organic compounds catalyzed by manganese β-diketonates indicates the ability of the metal compounds to assume a number of different catalytic roles depending on the nature of the organic cosubstrate. Three distinct reaction types have been illustrated in which manganese is predominantly divalent, trivalent, or intermediate between the two extremes.

Most of the experimental evidence strongly suggests that catalysis proceeds, at least in part, within a complex between metal ion, cosubstrate, and/or oxygen. In all of the reactions studied, excess chelating agent inhibited the rate of oxygen consumption. This effect is probably due to competition of diketone and cosubstrate (or oxygen) for coordination to manganese.

From a cursory inspection of the reaction rates and rate laws, the following mechanism, equation 109, can be eliminated from further discussion.

$$\mathrm{Mn(II)} \xrightarrow{O_2} \mathrm{Mn(III)} \quad \text{or} \quad \mathrm{Mn(IV)} \xrightarrow{SH_2} \text{Products} \qquad (109)$$

Benzoin, for example, either intercepts an intermediate formed in the autoxidation of $Mn(Acac)_2(ROH)_2$ in the absence of cosubstrate, possibly $Mn(Acac)_2(O_2)(ROH)$, or is oxidized in a complex between metal chelate and cosubstrate. This conclusion is suggested by the observations that the kinetic order in manganese(II) is reduced from approximately 3/2 in the absence of benzoin to first order, and the initial rates of manganese(III) appearance are greater in the presence of cosubstrate than in its absence.

Several completely general mechanisms have been proposed for metal-catalyzed autoxidation of organic compounds. One of these, illustrated by equation 109, has been eliminated as a possible explanation of these results. Weissberger and LuValle[64] presented a general mechanism for the autoxidation of compounds which initially form semi quinones, and classified individual mechanisms according to the relative kinetic importance of the individual reaction steps.

$$SH_2 + M^{+n} \rightleftharpoons (SH_2)M^{+n} \rightleftharpoons (SH\cdot)M^{(n-1)+} + H^+ \qquad (110)$$

$$(SH\cdot)M^{(n-1)+} \rightleftharpoons SH\cdot + M^{(n-1)+} \qquad (111)$$

$$(SH\cdot)M^{(n-1)+} + O_2 \rightleftharpoons (SH\cdot)M^{(n-1)+}(O_2) \rightarrow \text{Products} \qquad (112)$$

$$SH\cdot + O_2 \rightarrow S + OH_2\cdot \qquad (113)$$

$$M^{(n-1)+} + O_2 \rightarrow M^{n+} + HO_2\cdot \qquad (114)$$

Specific applications of this mechanism have been suggested by Yamazaki and Piette[33] and Homann[34] for the manganese catalyzed autoxidations of dihydroxyfumaric acid and 2,3-diketogulonate, respectively, equations 115-119.

$$\text{Initiation} \xrightarrow{k_i} \text{Mn(III)} \tag{115}$$

$$\text{Mn(III)} + SH_2 \xrightarrow{k_1} \text{Mn(II)} + SH\cdot \tag{116}$$

$$SH\cdot + O_2 \xrightarrow{k_2} S + OH_2\cdot \tag{117}$$

$$HO_2\cdot + \text{Mn(II)} + H^+ \xrightarrow{k_3} H_2O_2 + \text{Mn(III)} \tag{118}$$

$$2\,HO_2\cdot \xrightarrow{k_{t_1}} H_2O_2 + O_2 \tag{119}$$

A second termination step involving dismutation of SH· can be added to this mechanism.

Fallab[1,3] has been among the leading proponents of a third autoxidation mechanism, equations 120-122.

$$SH_2 + M^{+n} \rightleftharpoons (SH_2)M^{n+} \tag{120}$$

$$(SH_2)M^{+n} + O_2 \rightleftharpoons (SH_2)M^{+n}(O_2) \tag{121}$$

$$(SH_2)M^{+n}(O_2) \rightarrow \text{Products} \tag{122}$$

Fallab suggests that the role of the metal ion is to bring the substrate and oxidizing agent, O_2, together in a ternary complex. The d-orbitals of the metal ion serve as a conducting bridge for electrons from the organic molecule to oxygen; formal oxidation and reduction of the metal ion need not take place.

In the autoxidation of ascorbic acid, five of the eight β-diketonates studied react by a process which is half order in manganese concentration, and the rate constants for all except the (3-methylacetylacetonato)manganese(II) catalyzed autoxidation depend very little on the nature of the β-diketone ligand. The remaining three chelates catalyze a reaction which is first order in the concentration of the catalyst, and rate constants vary with the chelate used. All of the reaction rates appear to be independent of ascorbic acid concentration and proportional to the oxygen pressure.

A mechanism similar to the Weissberger-Luvalle mechanism[64] is consistent with the data if the restrictions $K_1 \gg 1$, $k_2 \gtrsim k_{-2} > k_3$

$$SH_2 + Mn^{II} \rightleftharpoons (SH_2)Mn^{II} \qquad (123)$$

$$(SH_2)Mn^{II} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SH\cdot + Mn^{I} + H^+ \qquad (124)$$

$$SH\cdot + O_2 \xrightarrow{k_3} S + HO_2\cdot \qquad (125)$$

$$Mn^{I} + H^+ + O_2 \xrightarrow{k_4} Mn^{II} + HO_2\cdot \qquad (126)$$

and k_4, $k_3(SH\cdot) \sim k_4(Mn^{I})$, and $(Mn^{II}) = (Mn)_T$ are invoked. Manganese(I) is a known oxidation state of manganese, but has been observed in only a few compounds coordinated by ligands, high in the spectrochemical series, which readily accept electron density from the metal ion by back-bonding. Oxygen donor ligands are not numbered among this class of ligands, and they probably could not stabilize a complex with manganese(I) sufficiently to justify its existence.

A mechanism which does not require production of manganese(I) has several features in common with a mechanism proposed for the autoxidation of manganese(II) β-diketonates in the absence of cosubstrates.

$$\mathrm{MnA_2 + 2\,SH_2 \overset{K_1}{\rightleftharpoons} Mn(SH)_2 + 2\,HA} \tag{127}$$

$$\mathrm{Mn(SH)_2 \overset{K_2}{\rightleftharpoons} Mn(SH)^+ + SH^-} \tag{128}$$

$$\mathrm{Mn(SH)^+ + O_2 \overset{K_3}{\rightleftharpoons} Mn(SH)(O_2)^+} \tag{129}$$

$$\mathrm{Mn(SH)(O_2)^+ \xrightarrow{k_4} Products} \tag{130}$$

$$\mathrm{Mn(SH)^+ + HA \overset{K_5}{\rightleftharpoons} Mn(SH)(HA)^+} \tag{131}$$

$$\mathrm{Mn(SH)(HA)^+ + O_2 \overset{K'}{\rightleftharpoons} Mn(SH)(HA)(O_2)} \tag{132}$$

$$\mathrm{Mn(SH)(HA)(O_2)^+ + Mn(SH)_2 \xrightarrow{k'} Products} \tag{133}$$

Both mechanisms propose a dissociation step which produces a singly chelated manganese(II) cation, and suggest that inhibition by neutral ligand is a competition reaction between ketone and oxygen for coordination to manganese(II). The mechanism represented by equations 127-133 is not a unique description of the kinetic data, but it does satisfactorily account for the majority of the experimental evidence obtained so far.

Ascorbic acid is a much stronger acid than seven of the eight β-diketones from which the manganese(II) catalysts were synthesized. Equilibrium constant K_1, equation 127, should be a large number in these seven examples since it measures the ratio of ionization constants of ascorbic acid and diketone, approximately 7.3×10^4, for example, in the case of $Mn(Acac)_2$ catalysis. At sufficiently high concentrations of neutral β-diketone, a new manganese(II) complex forms which cannot react directly with oxygen to give products, but must intercept a second molecule of manganese(II) prior to the rate determining step. The rate of the autoxidation in the presence of sufficient β-diketone should be proportional to the 3/2 power of the manganese(II) concentration which is observed. The observed ascorbic acid dependence in the presence of excess diketone could be due to participation of reaction 134 in addition to reaction 131.

$$Mn(SH)^+ + SH_2 \rightleftharpoons Mn(SH)(SH_2)^+. \qquad (134)$$

The mechanism proposed by Yamazaki and Piette[33] and Homann,[34] equations 115-119, also applies to the manganese(II) catalyzed autoxidation of ascorbic acid if it can be assumed that a steady state concentration of manganese(III) is rapidly attained. This assumption is valid because manganese(III) reacts quite rapidly with the cosubstrate and subsequent reactions of the radicals produced will be fast. Since the autoxidation of manganese(II) β-diketonates in alcohol solution apparently proceeds within a metal-oxygen complex, the mechanism similar to Fallab's general mechanism, equations 127-133, may be preferable to a mechanism which requires formation of manganese(III), equations 115-119. With the available data, however, it is not possible to differentiate between the two mechanisms.

Trifluoroacetylacetone ($pK_a = 6.7$; 20°, 50% dioxane) and ascorbic acid ($pK_a = 4.04$; 25°, 0.1 M KNO_3) are acids of comparable strength. The equilibrium of equation 127 may not lie completely to the right, and the manganese(II) complex containing both ascorbate and trifluoroacetylacetonate ligands might be able to react directly with oxygen.

It is a difficult task to explain the catalytic behavior of the dipivaloylmethanato, DPM, and ethylacetoacetato manganese chelates in terms of either proposed mechanism. Both β-diketones from which the compounds are derived are weaker acids than ascorbic acid, so that the rate constants observed should be independent of the β-diketonate catalyst if the mechanism proposed, equations 127-133, is correct. However, DPM^- is a much stronger ligand than $Acac^-$, and a kinetically significant concentration of manganese complexes containing DPM ligands may exist in solution. This is not true of the ethylacetoacetato manganese(II) compound which is partially dissociated in solution.

The same mechanisms suggested for the catalyzed autoxidation of ascorbic acid can be used to describe the manganese catalyzed autoxidation of dehydroascorbic acid. Study of this reaction is complicated by the limited solubility of the cosubstrate. The reactive form of dehydroascorbic acid could be either the triketone or the ring opened compound, 2, 3-diketogulonate. The open chain compound should form a stronger complex with manganese(II) than dehydroascorbic acid, but this possibility was not investigated.

The manganese catalyzed autoxidation of hydroquinone has been studied by Sym [31] and LaMer and Temple.[66] Their results indicated that the reaction rate was proportional to manganese(II) and oxygen concentrations and inversely proportional to the hydrogen ion concentration. In addition, Sym observed maximum autoxidation rates in neutral solution, reported inhibition by benzoquinone, and proposed that autoxidation occurs in a complex of hydroquinone and manganese(II) ion ($K = 15\,\underline{M}^{-1}$). Weissberger and LuValle [64] explained the results of LaMer and Temple [66] in terms of their semiquinone theory, equation 135.

$$Mn^{++} + HQ^{-} \rightleftharpoons (\overset{I}{Mn} - Q\cdot) + H^{+} \tag{135}$$

For reasons stated above, manganese(I) should not be formed when the surrounding ligands are composed entirely of oxygen donor atoms. A more likely mechanism would be the one outlined below.

$$MnA_2 + HQ \overset{K_1}{\rightleftharpoons} MnA_2(HQ) \tag{136}$$

$$MnA_2(HQ) + O_2 \overset{K_2}{\rightleftharpoons} MnA_2(HQ)(O_2) \tag{137}$$

$$MnA_2(HQ)(O_2) \xrightarrow{k_3} \text{Products} \tag{138}$$

$$MnA_2(HQ) + HA \rightleftharpoons MnA_2(HQ)(HA) \qquad (139)$$

In this example, hydroquinone is a weaker acid than acetylacetone, and the complex it forms with $Mn(Acac)_2(ROH)_2$ will not involve a proton transfer. Equilibrium constant K_1, equation 136, must be large to account for zero order in cosubstrate concentration.

The effect of benzoquinone on the autoxidation of hydroquinone was not investigated. Oxygen consumption by benzoquinone, catalyzed by $Mn(Acac)_2(ROH)_2$, was studied in separate experiments. A large fraction of the manganese is undoubtedly in the trivalent state, but it is not known whether manganese(II) or manganese(III) is the active catalyst.

The rate expressions and rates of oxygen consumption for the $Mn(Acac)_2(ROH)_2$ catalyzed autoxidation of benzoin and hydrazobenzene are similar, and it is quite possible that both reactions proceed by the same mechanism. Brintzinger, Zell, and Ehrlenmeyer[35] studied the manganese(II) catalyzed autoxidation of substituted hydrazines in phosphate and pyrophosphate buffers, and proposed a mechanism in which manganese(II) is first oxidized to manganese(III) by oxygen followed by reduction of manganese(III) by hydrazine. For reasons stated previously, this mechanism can not be applied to the oxidations in methanol catalyzed by $Mn(Acac)_2(ROH)_2$. Since no attempt was made to directly identify a complex between metal chelate and cosubstrate in solution, it is not possible to differentiate between oxidation in a substrate-metal-oxygen complex, or the following mechanism:

$$MnA_2 + O_2 \overset{K}{\rightleftharpoons} MnA_2(O_2) \tag{140}$$

$$MnA_2(O_2) + SH_2 \rightarrow Mn(III) + SH\cdot + HO_2^- \tag{141}$$

The role of manganese(III) which is produced during autoxidation of the cosubstrates has not been assessed, but it probably also functions as a catalyzing agent.

The manganese catalyst present during the autoxidation of pyrocatechol is predominantly in the trivalent state. From the stoichiometry of the initial reaction of $Mn(Acac)_2(ROH)_2$, pyrocatechol, and oxygen, the fast oxidation step is consistent with

$$MnA_2 + PcH \rightleftharpoons MnA_2(PcH) \tag{142}$$

$$MnA_2(PcH) + O_2 \rightarrow Pc\cdot + MnA_2^+ + HO_2^- \tag{143}$$

Peroxide produced in equation 143 should react rapidly with a second molecule of metal-cosubstrate complex to be consistent with the observation that $Mn(Acac)_2$ is readily oxidized by hydrogen peroxide in methanol solution.

The kinetic results of the second, slower reaction do not suggest a simple reaction mechanism involving neutral pyrocatechol. Quite possibly the dependence of the rate on pyrocatechol concentration is a mixed expression involving neutral and ionic species which react at different rates. For example, if the monoanion of pyrocatechol reacted preferentially during the slower reaction, equations 144-148 would be in agreement with the data.

$$\text{Pc-H} \overset{K_1}{\rightleftharpoons} \text{Pc}^- + \text{H}^+ \tag{144}$$

$$\text{Mn(III)} + \text{Pc}^- \overset{K_2}{\rightleftharpoons} [\text{Mn}^{\text{III}}(\text{Pc})]^- \tag{145}$$

$$[\text{Mn}^{\text{III}}(\text{Pc})]^- + \text{O}_2 \overset{K_3}{\rightleftharpoons} [\text{Mn}^{\text{III}}(\text{Pc})(\text{O}_2)]^- \tag{146}$$

$$[\text{Mn}^{\text{III}}(\text{Pc})(\text{O}_2)]^- \xrightarrow{k_4} \text{Products} \tag{147}$$

$$[\text{Mn}^{\text{III}}(\text{Pc})]^- + \text{HA} \overset{K_5}{\rightleftharpoons} [\text{Mn}^{\text{III}}(\text{Pc})(\text{HA})]^- \tag{148}$$

K_1 is small, 3.6×10^{-10} in aqueous solution, and if K_2 were small, the rate of oxygen consumption would be proportional to the concentrations of oxygen, manganese(III), and pyrocatechol anion, which would be proportional to the square root of the total cosubstrate concentration.

From these studies of manganese β-diketonate catalyzed autoxidation of organic compounds, a very interesting picture has emerged that deserves further, more detailed investigation. Despite the variety of cosubstrates studied, the autoxidation reactions apparently proceed by the same general mechanism, with formation of complexes among metal ion, cosubstrate, and oxygen.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Spectra in the ultraviolet, visible, and near infrared regions were observed on a Cary Recording Spectrophotometer, Model 14. Infrared spectra were recorded on a Beckman Infrared Spectrometer, Model IR7. Proton magnetic resonance spectra were obtained on a Varian Associates, Model A-60 spectrometer at room temperature.

Materials

Inorganic chemicals were reagent grade and used as received. Ascorbic acid (Eastman White Label), absolute ethanol (National Distiller's Corporation), catechol (Matheson, Coleman, Bell), dihydroxyfumaric acid and dehydroascorbic acid (obtained from C.-H. Wu) were used without further purification.

Benzene was distilled and the middle fraction stored in a tightly capped bottle for kinetic measurements. Methanol was fractionated from aluminum amalgam and higher alcohols were refluxed over magnesium metal and distilled. β-Diketones were distilled under reduced pressure before use with the exception of 1, 1, 1-trifluoroacetylacetone (b. p. 107°/760 mm) which was distilled at atmospheric pressure. Benzoin and hydrazobenzene were recrystallized under nitrogen and stored under vacuum. Manganese(II) chelates were also stored under vacuum. All other organic materials used in the kinetic studies were purified before use.

Manganese was analyzed by either EDTA titration in NH_4OH-NH_4Cl buffer with Eriochrome Black T indicator,[67] or by spectrophotometric analysis of permanganate.[68] Elemental analyses for carbon and hydrogen were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Bis(acetylacetonato)diaquomanganese(II). A solution of acetylacetone (10 g, 0.1 mole) in 100 ml of 1 F NaOH was added slowly to a well stirred solution of $MnCl_2 \cdot 4H_2O$ (10 g, 0.05 mole) in 50 ml of water. The bright yellow, amorphous product was filtered, washed well with water, and dried under vacuum. Yield, 11.0 g (37.7%). Mp 250° (lit.,[37] decomp. 60°). Anal. Calcd. for $Mn(C_{10}H_{14}O_4)(H_2O)_2$: Mn, 19.01. Found: Mn, 19.16.

To minimize oxidation by molecular oxygen, the chelate was dehydrated under vacuum at 100° C over P_2O_5. Samples of the dihydrate for kinetic experiments were prepared by recrystallizing 0.5 g of the anhydrous complex from 8 ml of 50% aqueous ethanol.

Bis(benzoylacetonato)manganese(II).[23] $MnCl_2 \cdot 4H_2O$ (1.22 g, 0.0062 mole) was dissolved in 3 ml of water and benzoylacetone (2.00 g, 0.0123 mole) in 25 ml acetone added. A rapid stream of nitrogen was passed through the mixture for about five minutes to remove dissolved oxygen. Concentrated NH_4OH was added slowly, dropwise as the mixture was stirred to precipitate the bright yellow complex. The chelate was filtered rapidly under nitrogen, washed with water and, finally, with acetone. Attempts to recrystallize the complex from methanol failed. Yield: 2.4 g (96%). Mp 103-105°

(lit.,[69] decomp. >140°). Anal. Calcd. for $Mn(C_{20}H_{18}O_4)$: Mn, 14.56. Found: Mn, 14.30.

Bis(dibenzoylmethanato)manganese(II). This chelate was prepared by the same method used to synthesize bis(benzoylacetonato)-manganese(II). The yield from 2.00 g (0.0089 mole) dibenzoylmethane and 0.89 g (0.0045 mole) $MnCl_2 \cdot 4H_2O$ was 1.8 g (80%). Mp, decomp. 218-222°. Anal. Calcd. for $Mn(C_{30}H_{22}O_4)$; Mn, 10.97. Found: Mn, 11.98.

Bis(1,1,1-trifluoroacetylacetonato)manganese(II). A solution of NaOH (1.6 g, 0.04 mole) in 25 ml water was added to a suspension of 1,1,1-trifluoroacetylacetone (6.56 g, 0.04 mole) in 50 ml of water and the mixture added to a solution of $MnCl_2 \cdot 4H_2O$ (4.0 g, 0.02 mole) in 50 ml water. Concentrated NH_4OH was added dropwise until precipitation of the product was complete. The chelate was recrystallized from 50% aqueous ethanol to give about 1 g of material, mp, 149-151. Anal. Calcd. for $Mn(C_{10}H_8F_6O_4)$: Mn, 15.23. Found: Mn, 15.11.

Bis(pivaloylacetonato)manganese(II). Pivaloylacetone (2,2-dimethyl-3,5-hexanedione) (0.72 g, 0.0051 mole) and $MnCl_2 \cdot 4H_2O$ (0.50 g, 0.0025 mole) were dissolved in 15 ml of 50% aqueous ethanol and added to the reaction vessel. An analogous procedure developed for the synthesis of bis(dipivaloylmethanato)diaquomanganese(II) (See Experimental Section, Part II) was used to prepare this chelate. Mp, decomp. 101-104. Anal. Calcd. for $Mn(C_{16}H_{26}O_4)$: C, 56.97; H, 7.72; Mn, 16.32. Found: C, 56.87; H, 7.83; Mn, 14.85.

Bis(ethylacetoacetato)manganese(II).[23] $MnCl_2 \cdot 4H_2O$ (0.5 g, 0.0025 mole) in 3 ml of water was added to ethylacetoacetate (3 g, 0.023 mole) in 20 ml of methanol. Dilute NH_4OH was added until product formation was complete. The chelate was filtered, washed with absolute methanol, and recrystallized from absolute methanol under nitrogen. The cream-white complex was successfully prepared only when water was excluded from the washing and recrystallizing steps. Mp, 217-218°, Anal. Calcd. for $Mn(C_{12}H_{18}O_6)$: Mn, 17.54. Found: Mn, 18.70.

Tris(acetylacetonato)manganese(III). The chelate was prepared according to a procedure developed by Cartledge.[70] The shiny black crystals melted at 162.8° (lit.,[71] decomp. $>150°$). Anal. Calcd. for $Mn(C_{15}H_{21}O_6)$: Mn, 15.55. Found: Mn, 15.65.

Bis(acetylacetonato)diaquomanganese(III) salts. These complexes were made by the method of Cartledge.[72] The chloride salt was prepared from $MnCl_2 \cdot 4H_2O$. Anal. Calcd. for $[Mn(C_{10}H_{14}O_4)(H_2O)_2]$-$(Cl) \cdot 2H_2O$: Mn, 15.24. Found: Mn, 15.44. The perchlorate was prepared from $Mn(ClO_4) \cdot 6H_2O$. Anal. Calcd. for $[Mn(C_{10}H_{14}O_4)(H_2O)_2]$-$(ClO_4) \cdot 4H_2O$: Mn, 11.93. Found: Mn, 11.98. Because these chelates tended to hydrolyze readily, they were washed with 50% acetone-water and ether before use.

Tris(benzoylacetonato)manganese(III). The method of Fay and Piper[73] was used to synthesize this chelate. Mp, 173-174° (lit.,[73] 173-173.5°). Anal. Calcd. for $Mn(C_{30}H_{27}O_6)$: Mn, 10.20. Found: Mn, 10.17.

Tris(dibenzoylmethanato)manganese(III). The chelate was prepared by the method of Fay and Piper.[73] Mp, >250°. Anal. Calcd. for $Mn(C_{45}H_{33}O_6)$: Mn, 7.58. Found: Mn, 7.61.

Tris(dipivaloylmethanato)manganese(III). A solution of $KMnO_4$ (0.32 g, 0.002 mole) in 25 ml of water was added rapidly to a vigorously stirred mixture of $MnCl_2 \cdot 4H_2O$ (1.59 g, 0.008 mole) and dipivaloylmethane (5.55 g, 0.03 mole) in 50 ml of water. The mixture was stirred overnight. Yield: 5.91 g (96%). Purification was accomplished by recrystallization from methanol or sublimation. Mp, 161-162° (lit.,[36] 165°). Anal. Calcd. for $Mn(C_{33}H_{57}O_6)$: Mn, 9.12. Found: Mn, 9.03.

Tris(3-methylacetylacetonato)manganese(III). Attempts to prepare this complex by the methods of Cartledge[70] and Fay and Piper[73] were unsuccessful. The chelate was prepared in low yield from bis(3-methylacetylacetonato)manganese(II) (0.35 g, 0.005 mole) and 3-methylacetylacetone (0.57 g, 0.005 mole) in 50 ml of benzene by passing a slow stream of oxygen through the mixture for two hours. The dark brown solution was filtered and evaporated to a small volume under reduced pressure. Long black needles which formed when ligroin was added to the residue, cooled in ice, were filtered and washed with ligroin. The complex decomposes slowly in air. Yield: 0.30 g (15.1%). Mp, decomp. >140°. Anal. Calcd. for $Mn(C_{18}H_{27}O_6)$: Mn, 13.96. Found: Mn, 13.90. The air sensitive manganese(II) chelate was prepared under nitrogen by the method of Graddon and Mockler[37] and was used without further purification after drying it over P_2O_5 under vacuum.

Pivaloylacetone (2, 2-dimethyl-3, 5-hexanedione). The ligand was synthesized by the condensation of pinacolone and ethyl acetate with $NaNH_2$.[74] Bp, 75-78°/20 mm (lit.,[74] 70-71°/20 mm).

Isobutyrylacetone (2-methyl-3, 5-hexanedione). The ligand was synthesized by the condensation of acetone and ethyl isobutyrate with $NaNH_2$.[74] Bp, 74-75/30 mm (lit.,[74] 66-67°/20 mm).

3-Methylacetylacetone. The procedure outlined by Johnson *et al.*[75] was used to prepare the ligand. Bp, 170-172°/760 mm (lit.,[75] 170-172/760 mm).

Kinetic Procedures

Manometric method. Measurements of oxygen uptake at constant pressure were obtained with an apparatus described by Boozer *et al.*[76] The temperature of the constant temperature bath was $30.0 \pm 0.1°$. In a number of runs, the error in the measurements, ~0.02 ml, was large relative to the total volume of oxygen consumed in the initial rate studies, which was often less than 0.5 ml. The manometric method was well suited, however, for reactions in which oxygen consumption was large, and for determination of reaction stoichiometry.

Spectrophotometric method. Rates of manganese(III) production were determined with a reaction vessel illustrated in Fig. 14. Kinetic experiments could be analyzed as pseudo-zero order in oxygen since less than 5% of the total oxygen in the system was consumed in any one run.

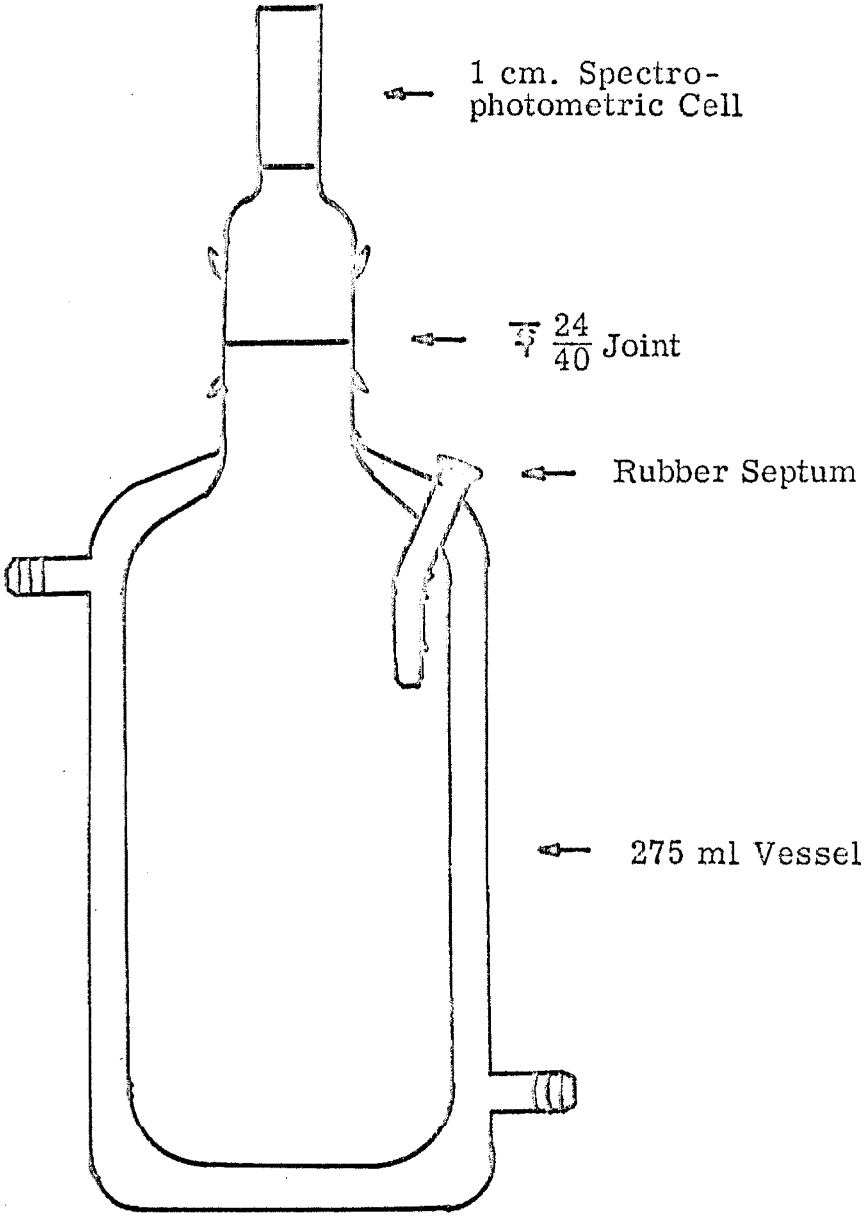


Fig. 14. Bulb Reactor for Monitoring Reaction Rates Spectrophotometrically in Beckman DU at Constant Gas Pressure.

A known amount of chelate and a stirring bar was added to the reaction vessel. The ground glass joints were greased lightly with Dow-Corning high vacuum silicone grease and held firmly together with springs. After the vessel had been evacuated to less than 1 mm pressure, solvent and all other reactants, except oxygen, were injected through the rubber septum. When the system had attained temperature equilibrium, $30° \pm 0.1°$ for most runs, air or oxygen was admitted to the cell and the pressure was quickly adjusted to atmospheric pressure. The zero time was taken as the moment the magnetic stirrer was started. Absorbance measurements were obtained by periodically inverting the vessel into the thermostatted cell compartment of the Beckman Spectrophotometer, Model DU. Measurements could be recorded every 30 sec , if necessary, while maintaining the solvent saturated with oxygen. Control experiments demonstrated that the reaction rates were independent of the rate of stirring at high stirring rates.

To establish an oxygen pressure less than 0.2 atm , a known volume of air was injected into the evacuated reaction vessel with a syringe. Results obtained were consistent with those obtained at 1 atm of air or oxygen.

Rates of manganese(III) appearance were followed by monitoring an absorbance maximum of the product in the near-infrared region. In the absence of excess chelating agent, manganese(III) production was observed at 960 mμ (ethanol) and 1100 mμ (benzene); in the presence of excess diketone, 1100 mμ (ethanol) and 1160 mμ (benzene).

Manganese(II) absorbance was essentially zero in this region.

Polarographic method. Rate constants for the consumption of a limited amount of oxygen under pseudo-zero order conditions for all other reactants were obtained with a Yellow Springs Instrument Company Biological Oxygen Monitor, Model 53. To minimize solvent attack on the probe assembly, a plunger made of Kel-F replaced the lucite plunger supplied by the manufacturer. Solutions in the reaction chambers were stirred with 1/8" × 1/2" teflon coated magnetic spinbars. The temperature of the water bath was maintained at $30.0 \pm 0.1°C$.

In a typical run, 3.0 ml of solution containing all reactants except the reaction initiating species were added to the cell and stirred for 3 min to saturate the solution with air. The plunger was carefully inserted to remove all air bubbles. When the current output from the probe had reached a steady value, indicating the system was in thermal equilibrium, 0.5 ml of solution containing the reaction inducing species was added by syringe, and the probe was quickly readjusted to remove air bubbles.

Rate constants for oxygen consumption varied ±10% over an extended period of time. The important sources of instrumental error could be traced to properties of the teflon membrane; variation in film thickness and methods of installing the membrane alters the permeability of the membrane and, hence, the current output of the sensor.

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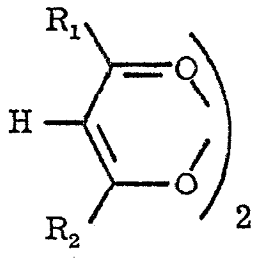
Part II

Synthesis of Dipivaloylmethane Chelates of Manganese(II)

INTRODUCTION

Metal complexes of β-diketones have been studied for over seventy-five years and a majority of the acetylacetonates(Acac) were characterized before the turn of the century. In the last few years, however, attention has been drawn to the structural and spectral properties of the chelates. The subject has been recently reviewed by Fackler.[1]



1a) $R_1=R_2=CH_3$

1b) $R_1=R_2=C(CH_3)_3$

β-Diketonate complexes of bivalent metals are square-planar or tetrahedral unless they can polymerize to form an octahedral configuration about the metal ion. Except for Cu(Acac)$_2$, 1a, which is square-planar, all bivalent first-row transition-metal acetylacetonates, M(Acac)$_2$, from manganese(II) to zinc(II) polymerize in the solid state and in non-donor solvents. Replacement of acetylacetonato ligands by dipivaloylmethanato ligands (DPM), 1b, prevents polymerization by steric hindrance from bulky tertiary butyl groups.[2] Ni(DPM)$_2$ is square-planar;[3] Fe(DPM)$_2$,[4] Co(DPM)$_2$,[5] and Zn(DPM)$_2$[6] are tetrahedral.

Replacing acetylacetonato ligands about a metal ion with dipivaloylmethanato ligands also results in greater formation constants for complexation,[7] and, for metals of variable valence, greater oxidation potentials.[8] Hammond, Nonhebel, and Wu[9] reported that Co(DPM)$_2$ was readily autoxidized in hydrocarbon solution, Mn(DPM)$_2$ charred on exposure to air, and attempts to prepare Fe(DPM)$_2$ gave considerable amounts of the ferric chelate. In comparison, the acetylacetonates of these bivalent metal ions can be prepared in air or with minimum precautions to exclude oxygen.

Synthesis of Mn(DPM)$_2$ has been repeated under oxygen-free conditions and physical properties have been reported. Structures of the compounds isolated are proposed and are discussed briefly with particular reference to the structures of other, known metal-DPM chelates.

RESULTS

Initial attempts to prepare a manganese(II) compound with dipivaloylmethane, HDPM, were conducted in methanol solvent in an apparatus illustrated in Fig. 2 (see Experimental Section). The bright yellow, amorphous solid precipitates from solution upon neutralization of the diketone with either piperidine or sodium hydroxide. Samples under a variety of conditions give essentially the same manganese analysis, 19.7 ± 1% (six preparations). The material can be synthesized with a slight excess of ligand or an excess of manganese(II) chloride with no distinct change in the manganese content of the sample.

Analyses of the β-diketone content of the substance indicate that the material is not the bis chelate expected, but a 1:1 complex of ligand to metal. The molecular weight of the substance, determined from the freezing point depression of benzophenone, is 540 ± 230 (3 values). The result is subject to large error and is questionable since oxidation of the manganese complex was noted at the melting point of the mixture. However, a compound with 19.7% manganese content should have a molecular weight of 280 for a monomer and 560 for a dimer. The room temperature magnetic susceptibility of the material is 5.96 B.M. (corr.), close to the value of 5.92 B.M. observed for most high-spin manganese(II) compounds.

The material is soluble in benzene, acetone, pentane, and dichloromethane, but only slightly soluble in alcohol, acetonitrile, and formamide. The dry compound is noticeably oxidized in air after one or two minutes, while the moist substance or the material in solution is oxidized immediately in the atmosphere. $Mn(DPM)_3$, identified after elution on a silica gel thin-layer chromatography plate, and at least one other manganese containing substance, insoluble in common solvents, constitute the products of oxidation.

When the manganese(II) chelate with dipivaloylmethane is synthesized in acetone-water solvent, a cream-white amorphous solid is isolated. The product was dried under high vacuum but prolonged, continuous evacuation results in slow decomposition; the cream-white solid slowly turns yellow and is ultimately transformed into a gummy yellow-brown solid. Manganese analyses for both the cream-white material and the yellow material, $13.4 \pm 1.0\%$, are consistently lower than those for the product prepared in methanol. Analyses of the ratio of ligand to metal indicate the product contains two β-diketone ligands, and the elemental analyses agree with the formula $Mn(DPM)_2(H_2O)_2$. The magnetic susceptibility is unusually high, 6.45 B.M. (corr.), but corresponds to that of a compound containing five unpaired electrons.

Ultraviolet spectra of the two DPM compounds were recorded in cyclohexane. The spectra of both compounds consist of one intense maximum in the ultraviolet region. The compound prepared in methanol also absorbs radiation in the low wavelength region of the ultraviolet. Neither compound exhibits an absorption maximum in the visible region. Both solutions were air oxidized and the spectra were remeasured. Differences in the two sets of spectra indicate that the manganese(II) samples were not contaminated with manganese(III). The spectra are reproduced in Fig. 1.

Infrared spectra for the two manganese(II)-DPM compounds were recorded as finely ground powders between salt plates to minimize contact with the air. The spectrum of $Mn(Acac)_2(H_2O)_2$ was recorded in a similar manner for comparison. Spectral bands and their relative intensities are listed in Table I. Spectra of $Mn(DPM)_2$ and $Mn(Acac)_2(H_2O)_2$ in KBr pellets were also recorded. The bands are sharper than those obtained with powdered samples, and the O–H absorption in the region of 3500 cm^{-1} is more pronounced. Appreciable oxidation of the DPM chelate occurred in the pellet as the spectrum was recorded, giving rise to a number of new bands. Except for the presence of bands in the 3500 cm^{-1} region (O–H stretch) and 1680 cm^{-1} (H–O–H bending) for $Mn(DPM)_2(H_2O)_2$ and their absence in the DPM derivative prepared in methanol, and some differences in the 800-1050 cm^{-1} region, the spectra of both DPM species are quite similar.

The band at 1033 cm^{-1} which appears in the spectrum of the DPM compound prepared in methanol is in the region where absorption of methoxy ligands is expected. In an attempt to determine whether or not this assignment is reasonable, a magnesium compound was synthesized by refluxing bis(dipivaloylmethanato)magnesium(II) and potassium hydroxide in methanol, a procedure which has been used to introduce methoxy ligands into several metal acetylacetonates.[10, 11] Magnesium analysis of this compound and a molecular weight determination indicate it is a polymer. The ligand to metal ratio is 1.0. Infrared

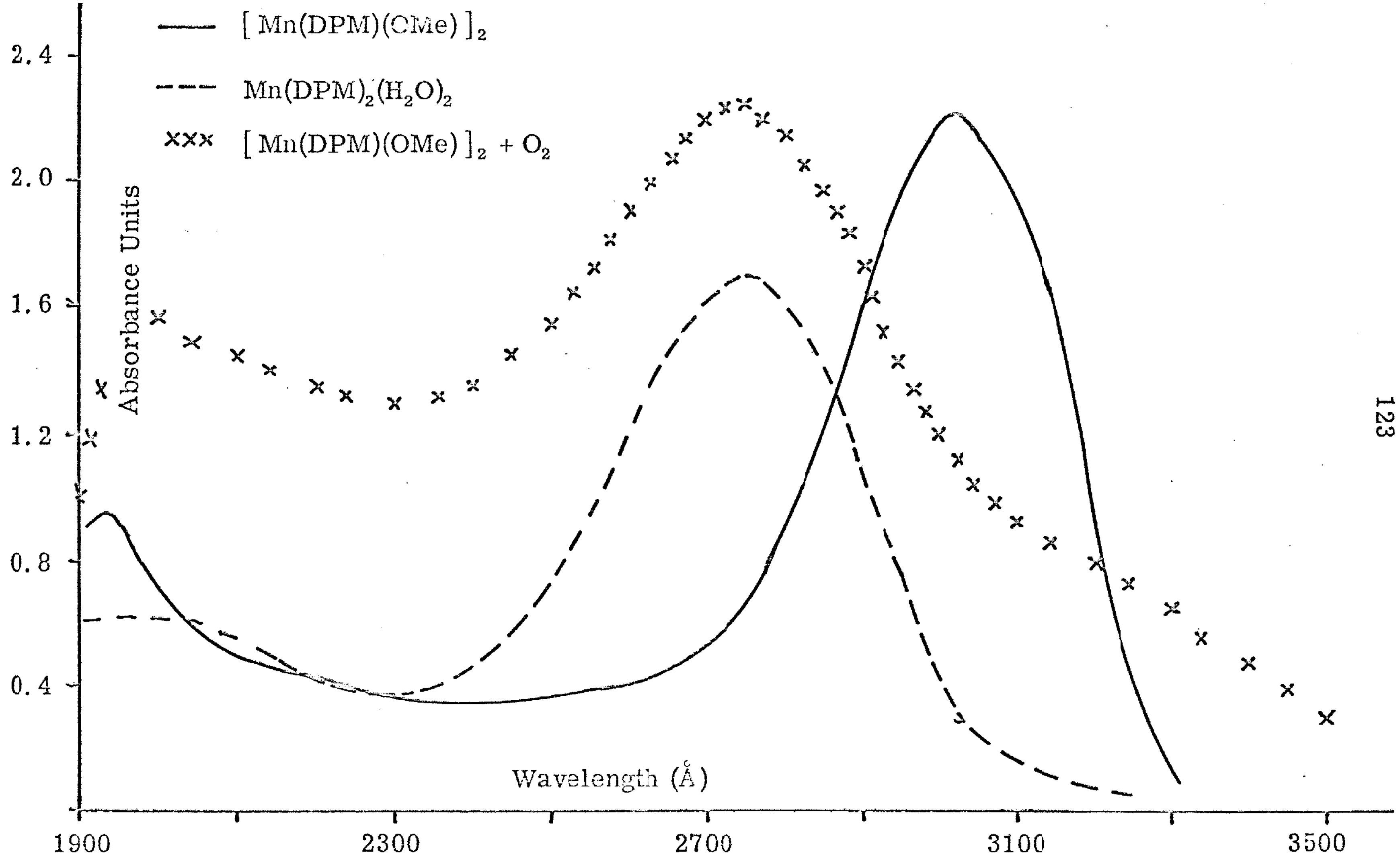


Fig. 1. Spectra of Manganese-DPM Species in Cyclohexane.

Table I

Infrared Spectral Bands of Manganese(II) Chelates

Mn(DPM)$_2$ $\bar{\nu}$(cm^{-1})	Mn(DPM)$_1$* $\bar{\nu}$(cm^{-1})	Mn(Acac)$_2$(H$_2$O)$_2$ $\bar{\nu}$(cm^{-1})
3410 MB	2950 MB	3380 WB
2970 M	2370 B	3250 WB
2870 Msh	2250 B	2970 WB
1680 WB	1586 S	1640 W
1592 M	1573 S	1590 S
1572 S	1535 S	1500 S
1543 MB	1503 S	1445 M
1508 S	1447 M	1380 S
1408 S	1408 SB	1340 Msh
1390 Ssh	1385 SB	1235 M
1363 S	1355 S	1180 W
1247 M	1278 M	1005 S
1224 M	1244 W	912 M
1190 W	1220 M	765 M
1134 M	1183 M	
1025 W	1131 M	
960 W	1033 S	
871 M	954 W	
795 W	930 WB	
763 W	866 S	
742 W	820 W	
	790 M	
	758 W	
	739 W	

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*Mn(DPM)$_1$ - Complex prepared from methanol solvent.
S - Strong; M - Medium; W - Weak; B - Broad; sh - Shoulder.

spectra of the magnesium compound containing a methoxy ligand and $Mg(DPM)_2$ are identical in the 2000 cm^{-1} to 700 cm^{-1} region, except for a sharp, strong doublet centered at 1040 cm^{-1} in the spectrum of the polymer which is missing in the spectrum of $Mg(DPM)_2$.

X-Ray diffraction powder patterns were recorded for both manganese(II)-DPM compounds as well as $Zn(DPM)_2$, and $Cu(DPM)_2$. Relative intensities of the diffraction lines and spacings between lines are subject to some error since the diffraction patterns for all but the copper(II) complex were weak and diffuse. By immediate inspection, the manganese(II) compounds are not isomorphous with the planar $Cu(DPM)_2$. Table II lists the d spacings and relative intensities of the first ten lines observed for the manganese(II) complexes, and the isomorphous tetrahedral chelates, $Zn(DPM)_2$ and $Fe(DPM)_2$.
The data in Table II indicate that neither manganese(II) compound is isomorphous with the tetrahedral zinc(II) and iron(II) chelates, and that the two manganese(II)-DPM compounds have different structures.

Table II

Spacings of X-Ray Powder Diffraction Lines for Metal-DPM Complexes[*]

$Zn(DPM)_2$	$Zn(DPM)_2$[‡] calc.	$Fe(DPM)_2$[φ]	$Mn(DPM)_2(H_2O)_2$	$Mn(DPM)_1$[**]
8.51 M	9.57	9.43 S	7.36 S	8.61 S
6.74 S	6.20	6.15 M	6.80 W	7.32 W
6.11 M	6.00		5.67 M	6.47 M
5.45 M	5.43	5.49 W	5.18 S	5.67 M
	5.34	5.30 W	4.83 W	5.18 W
4.89 S	4.79	4.79 M	4.61 W	4.34 M
4.66 S	4.66	4.62 S	4.40 W	3.88 W
4.27 M	4.03		4.18 S	3.60 W
3.99 W	3.99	3.97 W	3.94 W	3.30 W
3.63 M			3.74 M	3.11 W
3.29 W				

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[*] d spacings in Å.

[‡] Ref. 6. Calculated assuming tetragonal cell constants for $Zn(DPM)_2$ a = 10.67 Å, c = 21.76 Å.

[φ] Ref. 4a.

[**] $Mn(DPM)_1$ - Material prepared from methanol.

DISCUSSION

Two manganese(II) dipivaloylmethane chelates have been synthesized, one from methanol solvent, and the other from acetone-water solvent.

A. $Mn(DPM)_2(H_2O)_2$

The formula $Mn(DPM)_2(H_2O)_2$ is assigned to the compound prepared from acetone-water based on elemental analyses, the ligand to metal ratio of two, and the presence of an infrared absorption band at 3400 cm^{-1} in the region of the O–H stretching vibration.

The X-ray powder pattern indicates a structure other than tetrahedral, and the spectral properties of the compound, both its solution spectrum and color of the solid, cream-white, are consistent with a d^5 high-spin octahedral configuration. High-spin tetrahedral manganese(II) compounds are generally pale green to yellow-green in color, and exhibit a number of weak spectral bands in the visible region.[12]

Molecular models show that two water molecules can be bound in the <u>trans</u> positions of the <u>bis</u> DPM compound, but not the <u>cis</u> positions, although square planar or tetrahedral configurations are less crowded.

On the basis of the evidence presented, the compound formulated as $Mn(DPM)_2(H_2O)_2$ is six coordinate and octahedral, consistent with all known six-coordinate manganese(II) compounds. This conclusion is quite interesting since all other first-row divalent transition-metal ions which form octahedral or pseudo-octahedral acetylacetonates form four-coordinate DPM chelates. Cotton and Fackler[2] stated that the reduction in coordination number is due to the bulky tert-butyl groups which prevent polymerization of the chelates.

Of the bis DPM compounds besides manganese, only nickel forms a hydrate, $Ni(DPM)_2(H_2O)_2$, with presumably octahedral coordination, which readily loses water upon sublimation in vacuum to give a four-coordinate square-planar complex. Conceivably, the yellow material which forms when $Mn(DPM)_2(H_2O)_2$ is dried under vacuum for long periods of time could be the anhydrous compound, but samples of sufficient purity could not be obtained for complete elemental analysis.

Despite the fact that DPM ligands prevent polymerization of the bis chelates, an octahedral configuration about the metal ion can be maintained in principle by coordination with two donor molecules in the trans positions. Thus steric factors alone do not determine the stereochemistry of the bis DPM compounds. In a qualitative sense, the relative stability of octahedral and tetrahedral configurations for a given series of high-spin transition-metal ions is determined by ligand-field effects. Ligand-field stabilizations for octahedral and tetrahedral environments for divalent high-spin transition-metal ions are listed in Table III.[13]

Although manganese(II) and zinc(II) have no ligand-field stabilization, manganese(II) shows a marked preference for octahedral coordination while zinc(II) tends to form tetrahedral complexes. In the absence of ligand-field stabilization the change from octahedral to tetrahedral bonding should vary smoothly along the series of metal

Table III

Ligand-Field Stabilization Energies for Octahedral and Tetrahedral Environments of Divalent Metal Ions

Metal	No. of d electrons	Octahedral complex	Tetrahedral complex
Mn	5	0	0
Fe	6	$-2/5\ \Delta$*	$-3/5\ \Delta$
Co	7	$-4/5\ \Delta$	$-6/5\ \Delta$
Ni	8	$-6/5\ \Delta$	$-4/5\ \Delta$
Cu	9	$-3/5\ \Delta$	$-2/5\ \Delta$
Zn	10	0	0

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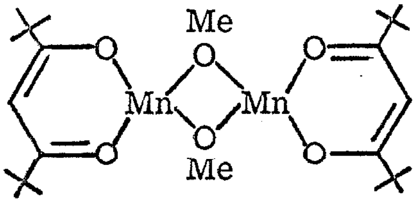
[*] Δ is the ligand-field splitting, the energy difference between t_{2g} and e_g orbitals.

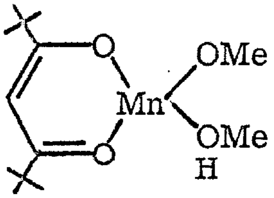
ions; in actual fact, the tendency to form tetrahedral complexes increases to a maximum at cobalt(II), while the maximum stabilization of octahedral coordination is observed at nickel(II). This stability order is followed for <u>bis</u> DPM complexes as manganese(II) and nickel(II) form six-coordinate species while the iron(II), cobalt(II), and zinc(II) compounds are tetrahedral. Steric effects are admittedly important since Fe(DPM)$_2$ is the only known tetrahedral iron(II) complex bound by four oxygen atoms.[4]

B. Mn(II)-DPM Compound from Methanol.

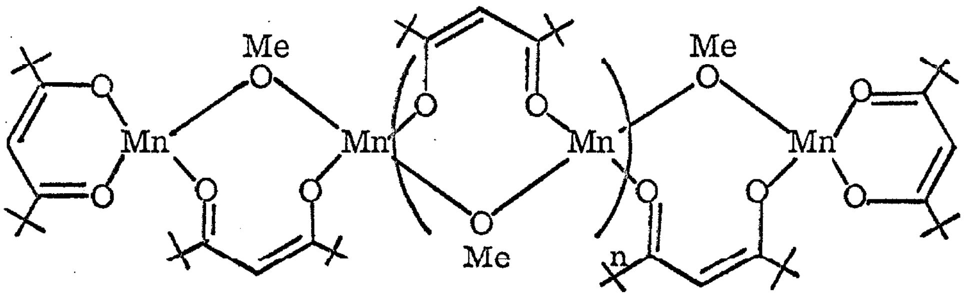
The manganese(II) compound with DPM prepared in methanol solution has an empirical formula $C_{12}H_{22.5}O_{3.5}Mn_1$ based on average values of the elemental analyses, and $C_{12-13}H_{21-24}O_{3-4}Mn_1$, using extreme values of the analytical data. The following proposed compounds are consistent with the elemental analyses and the ligand to metal ratio of one: (DPM)Mn(OCH_3)(CH_3OH) ($C_{13}H_{26}O_4Mn$); (DPM)Mn(OH)(CH_3OH) ($C_{12}H_{24}O_4Mn$); [(DPM)Mn(OCH_3)]$_2$ ($C_{12}H_{22}O_3Mn$)$_2$; given the analytical data, it is not possible to devise a structure with octahedral configuration. Three possible structures can be considered.



A



B



C

Structure C is one representation of a polymeric species which could be produced. On the basis of infrared evidence, structures A and C are preferred over structure B. The magnetic susceptibility of this material does not conflict with these choices, since there is no way of predicting beforehand whether spin pairing betwen the metal ions will occur.

Klein and Bailar[14] reported the synthesis of (3-NO_2Acac)-Be$(OCH_3)_2$Be(3-NO_2Acac), and Bertrand and Kaplan[11] characterized the compound, (Acac)Cu$(OCH_3)_2$Cu(Acac). These structures were confirmed partly on the basis of infrared evidence. Bertrand and Kaplan[11] stated that absorption of bridging methoxy groups should appear below 1040 cm^{-1}; that for the nonbridging methoxy groups, above 1060 cm^{-1}.

Hammond and Wu[15] isolated alkoxides of bis(dipivaloylmethanato)-iron(III) from the oxidation of iron(II) chloride in alcohol in the presence of added dipivaloylmethane and piperidine. Alkoxides of iron(III) β-diketonates were reported previously by Emmert.[16] Analytical data and molecular weight determinations suggest a dimer, $(DPM)_2$Fe-$(OR)_2$Fe$(DPM)_2$. The compound containing methoxy ligands has a strong infrared absorption at 1050 cm^{-1}. The magnesium chelate synthesized in this work undoubtedly contains bridging methoxy groups; it exhibits a sharp band at 1040 cm^{-1}.

Thus, it appears that the (dipivaloylmethanato)manganese(II) compound prepared in methanol, which shows a strong infrared band at 1033 cm^{-1}, contains bridging methoxy groups. Of the two structures, A and C, structure A is compatible with the molecular weight data which is, admittedly, subject to large error. The possibility also exists of forming mixtures of dimer and polymer.

Electronic spectra of metal β-diketonates have been reviewed briefly by Fackler.[1] The single band observed in the spectra of both manganese(II)-DPM species in cyclohexane can be assigned to a π-π^* transition. The large shift of the absorption band of $[Mn(DPM)(OCH_3)]_2$ to lower energy relative to the absorption maximum of $Mn(DPM)_2(H_2O)_2$ may be due to intramolecular ligand interactions. Mixing of π orbitals on the chelate ring with different sets of metal π orbitals in the four-coordinate dimer and the six-coordinate monomer may be a factor.

EXPERIMENTAL

Materials

Dipivaloylmethane (2, 2, 6, 6-tetramethyl-3, 5-heptanedione) (HDPM), obtained from C-H. S. Wu, was distilled before use. Bp, 100°/24 mm (lit.,[17] 93-94°/35 mm). Piperidine was distilled before use. Nitrogen, 99.9% pure, was bubbled through vanadous sulfate solution and passed through a column of silica gel. All other materials were reagent grade and used as received. Carbon and hydrogen analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Molecular weight determinations were conducted by Elek Microanalytical Laboratories, Torrance, California.

Methods

The cell shown in Fig. 2 was used to prepare the extremely air sensitive complexes. Nitrogen was passed through the coarse fritted disc from below for about 15 min to deoxygenate the solvent containing manganous salt and diketone. Base was added dropwise by syringe through the rubber septum. The reactants were mixed by the stream of gas and by manually shaking the apparatus. The flow of gas was switched to the upper inlet forcing the solvent from the cell. The complex was washed several times with 10 ml portions of deoxygenated solvent to remove excess starting material and any oxidation products which might have formed. Nitrogen was passed through the cell for 1 to 3 hrs; final traces of solvent were removed under vacuum. All other handling operations were performed in a glovebag (I^2R Model

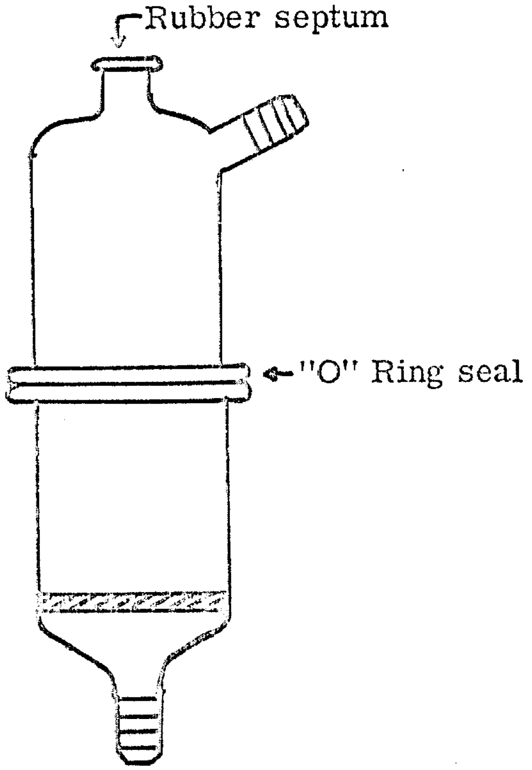


Fig. 2. Reaction Vessel for Synthesis of Oxygen Sensitive Chelates. Vessel is constructed from sintered glass filter, Kimax #30C. Overall dimensions are 4 cm × 18 cm.

X-17-17) filled with high-purity nitrogen.

Bis(dipivaloylmethanato)diaquomanganese(II). $MnCl_2 \cdot 4H_2O$ (0.54 g, 0.0027 mole) and HDPM (1.00 g, 0.0054 mole) were added to 5 ml water and 15 ml acetone in the reaction cell. NH_4OH (1:1) was added in slight excess to precipitate the cream-white amorphous solid. The product was washed with water and, finally, acetone. Mp, darkens 104-105, decomp. 145. Anal. Calcd. for $Mn(C_{22}H_{38}O_4)$-$(H_2O)_2$: C, 57.77; H, 9.19; Mn, 12.04. Found: C, 56.46, 56.34; H, 8.65, 8.62; Mn, 13.70. Ligand/Mn Calcd: 2.0. Found: 1.9.

Di-μ-methoxo-bis(dipivaloylmethanato)dimanganese(II). HDPM (1.85 g, 0.010 mole) and $MnCl_2 \cdot 4H_2O$ (1.00 g, 0.0050 mole) were dissolved in 20 ml methanol. The bright yellow, amorphous product formed upon addition of piperidine (1.19 ml, 0.012 mole), or NaOH (0.40 g, 0.010 mole) in 5 ml of methanol. The complex darkens at 97-100° and decomposes at 143-145°. Anal. Calcd. for $Mn(C_{12}H_{22}O_3)$ C, 53.5; H, 8.18; Mn, 20.4. Found: C, 51.90, 51.76; H, 8.02; 7.94; Mn, 19.7 ± 1.0. Ligand/Mn Calcd: 1.0. Found: 0.77.

Ligand/Mn analyses. A known amount of the chelate was hydrolyzed in conc. HCl under nitrogen and diluted with water. The ligand was extracted with 5×5 ml portions of $CHCl_3$ and diluted to 50 ml. The absorbance was determined at 2720 Å ($\epsilon = 1.11 \pm 0.06 \times 10^4$ ℓ mole^{-1} cm^{-1}). Total manganese was determined from the aqueous solution.

Bis(dipivaloylmethanato)copper(II). The chelate was prepared and purified by the procedures described by Hammond, Nonhebel, and

Wu.[9] Mp, 198° (lit.,[9] 198°).

Bis(dipivaloylmethanato)zinc(II). The method of Hammond, Nonhebel, and Wu[9] was followed to synthesize the complex. Mp, 143-144° (lit.,[9] 144°).

Magnesium-DPM Chelate with Bridging Methoxy Groups.

A procedure reported by Bertrand and Caine[10] was used to prepare this compound. Equimolar amounts of bis(dipivaloylmethanato)magnesium(II) and potassium hydroxide were refluxed in methanol 24 hrs. The white, crystalline product, insoluble in methanol, was isolated by filtration and washed thoroughly with methanol. Mp, 154-156°. Anal. Calcd. for $[Mg(C_{11}H_{19}O_2)(CH_3O)]_n$; Mg, 10.16. Found; Mg, 9.87. Mol wt: Found, 1110±10.

X-ray powder patterns. Powdered samples in 0.5 mm diameter thin-walled capillary tubes were mounted in the beam of a C.I.T. type X-ray diffraction powder camera. Cu-Kα radiation was filtered with nickel foil. Diffraction patterns for the dipivaloylmethane compounds with manganese(II) were compared with those of the copper(II) and zinc(II) derivatives.

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PROPOSITION I

Abstract: An investigation of the autoxidation of ruthenium(II) compounds in solution is proposed. The reaction is a particularly important one for understanding the factors which govern the mechanisms of metal ion autoxidations since the ruthenium(II) reactant and ruthenium(III) product are both substitution inert. Experiments are suggested to possibly determine whether oxygen is a one-electron or two-electron oxidant.

Autoxidation of ruthenium(II) species in aqueous solution is a known, often undesirable, reaction observed in studies of the lower oxidation states of ruthenium. Manchot and Schmid[1] reported that solutions of the chloro complexes of ruthenium(II) were slowly air oxidized to ruthenium(III). Rechnitz and Catherino[2] found that oxygen has no effect on the rate of $Ru(H_2O)_5Cl^+$ oxidation by water, thereby placing an upper limit of 4×10^{-5} sec^{-1} on the rate constant for autoxidation of this complex. Mercer and Buckley[3] prepared $Ru(H_2O)_6^{+2}$ and found that the product of reaction with oxygen was $Ru(H_2O)_6^{+3}$. The autoxidation of $Ru(NH_3)_6^{+2}$ was studied by Taube and Meyer[4] who found that the reaction proceeds at a moderately rapid rate, and identified the reaction product as $Ru(NH_3)_6^{+3}$. Study of this reaction is complicated by the fact that $Ru(NH_3)_6^{+2}$ solutions slowly decompose to give species which are rapidly oxidized to ruthenium(III) by cobalt(III) compounds and chlorine but not by oxygen.[5] Taube and Meyer[4] found no direct evidence for a two-electron oxidation but noticed that solutions of $Ru(NH_3)_6^{+3}$ obtained by autoxidation of $Ru(NH_3)_6^{+2}$ aged differently than solutions of $Ru(NH_3)_6^{+3}$ prepared by other means.

Complexes of ruthenium(II), (III), and (IV) are relatively inert to substitution. This property can be used to great advantage in studying oxidation-reduction reactions of these species. For example, if the reaction of ruthenium(II) with molecular oxygen proceeds at a faster rate than ligand substitution, the process is an outer-sphere electron-transfer reaction. If the reaction takes place by inner-sphere electron transfer, oxygen from molecular oxygen would be found in the ruthenium(III) product. According to the results of Meyer and Taube,[4] autoxidation of $Ru(NH_3)_6^{+2}$ gives $Ru(NH_3)_6^{+3}$ and the reaction is outer-sphere. The apparently slow rate of $Ru(H_2O)_5(Cl)^+$ oxidation may indicate that an inner-sphere reaction occurs in this case.

Because undesirable side reactions with ammino ligands and perchlorate[6] accompany studies of ruthenium(II), (III), and (IV), the autoxidation of $Ru(H_2O)_6^{+2}$ in an ionic medium of para-toluenesulfonate or tetra-fluoroborate is proposed. Classification of the reaction as inner sphere or outer sphere could be accomplished by comparing the rate of autoxidation with the rate of water exchange determined by experiments with H_2O^{18} or H_2O^{17} (NMR method), and looking for labeled oxygen from $(O_2)^{18}$ in the ruthenium(III) product.

Several criteria exist for determining whether a particular metal ion autoxidation reaction proceeds with one-electron or two-electron transfer.[7] Two potentially useful tests can be applied to the ruthenium(II) autoxidation reaction to test for the appearance of ruthenium(IV). The first involves addition of a reagent which will compete with ruthenium(II) for reduction of ruthenium(IV). An ideal reagent for competition studies of this kind is one which, in the reduced state, reacts much more slowly with oxygen and its intermediate reduction products than the metal ion does, and, in its oxidized form, does not readily oxidize the reduced substrate. Without knowing the rate constants for reaction of ruthenium(II) with ruthenium(IV), oxygen, and hydrogen peroxide, it is a difficult task to propose reagents which will fulfill the stated objective. The single electrode potentials for one-electron oxidation of hexaaquoruthenium(II) and one-electron reduction of ruthenium(IV) are -0.22 V and + 1.00 V, respectively. Reagents whose reduction half-cell potential is $+0.22\ \mathrm{V} > E > -1.0\ \mathrm{V}$, and which fulfill the other requirements stated above are potential trapping agents for ruthenium(IV).

Atwood and DeVries[8] studied the stepwise reduction of monomeric ruthenium(IV) species in perchloric acid solution polarographically and by titration with vanadium(II), obtaining evidence for the formation of a dimer containing ruthenium(III) and ruthenium(IV). If the dimer forms rapidly, reduction with excess ruthenium(II) by outer-sphere electron transfer[4] might produce a dimer of ruthenium(III) which could be identified by ion-exchange chromatography or spectrophotometrically.

A dimer of ruthenium(III) may have been observed by Dwyer, King, and Winfield[9] in their study of ruthenium(II) and ruthenium(IV) catalyzed decomposition of hydrogen peroxide. Their results indicated that the ruthenium(II) compounds were oxidized in one- and two-electron steps. Ruthenium(IV) produced in a two-electron oxidation apparently reacted with ruthenium(II) to produce a ruthenium(III) compound different from ruthenium(III) produced in a one-electron oxidation.

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PROPOSITION II

Abstract: An investigation of the autoxidation of manganese(II) phthalocyanine is proposed. The product of the reaction in pyridine has been identified by X-ray crystallography. Kinetic studies should provide additional, important information about the mechanism of the reaction.

After a communication appeared stating that manganese(II) phthalocyanine absorbed oxygen reversibly in pyridine solution,[1] equation 1, Calvin and co-workers[2] published an extensive series of

$$\begin{tikzcd}
\mathrm{Mn^{II}(Phth)(py)} + \mathrm{O_2} \arrow[r] & \text{Intermediate} \arrow[r] & \mathrm{(Phth)Mn^{IV}(O)} \arrow[d, "\text{heat to boiling}"] \\
 & & \mathrm{Mn^{II}(Phth)} + \mathrm{O_2}
\end{tikzcd}$$

(1)

experiments on the oxidation of manganese phthalocyanines with oxygen, and their reduction under certain conditions, repeating the work of Elvidge and Lever.[1] The reactions were of interest because of possible analogies between the manganese phthalocyanine system and the manganese found in the chloroplasts of plants which is recognized as an essential element for oxygen evolution in photosynthesis.[3] Results of the work of Calvin *et al.*,[2] are outlined in Fig. 1. Their

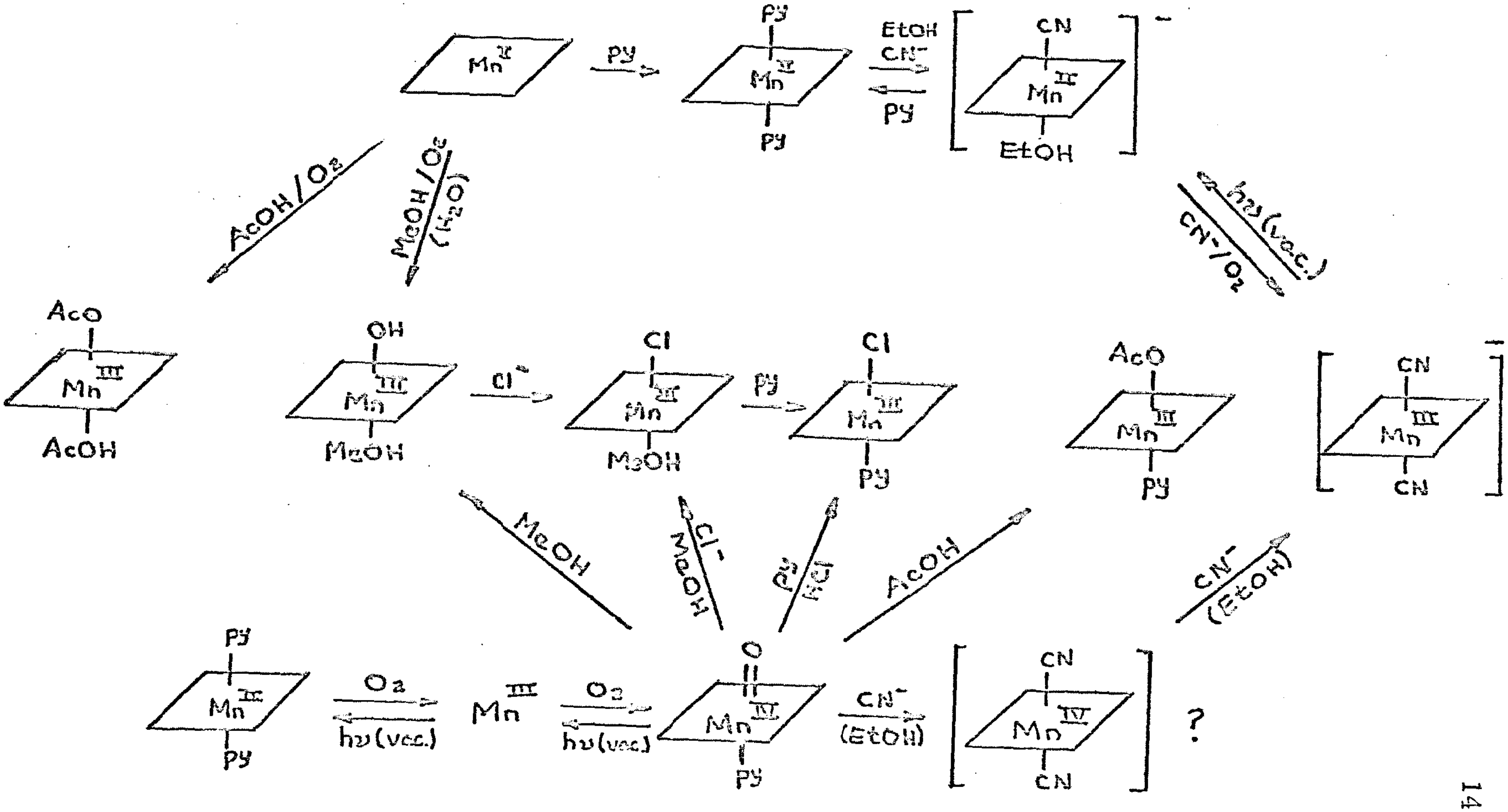
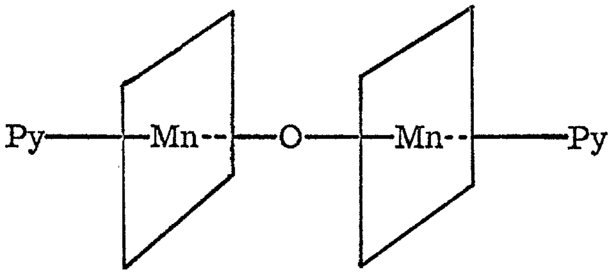


Fig. 1. Reactions of Manganese(II) Phthalocyanines 2

principle conclusions were that (1) oxygen is not reversibly absorbed by manganese(II) phthalocyanines, (2) manganese(III) is the stable oxidation product in weakly donor solvents such as alcohols, but manganese(IV) predominates in the presence of strong donors like pyridine or dimethyl sulfoxide, and (3) the reactions are catalyzed by light.

The crystal structure of the product obtained by Calvin from air oxidation of manganese(II) phthalocyanine in pyridine has been determined.[4] The compound is a dimer of manganese(III) rather than the manganese(IV) compound, $(\mathrm{Phth})(\mathrm{Py})\mathrm{Mn}^{\mathrm{IV}}=\mathrm{O}$, proposed by Calvin.



(2)

Thus, many of the results of Calvin et al.,[2] are in error. For example, the reduction of $(\mathrm{Phth})(\mathrm{Py})\mathrm{Mn}^{\mathrm{IV}}=\mathrm{O}$ to manganese(III) in alcohol or acetic acid solvent reported by Calvin is probably a solvolysis of the dimer, 2.

Knowing the molecular structure of one of the key products obtained by Calvin and co-workers does not lead immediately to a clear restatement of all their conclusions, and does not necessarily provide conclusive information about the mechanism of the autoxidation reaction. Calvin[2] suggested that the intermediate in the reaction of manganese(II) phthalocyanine with oxygen in pyridine, equation 3, was manganese(III), because the spectrum of this species was similar to spectra of known manganese(III) phthalocyanines.

$$(\mathrm{Phth})\mathrm{Mn}^{\mathrm{II}}(\mathrm{py})_2 \overset{O_2}{\rightleftharpoons} \mathrm{Mn}^{\mathrm{III}} \overset{O_2}{\rightleftharpoons} [(\mathrm{Phth})(\mathrm{py})\mathrm{Mn}^{\mathrm{III}}]_2(\mathrm{O}). \tag{3}$$

Unfortunately, it was not possible to isolate this intermediate and identify it directly.

A possible alternative to equation 3 is illustrated by the following mechanism.

$$\mathrm{Mn}^{\mathrm{II}}(\mathrm{py})_2 + O_2 \overset{K_1}{\rightleftharpoons} \mathrm{Mn}^{\mathrm{II}}(\mathrm{py})(O_2) + \mathrm{py} \tag{4}$$

$$\mathrm{Mn}^{\mathrm{II}}(\mathrm{py})(O_2) + \mathrm{Mn}^{\mathrm{II}}(\mathrm{py})_2 \overset{K_2}{\rightleftharpoons} (\mathrm{py})\mathrm{Mn}^{\mathrm{II}}-O_2-\mathrm{Mn}^{\mathrm{II}}(\mathrm{py}) + \mathrm{py} \tag{5}$$

$$(\mathrm{py})\mathrm{Mn}^{\mathrm{II}}-O_2-\mathrm{Mn}^{\mathrm{II}}(\mathrm{py}) \overset{k_3}{\rightarrow} 2\,(\mathrm{py})\mathrm{Mn}^{\mathrm{IV}}{=}\mathrm{O} \tag{6}$$

$$(\mathrm{py})\mathrm{Mn}^{\mathrm{IV}}{=}\mathrm{O} + \mathrm{Mn}^{\mathrm{II}}(\mathrm{py})_2 \xrightarrow{\text{fast}} (\mathrm{py})\mathrm{Mn}^{\mathrm{III}}-\mathrm{O}-\mathrm{Mn}^{\mathrm{III}}(\mathrm{py}) \tag{7}$$

$$\begin{aligned} \mathrm{Mn}^{\mathrm{II}} &\equiv (\mathrm{Phth})\mathrm{Mn}^{\mathrm{II}} \\ (\mathrm{py}) &\equiv \text{pyridine} \end{aligned}$$

If the intermediate observed is $[(\mathrm{Phth})(\mathrm{py})\mathrm{Mn}^{\mathrm{II}}]_2(O_2)$, a spectrum similar to those observed for manganese(III) phthalocyanine species would not be unexpected, since the extent of electron transfer from manganese(II) to the oxygen molecule in the dimer could be appreciable. In the absence of oxygen, the intermediate dimer could revert back to reactants or decompose to products, accounting for the disproportionation of manganese(III) reported by Calvin.[2] For this mechanism to be valid, formation of the binuclear intermediate should be proportional to the oxygen pressure and the square of the manganese(II) concentration; its decomposition to product should be unimolecular. Decomposition of the intermediate to the manganese(II) reactant should be faster in a stream of inert gas than under a static inert atmosphere.

A second mechanism can be proposed based on the direct reaction of manganese(II) phthalocyanine with oxygen to form a manganese(III) intermediate, equation 3.

$$(\mathrm{py})_2\mathrm{Mn}^{\mathrm{II}} + \mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \xrightarrow{k_1} (\mathrm{py})\mathrm{Mn}^{\mathrm{III}}(\mathrm{OH}) + \mathrm{HO}_2\cdot \tag{8}$$

$$2\,(\mathrm{py})\mathrm{Mn}^{\mathrm{III}}(\mathrm{OH}) \overset{K}{\rightleftharpoons} (\mathrm{py})\mathrm{Mn}^{\mathrm{III}}-\mathrm{O}-\mathrm{Mn}^{\mathrm{III}}(\mathrm{py}) + \mathrm{H}_2\mathrm{O} \tag{9}$$

$$(\mathrm{py})\mathrm{Mn}^{\mathrm{III}}(\mathrm{OH}) + \mathrm{O}_2 \xrightarrow{k_2} (\mathrm{py})\mathrm{Mn}^{\mathrm{IV}}{=}\mathrm{O} + \mathrm{HO}_2\cdot \tag{10}$$

$$(\mathrm{py})\mathrm{Mn}^{\mathrm{IV}}{=}\mathrm{O} + (\mathrm{py})_2\mathrm{Mn}^{\mathrm{II}} \xrightarrow{\text{fast}} (\mathrm{py})\mathrm{Mn}^{\mathrm{III}}-\mathrm{O}-\mathrm{Mn}^{\mathrm{III}}(\mathrm{py}) + \mathrm{py} \tag{11}$$

Further reaction of $\mathrm{HO}_2\cdot$ and other intermediate reduction products of oxygen with manganese(II) should be fast. An initial two-electron transfer to oxygen from manganese(II) would probably produce dimeric product directly and can be ruled out if this mechanism is correct. Decomposition of the intermediate manganese(III) back to manganese(II) in the absence of oxygen is not accounted for by equations 8 to 11. It is possible that a competing reaction for dimer formation is a redox reaction between manganese(III) and phthalocyanine[5] or solvent, pyridine.[2]

The above discussion has been based on the premise that manganese(IV) is not a stable species in pyridine solution. Reaction conditions can be adjusted, however, to favor formation of stable manganese(IV). Calvin[3] has found, for example, that porphyrin complexes of manganese(IV) are often stable in basic solution (pH 10-14). Reports that manganese(II) phthalocyanine is oxidized by oxygen to the tetravalent state in the presence of hydroxide ion[2,5] can not be dismissed until a comparison of the products of oxidation with the manganese(III) dimer is made. Two manganese phthalocyanines prepared from aerated solutions of alcoholic sodium hydroxide and alcoholic potassium cyanide have magnetic moments 3.88 B.M. and 3.77 B.M., respectively, corresponding to three unpaired electrons expected for manganese(IV).[5] Conceivably, these species could be produced by one-electron oxidation of monomeric manganese(III) or two-electron oxidation of dimeric manganese(III).

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PROPOSITION III

Abstract: Phosphorus trichloride, coordinated to certain metal ions, reacts with water and alcohols to form new compounds containing phosphite and phosphorous acid ligands. The objective of this proposed research is to determine if the reaction of coordinated phosphorus halide ligands with nucleophilic reagents is a general process.

In the last few years, great emphasis has been placed on reactions of coordinated ligands both from a practical and theoretical standpoint.[1,2,3,4] Several reports of reactions of coordinated phosphorus ligands have appeared[1,3,4] but the studies seem to have been confined mainly to hydrolysis and alcoholysis of halophosphine ligands. Much of the work, furthermore, was published over 75 years ago.

Typical examples of the reactions reported are shown below:

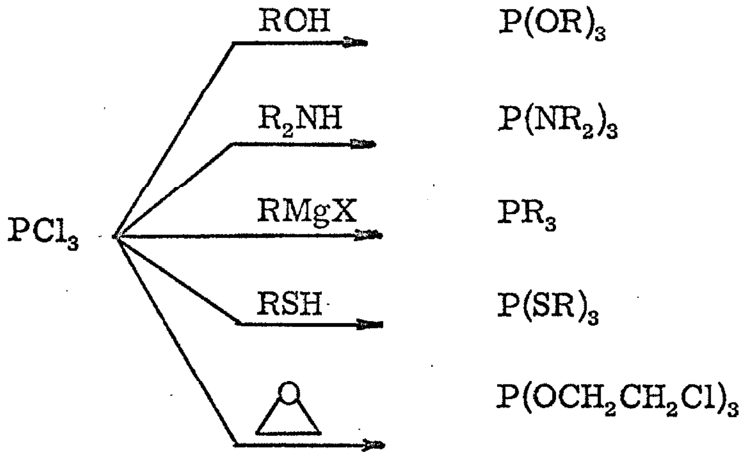
$$(Cl_3P)_2PtCl_2 + 6\,ROH \rightarrow [(RO)_3P]_2PtCl_2 + 6\,HCl \tag{1}$$

$$Cl{-}Au{-}PCl_3 + 3\,ROH \rightarrow Cl{-}Au{-}P(OR)_3 \tag{2}$$

$$Ni(PCl_3)_4 + 12\,KSO_2F \rightarrow Ni(PF_3)_4 + 12\,KCl + 12\,SO_2 \tag{3}$$

In addition, the reaction of dichloro-bis(phenyldichlorophosphine)-palladium(II) with ethylene glycol or catechol produces the corresponding coordinated phosphorus esters, but none containing multidentate ligands.[5] An important feature of these reactions is that coordination protects the phosphorus atom from oxidation. Tetrakis(trichlorophosphine)nickel(O) can be fluorinated readily, equation 3, under conditions which produce phosphates and thiophosphates from the free ligand.[6] The metal ion may strongly affect the reactivity of the phosphorus ligand by controlling the electron density at the phosphorus atom. In contrast to reaction 1, $[IrCl_3(PCl_3)_3]$ is unaffected by alcohol and cold sulphuric acid.[7]

Phosphorus(III) halides react readily with a large number of nucleophilic reagents to give new compounds, many of which are interesting and important ligands. Most of these reactions have not been reported with coordinated phosphorus halides.



(4)

There are several potential advantages of a synthesis of $M(L)_n(PX_3)_{m-n}$ from the starting material $M(L)_n(PCl_3)_{m-n}$. Trichlorophosphine replaces CO in metal carbonyls more readily than phosphines or phosphites which could lead to synthesis of compounds containing these ligands under relatively mild conditions. Metal compounds with chlorophosphine ligands are often nearly as stable to decomposition, in the absence of water, as the corresponding metal carbonyls. Synthesis of new compounds by the proposed method would be more direct than present methods since steps required for production and isolation of the free ligand would be eliminated. Protection of the reaction mixture from the atmosphere would not be necessary if the metal compound reactant is air stable.

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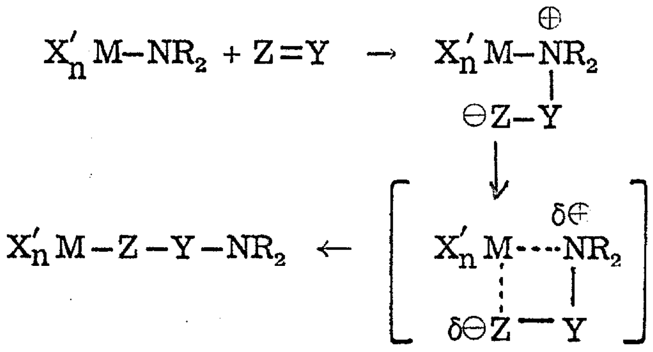
PROPOSITION IV

Abstract: Insertion reactions of amino compounds, $-M-NR_2$, generally involve attack by unsaturated electrophiles at the nitrogen atom. An exception to this rule is the reaction of aminophosphines with carbon disulfide. Experiments are proposed to determine the mechanism and scope of these interesting reactions.

In the last few years, numerous examples of insertion reactions, equation 1, have been reported. The results have been summarized

$$\begin{array}{c} X'_nM-X \\ + Z=Y \end{array} \rightarrow X'_nM-ZY-X \qquad (1)$$

in several reviews.[1, 2, 3] When M in equation 1 is a non-transition element and X is nitrogen, for example, a mechanism involving a four-center transition state is a reasonable explanation for most of the reactions.

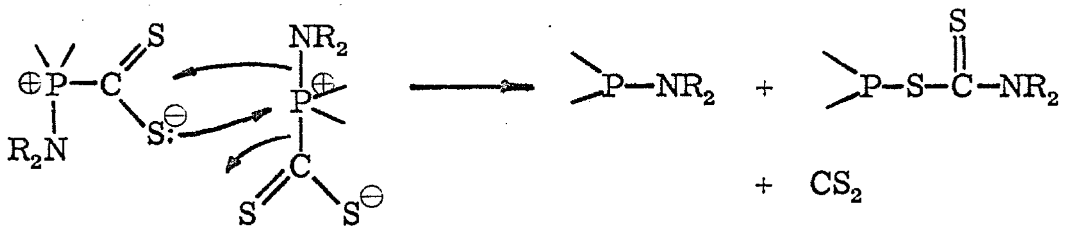


$$\begin{array}{ccc} X'_nM-NR_2 + Z=Y & \rightarrow & X'_nM-\overset{\oplus}{N}R_2\text{ with }\ominus Z-Y \text{ bonded to N} \\ & & \downarrow \\ X'_nM-Z-Y-NR_2 & \leftarrow & \left[\begin{array}{ccc} X'_nM & \cdots & \overset{\delta\oplus}{N}R_2 \\ \vdots & & | \\ \delta\ominus Z & - & Y \end{array} \right] \end{array} \qquad (2)$$

$$\begin{array}{lll} Z{=}Y \;=\; & CO_2 & CS_2 \text{ (depending on } X_n'M) \\ & RNCO & RCHO \\ & RNCS & RCOCl \end{array}$$

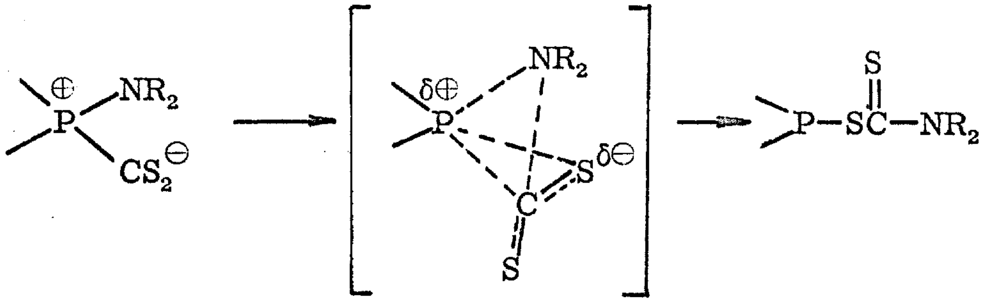
The reactions of aminophosphines, $(R_2N)_xP(R')_{3-x}$, with carbon disulfide is of special interest because rather convincing experimental evidence indicates that the first step of the reaction involves nucleophilic attack of phosphorus at carbon. When the reactions are conducted below room temperature,[4, 5, 6] a deep-violet transient is observed which is similar in color to the stable carbon disulfide adduct with tertiary phosphines.[7] Strong $p_\pi - d_\pi$ bonding between nitrogen and phosphorus in the aminophosphine-carbon disulfide zwitterion provides the driving force for adduct formation.

Although identification of the intermediate as a phosphorus-carbon disulfide adduct is not questioned, the manner in which the intermediate decomposes is still much in doubt. Vetter and Nöth[4] proposed a bimolecular reaction between two phosphonium species, reaction 3.



(3)

Cragg and Lappert[6] suggested that a unimolecular decomposition of the zwitterion occurred.



(4)

It is proposed that a kinetic study of the decomposition of an aminophosphine adduct with carbon disulfide be undertaken to distinguish between these two possible mechanisms.

Reaction of carbon disulfide with aminophosphites, $(RO)_x P(NR_2')_{3-x}$, has been reported.[5] Since the highly exothermic reactions were conducted at room temperature, any intermediates indicative of phosphorus-carbon disulfide adducts may not have been noticed. It is, of course, possible that the nitrogen atom is more nucleophilic than phosphorus when the latter is bound by alkoxy groups.[8] Kabachnik[9] proposed a reactivity series for nucleophiles, PX_3, $X = \text{alkyl} > \text{aryl} > \text{alkoxy}$; the position of the amino group should be between aryl and alkoxy groups. It would be of interest to study the reactions of aminophosphites with carbon disulfide at low temperatures to determine if the phosphorus atom is sufficiently nucleophilic to react at the unsaturated carbon center.

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PROPOSITION V

Abstract: An investigation of the reaction between platinum(IV) compounds and hexaaquochromium(II) is proposed. Analysis of the chromium(III) products should indicate whether platinum(IV) is reduced in one- or two-electron steps.

Studies of redox reactions in which the oxidant and reductant normally do not exchange equal numbers of electrons are often quite challenging. A number of problems arise during investigations of these non-complementary redox processes which are not faced when both reactants participate in one- or two-electron transfer reactions. A particular example, reaction of metal ions with molecular oxygen, was discussed in the Introduction to Part I of this thesis.[1] The methods used to determine the number of electrons transferred in non-complementary oxidation-reduction reactions and recent examples which have been studied are summarized by Basolo and Pearson[2] and Sykes.[3]

Beattie and Basolo[4] reported a kinetic study of the reduction of several platinum(IV) compounds by *tris*(bipyridine)chromium(II) ion. Their results indicated that the reactions involved net two-electron reduction of platinum(IV) to platinum(II) in a bimolecular reaction between platinum(IV) and chromium(II). *Tris*(bipyridine)chromium(II) normally reacts by outer-sphere electron transfer. The relative rate constants for the Pt(IV)/Cr(II) reactions paralleled the relative half-wave potentials for polarographic reduction of platinum(IV) complexes and rates of reduction of cobalt(III) complexes by tris(bipyridine)-chromium(II). Based on these facts, Beattie and Basolo suggested that the reaction proceeds by one-electron outer-sphere electron transfer. However, they were not able to conclusively rule out the complementary two-electron exchange

$$\mathrm{Pt(IV) + Cr(II) \rightarrow Pt(II) + Cr(IV)} \qquad (1)$$

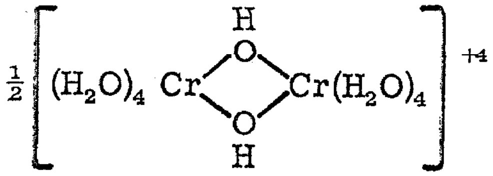
followed by

$$\mathrm{Cr(IV) + Cr(II) \rightarrow 2\,Cr(III)} \qquad (2)$$

Reaction of platinum(IV) complexes with hexaaquochromium(II) should settle the question of a possible initial two-electron transfer. Hexaaquochromium(II) reacts with one-electron oxidants and two-electron oxidants to give two distinct chromium(III) products [5, 6] which can be identified spectrophotometrically.

$$\mathrm{Cr(H_2O)_6^{+2} - 1\,e^- \rightarrow Cr(H_2O)_6^{+3}} \qquad (3)$$

$$\mathrm{Cr(H_2O)_6^{+2} - 2\,e^- \rightarrow}$$



(4)

Analysis of the reduction products of hexaamminoplatinum(IV) with chromium(II) would lead to a straightforward conclusion concerning the number of electrons transferred since the chromium(III) products would be hexaaquochromium(III) (one-electron transfer), equation 3, or the dimer (two-electron transfer), equation 4. Substituted platinum(IV) complexes could react with the chromium(II) ion by the following paths:

$$[Pt(NH_3)_5X]^{+3} + Cr(H_2O)_6^{+2} \xrightarrow{1e^-} [Cr(H_2O)_5X]^{+2} + Pt(III) + H_2O \quad (5)$$

$$Pt(III) + Cr(H_2O)_6^{+2} \xrightarrow{1e^-} Cr(H_2O)_6^{+3} + Pt(II) \quad (6)$$

$$[Pt(NH_3)_5X]^{+3} + Cr(H_2O)_6^{+2} \xrightarrow{2e^-} [Cr(H_2O)_5X]^{+3} + Pt(II) + H_2O \quad (7)$$

$$[Cr(H_2O)_5X]^{+3} + H_2O \rightleftharpoons Cr(H_2O)_6^{+4} + X^- \quad (8)$$

$$[Cr(H_2O)_5X]^{+3} + Cr(H_2O)_6^{+2} \rightarrow [Cr(H_2O)_5X]^{+2} + Cr(H_2O)_6^{+3} \quad (9)$$

$$Cr(H_2O)_6^{+4} + Cr(H_2O)_6^{+2} \rightarrow [(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{+4} + 2\,H^+ \quad (10)$$

X = Halogen

The chromium(III) products from a one-electron reduction of platinum(IV) should consist of equal amounts of $Cr(H_2O)_6^{+3}$ and $[Cr(H_2O)_5X]^{+2}$ since the chromium(II) ion generally reacts by an inner-sphere path and the platinum(III) intermediate would be labile.[7] Two-electron oxidation of chromium(II) should produce some dimeric chromium(III), the exact amount depending on the values of the rate constants and equilibrium constant involved.

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