Aromatic Oxidation by Electron Transfer. III.[1] Oxidation of 1- and 2-Methoxynaphthalene by Manganic Acetate[2]

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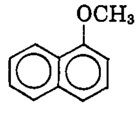
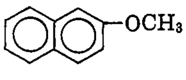
Abstract: Kinetic studies of the oxidations of 1- (I) and 2-methoxynaphthalene (II) by manganic acetate in acetic acid are reported. Both reactions follow the kinetic scheme established[3] for the analogous oxidation of *p*-methoxytoluene, indicating that the first step involves the reversible abstraction of an electron from the aromatic substrate by Mn^{III}. The products of oxidation at low conversions were 4-methoxy-1-napthyl acetate (IIIb) and 2-methoxy-1,4-naphthoquinone (IV), respectively.

Previous papers[1,3] of this series have indicated that the oxidation of aromatic ethers by manganic acetate in acetic acid probably involve a preliminary reversible electron transfer from the ether to Mn^{III}, giving an ion radical which undergoes a slow rate-determining reaction to form the final product. The purpose of the present investigation was to obtain further evidence for the mechanism proposed in part I[3] of this series by studying the kinetics of some further reactions of this type.

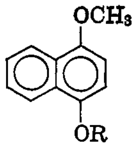
We were guided in our choice of substrates by the qualitative studies reported in part II[1] of this series; these seemed to suggest that 1- (I) and 2-methoxynaphthalene (II) undergo oxidation clearly *via* the corresponding cation radicals as intermediates, these combining with acetic acid in a slow rate-determining step to give neutral radicals which undergo rapid further oxidation to the final products.



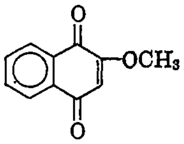
I



II.



III; a, R = H
b, R = Ac



IV

Experimental Section

Materials. Acetic acid and manganous and manganic acetates were prepared and/or purified by the methods described in part I.[3] The methoxynaphthalenes (I, II) were commercial samples (from Eastman Chemicals Co.); they were purified before use and were shown to be homogeneous by glpc.

Procedure. The reactions were carried out at 100° using the steam-jacketed vessel and procedure described in part I.[3] Initial rates were measured over the first 5–10% of the reaction, while the results over a range of conversions were analyzed as before, using the same computer program.

Products of Reaction. The products were obtained by carrying out runs under the usual kinetic conditions to *ca.* 10% conversion, followed by addition of ferrous chloride and water to quench the reaction and extraction with methylene chloride. The products were identified by comparison with authentic[1] specimens, using glpc and infrared and ultraviolet spectroscopy.

Results

Products of Reaction. Only a single product was obtained by oxidation of I or II with manganic acetate under the conditions of our kinetic runs. Oxidation of I gave 4-methoxy-1-naphthyl acetate (III), while oxidation of II gave 2-methoxy-1,4-naphthoquinone (IV). None of the other products previously[1] obtained from I could be detected.

Kinetics of Oxidation. Both reactions seemed to follow the kinetic scheme of part I,[3] *i.e.*

$$-\frac{d[Ar]}{dt} = \frac{k[Ar][Mn^{III}]}{[Mn^{II}]} \qquad (1)$$

where Ar represents the aromatic substrate. The initial rates of oxidation were first order with respect to Ar and Mn^{III}, and inverse first order with respect to Mn^{II}; illustrative plots for the oxidation of I are shown in Figures 1–3.

The kinetic runs were analyzed using the integrated form[3] of eq 1, the calculations being carried out with the CDC 1604 digital computer at the Computation Center of The University of Texas. The results are listed in Table I for I and in Table II for II.

Table I. Rate Constants Calculated from Integrated Rate Equation for 1-Methoxynaphthalene (I)

Initial concn, $ml^{-1} \times 10^{-3}$ I	Mn^{II}	Mn^{III}	Rate constant, $ml^{-1}\,sec^{-1} \times 10^{4}$ (calcd from titer) Time, sec 300	600
16.90	4.50	8.98	1.59	1.72
25.32	4.50	9.05	1.77	1.79
21.62	4.50	4.06	1.62	1.44
21.62	4.50	5.44	1.79	1.85
21.62	4.50	6.75	1.73	...
21.62	6.75	4.18	1;47	1.54
21.62	6.75	5.48	1.63	1.81
21.62	6.75	6.67	1.64	1.54
21.62	9.00	4.05	1.48	1.52
21.62	9.00	5.46	1.44	...
21.62	9.00	6.94	1.37	...

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[1] Part II: T. Aratani and M. J. S. Dewar, *J. Am. Chem. Soc.*, **88**, 5479 (1966).

[2] This work was supported by the Air Force Office of Scientific Research through Grant AF-AFOSR-1050-66.

[3] Part I: P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).

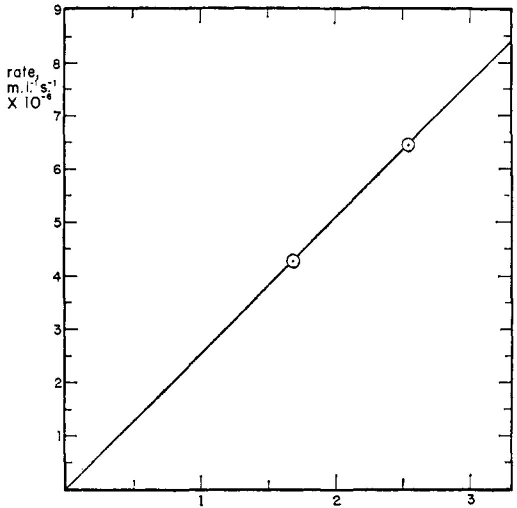


Figure 1. Plot of initial rate of oxidation of I at 100° *vs.* [II]; [Mn^{III}] = 9 × 10^{-3} ml^{-1}; [Mn^{II}] = 4.50 × 10^{-3} ml^{-1}.

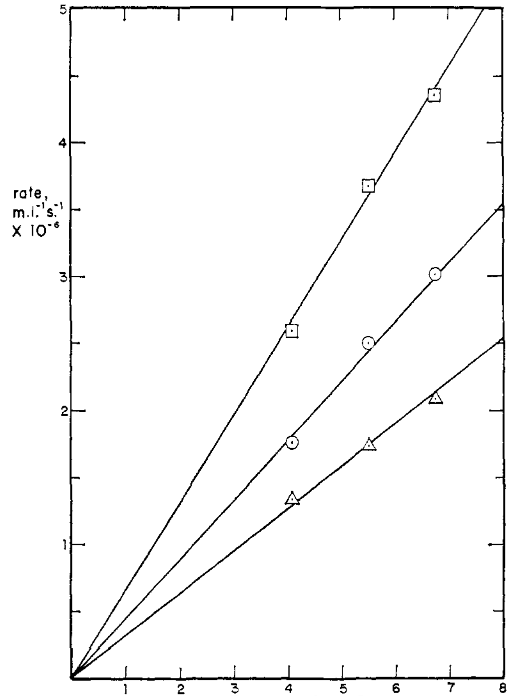


Figure 2. Plot of initial rate of oxidation of I at 100° *vs.* [Mn^{III}]; [II] = 2.16 × 10^{-2} ml^{-1}; [Mn^{II}] = 4.50 × 10^{-3} ml^{-1}, ⊡; 6.75 × 10^{-3} ml^{-1}, ⊙; 9.00 × 10^{-3} ml^{-1}, △.

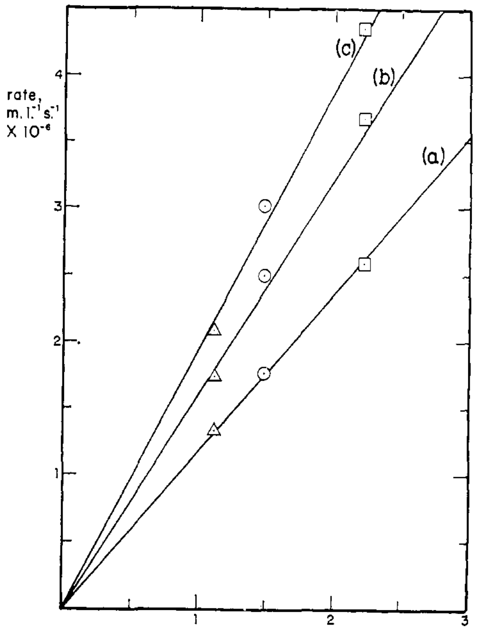


Figure 3. Plot of initial rate of oxidation of I at 100° *vs.* [Mn^{II}]$^{-1}$; [II] = 2.16 × 10^{-2} ml^{-1}; [Mn^{III}] = (a) 4.05 × 10^{-3} ml^{-1}; (b) 5.50 × 10^{-3} ml^{-1}; (c) 6.75 × 10^{-3} ml^{-1}.

Discussion

The results shown in Tables I and II and Figures 1–3 suggest that the oxidations of I and II do indeed follow the same kinetic scheme (eq 1) as that previously deduced[3] for the analogous oxidation of *p*-methoxytoluene. The general course of these oxidations therefore seems to follow the pattern suggested in part I,[3] *i.e.*

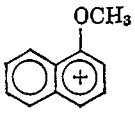
$$\mathrm{Ar} + \mathrm{Mn^{III}} \rightleftharpoons \mathrm{Ar^{+}} + \mathrm{Mn^{II}} + \mathrm{AcO^{-}} \qquad (2)$$

$$\mathrm{Ar^{+}} + \mathrm{AcO^{-}} \xrightarrow{\text{slow}} \mathrm{R} \xrightarrow[\text{fast}]{\mathrm{Mn^{III}}} \text{product} \qquad (3)$$

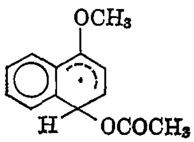
where Ar$^+$ represents a cation radical formed from Ar by abstraction of an electron, while R is a neutral radical formed from Ar$^+$ by reaction with acetic acid or acetate ion. In the oxidation of I the intermediates will be V and VI, respectively; in the oxidation of II they will be VII and VIII.

Table II. Rate Constants Calculated from Integrated Rate Equation for 2-Methoxynaphthalene (II)

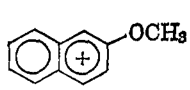
Initial concn, ml^{-1} × 10^{-3} II	Mn^{II}	Mn^{III}	Rate constant, ml^{-1} sec^{-1} × 10^4 (calcd from titer) Time, sec 300	600
16.90	4.50	8.92	1.11	1.21
25.32	4.50	9.00	1.17	1.18
21.62	4.50	4.03	1.24	1.25
21.62	4.50	5.54	1.15	1.23
21.62	4.50	6.66	1.19	1.33
21.62	6.75	4.03	1.16	1.09
21.62	6.75	5.40	1.22	1.30
21.62	6.75	6.76	1.18	1.25
21.62	9.00	4.04	1.20	1.21
21.62	9.00	5.45	1.32	1.23
21.62	9.00	6.67	1.35	1.52



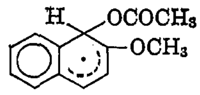
V



VI



VII



VIII

If this mechanism is correct, one might expect the over-all rate for a given type of oxidation to be determined mainly by the preequilibrium of eq 2, for the reactions of the intermediate ion radicals with acetate ion are likely to be very fast and so relatively unselective. If so, there should be a parallel between the ionization potential of the aromatic ether and its rate constant.

In order to apply this criterion to the rate constants for oxidation of I, II and *p*-methoxytoluene, it was necessary to know their relative ionization potentials. Unfortunately these have not been reported and we had no facilities for measuring them directly; we therefore made use of the well-known[4] relation between the ionization potentials of a series of aromatic compounds and the frequencies of the charge-transfer bonds of complexes formed by them with a suitable acceptor. For our purpose we chose tetracyanoethylene (TCNE).

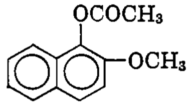
Table III shows the charge-transfer spectra observed for these complexes; each spectrum consisted of two bands, no doubt corresponding to ionization from the two highest occupied orbitals of the ether. Since the band at lower frequency must be the one that correlates with the ionization potential, one can then conclude that the ionization potentials fall in the order *p*-methoxytoluene (PMT) > II > I.

Table III. Charge-Transfer Maxima and Rate Constants for Aryl-Dependent Reactions

Compound	λ_{max}, mμ	Rate constant, ml^{-1} sec^{-1} $\times$ 10^5
I	657,432	7.96
		8.59
		8.87
		8.97
II	618,489	1.85
		2.02
		1.95
		1.97
PMT	565,395	3.01
		3.19

To compare these with the rates of oxidation, it is necessary to know the relative rates of oxidation of the three ethers under comparable conditions. These are given by dividing the over-all rate constants listed in part I[3] and Tables I and II by the number of equivalents of Mn^{III} taking part in the reaction, for the listed rate constants refer to the rate of disappearance of Mn^{III} rather than the rate of the primary attack on the ether. The products of reaction indicate that the oxidation of PMT or I required 2 equiv of Mn^{III} while that of II required 6 equiv; the corresponding corrected rates are shown in Table III. It will be seen that I was oxidized much more rapidly than II, as one would expect in view of its lower ionization potential; however II was oxidized more slowly than PMT although the ionization potential of II was the lower. This difference can be attributed to the different nature of the subsequent reaction of the ion radical with base (*i.e.*, acetate); in the case of I or II, the ion radical (V or VII) combines with acetate ion to form VI or VIII, whereas the ion radical from PMT reacts with base to form *p*-methoxybenzyl. The latter process might well be easier since it must certainly be much more exothermic, for the conversion of V to VII, or of VI to VIII, involves a decrease in π-bond energy, while the conversion of PMT to *p*-methoxybenzyl involves an increase.

One final point deserves attention. In the earlier qualitative work,[1] using high concentrations of manganic acetate and carrying reactions to high conversion, it was observed that I gave, in addition to III, products apparently derived from its further oxidation. The fact that III was the sole product under conditions where I was present in excess, and the conversion very small, supports the suggestion[1] that the other products were indeed formed by secondary attack on III, and that these secondary reactions were relatively slow. However the sole product from II was the quinone IV even under the conditions used here; no significant amount of the intermediate ester (IX) could be found in the product. If therefore IX is formed as an intermediate, it must undergo further oxidation extremely easily—and it is not immediately obvious why it should differ so greatly from III in this respect.



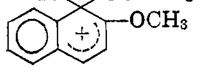
IX

One possible explanation might be that manganic acetate can act as a donor of acetyl radicals, leading to an intermediate such as X; however, it seems unlikely on the basis of available analogies that a reaction of this type could take place so very much more easily in the case of IX than III, acetate radicals being relatively unselective reagents. It seems to us more probable that the distinction arises at an earlier stage, before III or IX is formed. Thus the radical VI, being cross conjugated, should have a higher ionization potential than VIII; it may well be that VI prefers to react directly with manganic acetate by transfer of a hydrogen atom, rather than by electron transfer

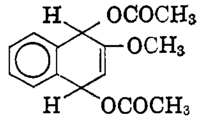
$$\mathrm{VI} + \mathrm{Mn(OAc)_3} \longrightarrow \mathrm{III} + \mathrm{HOAc} + \mathrm{Mn(OAc)_2} \qquad (4)$$

whereas VIII reacts by electron transfer followed by a recombination of ions, giving a product (X) which would be expected to undergo rapid oxidation to 2-methoxynaphthaquinone.

$$\mathrm{VIII} + \mathrm{Mn(OAc)_3} \longrightarrow \qquad (5)$$



$+ \mathrm{AcO^-} + \mathrm{Mn(OAc)_2}$



X

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(4) See G. Briegleb, "Elektronen-Donator-Acceptor-Complexe," Springer-Verlag, Berlin, 1961, Chapter VI.