Aromatic Oxidation by Electron Transfer. I. Oxidations of *p*-Methoxytoluene[1]

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Abstract: This paper reports a detailed kinetic study of the oxidation of *p*-methoxytoluene (PMT) by manganic acetate in acetic acid, and a comparison of the products formed from PMT by oxidation with manganic acetate and other oxidizing agents. The oxidation by manganic acetate seems to involve an initial reversible electron transfer, yielding the ion radical (PMT)+; this then loses a proton in a slow, rate-determining step to form a radical which undergoes rapid further oxidation to *p*-methoxybenzyl acetate.

Although electron-transfer reactions have been a major preoccupation of inorganic chemists in recent years,[2] and although the theory of such processes now seems to be well understood,[3] surprisingly little work has been done on reactions where similar processes occur between organic molecules acting as electron donors and suitable oxidizing agents. Much of the work in this field has, moreover, been concerned with reactions in which stable free radicals are formed as intermediates or products, the main interest lying in the esr spectra of such radicals rather than in the mechanisms of the reactions by which they are formed.

Chemical studies have been mostly confined to oxidations of aliphatic materials, either at an anode, or by metals in high valence states. The Kolbe reaction is the classic example of such an anodic oxidation, while typical examples of reactions involving metal ions are the oxidations by $\mathrm{Co^{III}}$ of formic acid,[4] alcohols and aldehydes,[4] formaldehyde,[5] cyclohexanol,[6] *t*-butyl alcohol,[6] diethyl ketone,[6] and aromatic aldehydes,[7] and oxidations by various metal ions ($\mathrm{Cr^{VI}}$, $\mathrm{V^{V}}$, $\mathrm{Co^{III}}$, $\mathrm{Mn^{III}}$) of formaldehyde, formic acid, and α-hydroxy acids.[8] Similar studies of aromatic systems have been almost entirely confined to cases where relatively stable radicals, formed as intermediates, dimerize, *e.g.*, the oxidative coupling of phenols (Dianin reaction) and the anodic oxidation of dimethylaniline to tetramethylbenzidine.[9] Otherwise the oxidation of aromatic compounds by electron transfer has been a largely neglected field.

This is surprising, for aromatic compounds have relatively low ionization potentials and so should readily undergo oxidation by electron transfer; moreover one might expect such reactions to be of potential synthetic value since the products could well differ from those given by other types of oxidation. There are, moreover, indications in the literature that this may be so. For example the oxidation of methyl substituents in naphthalene to carboxyl by alkaline ferricyanide[10] is an unusual reaction which can be well rationalized in terms of electron transfer; *e.g.*

$$\mathrm{ArCH_3 + Fe(CN)_6^{3-} \longrightarrow (ArCH_3)^+ + Fe(CN)_6^{4-}}$$
$$\mathrm{(ArCH_3)^+ + HO^- \longrightarrow ArCH_2\cdot + H_2O}$$
$$\mathrm{ArCH_2\cdot + Fe(CN)_6^{3-} \longrightarrow ArCH_2^+ + Fe(CN)_6^{4-}\ etc.} \qquad (1)$$

Another possible example is the oxidation of *p*-xylene to *p*-toluic acid by air in presence of a cobalt catalyst in acetic acid, a reaction of practical importance since it forms the first step in the Shell process for manufacturing terephthalic acid. If this involves a normal radical chain autoxidation, it is difficult to see why it should stop at *p*-toluic acid—the more so since methyl *p*-toluate oxidizes easily under the same conditions. The difference between the acid and its ester could be rationalized in terms of the greater radical-stabilizing effect of an ester group; in *p*-toluic acid the methyl group may not be sufficiently activated to allow ready abstraction of hydrogen atoms by peroxide radicals. However in this case *p*-xylene would be expected to react still less readily. These difficulties could be avoided if the oxidation of *p*-xylene involves a different type of chain reaction in which electron transfer is involved; a possible propagation cycle would be

$$\mathrm{ArCH_3 + Co^{III} \longrightarrow (ArCH_3)^+ + Co^{II}}$$
$$\mathrm{(ArCH_3)^+ + AcOH \longrightarrow ArCH_2\cdot + AcOH_2^+}$$
$$\mathrm{ArCH_2\cdot + O_2 \longrightarrow ArCH_2O_2\cdot}$$
$$\mathrm{ArCH_2O_2\cdot + Co^{II} \longrightarrow ArCH_2O_2^- + Co^{III}}$$
$$\mathrm{ArCH_2O_2^- + AcOH_2^+ \longrightarrow ArCH_2O_2H + AcOH} \qquad (2)$$

These examples are of course speculative but they

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(2) See H. Taube, Special Publication No. 13, The Chemical Society, London, 1959, p 57; *Advan. Inorg. Radiochem.*, **1**, 1 (1959); J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 7 (1960); J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

(3) See R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **37**, 853 (1962).

(4) C. E. H. Bawn and A. G. White, *J. Chem. Soc.*, 339, 343 (1915).

(5) G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, **51**, 786 (1955).

(6) D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 965, 971 (1962).

(7) T. A. Cooper and W. A. Waters, *ibid.*, 1538 (1964).

(8) T. J. Kemp and W. A. Waters, *Proc. Roy. Soc.* (London), **A274**, 480 (1963); *J. Chem. Soc.*, 339, 1192, 3193 (1964).

(9) See Z. Galus, R. M. White, F. S. Rowland, and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 2065 (1962).

(10) See R. Weissgerber and O. Kruber, *Ber.*, **52**, 346 (1919); O. Kruber and W. Schade, *ibid.*, **68**, 11 (1935); L. Ruzicka and E. A. Rudolph, *Helv. Chim. Acta*, 10, 915 (1927).

Table I. Oxidation Products from *p*-Methoxytoluene

Expt no.	Oxidizing agent	Temp, °C	Mole ratio, oxidant: PMT	Products, mole %					
				PMT	Anisyl acetate	Anisaldehyde	*p*-Methoxybenzyl acetate	Anisic acid	Efficiency
1	$Mn(OAc)_3$	70	1:10	94.4	5.27	0.30	...	...	117
2	$Mn(OAc)_3$	70	1:1	54.1	40.5	4.62	0.86	...	101
3	$Mn(OAc)_3$	70	2:1	26.8	58.5	11.9	1.69	1.0	90
4	$Mn(OAc)_3$	117	2:1	38.0	50.2	7.4	4.5	...	70
5	$Mn(OAc)_3 + O_2$	25	1:10	93.2	50.82	0.83	0.20	...	150
6	$Co(OAc)_3$	25	1:10	93.4	5.38	1.18	...	...	150
7	$Co(OAc)_3$	25	1:1	72.0	23.4	4.3	...	0.3	57
8	$Co(OAc)_3$	25	2:1	60.9	34.9	3.9	...	0.5	44
9	$KMnO_4$	25	1:10	99.8	...	...	...	0.2	...
10	$KMnO_4$	25	1:1	87.4	10.4	0.77	...	1.4	30
11	$KMnO_4$	25	2:1	70.1	16.1	2.12	3.89	7.75	42
12	$Pb(OAc)_4$	70	1:1	57.4	41.4	1.2	...	...	90
13	$Pb(OAc)_4$	70	2:1	35.8	61.5	1.34	1.37	...	70
14	CrO_3	25	1:10	97.3	...	2.63	...	1.0	165
15	CrO_3	25	1:1	93.8	0.57	5.51	...	7.0	80
16	CrO_3	25	2:1	65.5	0.64	33.8	...	18.0	110

seem to emphasize the potential interest of aromatic electron-transfer reactions and the need for further experimental work. This paper is the first of a series describing a general survey of aromatic oxidations under conditions that might lead to electron transfer, from the viewpoint both of mechanism and potential use in synthesis. Our object here was to study in detail one reaction of this type, to see if we could find definite evidence for electron transfer.

Preliminary Studies

Our first objective was to find a suitable system for kinetic study. For this we needed a homogeneous reaction in which some suitable organic substrate would be oxidized cleanly to a single product, using an oxidizing agent which would be expected from analogy to act by electron transfer. A survey of the literature, together with extensive preliminary experiments, led us to select manganic acetate in acetic acid as the oxidizing agent and *p*-methoxytoluene (PMT) as the substrate. These react together at a convenient rate to form anisyl acetate as the main product, the over-all reaction being

$$MeOC_6H_4CH_3 + 2Mn(OAc)_3 \longrightarrow MeOC_6H_4CH_2OAc + AcOH + 2Mn(OAc)_2 \quad (3)$$

Table I shows the proportions of products formed by oxidizing PMT with various oxidizing agents in acetic acid, the reactions being carried out in stoppered flasks, but without exclusion of air. The anisaldehyde was probably an artifact, formed by pyrolysis of *p*-methoxybenzylidenediacetate during analysis by glpc. The last column lists the efficiency with which PMT was removed, calculated from the rate of disappearance of Mn^{III} and eq 3 (*i.e.*, 100% efficiency corresponds to loss of 1 mole of PMT per 2 moles of manganic ion reduced).

Several conclusions follow at once from these results.

(a) The main product from PMT and manganic acetate is indeed anisyl acetate; the relatively small yield of anisaldehyde, even in the presence of large amounts of Mn^{III}, implies that secondary oxidations were relatively slow.

(b) Autoxidation can play an important role, particularly at 70°; this is indicated by the high efficiencies, and by the increase in efficiency in an experiment (no. 5) where oxygen was bubbled through the reacting solution. The products, however, remained essentially unchanged.

(c) The oxidizing agents seem to fall into three distinct groups. Lead tetraacetate gave anisyl acetate as almost the sole product, even when present in large mole ratio; Mn^{III} and Co^{III} also gave anisyl acetate predominantly, but here anisaldehyde was a major byproduct; chromium trioxide and potassium permanganate differed from the other oxidants in giving large amounts of anisic acid.

Small amounts of other products were also formed in these reactions; these included 2- and 3-acetoxy-4-methylanisole and 1,2-bis(*p*-anisyl)ethane.

Kinetic Results and Analysis

Two series of rate measurements were carried out for the reactions between PMT and manganic acetate in acetic acid, at 70° and at 100°; oxygen was carefully excluded in each case to avoid interference from autoxidation. The reactions were followed by iodometric titration of Mn^{III}. Since Mn^{II} acts as a retarder and is formed in the reaction, individual runs followed no simple kinetic law; in preliminary work we therefore followed only the early stages (*ca.* 10%) of the reaction, assuming that the average rate over this period could be equated to the initial rate. The "initial rates" so found, for reactions at 70°, are shown in Table II.

Figure 1 shows a plot of "initial rate" *vs.* initial concentration of PMT, the initial concentration of Mn^{III} being constant and no Mn^{II} being added initially; the linearity of this plot suggests that the over-all reaction is of first order with respect to PMT. Figure 2 shows a similar plot of "initial rate" *vs.* the reciprocal of initial Mn^{II} concentration; evidently the reaction seems to be of inverse first order with respect to Mn^{II}. Figure 3 shows a similar plot of "initial rate" *vs.* initial concentration of Mn^{III}; here again a linear plot is obtained, implying a first-order dependence. It is true that the line does not pass through the origin, as it should; however this discrepancy could well be due to errors in equating average rates over the first part of the reaction to true initial rates—particularly in the case

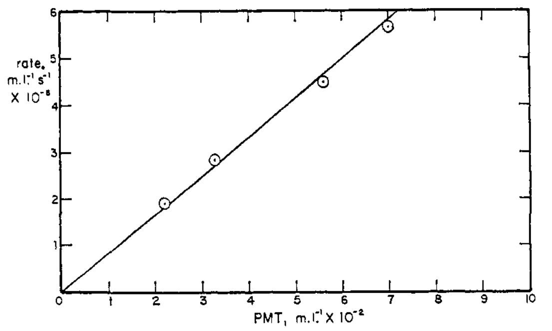

Figure 1. Plot of "initial rate" *vs.* initial concentration of PMT; initial concentration of Mn^{III}, 6.33 × 10^{-2} ml^{-1}; no Mn^{II} added initially.

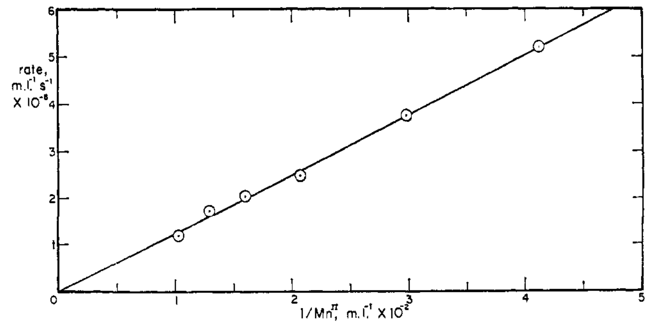

Figure 2. Plot of "initial rate" *vs.* reciprocal of initial concentration of Mn^{II}; initial concentrations of PMT, 0.142 ml^{-1}; of Mn^{III}, 0.134 ml^{-1}.

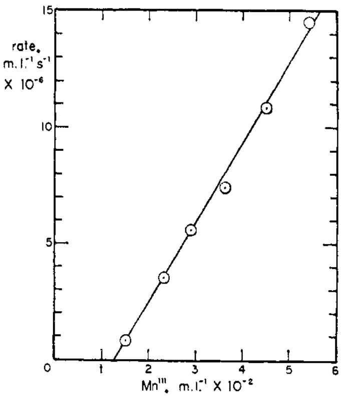

Figure 3. Plot of "initial rate" *vs.* initial concentration of Mn^{III}; initial concentration of PMT, 0.2 ml^{-1}; no Mn^{II} added initially.

of runs where no Mn^{II} was added initially, the reaction being very sensitive to the concentration of Mn^{II} when this is low. These preliminary studies therefore indicated that the kinetics of the reaction are probably consistent with the following rate law.

Table II. "Initial Rates" of Oxidation of PMT by Manganic Acetate in Acetic Acid at 70°

Initial concn, ml^{-1} × 10^2			"Initial rate" of reduction of Mn^{III}, ml^{-1} sec^{-1} × 10^6
PMT	$Mn(OAc)_3$	$Mn(OAc)_2$	
2.19	6.33	0	1.90
3.28	6.33	0	2.85
5.60	6.33	0	4.48
7.00	6.33	0	5.66
14.2	3.14	0.243	5.20
14.2	3.14	0.336	3.75
14.2	3.14	0.485	2.50
14.2	3.14	0.626	2.05
14.2	3.14	0.777	1.73
14.2	3.14	0.970	1.18
20.0	1.51	0	0.79
20.0	2.31	0	3.53
20.0	2.88	0	5.51
20.0	3.61	0	7.41
20.0	4.51	0	10.86
20.0	5.41	0	14.50

$$-\frac{d[Mn^{III}]}{dt} = \frac{k[Mn^{III}][PMT]}{[Mn^{II}]} \tag{4}$$

Since the reaction gives *p*-anisyl acetate (PAA) as almost the sole product, the over-all course of the reaction must presumably be

$$PMT + 2Mn(OAc)_3 \longrightarrow PAA + 2Mn(OAc)_2 + AcOH \tag{5}$$

In that case

$$\frac{d[PMT]}{dt} = \frac{1}{2}\frac{d[Mn^{III}]}{dt} \tag{6}$$

To check this kinetic expression, we carried out an extensive series of runs at 100° in which the reaction was followed to high conversions, and analyzed the results rigorously in terms of eq 4. Integration of this leads to the following expression for the constant *k*

$$k = \frac{2}{t(2b - a)}(a + c) \log \frac{a}{x} - (2b + c) \log \frac{2b}{x + 2b - a} \tag{7}$$

where *a*, *b*, *c* are the initial concentrations of Mn^{III}, PMT, and Mn^{II}, respectively, and *x* is the concentration of Mn^{III} at time *t*. Table III shows rate constants calculated for a range of initial concentrations of the reactants, using eq 7 and a CDC 1604 computer. Although these values show some scatter, there is no systematic variation, apart from a tendency for *k* to be high in runs at the lowest (0.015 *M*) concentrations of Mn^{III}, particularly at high conversions. If this effect were real, it would be very puzzling, for it would imply that order of the reaction with respect to Mn^{III} becomes *less* than unity at low concentrations of Mn^{III}. It seems more likely that the drift was due to the presence of undetected traces of oxidizable impurities in the solvent, in spite of the precautions taken to purify it. Apart from this one discrepancy, the results in Table IV suggest that the reaction does follow the rate law of eq 4 reasonably well.

To provide further insight into the reaction, we also studied the effect of added base (sodium acetate) on the "initial rate" of the reaction at 70°, and the effect of replacing the α-hydrogen atoms of PMT by deuterium; the results are shown in Tables IV and V.

Some experiments were also carried out on the oxidation of compounds other than PMT; Table VI shows initial rates of oxidation of anisyl alcohol, anisyl acetate, and anisyl methyl ether, as functions of substrate concentration. All three reactions were of

Table III. Rate Constants Calculated from Equation 7

No. of measurements	Initial concn, ml^{-1} × 10^2 PMT	Mn^{II}	Mn^{III}	Rate constant, ml^{-1} sec^{-1} × 10^5
22	2.19	0	5.32–5.85	5.00
28	3.28	0	5.34–5.77	5.34
19	5.60	0	5.34–5.82	5.07
17	7.00	0	5.37–5.76	5.30
9	20.00	0	1.50–1.54	6.31
11	20.00	0	2.29–2.33	6.44
10	20.00	0	2.93	5.87
13	20.00	0	3.51–3.66	5.59
8	20.00	0	4.51	6.01
12	20.00	0	5.46–5.78	5.46
10	20.00	0.45	1.46–1.55	10.27
16	20.00	0.45	2.25–2.39	8.25
8	20.00	0.45	2.97–3.00	7.96
8	20.00	0.45	3.55–3.58	6.98
7	20.00	0.45	4.33–4.48	7.02
12	20.00	0.45	5.26–5.36	7.65
12	1.42	0.24	3.09–3.12	7.42
12	1.42	0.34	3.10–3.12	5.95
12	1.42	0.49	2.90–3.11	5.95
16	1.42	0.63	3.11	5.75
16	1.42	0.78	3.11–3.14	6.35
11	1.42	0.97	3.09–3.17	5.99

Table IV. Effect of Sodium Acetate on the "Initial Rate" of Oxidation of PMT by Mn(OAc)$_3$ at 70°

Initial concn, ml^{-1} × 10^2			"Initial rate" of reduction of Mn^{III}, sec^{-1} × 10^5
PMT	Mn(OAc)$_3$	NaOAc	
14.2	3.15	0	1.18
		0.257	1.21
		2.05	1.18
		4.12	1.20
2.19	6.33	0	0.17
		2.05	0.19

Table V. Measurement of Deuterium Isotope Effect in Oxidation of PMT-α,α,α-d_3 by Mn(OAc)$_3$ (0.0633 *M*) at 70°

Initial concn of PMT or PMT-α,α,α-d_3, ml^{-1} × 10^2	"Initial rate" of reduction of Mn^{III}, ml^{-1} sec^{-1} × 10^6		
	PMT-α,α,α-d_3	PMT^a	Ratio
1.19	0.228	1.17	5.1
3.56	0.667	2.98	4.5

[a] Interpolated from Figure 1.

Table VI. "Initial Rates" of Oxidation of Anisyl Derivatives in Acetic Acid at 70° by Manganic Acetate (0.0633 *M*)

Compound	Concn, ml^{-1} × 10^2	"Initial rate" of reduction of Mn^{III}, ml^{-1} sec^{-1} × 10^6
Anisyl alcohol	0.657	0.428
	1.10	0.828
	1.75	1.33
	2.19	1.69
	3.29	2.53
Anisyl methyl ether	3.29	0.673
	6.33	1.15
	9.50	1.70
	12.7	2.13
	15.8	2.68
Anisyl acetate	23.4	0.76
	35.1	1.01
	46.8	1.32
	58.5	1.61

Table VII. Relative Rates of Oxidation of Anisyl Derivatives by Manganic Acetate in Acetic Acid at 70°, at Equal Concentrations of Mn^{III} and Substrate

Compound	Relative rate
PMT	1
Anisyl alcohol	0.95
Anisyl methyl ether	0.21
Anisyl acetate	0.035

first order with respect to the anisyl derivative; at equal initial concentrations of Mn^{III} and anisyl derivative, the relative rates of oxidation were as shown in Table VII.

Discussion

The most salient point about the PMT-Mn^{III} reaction is the inverse dependence of the rate on the concentration of Mn^{II}. There are three ways in which this dependence might arise.

(a) The oxidation might be a radical chain process in which Mn^{II} acts as a retarder; this seems extremely unlikely. The reaction shows none of the characteristics of chain reactions, and the rate is relatively little affected by the presence or absence of oxygen.

(b) The Mn^{II} might act by removing either Mn^{III} or PMT by forming an inert complex; however this could lead to a simple inverse dependence of the rate on Mn^{II} concentration only if the latter were much greater than the concentration of the other species involved. In fact the inverse dependence holds even when the concentration of Mn^{II} is less than that of either PMT or Mn^{III}.

(c) The only remaining alternative is that the oxidation takes place in steps. If Mn^{III} is converted to Mn^{II} in a reversible step preceding the rate-determining step, and if the equilibrium constant for this is small, then the over-all rate will vary inversely as the concentration of Mn^{II}.

This reversible step cannot be a disproportionation of Mn^{III} to Mn^{II} and Mn^{IV}, as has been postulated by Rosseinsky[11] in the reaction between mercurous and manganic ions, for a mechanism of this type, *e.g.*

$$\begin{aligned} 2\mathrm{Mn^{III}} &\rightleftharpoons \mathrm{Mn^{II}} + \mathrm{Mn^{IV}} \\ \mathrm{Mn^{IV}} + \mathrm{PMT} &\longrightarrow \text{product} \end{aligned} \tag{8}$$

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[11] D. R. Rosseinsky, *J. Chem. Soc.*, 1181 (1963). Rosseinsky states that his rate expression cannot be derived from a kinetic scheme in which $\mathrm{Hg_2}^{2+}$ reacts with Mn^{III}; this, however, is not the case. The following scheme leads to the same rate expression for the oxidation of $\mathrm{Hg_2}^{2+}$ (*i.e.*, first order in $\mathrm{Hg_2}^{2+}$, second order in Mn^{III}, inverse first order in Mn^{II}) if k_1/k_{-1} is small and the initial equilibrium is established rapidly.

$$\mathrm{Hg_2}^{2+} + \mathrm{Mn^{III}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Hg_2}^{3+} + \mathrm{Mn^{II}}$$

$$\mathrm{Hg_2}^{3+} + \mathrm{Mn^{III}} \xrightarrow{k_2} 2\mathrm{Hg}^{2+} + \mathrm{Mn^{II}}$$

The other term in Rosseinsky's expression, representing the oxidation of Hg^0 by Mn^{III}, would remain unchanged.

would not lead to a first-order dependence of the rate on the concentration of $\mathrm{Mn^{III}}$. We therefore seem to be forced to the conclusion that the reversible reaction must be one between PMT and $\mathrm{Mn^{III}}$ to form an intermediate X. This is then converted to the products in a slow rate-determining step in which neither $\mathrm{Mn^{III}}$ nor $\mathrm{Mn^{II}}$ is involved; *i.e.*

$$\mathrm{Mn^{III}} + \mathrm{PMT} \overset{K}{\rightleftarrows} \mathrm{Mn^{II}} + \mathrm{X}$$

$$\mathrm{X} \xrightarrow{k'} \text{product} \qquad (9)$$

This will lead to a rate expression of the correct form (eq 4) if K is small; the constant k in eq 4 is then given by

$$k = Kk' \qquad (10)$$

Now the reaction shows a large deuterium isotope effect (Table V); evidently the breaking of the bond to the α hydrogen takes place in the slow rate-determining step. This argument seems to leave us with no alternative but to suppose that X is an ion radical derived from PMT by loss of an electron; the slow reaction must then be loss of a proton from X to give an anisyl radical. Since the ionization potential of this radical must be much less than that of PMT, it would be expected to undergo rapid oxidation by $\mathrm{Mn^{III}}$ to the corresponding carbonium ion—which would of course at once combine with solvent to form anisyl acetate. The evidence therefore strongly supports the following mechanism for the over-all reaction (Ar = *p*-methoxyphenyl).

$$\mathrm{ArCH_3} + \mathrm{Mn^{III}} \overset{K}{\rightleftarrows} (\mathrm{ArCH_3})^+ + \mathrm{Mn^{II}}$$

$$(\mathrm{ArCH_3})^+ \xrightarrow{k'} \mathrm{ArCH_2}\cdot + \mathrm{H^+}$$

$$\mathrm{ArCH_2}\cdot + \mathrm{Mn^{III}} \xrightarrow{\text{fast}} \mathrm{ArCH_2^+} + \mathrm{Mn^{II}}$$

$$\mathrm{ArCH_2^+} + \mathrm{AcOH} \xrightarrow{\text{fast}} \mathrm{ArCH_2OAc} + \mathrm{H^+} \qquad (11)$$

In this mechanism the rate-determining step is loss of a proton from the ion radical $\mathrm{PMT^+}$. How then can we explain the insensitivity of the rate to the presence of added base (Table IV)? The explanation probably lies in the fact that the dissociation constants of metal acetates in acetic acid are low (1.3×10^{-6} for sodium acetate,[12] 5.5×10^{-11} for manganous acetate[13]). If manganic acetate is essentially undissociated in acetic acid, the first step in the oxidation of PMT will be a reaction between neutral PMT and undissociated $\mathrm{Mn(OAc)_3}$. When the ion radical $\mathrm{PMT^+}$ is formed, an acetate ion will be formed simultaneously; these will exist for an appreciable period as an intimate ion pair. If the radical $\mathrm{ArCH_2}\cdot$ is formed by internal proton transfer inside this ion pair, then of course added base would not be expected to have a significant effect on the rate. If this explanation is accepted, eq 11 should be modified thus

$$\mathrm{ArCH_3} + \mathrm{Mn(OAc)_3} \overset{K}{\rightleftarrows} [(\mathrm{ArCH_3})^+, \mathrm{AcO^-}] + \mathrm{Mn(OAc)_2}$$

$$[(\mathrm{ArCH_3})^+, \mathrm{AcO^-}] \xrightarrow{k'} \mathrm{ArCH_2}\cdot + \mathrm{AcOH} \qquad (12)$$

The mechanism of eq 12 is also consistent with our other observations. Thus while the over-all rate of the reaction is little affected by the presence of oxygen, the efficiency of the reaction increases (Table I); this can be attributed to an alternative reaction of the intermediate anisyl radicals with oxygen instead of with $\mathrm{Mn^{III}}$. Again, the retarding effect of methoxyl and acetoxyl might be expected (Table VII), for since these are +I groups, the ionization potentials of anisyl acetate and anisyl methyl ether must be significantly greater than that of PMT, and the equilibrium constants k_1 correspondingly smaller. This decrease in k_1 will be offset to some extent by an increase in k_2, due to the stabilizing effect of methoxyl or acetoxyl on the anisyl radical—but these groups are poor stabilizers of radicals. The fact that anisyl alcohol reacted faster than its acetate or methyl ether is also easily understood; the hydroxyl group is known to be a much less electron-withdrawing substituent in solvents such as acetic acid, due to hydrogen bonding between it and the solvent.

Thus there seem to be good reasons for believing that the oxidation of PMT by $\mathrm{Mn^{III}}$ is an electron-transfer process; if so, it would be easy to explain the differences between different oxidizing agents (Table I) in terms of different reaction mechanisms. There are three different basic processes by which PMT might be oxidized to anisyl acetate, the key steps involving abstraction of an electron, hydrogen atom, or hydride ion, respectively, from the PMT; different mechanisms could lead to different products.

Acetoxylation by lead tetraacetate seems as a rule to be a radical chain process, involving the following propagation cycle

$$\mathrm{R}\cdot + \mathrm{Pb(OAc)_4} \longrightarrow \mathrm{ROAc} + \mathrm{Pb(OAc)_3}\ (\text{or } \mathrm{Pb(OAc)_2} + \mathrm{AcO}\cdot)$$

$$\mathrm{RH} + \mathrm{Pb(OAc)_3}\ (\text{or } \mathrm{Pb(OAc)_2} + \mathrm{AcO}\cdot) \longrightarrow \mathrm{R}\cdot + \mathrm{Pb(OAc)_2} + \mathrm{AcOH} \qquad (13)$$

Reactions of this type can easily be controlled to give monoacetoxylation, the product undergoing further oxidation with relative difficulty; this presumably is due to the small radical-stabilizing effect of the acetoxy group, combined with steric and electrostatic repulsions between it and the oxidizing agent. The differences in products between lead tetraacetate on the one hand, and $\mathrm{Mn^{III}}$ and $\mathrm{Co^{III}}$ on the other, could well be explained on this basis; $\mathrm{Co^{III}}$ presumably resembles $\mathrm{Mn^{III}}$, acting as an electron acceptor.

Oxidation of arylmethanes by chromium trioxide seems on the other hand to involve hydride abstraction, there being good evidence that the intermediates are carbonium ions rather than radicals.[14] If the oxidation of PMT by chromium trioxide follows a mechanism of this kind, *e.g.*

$$\mathrm{ArCH_3} + \mathrm{CrO_3} \longrightarrow \mathrm{ArCH_2^+} + \mathrm{HCrO_3^-}$$

$$\mathrm{ArCH_2^+} + \mathrm{AcOH} \longrightarrow \mathrm{ArCH_2OAc} + \mathrm{H^+} \qquad (14)$$

one could easily understand the strong tendency toward further oxidation (Table I), for since acetoxy is a −E group, it should act as a powerful stabilizer toward carbonium ions, and so the further oxidation of anisyl acetate, leading ultimately to anisic acid, could compete with attack on unchanged PMT.

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Experimental Section

Manganic Acetate. Manganic acetate dihydrate ($Mn(OAc)_3 \cdot 2H_2O$) was prepared by a modification of Christiansen's procedure.[15] A mixture of anhydrous manganous acetate (303 g) and glacial acetic acid (4.4 kg) was boiled under reflux for 2 hr; potassium permanganate (68.2 g) was then added and the mixture stirred under reflux for 45 min, then allowed to cool while water (750 ml) was added dropwise. The crude $Mn(OAc)_3 \cdot 2H_2O$ was collected after 3 days and recrystallized from a mixture of glacial acetic acid (2.1 l.) and water (425 ml).

Anal. Calcd for $C_6H_{13}O_8Mn$: C, 26.87; H, 4.85; Mn, 20.52. Found: C, 26.70; H, 4.67; Mn, 20.77.

4-Methoxybenzylidene Diacetate. Anisaldehyde (12 ml) was added over 20 min to acetic anhydride (18 ml) and Dowex 50WX8 resin (1 g), the mixture being maintained at 60° by controlling the rate of addition. After a further 10 min at 60°, the mixture was filtered into water (200 ml) and excess sodium bicarbonate. A solution of the crude product in ether was poured through a 1 × 20 cm of Woelm neutral alumina and evaporated to dryness, and the residue was crystallized twice from petroleum ether (bp 30–35°) giving white plates (6.1 g, 25%), mp 65–66°.

Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.5; H, 5.9. Found: C, 60.8; H, 6.1.

2-Acetoxy-4-methylanisole. 2-Amino-4-methylanisole (50 g, technical grade) was recrystallized from petroleum ether (bp 30–35°) and dissolved in water (150 ml) and 98% sulfuric acid (50 g), and the insoluble impurities were extracted with chloroform. The solution was diazotized at 0° and then added slowly to a boiling mixture of water (750 ml), 98% sulfuric acid (5 ml), copper sulfate (200 g of $CuSO_4 \cdot 5H_2O$), urea (22 g), and charcoal (2 g), and the resulting phenol was steam distilled and acetylated with acetic anhydride containing a little sulfuric acid. Dilution with water and recrystallization from petroleum ether (bp 30–35°) gave 2-acetoxy-4-methylanisole (12 g, 16%), mp 59.5–60° (lit.[16] 56–57°).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.7; H, 6.7. Found: C, 66.7; H, 6.6.

3-Acetoxy-4-methylanisole. Hydrazine hydrate (24 ml) was added slowly to a refluxing mixture of 3-nitro-4-methylanisole[17] and palladized charcoal (0.2 g, 10%) in ethanol (150 ml). The solution was filtered into water (850 ml) and extracted with methylene chloride, and the dried organic layer was treated with excess hydrogen chloride. The resulting 3-amino-4-methylanisole hydrochloride was converted as above into 3-hydroxy-4-methylanisole which was acetylated with acetic anhydride–pyridine and distilled at 138° (16 mm) as an oil (14 g), $n^{27}D$ 1.5085, which solidified on cooling, mp 22°.

Anal. Found: C, 66.8; H, 6.9.

3-Acetoxy-4-methylbenzyl Acetate. Prepared by borohydride reduction of isovanillin followed by acetylation with acetic anhydride–pyridine, the diacetate after recrystallization from petroleum ether (bp 30–35°) had mp 64–65°.

Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.5; H, 5.9. Found: C, 60.6; H, 6.1.

***p*-Methoxytoluene-α,α,α-d_3.** A solution of aluminum chloride (17 g) in dry ether (50 ml) was added over 5 min with stirring to one of lithium aluminum deuteride (2.1 g, 96%) in dry ether (40 ml). Redistilled anisoyl chloride (5 g) was added dropwise, the solution boiled under reflux for 30 min, then cooled, and excess methyl formate added. The ethereal solution was washed with dilute hydrochloric acid, dried ($MgSO_4$), and evaporated, and the residual oil was distilled, giving 4-methoxytoluene-α,α,α-d_3 in 85% yield, bp 76–77° (10 mm), $n^{30}D$ 1.5067, deuterium content (nmr), 96%.

The remaining materials were of reagent grade, from Matheson Coleman and Bell Co. Acetic acid was purified by the procedure of Orton and Bradfield.[18] Anhydrous manganous acetate was prepared by dehydrating the tetrahydrate under vacuum at 100° for not less than 3 days.

Procedure. The kinetic apparatus consisted of a 400-ml jacketed glass reaction vessel, with jacket inlet at the bottom and outlet at the top, three jacketed joints of varying sizes for condenser, thermometer, and for the admission of reactants, and a flat bottom permitting the use of a magnetic stirrer. A copious flow of steam was passed through the jacket and condensed by contact with water in a Vigreux column. In this way the temperature inside the reaction vessel could be easily maintained within a 0.1° range. Glacial acetic acid (200 ml) was first heated to the reaction temperature (99°) and weighed samples of manganic acetate, and (if required) of manganous acetate, were then added. When thermal equilibrium had been reattained (*ca.* 4 min), a sample of the solution was withdrawn for analysis, and a weighed amount of preheated PMT then added. Further samples were withdrawn at appropriate intervals. Each sample was rapidly chilled in ice–water and two or three separate estimations of Mn^{III} were carried out iodometrically on 1-ml portions.

Glpc Analysis of Products. Analytical glpc's were run on an F & M Model 500 chromatograph, using an 8 ft × 1/8 in. stainless steel column packed with 20% silicone gum rubber on Chromosorb P with a helium flow rate of 50 cc/min and a column temperature of 175°. Peak heights were calibrated for each component and the accuracy (±1%) of the analyses checked by running synthetic mixtures.

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