Oxidation by Metal Salts. III.[1] The Reaction of Manganic Acetate with Aromatic Hydrocarbons and the Reactivity of the Carboxymethyl Radical

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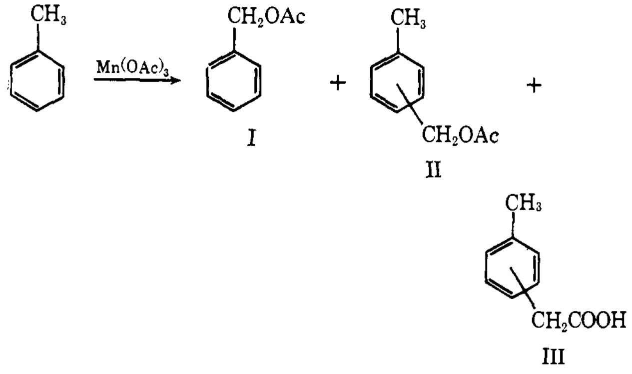
Abstract: The manganic acetate oxidation of aromatic hydrocarbons proceeds by two competing mechanisms: (a) a free-radical mechanism resulting from the interaction of the aromatic hydrocarbon with the carboxymethyl radical ($\cdot CH_2COOH$) generated directly by the thermolysis of manganic acetate; (b) an electron transfer mechanism which is of importance in the oxidation of aromatic hydrocarbons having ionization potentials of ≤ 8 eV. The relative extent of the electron transfer pathway can be suppressed by carrying out the reaction under anhydrous conditions or in the presence of potassium acetate. The relative reactivity of the carboxymethyl radical toward hydrogen abstraction from substituted toluenes was determined yielding a ρ value of -0.63 (correlated with σ^+). The observed relative rate ratio of hydrogen atom abstraction from toluene–diphenylmethane–triphenylmethane is 1:12:39, respectively. A study of the relative rates of addition of the $\cdot CH_2COOH$ radical to substituted benzenes revealed that the reactivity toward addition is guided by the stability of the radical intermediate irrespective of whether the groups are electron withdrawing or electron donating.

Unlike the oxidation of aromatic hydrocarbons by lead tetraacetate, which has been extensively studied, the manganic acetate oxidation reaction in the absence of oxygen has received surprisingly little attention. The few studies that have been reported[2–4] have been concerned primarily with aromatic ethers and amines and other aromatic compounds having relatively low ionization potentials.

In view of our interest in oxidation by metal salts, we have previously investigated the mechanism of the oxidation of aromatic hydrocarbons by lead tetraacetate.[5] As a continuation of this work, we have now investigated the oxidation of aromatic hydrocarbons by manganic acetate in some detail.

Results

Oxidation of Toluene. The oxidation of toluene by manganic acetate in refluxing acetic acid yielded three major products:[6] benzyl acetate (I), the isomeric methylbenzyl acetates (II) (predominantly *ortho*), and tolylacetic acid (III). No xylenes were detected under our reaction conditions.



In a typical experiment, $Mn(OAc)_3 \cdot 2H_2O$ (18.94 mmol) and excess toluene (80 mmol) dissolved in 400 ml of glacial acetic acid containing 0.4 mol of potassium acetate were refluxed under nitrogen until the characteristic brown color of manganic acetate disappeared. The following yields of products were obtained: benzyl acetate (1.25 mmol), methylbenzyl acetate (1.54 mmol), and tolylacetic acid (2.58 mmol) thereby accounting for 73% of the manganic acetate used.[7]

In a different experiment in which a 1.12 *M* solution of toluene in glacial acetic acid was heated at 90° for 76 hr with $Mn(OAc)_3 \cdot 2H_2O$ (0.18 *M*), methylbenzyl acetate and benzyl acetate were obtained in a 3:1 molar ratio. The yield of the $-CH_2OAc$ adduct was obtained in 59% yield based on the Mn(III) consumed.

Oxidation of Anisole. A 0.36 *M* solution of anisole in glacial acetic acid, heated at 90° for 66 hr in the presence of 0.07 *M* $Mn(OAc)_3 \cdot H_2O$, gave the isomeric methoxybenzyl acetates in 84% yield based on the Mn(III) consumed. The isomer distribution was 78% *ortho*, 5% *meta*, and 17% *para*.

Oxidation of 2-Methylnaphthalene. A 0.28 *M* solution of 2-methylnaphthalene in glacial acetic acid, heated at 90° for 68 hr in the presence of 0.18 *M* $Mn(OAc)_3 \cdot 2H_2O$ yielded three major products: the isomeric $-CH_2OAc$ adducts (40% yield based on Mn(III) consumed), 1-acetoxy-2-methylnaphthalene (21%), and

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[1] Previous article by E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 2706 (1968).

[2] (a) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *ibid.*, **88**, 5473 (1966); (b) T. Aratani and M. J. S. Dewar, *ibid.*, **88**, 5479 (1966); (c) P. J. Andrulis, Jr., and M. J. S. Dewar, *ibid.*, **88**, 5483 (1966).

[3] L. Eberson, *ibid.*, **89**, 4669 (1967).

[4] R. Van Helden and E. C. Kooyman, *Rec. Trav. Chim.*, **80**, 57 (1961). After the completion of this study, a paper appeared by R. E. Van Der Ploeg, R. W. DeKorte, and E. C. Kooyman, *J. Catalysis*, **10**, 52 (1968), in which the manganic acetate oxidation of benzene, chlorobenzene, and toluene was discussed.

[5] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 1082 (1968).

[6] Minor amounts of benzaldehyde and methylbenzaldehyde were also observed.

[7] This calculation is based on the stoichiometry of 2 mol of manganic acetate/mol of I and III produced, and 4 mol of manganic acetate/mol of II obtained. This stoichiometry is required by the mechanism presented in this paper.

2-acetoxymethylnaphthalene (8%). When the same reaction was run in the presence of 1.2 *M* potassium acetate, the yield of the isomeric $-CH_2OAc$ adducts increased to 56% while the yields of both 1-acetoxy-2-methylnaphthalene and 2-acetoxymethylnaphthalene decreased to 3% each.

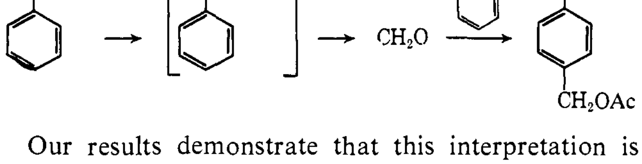
Oxidation of *p*-Methoxytoluene. A solution of *p*-methoxytoluene in glacial acetic acid, heated at 130° in a sealed tube in the presence of $Mn(OAc)_3 \cdot 2H_2O$, yielded three major nonacidic products. In addition to the major product, *p*-methoxybenzyl acetate, two isomeric $-CH_2OAc$ adducts of molecular weight 194 were isolated. The two isomers had similar nmr and infrared spectra. The major isomer was identified as 2-methoxy-5-methylbenzyl acetate by comparison of its infrared and nmr spectra as well as vpc retention time with those of an authentic sample prepared by chloromethylation of *p*-methylanisole.[8]

The possibility of the minor isomer being 3-methyl-4-methoxybenzyl acetate was excluded by comparison with an authentic sample prepared by chloromethylation of *o*-methoxytoluene[9] followed by acetate solvolysis. The minor isomer was therefore assumed to be 2-methyl-5-methoxybenzyl acetate. A fourth product was obtained in small quantities by acidification of the basic extracts as a white solid, mp 131–132°. This was identified as 2-methoxy-5-methylphenyl acetic acid.

Discussion

Formation of $-CH_2OAc$ Adducts. The formation of products in low yields in which the $-CH_2OAc$ group had been added to the aromatic ring was reported by Aratani and Dewar[2b] for the oxidation of methoxybenzenes by manganic acetate. Significant amounts of $-CH_2OAc$ adducts with *p*-methoxytoluene were apparently[9] observed by Eberson[3] when the reaction was run in acetic acid preconditioned with acetic anhydride, although no such products were found in glacial acetic acid alone.[2a]

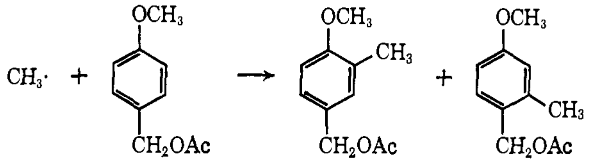
Two different explanations for the formation of these adducts were presented by these authors. Aratani and Dewar[2b] attributed these products to condensation of the aromatic ether with formaldehyde produced by decomposition of α-acetoxy ethers. The acetoxy ether was assumed to form during the course of the reaction.



Our results demonstrate that this interpretation is incorrect. First, the $-CH_2OAc$ adducts were formed even with toluene and 2-methylnaphthalene where no possibility exists for formaldehyde formation. Second, the isomer distribution observed in the oxidation of anisole (78% *ortho*, 5% *meta*, and 17% *para*) is comparable to that found in the free-radical methylation of anisole.[10] The isomer distribution is clearly inconsistent with an ionic mechanism since the chloromethylation of anisole yields a product which is 90% *para* and 10% *ortho*.[11]

Eberson,[3] in his studies on the oxidation of *p*-methoxytoluene, observed products having a molecular ion peak at mass number 194. He assumed these products to be methylated derivatives of the major product, *p*-methoxybenzyl acetate. He suggested a free-radical mechanism in which methyl radicals, formed by the manganic ion oxidation of acetate ion, added to the initially formed *p*-methoxybenzyl acetate.

$$Mn^{3+} + {}^{-}OAc \longrightarrow CH_3\cdot + CO_2 + Mn^{2+}$$



IV V

This interpretation, also, is inconsistent with our observation that no xylenes are produced in the presence of a large excess of toluene as would be expected if methyl radicals were involved, as was the case with lead tetraacetate.[5] Furthermore, our results indicate that the two isomeric $-CH_2OAc$ adducts, formed in the oxidation of *p*-methoxytoluene with manganic acetate, have the methyl group *para* to the methoxy group, unlike the structures (IV and V) suggested by Eberson. The fact that the $-CH_2OAc$ adduct to *p*-methoxytoluene had the structure in which the methyl group remained *para* to the methoxy group clearly indicated that it was a $-CH_2OAc$ group that was added to the ring and not a methyl group.

Mechanism. The isolation of arylacetic acids as major products in the oxidation of aromatic hydrocarbons suggests that they are the precursors of the $-CH_2OAc$ adducts formed, and that a free-radical mechanism similar to that of lead tetraacetate[6] is operative. This mechanism is shown in Scheme I where it is assumed the $\cdot CH_2COOH$ radical is oxidized relatively slowly to the corresponding carbonium ion, in contrast to the benzylic radical[12] or the cyclohexadienyl radical, due to its relatively high ionization potential.[13] The high yield of benzylacetate, methylbenzyl acetate, and tolylacetic acid obtained indicates that the $\cdot CH_2COOH$ radical reacts with toluene faster than it is oxidized by Mn(III). This fact was illustrated by the addition of trace amounts (4 mmol) of $Cu(OAc)_2$ to the typical reaction mixture mentioned above. Cu(II), which oxidizes the $\cdot CH_2COOH$ radical at a high rate,[14] decreased by more than 90% the yield of these products based on Mn(III) consumed.

While the above proposed mechanism is similar to that proposed for lead tetraacetate, several distinct differences in the oxidation of toluene by manganic acetate should be noted. Unlike the lead tetraacetate oxidation, no xylenes were detected, indicating that the free methyl radicals are not produced from man-

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[8] R. Quelet, *Bull. Soc. Chim. France*, [4] **53**, 851 (1933).

[9] Only mass spectral evidence was reported.

[10] B. R. Cowley, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 1799 (1959).

[11] R. Quelet and M. Anglade, *Compt. Rend.*, **203**, 262 (1936).

[12] J. K. Kochi, J. D. Bacha, and T. W. Bethea, III, *J. Am. Chem. Soc.*, **89**, 6538 (1967).

[13] Gas phase IP of $\cdot CH_2COOH$ is expected to be similar to cyanomethyl radical whose IP = 10.87 eV, while that of benzylic radical is 7.76 eV. R. W. Kaiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 319.

[14] Preliminary experiments indicate that Cu(II) oxidizes secondary alkyl radicals at least 100 times faster than Mn(III).

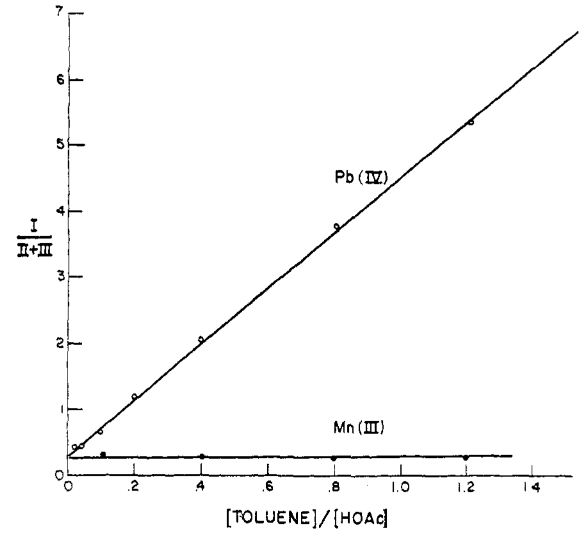
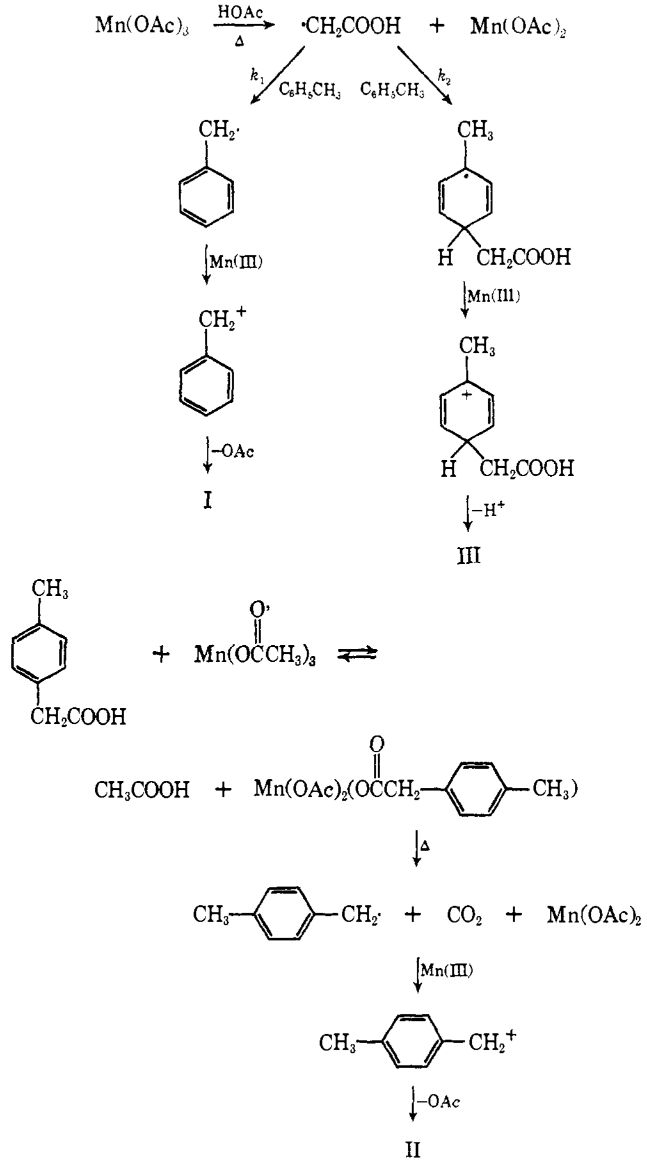


Figure 1. Oxidation of toluene; effect of toluene/acetic acid ratio on the product distribution.

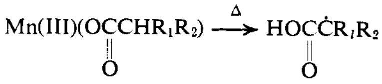
ganic acetate. In addition, the relative yield of I to the sum of II and III was found to be independent of the toluene/acetic acid ratio used, which is unlike the linear variation observed with lead tetraacetate (see Figure 1). This suggests that the $\cdot CH_2COOH$ radicals are formed directly from the manganic acetate complex, by a mechanism that as yet is not fully understood.

Scheme I

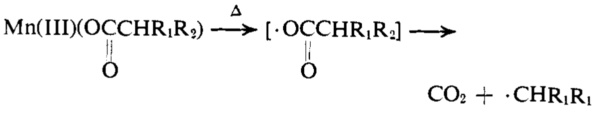


The manganic acetate oxidation differs from the lead tetraacetate oxidation in one additional respect. It is not a chain reaction. This is not unexpected since the oxidation by Mn(III) involves only a one electron reduction to Mn(II), while Pb(IV) undergoes two consecutive one-electron-transfer processes.[12,15]

An interesting feature of the thermolysis of manganic acetate is that it leads predominantly to a carbon radical. In general, the thermolysis of manganic carboxylates proceeds by two distinct pathways, one leading to a carboxyalkyl radical (eq 1) while the other pathway leads to the corresponding acyloxy radical (eq 2).


(1)

$$\mathrm{Mn(III)(O\underset{\underset{O}{\|}}{C}CHR_1R_2)} \xrightarrow{\Delta} \mathrm{HO\underset{\underset{O}{\|}}{C}\dot{C}R_1R_2} \qquad (1)$$


(2)

$$\mathrm{Mn(III)(O\underset{\underset{O}{\|}}{C}CHR_1R_2)} \xrightarrow{\Delta} [\cdot\mathrm{O\underset{\underset{O}{\|}}{C}CHR_1R_2}] \longrightarrow \mathrm{CO_2} + \cdot\mathrm{CHR_1R_1} \qquad (2)$$

The extent of the thermolysis by either of these two pathways depends on the structure of R_1 and R_2. When $R_1 = R_2 = H$, thermolysis proceeds almost exclusively by pathway 1 (at least 97–99.3% depending on conditions used). If, however, R_1 or R_2 = an alkyl group as in manganic propionate, relatively more thermolysis *via* pathway 2 is observed.[16] When R_1 or R_2 is benzylic, as in phenyl acetic or tolylacetic acids, thermolysis appears to proceed predominantly *via* pathway 2. Similar results were obtained independently by Van Der Ploeg, DeKorte, and Kooyman,[4] who demonstrated that the $\cdot CH_2COOH$ radical is the primary product of the thermolysis of manganic acetate and that the rate of decomposition of manganic acetate is not dependent on the presence of organic substrates such as benzene and chlorobenzene. They have also shown that phenylacetic acid is decarboxylated *via* pathway 2 by manganic acetate.

The determined ratio of I/(II + III) = 0.3 using manganic acetate agrees well with the value obtained from the oxidation of toluene by lead tetraacetate extrapolated to infinite toluene dilution. This ratio, 0.3, represents the relative rate constants of α-hydrogen abstraction (k_1) to that of nuclear addition (k_2) by the $\cdot CH_2COOH$ radical. It should be noted here that the $\cdot CH_2COOH$ radical, unlike the more reactive methyl radical,[5] adds to toluene faster than it abstracts the benzylic hydrogen atom. The difference in behavior of this radical can be attributed to the greater stability of $\cdot CH_2COOH$ radical and to some extent to its electrophilicity. The more stable radical would be expected to favor the reaction of lower activation energy, which in this case is addition to the ring.[17]

Oxidation of Aromatic Hydrocarbons Having Low Ionization Potentials. The manganic acetate oxidation

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(15) J. K. Kochi, *J. Am. Chem. Soc.*, 87, 3609 (1965).

(16) Under the conditions where the thermolysis of manganic acetate proceeds to less than 0.7% *via* pathway 2, manganic propionate undergoes thermolysis to about 6% *via* pathway 2 (work to be published).

(17) M. Cher, C. S. Hollingsworth, and F. Sicilio, *J. Phys. Chem.*, 70, 877 (1966).

of aromatic hydrocarbons having ionization potentials lower than toluene also occurs to a large extent by a free-radical mechanism, as evidenced by the high yields of $-CH_2OAc$ adducts obtained (see Table I). In fact, anisole gave yields of better than 80% of the isomeric $-CH_2OAc$ adducts with either manganic acetate or lead tetraacetate.

Table I. Products of Oxidation of Various Aromatic Hydrocarbons by Manganic Acetate and Lead Tetraacetate

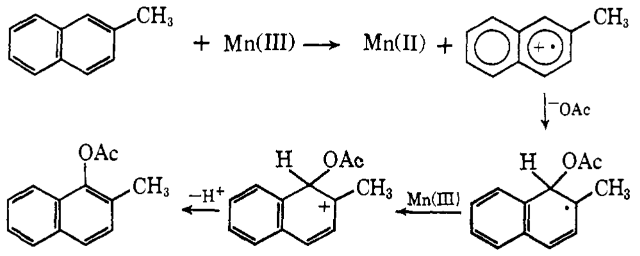
			Product yields,[a] %		
Hydrocarbon (IP, eV)	Oxidant	KOAc, *M*	Side-chain acetate	$-CH_2$-OAc[b] adducts	Nuclear acetate
Toluene[c] (8.82)	Mn(III)		9	59	
	Mn(III)	1.2	12	30	
	Pb(IV)		24	35	
Anisole[d] (8.22)	Mn(III)		Trace	84	
	Mn(III)	1.2	Trace	75	
	Pb(IV)		3	80	11
2-Methylnaphthalene[e] (7.96)	Mn(III)		8	40	21[f]
	Mn(III)	1.2	3	56	3
	Pb(IV)		22	22	38

[a] Based on oxidant reacted, assuming 2 equiv per side chain and nuclear acetate and 4 equiv per $-CH_2OAc$ adduct. [b] Yields of acids were not determined. In general, the addition of potassium acetate drastically increased the relative ratio of arylacetic acid to $-CH_2OAc$ adduct formed. [c] [HC] = 1.12 *M*, [Mn(III)] = 0.18 *M*, [Pb(IV)] = 0.08 *M*, temperature 90°. [d] [HC] = 0.36 *M*, [Mn(III)] = 0.07 *M*, [Pb(IV)] = 0.08 *M*, temperature 90°. [e] [HC] = 0.28 *M*, [Mn(III)] = 0.18 *M*, [Pb(IV)] = 0.08 *M*, temperature 90°. [f] 1-Acetoxy-2-methylnaphthalene.

While the major pathway by which manganic acetate oxidizes aromatic compounds is a free-radical process, a second pathway involving electron-transfer does in fact operate with hydrocarbons of relatively low ionization potential (≤ 8.0 eV) under certain conditions. The reaction of manganic acetate with *p*-methoxytoluene in refluxing acetic acid yielded *p*-methoxybenzyl acetate as the predominant product, along with the isomeric $-CH_2OAc$ adducts in a 20:1 ratio (the free acid formed was negligible). The extremely large preference for side-chain attack is inconsistent, as shown later, with the established reactivity of the $\cdot CH_2COOH$ radical. Since the $\cdot CH_2COOH$ radical abstracts benzylic hydrogen atoms from *p*-methoxytoluene only 3.6 times faster than from toluene and since its rate of addition to toluene is approximately 3.3 times greater than its rate of hydrogen abstraction from toluene, approximately equal amounts of side-chain attack and nuclear addition would be expected for *p*-methoxytoluene, assuming the rate of addition to *p*-methoxytoluene to be the same as for toluene. Actually the rate of addition of $\cdot CH_2COOH$ to *p*-methoxytoluene is most probably greater than that of toluene, in view of the fact that anisole reacts three times faster than *t*-butylbenzene. The large preponderance of side-chain acetoxylation in the manganic acetate oxidation of *p*-methoxytoluene is clearly inconsistent with the free-radical scheme alone. This indicates the existence of a second competing pathway which leads exclusively, or almost exclusively, to *p*-methoxybenzyl acetate. Most probably, this pathway is the electron-transfer process originally suggested by Dewar, *et al.*[2a]

The manganic acetate oxidation of 2-methylnaphthalene, whose ionization potential (7.92 eV) is comparable to that of *p*-methoxytoluene, apparently also involves both competing pathways. The existence of a free-radical pathway is indicated by the high yields of $-CH_2OAc$ adducts obtained, while the ionic electron-transfer process is suggested, although not proven, by the existence of significant amounts of nuclear acetates (see Table I). The formation of nuclear acetates can best be explained by Scheme II, which is similar to that suggested by Dewar[2c] for the oxidation of methoxynaphthalenes. The mechanism for nuclear acetoxylation by manganic acetate is similar to the mechanism of electrochemical acetoxylation which is presumed to involve radical cation intermediates.[18]

Scheme II



Competitive Free-Radical and Electron-Transfer Pathways. Competition between these two competing pathways described above can be drastically affected by the addition of acetate ion and by rigorous drying of the system with acetic anhydride. Thus, the addition of 1.2 *M* potassium acetate to the manganic acetate oxidation of 2-methylnaphthalene reduced the yields of the side-chain and nuclear acetates, while the yield of the $-CH_2OAc$ adducts increased (see Table I). The nuclear acetates derived entirely from the electron-transfer pathway and the side-chain acetate at least partly by this mechanism, while the $-CH_2OAc$ adducts are formed by the competing free-radical process. We have found that the rate of free-radical decomposition of manganic acetate is accelerated three- to fourfold at 140° by the addition of potassium acetate. A similar rate acceleration by acetate ion has been reported for lead tetraacetate.[19] By analogy to lead tetraacetate, a new manganic acetate complex, possibly $Mn(OAc)_4^-$, is formed in the presence of added acetate ion, and this complex decomposes to $\cdot CH_2COOH$ radicals more rapidly than does the neutral complex.

The effect of acetate ion was also observed with *p*-methoxytoluene. In refluxing acetic acid, the side-chain acetate predominated over the $-CH_2OAc$ adducts by a ratio of about 20:1 (Table II). In the presence of added potassium acetate (300 g/l. of acetic acid), the relative yield of $-CH_2OAc$ adducts increased to one-third of the side-chain acetate. Rigorous drying of the reaction system by preconditioning with acetic anhydride and using anhydrous manganic acetate caused a further dramatic increase in the relative yield of the $-CH_2OAc$ adducts, to the point where they constituted the major product of the reaction. The rate of reaction was also greatly increased under these conditions.

The effect of acetic anhydride is similar to the effect of acetate ion in that it accelerates the free-radical

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(18) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 4139 (1964); **79**, 4088 (1967).

(19) D. Benson, L. H. Sutcliffe, and J. Walkley, *ibid.*, **81**, 4488 (1959).

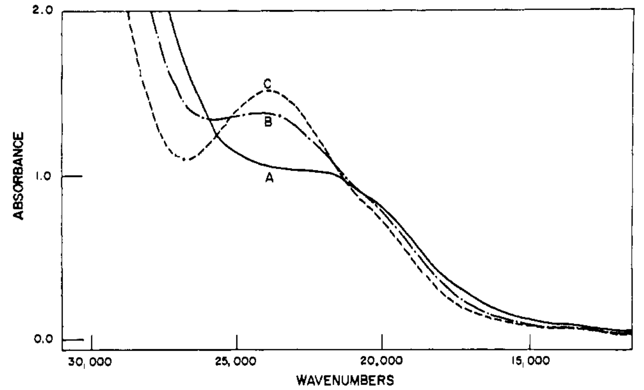

Figure 2. Visible absorption spectra of manganic acetate: A, 3×10^{-3} *M* $Mn(OAc)_3 \cdot 2H_2O$ in HOAc; B, 3×10^{-3} *M* $Mn(OAc)_3 \cdot 2H_2O$ in 1 *M* KOAc–HOAc; C, 3×10^{-3} *M* anhydrous $Mn(OAc)_3$ in anhydrous 1 *M* KOAc–HOAc.

pathway relative to the electron-transfer pathway. Apparently a new manganic complex is formed, possibly one in which a water ligand is replaced by acetate ion. The similarity between the new complexes formed in both cases is suggested by the changes in the visible spectrum of manganic acetate (Figure 2) which shows enhanced absorption at 24,000 cm^{-1}.

Table II. Effect of Reaction Conditions on the Products of the Oxidation of *p*-Methoxytoluene by Manganic Acetate

Conditions	$-CH_2OAc$ adducts/side-chain acetate
Glacial HOAc, 130°	0.04
1 *M* KOAc, 130°	0.10
1 *M* KOAc + 0.2 *M* Mn(II),[a] 130°	0.22
1 *M* KOAc, Ac_2O, anhydrous Mn(III), 130°	0.73
300 g of KOAc/1000 cc of HOAc, 138°	0.34[b]
300 g of KOAc/1000 cc of HOAc, 138°, anhydrous Mn(III), Ac_2O dried	1.50[b]

[a] This is twice the initial Mn(III) concentration. [b] Some carboxylic acid was detected.

The relative yield of the $-CH_2OAc$ adducts was also increased by the addition of Mn(II) acetate. This effect can be explained by the retarding influence of Mn(II) on the electron-transfer pathway, whose rate was shown to be inversely proportional to the manganous ion concentration.[2a]

The Relative Reactivity of the Carboxymethyl Radical toward Benzylic Hydrogen Abstraction. The thermolysis of manganic acetate in acetic acid yields the carboxymethyl radicals uncontaminated with other competing radicals. This system, therefore, is the most suitable for the study of the reactivity of the carboxymethyl radical toward hydrogen abstraction from substituted toluenes. The relative reactivities were carried out by a competitive technique and were calculated from the relative ratios of the pertinent reaction products, namely, the corresponding benzylic acetates. Tables III and IV show the relative reactivity of substituted toluenes and the relative rate ratios of hydrogen abstraction by carboxymethyl radical from substituted toluenes. A good linear Hammett σ–ρ fit was obtained for seven of the compounds studied. As can be seen from Tables III and IV, however, *p*- and *m*-methoxytoluene and *p*-phenyltoluene showed higher reactivities than expected on the basis of this plot. What these three compounds have in common is the fact that their ionization potentials are lower than the other substituted toluenes studied. The high reactivity of these three compounds indicates that with these compounds the corresponding benzylic acetates are produced by both radical and electron-transfer pathways. When the reaction with these compounds was carried out under anhydrous conditions (using acetic anhydride), conditions previously shown to suppress the contribution of the electron-transfer pathway relative to the free-radical pathway, the relative rates of hydrogen abstraction from these three compounds were reduced to the point where they approached the line determined by the other seven compounds. The good linear σ–ρ fit obtained for all ten substituted toluenes indicates that a single free-radical mechanism is operative for all of these compounds.

Table III. Competitive Experiments—Relative Reactivity of Substituted Toluenes at 130°

Compound A	Compound B	B-acetate/ A-acetate
p-F toluene	*m*-Br toluene	0.52
Toluene	*p*-Br toluene	0.87
p-Cl toluene	*m*-Br toluene	0.61
p-CH_3 toluene	*p*-Br toluene	0.26
m-CH_3 toluene	*p*-Br toluene	0.37
p-CH_3 toluene	*m*-Br toluene	0.18
m-CH_3 toluene	*m*-Br toluene	0.25
p-Cl toluene	*p*-Br toluene	1.06
Toluene	*m*-Br toluene	0.58
p-CH_3 toluene	Diphenylmethane	2.36
Diphenylmethane	Triphenylmethane	1.67
p-CH_3 toluene	*p*-CH_3O toluene	27.6
p-CH_3 toluene	*p*-CH_3O toluene[a]	1.10
p-CH_3 toluene	*m*-CH_3O toluene	0.40
p-CH_3 toluene	*m*-CH_3O toluene[a]	0.28
p-CH_3 toluene	*p*-C_6H_5 toluene	0.88
p-CH_3 toluene	*p*-C_6H_5 toluene[a]	0.88
Toluene-α-d_3	*p*-Br toluene	4.75

[a] Anhydrous conditions using acetic anhydride.

Table IV. Relative Rates of Hydrogen Abstraction by Carboxymethyl Radical from Substituted Toluenes at 130°

Compound	k/k_0[a]
Toluene	1.00
p-F toluene	1.11
p-Cl toluene	0.89
p-Br toluene	0.87
m-Br toluene	0.58
p-CH_3 toluene	1.66
m-CH_3 toluene	1.19
p-CH_3O toluene	3.64[b] (91.4)
m-CH_3O toluene	0.92[b] (1.33)
p-C_6H_5 toluene	1.60[b] (2.91)
Diphenylmethane	11.7
Triphenylmethane	39
Toluene-α-d_3	0.18

[a] Relative reactivity per benzylic hydrogen atom with toluene as standard (k_0). [b] These values were obtained under anhydrous conditions using acetic anhydride while the figures in parentheses are those found under the usual conditions (see Experimental Section).

The relative reactivity of substituted toluenes shows a good correlation with σ^+ (Figure 3), the plot of Figure

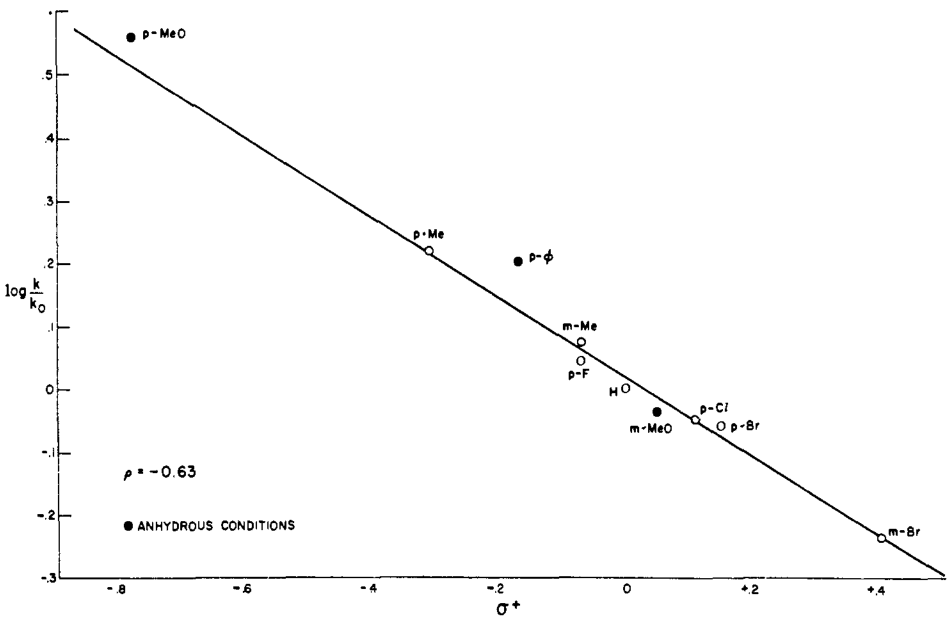

Figure 3. Relative reactivity of substituted toluenes toward hydrogen abstraction by the carboxymethyl radical at 130°.

3 yielding a ρ value of -0.63 when the reactivity values for *p*- and *m*-methoxytoluene and *p*-phenyltoluene are excluded and a ρ value of -0.68 when their reactivity values are included.

The fact that the hydrogen abstraction by the $\cdot CH_2COOH$ radical shows a better correlation with σ^+ rather than with σ constants indicates that the hydrogen abstraction proceeds through a transition state in which there is already pronounced C–H bond breakage as evidenced by the large isotope effect observed ($k_H/k_D = 5.46$).

The observed relative ratio of hydrogen abstraction from toluene–diphenylmethane–triphenylmethane of 1:11.7:39 is comparable to that reported for the trichloromethyl radical of 1:12:50.[20] The ρ value of -0.63 observed for the $\cdot CH_2COOH$ radical could suggest that the $\cdot CH_2COOH$ radical is less electrophilic than the $\cdot CCl_3$ radical[21] which has a ρ value of -1.46 at 55°. However, the difference in temperature between the two studies precludes a definite conclusion.

The Reactivity of the Carboxymethyl Radical toward Addition to Substituted Benzenes. The carboxymethyl radical generated from the thermolysis of manganic acetate undergoes, besides hydrogen abstraction from the side chain, addition to the aromatic ring. The products resulting from addition are, predominantly, the isomeric benzyl acetates and the corresponding phenylacetic acids. We have determined the reactivity of the $\cdot CH_2COOH$ radical toward addition to substituted benzenes by using a competitive technique in which the $\cdot CH_2COOH$ radical competes for two substrates. The relative reactivities toward addition were followed by the disappearance of the two hydrocarbons. The results obtained for the relative rates of addition of the $\cdot CH_2COOH$ radical are listed in Table V. As can be seen from Table V, both electron-withdrawing and electron-donating substituents accelerate the rate of carboxymethyl radical addition to the aromatic ring. The rate of addition appears to be governed by both the electrophilicity of the $\cdot CH_2COOH$ radical as well as the stability of the cyclohexadienyl radical intermediate. Electron-withdrawing substituents such as Cl, Br, or NO_2 tend to deactivate the ring toward addition while their contribution to the stabilization of the cyclohexadienyl radical intermediate tends to accelerate the rate of the $\cdot CH_2COOH$ radical addition. Although these are opposing effects, the stabilization of the radical intermediate appears to be the more important factor of the two.

Table V. Relative Rates of Addition of Carboxymethyl Radical to Substituted Benzenes at 130°

Compd	Rel rate	Compd	Rel rate
C_6H_6	1.0	$C_6H_5COOCH_3$	1.3
C_6H_5Br	1.0	$C_6H_5NO_2$	1.5
C_6H_5Cl	1.0	$C_6H_5OCH_3$	3.0
C_6H_5-*t*-Bu	1.1		

Experimental Section

The organic compounds used were purchased in the purest quality available and carefully checked for impurities by vapor phase chromatography. Where necessary, pure reference samples were trapped by preparative vpc. Toluene-α-d_3, 99.5%, was obtained from Stohler Isotope Chemicals.

Preparation of $Mn(OAc)_3 \cdot 2H_2O$. A modified procedure of Christensen[22] was used for the oxidation of manganous acetate. In a 5-l., four-necked, round-bottomed flask fitted with a stirrer, condenser, and a thermometer, 428.7 g of $Mn(OAc)_2 \cdot 4H_2O$ in 3 l. of glacial acetic acid was heated to 110°. Ground potassium permanganate (68.2 g) was added in small portions through the condenser over a 20-min period, while the temperature was maintained at 110°. The reaction mixture was heated an additional 20 min, cooled, poured into water (750 ml), and left to crystallize overnight. The solid was filtered off, washed with ether, and air dried. The yield was 496 g (82%) which was assayed by iodometric titration.

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(20) These values were determined at 91.5°, E. C. Kooyman, *Discussions Faraday Soc.*, **10**, 163 (1951).

(21) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).

(22) O. T. Christensen, *Z. Anorg. Allgem. Chem.*, **27**, 325 (1901).

Anal. Calcd for $Mn(OAc)_3 \cdot 2H_2O$: C, 26.87; H, 4.85; Mn, 20.5. Found: C, 26.6; H, 4.85; Mn, 20.2. Titration = 3.72 ± 0.09 mequiv/g; theory = 3.73 mequiv/g.

Preparation of Anhydrous $Mn(OAc)_3$. The procedure of Chre'tein and Varga[23] was used. A mixture of $Mn(NO_3)_2 \cdot 6H_2O$ (60 g) and acetic anhydride (225 ml) was stirred vigorously in a 4-l. beaker and heated cautiously until the cloudy mixture suddenly turned clear. The heating was stopped and a vigorous reaction followed during which there was copious evolution of NO_2. The product was allowed to crystallize overnight, filtered, washed with acetic anhydride, and dried over phosphorus pentoxide. The anhydrous manganic acetate thus obtained titrated as 90–98% $Mn(OAc)_3$, yields were 70–90%.

Anal. Calcd for $Mn(OAc)_3$: C, 31.03; H, 3.91. Found: C, 30.17; H, 4.19.

The Reaction of Manganic Acetate with Toluene. In a typical experiment, $Mn(OAc)_3 \cdot 2H_2O$ (18.94 mmol) and excess toluene (80 mmol) dissolved in 400 ml of glacial acetic acid containing 0.4 mol of potassium acetate were refluxed under nitrogen until the characteristic brown color of manganic acetate had disappeared. When an internal standard was used, 2 mmol of methyl benzoate was added to the cooled reaction mixture. The reaction mixture was added to 500 ml of ether which was then extracted four times with ice–water (1000 cc each time). The ether layer was dried over anhydrous sodium sulfate, filtered, and stripped on a rotary evaporator. The residue was then analyzed by vapor phase chromatography.

In all cases where the product distribution was studied, large molar excesses of toluene over manganic acetate were used to minimize subsequent reactions of products. All products were identified by comparison with authentic samples.

Quantitative vpc analyses were performed on an F & M Model 5750 gas chromatograph with dual thermal conductivity detectors using 6 ft × 0.25 in. 5% Silicone OV-17 columns and temperature programming (130–300° at 8°/min, He flow ~90 cc/min). Samples were also analyzed on a 6 ft × $^1/_8$ in. Silicone SE-30 column using dual flame detectors and temperature programming (95–300° at 8°/min, post-injection interval = 5 min, He flow ~25 cc/min). Peak areas were measured either with a planimeter or with a Varian Aerograph Model 475 automatic integrator. Peak responses were calibrated with mixtures prepared from authentic samples. The accuracy of these analyses was generally ±1–2% except for the tolylacetic acid peak which had an error of ±5–10% associated with it.

The Reaction of Manganic Acetate with 2-Methylnaphthalene. A solution of 2-methylnaphthalene (0.28 *M*) in glacial acetic acid was heated at 90° for 68 hr in the presence of $Mn(OAc)_3 \cdot 2H_2O$ (0.18 *M*). The reaction mixture was poured onto ice–water, extracted with ether, washed four times with ice–water, dried over anhydrous sodium sulfate, and evaporated. The residue was analyzed by vpc (10 ft 15% Silicone SE-30 on Diatoport S) and showed three major products. These products were characterized as: (a) 1-acetoxy-2-methylnaphthalene (21%) (hydrolysis of this material converted it to 1-hydroxy-2-methylnaphthalene which was identical with an authentic sample (vpc retention time and mixture melting point)); (b) 2-acetoxymethylnaphthalene (8%) (this compound exhibited the expected infrared and nmr spectra; nmr: singlet at τ 8.03 (3 H), singlet at 4.92 (2 H), multiplet in 2.8–2.2 region (8 H)); (c) acetoxymethyl-2-methylnaphthalene (40%) (the structure of this compound was deduced from its infrared and nmr spectra; infrared showed absorption at 1740 cm^{-1}; nmr: τ 2.3 (6 H), 4.6 (2 H), 7.6 (3 H), and 8.1 (3 H)).

When the effect of potassium acetate was studied, the reaction was carried out under the same conditions but in the presence of 1.2 *M* potassium acetate.

The Reaction of Manganic Acetate with Anisole. A solution of anisole (0.36 *M*) in glacial acetic acid was heated at 90° for 66 hr in the presence of $Mn(OAc)_3 \cdot 2H_2O$ (0.07 *M*). The reaction mixture was poured onto ice–water, extracted with ether, washed three times by cold water, dried over anhydrous sodium sulfate, and evaporated. The residue was analyzed by vpc using a 12-ft column 15% Silicone rubber (SE-30) on Diatoport S. One major product, methoxybenzyl acetate, was obtained in 84% yield (based on Mn(III) consumed). The compound was identified by comparison of the infrared and nmr spectra and vpc retention time with an authentic sample prepared from the alcohol. The isomer distribution was shown to be 78% *ortho*, 5% *meta*, and 17% *para* by vpc using a 12-ft column 10% Silicone SE-30 column.

The Reaction of Manganic Acetate with *p*-Methoxytoluene. *p*-Methoxytoluene (3.6 g, 0.03 mol) and 100 ml of glacial acetic acid were added to a tube containing 0.01 mol of $Mn(OAc)_3 \cdot 2H_2O$. The reaction mixture was flushed with nitrogen and the tube sealed and placed in a constant temperature bath maintained at 130 ± 1°. The sealed tube was left in the bath for 20 min, by which time the brown manganic color had disappeared. After cooling the reaction tube, the mixture was added to 500 cc of ether which was then extracted six times with 500 cc of water each. The ether layer was then dried over sodium sulfate, filtered, and stripped down on a rotary evaporator. The residue was then analyzed by vpc.

A similar reaction was run using 100 ml of 1 *M* potassium acetate in acetic acid instead of the glacial acetic acid, and was then worked up in the identical manner.

A third reaction in which 0.02 mol of $Mn(OAc)_2 \cdot 4H_2O$ was added to the potassium acetate containing reaction mixture was performed in the identical manner.

An anhydrous reaction was also run using 100 ml of preconditioned 1 *M* potassium acetate–acetic acid solution and 0.01 mol of anhydrous $Mn(OAc_3)$. The solution was preconditioned by refluxing overnight in the presence of 10% (by volume) acetic anhydride. This reaction was worked up in the usual manner.

Several runs, especially those for preparative purposes, were performed in refluxing systems containing 300 g of potassium acetate/l. of glacial acetic acid. The reflux temperature of these reactions was about 138°. The work-up in general was similar to that described above except for a final washing with aqueous sodium carbonate to separate out acidic products. The acidic products were isolated from the basic wash by acidification and extraction.

Product Analyses. The reaction mixture was analyzed on an F & M Model 810 gas chromatograph with dual flame detectors using 12-ft 15% Silicone SE-30 columns and temperature programming. Vpc analysis indicated the presence of three major products identified as *p*-methoxybenzyl acetate and the two isomeric $-CH_2OAc$ adducts to *p*-methoxytoluene. The *p*-methoxybenzyl acetate was characterized by comparison if its infrared and nmr spectra and vpc retention times with an authentic sample prepared from the corresponding alcohol. The two other products were isolated by vpc, with a 6-ft 10% neopentyl glycol succinate column being best for separation of the two isomers. A sample which contained both isomers satisfactorily analyzed for $C_{11}H_{14}O_3$.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.00; H, 7.27. Found: C, 68.29; H, 7.27.

The low voltage (~8 eV) mass spectrum of each compound indicated a structure of molecular weight 194 and a formula of $C_{11}H_{14}O_3$ (calculated from the isotopic peaks). The two isomers had similar infrared spectra (carbonyl peak at 5.73 μ) and nmr spectra. The nmr spectrum (in τ values) of each isomer consisted of a singlet (3 H) at 8.05, another singlet (3 H) at 7.8, a singlet (3 H) at 6.3, and a fourth singlet (2 H) at 5.0, as well as broad absorption (3 H) in the 2.9–3.5 region. The pattern of lines in the 2.9–3.5 region however was distinctly different for the two isomers. The major isomer, which had the shorter retention time of the two, was identified as 2-methoxy-5-methylbenzyl acetate by comparison of its spectra and retention times with those of an authentic sample. The authentic sample, bp 99–100° (0.1 mm), was prepared by chloromethylation of *p*-methoxytoluene[8] followed by solvolysis with potassium acetate in acetic acid. Another possible isomer, 3-methyl-4-methoxybenzyl acetate, was prepared by chloromethylation of *o*-methoxytoluene[8] followed by solvolysis with acetic acid, and this compound differed from either of the two isomers as shown by its nmr spectrum and retention time.

In addition, a fourth product was obtained from the basic extracts in the form of a white solid, mp 131–132°. This was identified as 2-methoxy-5-methylphenylacetic acid.[24] The infrared spectrum showed broad absorbtion in the 3–4-μ range as well as a peak at 5.85. The nmr spectrum in $CDCl_3$ contained a singlet (3 H) at τ 7.8, another singlet (2 H) at 6.4, and a singlet (3 H) at 6.25, as well as a multiplet (3 H) in the 2.9–3.5 region, and a broad peak (1 H) at −1.0. The mass spectrum showed a parent peak at *m/e* 180.

Relative Reactivity of Substituted Toluenes. Competitive Procedure. In a typical experiment, 50 ml of an acetic acid solution, 0.2 *M* in each of the two hydrocarbons under study and 1 *M* in potassium acetate, was mixed with 50 ml of a 0.0947 *M* solution of

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[23] A. Chre'tein and G. Varga, *Bull. Soc. Chim. France*, [5] **3**, 2387 (1936).

[24] O. Dann, J. Lang, and H. Vohl, *Ann.*, **631**, 116 (1960).

Table VI. Competitive Reactions of Substituted Benzenes

A	B	A_0/Std	A/Std	B_0/Std	B/Std	Std	k_B/k_A
C_6H_6	C_6H_5Br	1.62	1.39	1.55	1.33	20 μl of toluene	1.00
C_6H_6	C_6H_5Cl	1.62	1.34	1.51	1.24	20 μl of toluene	1.04
C_6H_5Cl	C_6H_5Br	1.25	1.01	1.24	1.00	20 μl of cumene	1.01
C_6H_5-tBu	C_6H_5Cl	2.06	1.72	1.19	0.98	20 μl of cumene	1.07
C_6H_5Br	$C_6H_5COOCH_3$	1.49	1.23	1.66	1.29	20 μl of *o*-dichlorobenzene	1.32
C_6H_5Br	$C_6H_5NO_2$	1.15	1.02	1.05	0.88	25 μl of *o*-dichlorobenzene	1.47
C_6H_5Cl	$C_6H_5OCH_3$	1.55	1.29	1.63	0.95	15 μl of *o*-xylene	2.93

$Mn(OAc)_3 \cdot 2H_2O$ in acetic acid, also 1 *M*, in potassium acetate. The reaction mixture was placed in a tube, flushed with nitrogen and sealed. The reactions were run in a constant temperature bath maintained at 130 ± 1° for a period of 2 hr by which time the brown manganic color had disappeared. When the reaction was over, the tube was cooled and the reaction mixture diluted with 500 ml of ether. The ether solution was extracted twice with ice water and three more times with cold saturated sodium bicarbonate solution. The ether extract was then dried over sodium sulfate and after filtration, the ether was removed on a rotary evaporator. The resulting reaction residue was then analyzed by vapor phase chromatography.

The relative amounts of the two benzyl acetates formed were determined by the areas of the corresponding peaks in the gas chromatogram, corrected for differences in response for the two compounds. This correction factor was obtained from a known mixture of authentic samples prepared by conventional methods from the corresponding benzyl alcohols or halides. Vpc analyses were conducted on an F & M Model 810 gas chromatograph with dual thermal conductivity detectors using 2–12-ft 10% Silicone SE-30 columns and temperature programming. Peak areas were obtained by a Varian Aerograph Model 475 automatic integrator. In general, each reaction was run in duplicate and analyzed twice by vpc. Average deviations were usually less than 2%.

In the reactions run under anhydrous conditions, 200 ml of glacial acetic acid, 60 g of potassium acetate, and 20 ml of acetic anhydride were heated at 130° under a stream of nitrogen. After 6 hr, 25 mmol each of the two hydrocarbons of interest were added along with 12.4 mmol of anhydrous $Mn(OAc)_3$. When the reaction was over, the reaction mixture was worked up and analyzed in the usual manner.

Relative Reactivity of Substituted Benzenes. Competitive Procedure. Each substituted benzene was dissolved in glacial acetic acid to give a 0.14 *M* solution of hydrocarbon. Twenty milliliters of each of two hydrocarbon solutions were then mixed, and 4-ml aliquots of the resulting mixture were then added to six ampoules, three of which contained 700 mg of $Mn(OAc)_3 \cdot 2H_4O$. The ampoules were then purged with nitrogen and sealed. The sealed ampoules were placed in a constant-temperature bath maintained at 130 ± 1° until the reaction mixtures containing manganic acetate turned clear, usually about 5 hr. The ampoules were then cooled in ice–water and opened. A specific amount of standard (usually 15–25 μl) was then added to each tube. The standard used varied with the two hydrocarbons under study as shown in Table VI. Analyses were performed on an F & M Model 5750 gas chromatograph with dual flame detectors using $^1/_8$ in. 3- or 6-ft Polypak No. 1 columns and temperature programming. Pea kareas were determined with a planimeter, and each reaction and control was analyzed at least twice. The average area ratios are shown in Table VI. The relative reactivities of the substituted benzenes were calculated from the equation

$$k_A/k_B = \log(A_0/A)/\log(B_0/B)$$

where A_0 and B_0 are the relative areas obtained from the control runs (*i.e.*, before reaction), and A and B are the relative areas of the completed reactions.

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Reactions of Triarylsulfonium Salts with Bases[1]

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Contribution from the Chemistry Departments of the University of Massachusetts, Amherst, Massachusetts 01002, and Johnson State College, Johnson, Vermont 05656. *Received August 7, 1968*

Abstract: Triphenylsulfonium and tri-*p*-tolylsulfonium fluoroborate, iodide, bromide, and chloride salts have been prepared and subjected to reaction with sodium methoxide in methanol solution. In all cases, a mixture of aromatic hydrocarbons, biaryls, methyl aryl ethers, diaryl sulfides, and products of relatively high molecular weight were obtained. However, the molar ratios of these products differed markedly from one system to another. An interpretation of these results and of those of the reactions of some of the same triarylsulfonium salts with other sodium alkoxides is offered in terms of competing free-radical and aromatic bimolecular nucleophilic substitution reactions. Preliminary examinations of the thermal decomposition of triphenylsulfonium hydroxide and of the photolysis of triphenylsulfonium salts have also been made.

Reactions of triphenylsulfonium and tri-*p*-tolylsulfonium fluoroborate, iodide, bromide, and chloride salts with sodium methoxide in methanol solution have been carried out at 72° for 60 hr. The results are summarized in Table I. Similar reactions have also been carried out with triphenylsulfonium iodide, triphenylsulfonium bromide, and tri-*p*-tolylsulfonium bromide and sodium ethoxide, sodium *n*-butoxide, and sodium isopropoxide, respectively, the corresponding alcohols being used as solvents. The results of these reactions are summarized in Table II.

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(1) A preliminary report of some of this work has been published: J. W. Knapczyk, G. H. Wiegand, and W. E. McEwen, *Tetrahedron Letters*, 2971 (1965).