The following relative intensities were found for I-H, measured (corrected): *m/e* 252, 0.1842 (0.1915[32]); *m/e* 251, 1.0000 (1.0000); and *m/e* 250, 0.207.

The corrected relative intensities were obtained by subtracting 0.207 times the measured 252 intensity from the measured 251 intensity. In subsequent deuterium determinations of mixtures of I-H and I-D, eq 25 and 26 were used to convert observed intensities [$(251)_{\text{obsd}}$ and $(252)_{\text{obsd}}$)] into corrected intensities [$(251)_{\text{cor}}$ and $(252)_{\text{cor}}$].

$$(252)_{\text{obsd}} = (252)_{\text{cor}} + 0.191(251)_{\text{cor}} \qquad (25)$$

$$(251)_{\text{obsd}} = (251)_{\text{cor}} + 0.207(252)_{\text{cor}} \qquad (26)$$

Because of the complexity of fragmentation, analyses were performed with a calibration curve. Standard mixtures were prepared by weighing amounts of I-H$_{\pm}$ and I-D$_{+}$ totalling 100 mg into flasks, dissolving the solids in ether, evaporating the solvent, and thoroughly grinding the recovered solid in a mortar to ensure isotopic homogeneity. Analytical data for the standards are reported below. Results were reproducible to ±0.003 atom of D per molecule. A standard containing 0.488 atom of D per molecule was prepared from I-H$_{+}$ and I-D$_{+}$. Its analysis was indistinguishable from that reported in the data below, demonstrating that racemate and antipode of I do not fractionate during vaporization into the heated inlet system of the mass spectrometer. All intensity ratios are medians of ratios obtained from three to five separate introductions of the sample into the instrument. Only samples of nearly equal deuterium content were analyzed at one time because amide I had a strong affinity for the walls of the inlet and source of the mass spectrometer, which gave a memory effect. Samples of racemate and antipode from both reresolutions described above and sample J from partial exchange of I-D$_{+}$ in *t*-butyl alcohol were analyzed by this procedure. The calculated fraction of deuterium in each unknown sample was corrected by interpolation from the deviations reported for standards (Table VIII).

Table VIII

Known fraction D	$(252)_{\text{obsd}}/(251)_{\text{obsd}}$	Calcd fraction D	Deviation
0.295	0.556	0.292	−0.003
0.488	0.917	0.473	−0.015
0.681	1.474	0.649	−0.032

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(32) J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry," Elsevier Publishing Co., New York, N. Y., 1963, report 0.1906 for naturally occurring isotopes in $C_{17}H_{17}NO$.

Studies on Electrolytic Substitution Reactions. III.[1] Isomer Distributions and Isotope Effects in Nuclear and Side-Chain Anodic Acetoxylation of Aromatic Compounds

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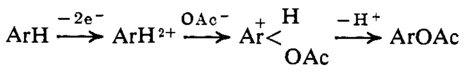
Abstract: Using the determination of isomer distributions as an experimental tool, the anodic acetoxylation of representative aromatic compounds in acetic acid–acetate has been investigated with respect to a number of experimental variables, such as the influence of changing the anode potential, the nature of the cation, and the concentration of the acetate ion. As regards the nature of the anion, it has been found that the presence of acetate ion is essential for *nuclear* acetoxylation to occur. A concerted mechanism, involving a two-electron transfer from the π-electron system of the aromatic compound simultaneously with the formation of a C–O bond to an acetate ion, is proposed for this reaction. This type of mechanism is closely similar to that generally assumed to be valid for electrophilic aromatic substitution reactions. Results from isomer distribution studies for anodic nuclear acetoxylation of a number of simple aromatic compounds confirm the validity of this analogy, as do also isotope effect determinations. In sharp contrast to nuclear acetoxylation, it has been found that *side-chain* acetoxylation of alkylaromatic compounds can also be achieved in acetic acid containing salts of other anions, such as perchlorate and tosylate. For side-chain acetoxylation of ethylbenzene an isotope effect $k_H:k_D$ of 2.6 ± 0.3 was determined. The similarity between the product distributions of anodic and manganic acetate acetoxylation of *p*-methoxytoluene further supports the view that benzyl cations are intermediates in side-chain acetoxylation, although existing data do not allow a differentiation between different mechanisms for their formation.

On the basis of polarographic measurements and preparative electrolyses at controlled anode potential (cpe), it was recently proposed[2] that the anodic acetoxylation of aromatic compounds observed during electrolysis in glacial acetic acid–sodium acetate proceeds *via* an initial two-electron transfer from the π-electron system of the aromatic compound to the anode, followed by a nucleophilic attack of acetate ion on the intermediate dicationic species (eq 1).



$$\mathrm{ArH} \xrightarrow{-2e^-} \mathrm{ArH^{2+}} \xrightarrow{\mathrm{OAc^-}} \overset{+}{\mathrm{Ar}}\!<^{\mathrm{H}}_{\mathrm{OAc}} \xrightarrow{-\mathrm{H^+}} \mathrm{ArOAc} \qquad (1)$$

The simultaneously occurring acetoxylation of the α-carbon atom of a side chain of an alkylaromatic compound was accounted for by a similar mechanism,[2] involving an initial two-electron transfer to the anode and loss of a proton to form a benzyl cation which then re-

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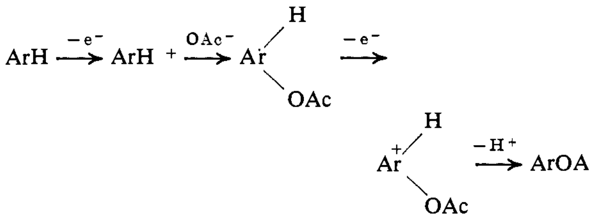
(1) Part II: L. Eberson and K. Nyberg, *Tetrahedron Letters*, 2389 (1966).

(2) L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966); *Acta Chem. Scand.*, **18**, 1568 (1964).

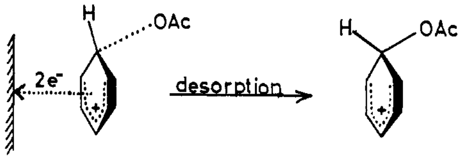
acts with acetate ion (eq 2). Polar mechanisms have also been invoked to explain the anodic addition of acetoxy groups across double bonds, *e.g.*, in the case of *trans*-stilbene[3] and cyclooctatetraene.[4]

$$\mathrm{ArCH_3} \xrightarrow{-2e^-} \mathrm{ArCH_3}^{2+} \xrightarrow{-H^+} \mathrm{ArCH_2}^{+} \xrightarrow{OAc^-} \mathrm{ArCH_2OAc} \quad (2)$$

The important feature of these mechanisms is of course the realization of the fact that it is the added aromatic substrate which participates in the primary electrode process and that the acetoxy radical does not play the role of a substituting (or adding) species in these reactions, as has been suggested earlier.[5] In other respects eq 1 and 2 represent simplifications, since they neglect the heterogeneous nature of the process and merely regard the electrode as a source of cationic intermediates. Thus, one cannot ignore the fact that the mechanism should be written as a series of consecutive one-electron transfer steps, as suggested by Perrin[6] (eq 3), or that the acetate ion actually assists in the electron-transfer step[2] (eq 4). In fact, a concerted mechanism involving an acetate ion assisted electron transfer leading directly to a Wheland-type intermediate (eq 4) would be a close analog to the mechanism of electrophilic aromatic substitution in homogeneous phase.[7]



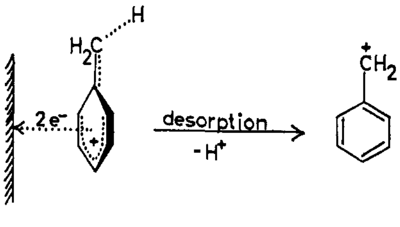
$$\mathrm{ArH} \xrightarrow{-e^-} \mathrm{ArH}^{+} \xrightarrow{OAc^-} \mathrm{Ar}\!<^{\mathrm{H}}_{\mathrm{OAc}} \xrightarrow{-e^-} {}^{+}\mathrm{Ar}\!<^{\mathrm{H}}_{\mathrm{OAc}} \xrightarrow{-H^+} \mathrm{ArOAc} \quad (3)$$



(4)

Likewise, one can describe the side-chain acetoxylation reaction as two consecutive electron transfers (eq 5), a mechanism similar to that proposed by Dewar, *et al.*,[8-10] for the oxidation of aromatic compounds by manganic acetate in acetic acid, or as a simultaneously occurring two-electron transfer and cleavage of the α-C–H bond to form a benzyl cation directly (eq 6). In order to attempt to make a differentiation between these mechanistic alternatives, a study of isomer distributions and isotope effects in the anodic acetoxylation of simple aromatic compounds has been undertaken, and the results of this study are presented in this paper.

$$\mathrm{ArCH_3} \xrightarrow{-e^-} \mathrm{ArCH_3}\cdot^{+} \xrightarrow{-H^+} \mathrm{ArCH_2}\cdot \xrightarrow{-e^-} \mathrm{ArCH_2}^{+} \xrightarrow{OAc^-} \mathrm{ArCH_2OAc} \quad (5)$$



(6)

Results

Analytical Procedure. In order to determine true isomer ratios in anodic acetoxylation it is of the utmost importance to note that the monoacetates primarily formed are often much less resistant toward oxidation than the starting material, and, besides, that isomeric acetates are oxidized at different rates.[2] Thus, anisole, with a half-wave potential *vs.* the saturated calomel electrode (sce) of 1.67 v in glacial acetic acid–sodium acetate, is oxidized to a mixture of *o*-, *m*-, and *p*-acetoxyanisole with half-wave potentials of 1.74, 1.25, and 1.12 v, respectively. This means that at a fixed anode potential the *meta* and *para* isomers will be consumed preferentially as the electrolysis progresses with a resultant increase in the *ortho*:*para* ratio, as indeed preparative runs have shown.[2] To avoid these secondary reactions it is necessary to analyze the product mixture in very early stages of the run. Consequently, samples were withdrawn and analyzed after passage of 1, 2, 3, and 4% of the charge calculated for a two-electron transfer process, and the mean value was then taken to be the isomer distribution. In all cases except one (*p*-methoxytoluene) no definite trend could be observed during this early period of the reaction, and the average value must therefore represent a close approximation of the true isomer distribution.

After about 10% reaction a gradual change in isomer distribution usually took place, and in cases where half-wave potentials of the isomeric acetates were known,[2] the change was qualitatively in agreement with predictions based on these values. Since previous investigators[5a,11] have analyzed their products after even higher conversions, the preferential oxidation of particular isomer is probably the main reason for the discrepancies between their results and ours (see Table IV).

Influence of the Anode Potential. Next, it was of interest to examine the effect of changing the anode potential upon product distribution. The compounds chosen for investigation differ widely in their susceptibility toward anodic oxidation, as evidenced by the half-wave potentials given in the third column of Table IV. These values are taken from the work of Lund[12] and Neikam, *et al.*,[13] and have been measured in the system acetonitrile–sodium perchlorate. No attempts were made to determine half-wave potentials in acetic acid–sodium acetate for all the compounds studied, since this electrolyte shows a high background current at potentials above 2 v which would make mea-

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[3] F. D. Mango and W. A. Bonner, *J. Org. Chem.*, **29**, 1367 (1964).

[4] L. Eberson, K. Nyberg, M. Finkelstein, R. C. Peterson, S. D. Ross, and J. J. Uebel, *J. Org. Chem.*, **32**, 16 (1967).

[5] (a) D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 4860 (1964); (b) C. L. Wilson and W. T. Lippincott, *J. Am. Chem. Soc.*, **78**, 4291 (1956); (c) R. P. Linstead, J. C. Bunt, B. C. L. Weedon, and B. R. Shephard, *J. Chem. Soc.*, 3624 (1952).

[6] C. L. Perrin, *Progr. Phys. Org. Chem.*, **3**, 165 (1965).

[7] The bookkeeping of electrons in the mechanism of electrophilic aromatic substitution can easily be made to conform to the scheme outlined in eq 4 if the attacking electrophile is allowed to play the electron-accepting role of the anode. Although this procedure is of formal interest only, it is not unreasonable in view of the fact that most electrophiles involved in aromatic substitution must be considered to be very strong oxidants.

[8] P. J. Andrulis, Jr., M. J. S. Dewar, R. Rietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).

[9] T. Aratani and M. J. S. Dewar, *ibid.*, **88**, 5479 (1966).

[10] P. J. Andrulis, Jr., and M. J. S. Dewar, *ibid.*, **88**, 5483 (1966).

[11] S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **86**, 4139 (1964).

[12] H. Lund, *Acta Chem. Scand.*, 11, 1323 (1957).

[13] W. C. Neikam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, 111, 1190 (1964).

surements on compounds resistant to oxidation difficult and inaccurate. However, the good linear correlation between the two sets of half-wave potentials observed previously[2] shows that the values measured in acetonitrile reflect the same order of oxidation susceptibility as in acetic acid.

Now, in orientation studies, it becomes necessary to compare product ratios from different reactions run at different anode potentials, and this might be a possible source of systematic error. To examine the magnitude of this effect, anisole was electrolyzed at five different anode potentials in the region 1.2–2.0 v and the product ratio determined. The results, given in Table I, show no significant trend as regards isomer distribution. Naphthalene and ethylbenzene were treated similarly with the same result. Therefore, we feel justified in comparing product ratios obtained at different anode potentials.

Table I. Anodic Acetoxylation of Anisole at Different Anode Potentials[a]

Anode potential *vs.* sce, v	Isomer distribution, % *ortho*	*meta*	*para*
1.20	68.1	3.7	28.2
1.40	67.4	3.5	29.1
1.60	66.8	3.7	29.5
1.80	67.0	3.3	29.6
2.00	68.3	3.3	28.4

[a] [OAc$^-$] = 1.00 *M*, [PhOCH$_3$] = 0.60 *M*.

Influence of the Cation. Alkali metal acetates have low dissociation constants[14,15] in acetic acid (of the order of 10^{-7} *M*) and must therefore exist predominantly as ion pairs under the reaction conditions employed. One might therefore expect that the steric requirements of the ion pair should increase with increasing size of the cation, and that a steric effect should be observable. To test this assumption, *t*-butylbenzene was electrolyzed in HOAc–MOAc, where M was Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, and Bu$_4$N$^+$. *t*-Butylbenzene was chosen in order to have a substituent with large steric requirements of its own, so that any effect of the cation would represent an upper limit. Table II shows that there is a weak trend toward diminishing *ortho*:*para* ratios with increasing size of the cation, indicating that it actually may be involved in the process. However, the effect is small and not entirely regular (LiOAc), even in a system where it would be expected to operate at its maximum, so it appears safe to conclude that the cation does not play any critical role in determining isomer distribution ratios.

Table II. Anodic Acetoxylation of *t*-Butylbenzene in HOAc–MOAc[a]

Cation	Isomer distribution, % *ortho*	*meta*	*para*	*ortho*: *para*
Li$^+$	32.3	21.3	46.4	0.70
Na$^+$	35.4	22.1	42.5	0.83
K$^+$	33.1	22.0	44.9	0.74
Rb$^+$	31.0	22.2	46.8	0.66
Cs$^+$	30.1	24.6	45.3	0.66
Bu$_4$N$^+$	28.2	25.0	46.5	0.61

[a] Anode potential 1.90 v *vs.* sce, [MOAc] = 1.00 *M*, [Ph-*t*-Bu] = 0.60 *M*.

Influence of the Concentration and Nature of the Anion. The variation in the isomer distribution with changes in the sodium acetate concentration is shown for anisole in Table III. On decreasing the acetate ion concentration by a factor of 10, there is a slight decrease in the *ortho*:*para* ratio, which may possibly be ascribed to a change in the distribution of species containing acetate ion accompanying changes in [NaOAc].

Table III. Anodic Acetoxylation of Anisole in HOAc–NaOAc[a]

[NaOAc]	Isomer distribution, % *ortho*	*meta*	*para*
1.00	67.4	3.5	29.1
0.33	57.3	3.2	39.5
0.10	60.2	2.2	37.6

[a] Anode potential *vs.* sce 1.40 v, [PhOMe] = 0.60 *M*.

Of much more interest is the abrupt change which takes place when acetate ion is replaced by other anions. In this case a fundamental difference between the side-chain and nuclear acetoxylation reactions appears, since *the side-chain reaction does not require the presence of acetate ion in order to occur. In sharp contrast, nuclear acetoxylation cannot be achieved in the absence of acetate ion.* Thus, ethylbenzene gives exclusively the α-acetoxy derivative when electrolyzed in HOAc–NaClO$_4$ or HOAc–Et$_4$N$^+$OTs$^-$, whereas in HOAc–NaOAc the products are partitioned in an approximate 1:1 ratio between the α-acetoxy compound and the three isomeric ethylphenyl acetates (see Table IV). On the other hand, neither anisole nor *t*-butylbenzene give any trace of nuclear acetoxylation products on electrolysis under those conditions (and also in HOAc–(NH$_4$)$_2$SO$_4$). In these cases, intensely colored solutions were formed, the nature of which have not yet been investigated. Nuclear acetoxylation of anisole could be effected by electrolysis in HOAc–KF, but in this medium species containing acetate ion must be present since fluoride ion is a fairly strong base (the solution had very strong glass-etching properties, indicating the presence of HF).[16]

That acetic acid is not essential as a medium for nuclear acetoxylation is shown by the fact that acetoxyanisoles were formed by electrolyzing anisole in 80% acetonitrile–20% water–(saturated solution) sodium acetate. The *ortho*:*meta*:*para* ratio was 66:5:29, not much different from the results obtained in HOAc–NaOAc (Table I).

The differentiation between nuclear and side-chain acetoxylation now possible is important for preparative applications. Nuclear acetoxylation generally tends to give fairly low yields of monoacetates because of secondary reactions, whereas this problem is not serious for the much more oxidation-resistant side-chain ace-

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[14] P. J. Proll and L. H. Sutcliffe, *Trans. Faraday Soc.*, **57**, 1078 (1961).

[15] O. W. Kolling and J. L. Lambert, *Inorg. Chem.*, **3**, 202 (1964).

[16] Dr. S. D. Ross at the Sprague Electric Co., North Adams, Mass., has kindly informed us that he has observed the same differentiation between side-chain and nuclear acetoxylation upon changing the nature of the anion. Toluene undergoes exclusive side-chain acetoxylation in HOAc–NH$_4$NO$_3$ with no trace of nuclear acetoxylation product observable. We have restricted ourselves to the use of salts of anions which are oxidized with difficulty, since there is no problem about the nature of the primary electrode process in these cases. Nitrate ion is discharged at much lower anode potentials, and hence radical intermediates must be considered in the discussion of possible mechanisms [*cf.* S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **88**, 4657 (1966)].

Table IV. Isomer Distribution in Anodic Acetoxylation of Aromatic Compounds, [NaOAc] = 1.00 *M*, [Substrate] = 0.60 *M*

Compound	Anode potential *vs.* sce, v	Half-wave potential[a] *vs.* Ag/Ag$^+$, v	Isomer distribution, % *ortho* or 1-	*meta* or 2-	*para*	α[b]
Toluene[c]	1.90	1.98, 1.93	43.2	11.1	45.7	28.6
Ethylbenzene[d]	1.90	1.96	43.8	10.2	46.0	50.5
Isopropylbenzene	1.90	1.87	44.0	16.5	39.5	46.7
t-Butylbenzene[e]	1.90	1.87	35.4	22.1	42.5	
Diphenylmethane	1.90		42.9	11.8	45.3	18.7
Fluorobenzene	1.96		34.1	8.2	57.7	
Chlorobenzene	2.00	2.07	36.8	5.5	57.7	
Bromobenzene	2.00	1.98	29.8	3.5	66.7	
Iodobenzene[f]	1.75	1.77	17.3	4.3	78.4	
Anisole[g]	1.40	1.35	67.4	3.5	29.1	
Phenyl acetate[h]	1.80		40.1	5.0	54.9	
Biphenyl	1.80	1.48	30.7	0.9	68.4	
Naphthalene[i]	1.70	1.34, 1.31	96.1	3.9		
Benzotrifluoride	2.4	2.6[j]		No acetates formed		
Methyl benzoate	2.4	2.4[j]		No acetates formed		

[a] Data taken from ref 12 and 13. [b] Percentage of total amount of acetoxylation products. [c] Lit.[5a] *ortho* 47.7, *meta* 11.2, and *para* 41.1% at high conversion and non-cpe conditions. [d] Lit.[11] *ortho* 48, *meta* 12, *para* 40, and α 44.5% at high conversion and non-cpe conditions. [e] Lit.[11] *ortho* 28, *meta* 27, and *para* 45% at high conversion and non-cpe conditions. [f] Analyzed after 15–20% conversion. About 90% of product appears as iodoxybenzene. [g] Lit.[5a] *ortho* 69.9, *meta* 1.8, and *para* 28.3% at high conversion and non-cpe conditons. [h] Lit.[11] *ortho* 56 and *para* 44% at high conversion and non-cpe conditions. [i] Lit.[11] 1- 84 and 2- 16% at high conversion and non-cpe conditions. [j] Estimated value.

toxylation products. The possibility of obtaining the side-chain acetoxylation product exclusively in media as HOAc–$NaClO_4$ or HOAc–Et_4^+ OTs^- would therefore be synthetically valuable.

Isomer Distribution Studies. Having established that the anode potential, the nature of the cation, and the concentration of acetate ion influence the isomer distribution in representative systems to a small extent only, the reaction conditions for a systematic study of isomer distributions could be fixed to the use of glacial acetic acid 1.00 *M* in sodium acetate and 0.60 *M* in substrate. If possible, the anode potential was kept at a value lower than the half-wave potentials given in Table IV in order to keep it lower than the critical potential for discharge of acetate ion. The temperature of the electrolyte was kept at 30°.

Following the analytical procedure described above, the isomer distributions shown in Table IV were obtained. It should be noted that the percentage of side-chain acetoxylation product is based on the total amount of products, whereas the figures for the *ortho*, *meta*, and *para* isomer of an alkylaromatic compound are based on the amount of nuclear acetoxylation products only in order to facilitate comparisons with other data.

In one case, iodobenzene, the reaction had to be run to an extent of 15–20% before acetoxylation products sufficient for satisfactory analyses had accumulated. This is due to the factor that the major pathway for anodic oxidation of iodobenzene gives rise to products in which the oxidation state of the iodine atom has changed. In this particular case iodoxybenzene could be identified among the products (no doubt small amounts of iodosobenzene and/or its diacetate were also formed), as has been found also in the electrolysis of iodobenzene in aqueous acetic acid.[17] Recent studies by Miller and Hoffman[18] have demonstrated that a similar reaction is predominant in cpe of iodobenzene in acetonitrile–lithium perchlorate, leading to 4-iodophenyliodonium perchlorate.

In good agreement with the postulate that the primary electrode process is an electron transfer from the aromatic compound to the anode, benzene derivatives containing strongly electron-withdrawing substituents (CF_3, COOMe) do not undergo acetoxylation under the conditions employed. Such substituents lower the energy of the highest filled π orbital of the molecule and hence it is more difficult to remove electrons from this orbital. From the excellent correlation between half-wave potentials in acetonitrile–sodium perchlorate and photoionization potentials,[13] it can be estimated from the photoionization potential of benzotrifluoride[19] (9.68 ev) that its half-wave potential in this medium would be about 2.6 v and hence about 2.9 v in HOAc–NaOAc *vs.* sce.[2] The photoionization potential of methyl benzoate does not appear to be known, but the value for benzaldehyde (9.51) gives 2.7 v as a crude estimate of the half-wave potential in HOAc–NaOAc. Thus, before one can attain an anode potential high enough for oxidizing these compounds, discharge of acetate ion will take place and be the predominant electrode reaction. This constitutes another piece of evidence speaking strongly against the intervention of acetoxy radicals as substituting species in anodic acetoxylation, since aromatic compounds with strongly electron-withdrawing substituents are actually very good substrates in homolytic substitution processes, *e.g.*, in homolytic hydroxylation by Fenton's reagent[20] or H_2O_2–Fe^{III}–catechol.[21] The situation is similar in homolytic alkylation and arylation processes,[20,22] and also in cases where the substituting radicals are produced anodically.[23]

Isotope Effects. To see if a primary deuterium isotope effect could be observed in side-chain acetoxylation, a preparative electrolysis of ethylbenzene-α-*d* in

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(17) F. Fichter and P. Lotter, *Helv. Chim. Acta*, **8**, 438 (1925).

(18) L. L. Miller and A. K. Hoffman, *J. Am. Chem, Soc.*, **89**, 593 (1967).

(19) D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966).

(20) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Inc., New York, N. Y., 1960, p 110 ff; R. O. C. Norman and G. K. Radda, *Proc. Chem. Soc.*, 138 (1962).

(21) G. A. Hamilton, J. W. Hanifin, Jr., and J. P. Friedman, *J. Am. Chem. Soc.*, **88**, 5269 (1966).

(22) J. R. Shelton and C. W. Uzelmeier, *ibid.*, **88**, 5222 (1966).

(23) For a summary, see L. Eberson in "Chemistry of the Carboxyl Group," S. Patai, Ed., Interscience Publishers, Inc., London, in press.

Table V. Anodic Acetoxylation of Ethylbenzene-α-d[a]

Compound	Isomer distribution, % of total products *ortho*	*meta*	*para*	α
Ethylbenzene	21.5	5.1	23.5	49.9
Ethylbenzene-α-d	25.4	5.9	26.2	42.5

[a] Anode potential 2.00 v *vs.* sce, [NaOAc] = 1.00 *M*.

Table VI. Anodic Acetoxylation of Deuterated Anisoles[a]

Compd	Isomer distribution, % *ortho*	*meta*	*para*
Anisole	67.4	3.5	29.1
Anisole-*o*-*d*	67.3	3.0	29.7
Anisole-*p*-*d*	64.9	4.2	30.9

[a] [NaOAc] = 1.00 *M*, anode potential 1.40 v *vs.* sce.

Table VII. Manganic Acetate Oxidation of PMT in Glacial HOAc at 70°[a]

Time, hr	Total yield of products, %	Product distribution, mole % *p*-Methoxybenzaldehyde	*p*-Methoxybenzyl acetate	2-Acetoxy-4-methylanisole	Ratio aldehyde/acetate
0.5	1.8	40	60	<0.1	0.67
1	2.8	34	66	<0.1	0.51
2	4.9	30	70	<0.1	0.43
5	8.3	25	75	<0.1	0.33
25	19.0	13	87	<0.1	0.15
52	31	9	91	<0.1	0.10
80	36	10	90	<0.1	0.11
∞	46	9[b]	91	<0.1	0.10
∞	47	10[c]	90	Not reported	0.11

[a] [PMT] = $[Mn(OAc)_3 \cdot 2H_2O]$ = 0.125 *M*. [b] Nmr analysis on the crude mixture gave an aldehyde/acetate ratio of 12:88. [c] Data from ref 8.

HOAc–NaOAc was performed. After hydrolysis, 1-phenylethanol was isolated and the percentage of deuterium label in the α position was determined (by nmr) to be 65 ± 2%, corresponding to a $k_H:k_D$ ratio of 2.6 ± 0.3. A similar but less accurate figure, 2.3 ± 0.7, could be calculated from the change in isomer distribution observed in the acetoxylation of ethylbenzene and ethylbenzene-α-d, respectively (Table V). Thus, C–H bond loosening is implied in the transition state of the rate-determining reaction, which is similar to what is observed[8] in the homogeneous side-chain acetoxylation of the methyl group of *p*-methoxytoluene by manganic acetate in glacial acetic acid, postulated to occur *via* an electron-transfer mechanism of the same type as that depicted in eq 5 (see eq 7 below). In this case the $k_H:k_D$ ratio was about 5, although for reasons discussed below this value may not be correct.

To study the effect of deuterium substitution in nuclear acetoxylation, *o*- or *p*-deuterioanisole was electrolyzed in HOAc-NaOAc and the isomer distribution determined. The mean value from several runs gave small deviations from the isomer ratio obtained with the protio compound, but the calculated isotope effects, $(k_H/k_D)_p$ = 0.9 ± 0.1 and $(k_H/k_D)_o$ = 1.0 ± 0.1, are hardly significantly different from unity (see Table VI).

Anodic *vs.* Manganic Acetic Oxidation of *p*-Methoxytoluene. The publication of a series of papers on aromatic oxidation by electron transfer[8–10] immediately suggested a comparison between anodic and manganic acetate acetoxylation of *p*-methoxytoluene (PMT) in order to see if there are any differences with regard to product distribution between these processes.

The products isolated from manganic acetate oxidation of PMT in HOAc at 70° (molar ratio of oxidant to PMT = 1:1) were recovered PMT (54.1%), *p*-methoxybenzyl acetate (40.5%), 2- and 3-acetoxy-4-methylanisole (yield not specified but claimed to be small), *p*-methoxybenzaldehyde (4.6%), and 1,2-bis(*p*-methoxyphenyl)ethane (yield not specified but claimed to be small).[8] Kinetic studies, mainly concerned with the determination of "initial rates" of disappearance of manganic acetate (during the first 10% of the reaction), made probable a mechanism of the electron-transfer type (eq 7).[8]

$$\begin{aligned}
&ArCH_3 + Mn(OAc)_3 \rightleftarrows \underset{\text{intimate ion pair}}{(ArCH_3^+), OAc^-} + Mn(OAc)_2 \\
&[(ArCH_3^+), OAc^-] \longrightarrow ArCH_2\cdot + AcOH \\
&ArCH_2\cdot + Mn^{III} \longrightarrow ArCH_2^+ + Mn^{II} \\
&ArCH_2^+ + AcOH \longrightarrow ArCH_2OAc + H^+ \qquad (7)
\end{aligned}$$

However, following our practice of analyzing the product at early stages of the run in order to minimize secondary reactions, quite different product distributions were observed. Specifically, it was hoped that the formation of *p*-methoxybenzaldehyde, assumed[8] to be formed *via* further oxidation of *p*-methoxybenzyl acetate to the aldehyde diacetate (which analyzes as the aldehyde on vpc), would be suppressed during the first few per cent of the reaction. Contrary to expectations, an initially high aldehyde to acetate ratio was observed, and this ratio then slowly decreased to a final value close to that reported previously[8] (see Table VII). Nmr analysis of the crude product mixture demonstrated that the aldehyde was formed as such and not as its diacetate.

Since manganic acetate contains two molecules of crystal water it seemed reasonable to assume that water, possibly preferentially bound to the manganic ion, partially replaces acetate ion as a nucleophile during the early phases of the reaction, resulting in the formation of *p*-methoxybenzyl alcohol. This is known[8] to be oxidized by manganic acetate at approximately the same rate as the starting material (relative alcohol:PMT = 0.95:1). *p*-Methoxybenzyl acetate cannot possibly be the precursor of the aldehyde, since the diacetate is not formed and the ratio between the oxidation rates of PMT and the acetate is 1:0.035, far too high to account for more than a small proportion of the aldehyde actually formed.

To study the possible role of water during the early stages of the reaction, it was run with 2.5% of water added (Table VIII) and in a medium consisting of

Table VIII. Manganic Acetate Oxidation of PMT in Wet[a] Acetic Acid at 70° [b]

Time, hr	Product distribution, mole %: *p*-Methoxybenzaldehyde	*p*-Methoxybenzyl acetate	2-Acetoxy-4-methylanisole	Ratio aldehyde/acetate
0.5	58	42	<0.1	1.38
1	48	52	<0.1	0.92
2	40	60	<0.1	0.67
5	24	76	<0.1	0.32
25	13	87	<0.1	0.15
∞	10	90	<0.1	0.11

[a] 2.5% water added. [b] [PMT] = [$Mn(OAc)_3 \cdot 2H_2O$] = 0.125 *M.*

Table IX. Manganic Acetate Oxidation of PMT in Preconditioned[a] Medium at 70° [b]

Time, hr	Product distribution, mole %: *p*-Methoxybenzaldehyde	*p*-Methoxybenzyl acetate	2-Acetoxy-4-methylanisole	Ratio aldehyde/acetate
0.5	4.8	95.2	<0.1	0.051
1	3.1	96.9	<0.1	0.032
2	1.7	98.3	<0.1	0.017
5	1.1	98.9	<0.1	0.011
25	1.4	98.6	<0.1	0.014
∞[c]	1.5	98.3	0.20	0.015

[a] $Mn(OAc)_3 \cdot 2H_2O$ was added to HOAc containing 4% of acetic anhydride and kept at 70° for 20 hr. Shorter preconditioning periods resulted in higher aldehyde/acetate ratios. [b] [PMT] = [$Mn(OAc)_3 \cdot 2H_2O$] = 0.125 *M.* [c] The product distribution is calculated only on the basis of the products mentioned in the table. Two unknown compounds, each having a molecular ion mass number of 194, were also visible in the gas chromatograms. These comprised 15.8 and 2.6%, respectively, of the *total* product mixture.

Table X. Anodic *vs.* Manganic Acetate Oxidation in PMT

Oxidant, medium	Amount of charge, % of theoret	Product distribution, mole %: *p*-Methoxybenzaldehyde	*p*-Methoxybenzyl acetate	2-Acetoxy-4-methylanisole	3-Acetoxy-4-methylanisole
Anodic oxidation in HOAc, preconditioned with acetic anhydride, at 30°	1.5	7.8	89.5	2.7	0.1
	2.5	6.6	91.3	2.0	0.07
	3.8	3.9	92.4	3.5	0.2
	7.5	3.4	93.1	3.4	0.1
	14	3.5	91.0	4.9	0.6
	40	11.4	83.8	4.3	0.5
Anodic oxidation in HOAc, preconditioned with acetic anhydride, at 70°	2.5	5.7	93.4	0.85	0.05
	5.0	3.6	95.4	0.9	0.1
	9.0	3.5	95.2	1.1	0.2
$Mn(OAc)_3$ oxidation in HOAc, preconditioned with Ac_2O, at 70°	3[a]	1.7	98.3	<0.1	
	5[a]	1.1	98.9	<0.1	

[a] Estimated per cent conversion.

$Mn(OAc)_3 \cdot 2H_2O$ in glacial acetic acid, preconditioned with 5% of added acetic anhydride for 20 hr at 70° before the addition of PMT (Table IX). The drastic effect on the aldehyde to *p*-methoxybenzyl acetate ratio clearly demonstrates that the water content of manganic acetate creates a different situation during the first 10–20% of the reaction as compared to the anhydrous case. Fortunately, *p*-methoxybenzyl alcohol is oxidized at nearly the same rate as PMT, so conclusions based on initial rate measurements are probably not much affected. On the other hand, oxidation rates are not known for PMT-α,α,α-d_3 and *p*-methoxybenzyl alcohol-α,α-d_2, so that the isotope effect reported[8] may be in error.

Having identified this source of error, comparisons between anodic and manganic acetate oxidation of PMT were based on runs in media which had been preconditioned by a small amount of acetic anhydride. The results are shown in Table X. Two products, not previously observed and as yet unidentified, both having a molecular ion peak at mass number 194 (corresponding to *p*-methoxybenzyl acetate + a methylene group), were found in the final product mixture from manganic acetate oxidation of PMT. It appears reasonable to assume that the slow spontaneous decomposition[9] of manganic acetate is responsible for the formation of these compounds. In a manner similar to the cobaltic ion oxidation of acetate ion[24] this reaction would produce methyl radicals which would then have a chance to be captured by PMT and/or its acetoxylation products. Lead tetraacetate oxidations of aromatic compounds are complicated by the same type of reaction.[5a,25]

Even if care has been taken to remove water as completely as possible from the media used there is still a trend toward initially high aldehyde to acetate ratios both in the anodic and manganic acetate case (Tables IX and X). Autoxidation of an intermediate benzyl radical is a possible explanation for this effect, since no special precautions were taken to remove oxygen completely from the solutions.

If the comparison between the two types of oxidations is restricted to an interval where the aldehyde percentage has assumed a steady value (*i.e.*, in the range of 5–10% reaction), one notes that the product distributions are closely similar, except possibly for the fact that nuclear acetoxylation occurs to a larger extent in the anodic case. Another noticeable feature of Table X is the temperature effect on the anodic process, the proportion of side-chain acetoxylation product increasing with temperature.

Discussion

Nuclear Acetoxylation. Our previous suggestion[2] that the anodic acetoxylation of an aromatic nucleus should be described by the mechanism depicted in

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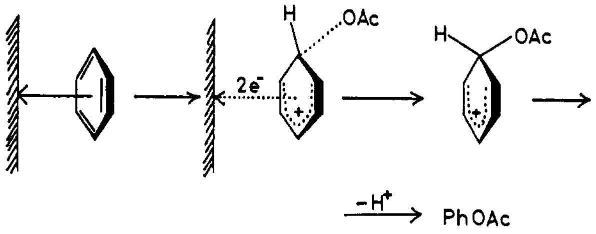
(24) A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 2796 (1965).

(25) R. Crigee in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965 p 277.

eq 1 (or eq 3, as preferred by Perrin[6]) was mainly intended to emphasize that electron transfer from the aromatic compound to the anode is the primary electrochemical step. The possibility that the nucleophile might actually assist in the electron-transfer step was discussed and by no means ruled out, but at that time existing data did not allow a decision between these alternatives. Some indications that one-electron transfers are favored in very weakly nucleophilic media and that nucleophile-assisted two-electron transfers are favored in more nucleophilic media were indeed to be found,[2] but these results did not easily lend themselves to an extrapolation to the behavior of the acetic acid–acetate system.

The finding that the presence of acetate ion is essential for the occurrence of nuclear acetoxylation and that the isomer distribution in anodic acetoxylation of anisole is somewhat dependent on the acetate ion concentration (Table III) strongly supports the view that acetate ion or an acetate–metal ion pair assists the electron-transfer step. Since the alkali metal acetates (and probably also $Bu_4N^+OAc^-$ [26]) have dissociation constants of the order of 10^{-7} *M* in HOAc, the predominant acetate ion containing species must be the ion pair. This would therefore likely be the active species, although one cannot exclude the fact that the field gradient near the anode forces a separation of the two ions. The weak steric effect of the cation (Table II) would seem to favor the ion pair as the active species, although opinion must be reserved at this point since the dissociation constants of different alkali metal acetates exhibit slight differences. An additional source of uncertainty is that data from different investigations disagree to a certain extent,[15,16] and hence a more detailed treatment must await further experimentation. The important conclusion that acetate ion in some form is involved in the product-determining step is not affected by these marginal problems.

Thus, the first refinement of eq 1 would be to include acetate ion in the product-determining step. Equation 8 is an attempt to do this. It consists of an adsorption step in which the aromatic compound is adsorbed to the anode, most likely *via* its π-electron system. In the second and rate-determining step, two electrons are transferred to the anode simultaneously with the formation of a carbon to oxygen bond to an acetate ion, resulting in the formation of a Wheland-type intermediate which is desorbed from the anode and gives product by loss of a proton.



(8)

Equation 8 represents a mechanism entirely analogous to that generally assumed to be valid for electrophilic aromatic substitution in homogeneous phase (π-complex formation between substrate and electrophile, a rate-determining attack of the electrophile on one of the ring carbons, formation of a Wheland intermediate, followed by rapid proton loss). If one postulates this kind of mechanism, one would expect that anodic acetoxylation would show the general characteristics of electrophilic aromatic substitution reactions, with regard to both isomer distribution and isotope effects.

The results shown in Table IV do indeed demonstrate a close resemblance between anodic acetoxylation and electrophilic aromatic substitution. Although the data cannot be treated quantitatively according to the Brown–Stock selectivity treatment[27] because of the lack of suitable data correlating relative rates of the substrates used, the fairly high proportion of *meta* derivatives observed in most cases (anisole, alkyl- and halobenzenes) suggests that the system anode–acetate should preferably be described as a low-selectivity "reagent." Some ambiguity is attached to this conclusion, though, since the result for biphenyl does not fit in very well.

A weak steric effect is indicated by the decreasing *ortho*:*para* ratios in the halobenzene series and for the pair isopropylbenzene–*t*-butylbenzene.

The absence of a significant positive deuterium effect on the *ortho* and *para* acetoxylation of anisole is another important similarity with electrophilic substitution reactions of this compound[28] (Table VI).

We do not think it worthwhile to discuss the orientation data and isotope effects in more detail at present, since too far reaching comparisons with homogeneous processes might lead to faulty conclusions. We are forced to conclude, however, that anodic acetoxylation has many of the characteristic features of an electrophilic aromatic substitution reaction, and therefore that the mechanism given in eq 8 should provide the best picture of nuclear anodic acetoxylation.

Side-Chain Acetoxylation. Equation 2 shows the mechanism previously suggested for side-chain acetoxylation.[2] The formation of a benzyl cation *via* an initial two-electron transfer from the alkylaromatic compound to the anode and subsequent loss of a proton from an α carbon are clearly the most important features of this mechanism. It has now been established that the presence of acetate ion is not a necessary requirement for side-chain acetoxylation to occur, and that acetic acid containing salts of different electrochemically inert anions (ClO_4^-, OTs^-, SO_4^{2-}) is just as good or even better as a medium. Moreover, alkylbenzenes have been shown to undergo anodic side-chain acetamidation on electrolysis in acetonitrile–sodium perchlorate[1] which is very difficult to rationalize if the intermediacy of benzyl cations is not postulated.

Accordingly, a benzyl cation is the most probable intermediate in side-chain acetoxylation, even if the mechanism in eq 2 must be slightly modified to accommodate the isotope effect observed. This was found to be 2.6 ± 0.3, implying a certain amount of C–H bond breaking in the transition state of the rate-determining step. This means that a concerted mechanism (eq 6), a rate-determining proton loss from the dication of eq 2, or a rate-determining proton loss from the cation radical of eq 5 must be considered. Existing data do not allow a differentiation between these alternatives, although the close similarity between anodic and

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[26] *Cf.* E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 2956 (1964).

[27] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[28] For a review, see H. Zollinger, *ibid.*, **2**, 163 (1964).

Table XI. Vpc Conditions for Analysis of Acetate Mixtures

Compound	Column[a]	Temp, °C	Retention time of acetate, min[b] ortho or 1-	meta or 2-	para	α
Toluene	A[c]	120	18.0	25.0	23.2	7.4
Ethylbenzene	B	120	10.3	13.0	14.0	8.4
Isopropylbenzene	B	110	15.8	21.2	24.2	12.2
t-Butylbenzene	C	120	22.8	25.4	32.0	
Diphenylmethane	B	180	16.4	24.0	27.0	13.0
Fluorobenzene	D	80	71.4	78.0	82.0	
Chlorobenzene	B	120	13.2	15.6	16.6	
Bromobenzene	B	130	14.9	18.4	19.6	
Iodobenzene	E	140	43.4	54.4	57.8	
Anisole	B	130	13.1	17.9	19.6	
Phenyl acetate	F	150	30.0	41.0	43.4	
Biphenyl	B	180	9.4	23.6	26.4	
Naphthalene	C	180	15.0	16.8		

[a] Column A, 2 m × 0.3 cm 10% trixylenyl phosphate on Chromosorb W 80–100; B, 2 m × 0.3 cm 5% neopentyl glycol succinate on Chromosorb P 80–100; C, 2 m × 0.3 cm 10% Apiezon L on Chromosorb P 80–100; D, same as C but 4 m in length; E, 2 m × 0.3 cm 10% butanediol succinate polyester on Chromosorb W 80–100 in combination with column B; F, same as B but 4 m in length. [b] Nitrogen flow rate 30 cc/min. [c] Analyzed as a mixture of cresols and benzyl alcohol.

manganic acetate acetoxylation (Table X) of PMT would seem to favor the last-mentioned one.

Concluding, we wish to emphasize that anodic acetoxylation can be described mechanistically in very much the same way as similar homogeneous processes of the electrophilic type. Differences which can be traced back to the heterogeneous nature of the electrolytic reaction have not yet been found. It is hoped that stereochemical studies of the side-chain acetoxylation reaction will provide some insight into this complex problem.

Experimental Section

Materials. Analytical grade acetic acid was distilled through a ten-plate column before use, a middle fraction comprising about 70% of the batch being collected. Analytical grade inorganic reagents were used throughout for preparing the electrolytes. Manganic acetate was prepared according to the method given by Dewar, *et al.*[8]

The organic compounds studied were purchased in the purest quality available and carefully checked for impurities by vpc. If the region in which the corresponding monoacetates eluted was not entirely clean at high attenuations, the compound was further purified by distillation or preparative vpc. For use as reference compounds, all the monoacetates of the compounds listed in the first column of Table IV (except benzotrifluoride, in which case only the *m*-acetate was prepared) were synthesized from commercially available phenols according to well-known procedures. 4-Methoxybenzylidene diacetate and 2- and 3-acetoxy-4-methylanisole were prepared according to the methods given by Dewar, *et al.*[8] The deuterium-labeled compounds were synthesized by treating the appropriate Grignard reagent with D_2O.

Procedure. The isomer distribution experiments were carried out using the same electrolysis cell set-up as that described earlier,[2] except that the volume of the vessel was 60 ml. The appropriate electrolyte (50.0 ml, 0.6 *M* in substrate and 1.00 *M* in supporting electrolyte in the case of the acetates, unless otherwise required, and saturated with respect to other supporting electrolytes referred to above) was poured into the cell and allowed to reach thermal equilibrium (30°). The anode potential was controlled by means of a Model 557 potentiostat from Amel, Milan, Italy, and the charge passed through the electrolyte was measured by means of the Model 558 integrator from the same company. After starting the electrolysis, 2.00-ml samples were withdrawn after passage of 1, 2, 3, and 4% of the theoretically calculated amount of charge (except in the case of iodobenzene, as mentioned above). Each sample was worked up by pouring it into saturated bicarbonate solution (20 ml), extracting the organic components with analytical grade ether, and washing the ether extracts with saturated bicarbonate solution. Finally, the ether solution was concentrated to a volume of about 0.4 ml, and the products were analyzed by vpc (Perkin-Elmer 880 gas chromatograph, equipped with a disk integrator) under the conditions given in Table XI. Adequate checks on the work-up procedure using acetic acid solutions of known composition were made. It is estimated that the percentages given are correct to ±0.5% (absolute value).

In cases where monoacetates have not been isolated and identified previously,[2,11] identification was based on vpc comparisons with authentic samples at several temperatures on several columns. Mass spectrometry was also used for identification in some cases (LKB A-9000 mass spectrometer, equipped with a gas chromatography inlet).

Anodic Oxidation of Iodobenzene. Iodobenzene (0.15 mole) in 250 ml of acetic acid–sodium acetate (1.00 *M*) was electrolyzed at an anode potential of 1.80 v *vs.* sce until 9000 coulombs had passed through the electrolyte. The solution was then dropped into a vigorously stirred slurry of sodium bicarbonate (320 g) in water (700 ml). One extraction with ether removed ether-soluble organic materials, and then the aqueous layer was allowed to stand for 1 week. A small amount of a solid (0.9 g) was collected by filtration. A sample was recrystallized from water; explosion point of the pure product was about 240°, infrared spectrum identical with that of authentic iodoxybenzene.

Anodic Oxidation of Ethylbenzene-*α*-*d*. Ethylbenzene-*α*-*d* (0.15 mole, containing 7 ± 0.5% of protio compound according to nmr analysis) in 250 ml of acetic acid–sodium acetate (1.00 *M*) was electrolyzed at an anode potential of 2.00 v *vs.* sce until vpc analysis of a small sample indicated a 35–40% conversion into acetates. The solution was dropped into a vigorously stirred slurry of sodium bicarbonate (320 g) in water (700 ml). The organic product was taken up in ether (three 100-ml portions) and then the ether evaporated *in vacuo*. The residue was treated with a solution of potassium hydroxide (3.5 g), ethanol (60 ml), and water (20 ml) overnight at room temperature. After distilling off most of the ethanol *in vacuo*, water was added, and the organic products were taken up in ether. The cresols were removed by washing with 0.1 *M* potassium hydroxide (three 50-ml portions) and water (20 ml). After drying with anhydrous magnesium sulfate, distillation gave 1-phenylethanol (1.2 g), bp 50–51° (0.3 mm). Nmr analysis of this product gave the percentage of 1-phenylethanol-1-*d* as 65 ± 1% (integration of all signals) and 64 ± 1% (integration of methyl group signal only).

Anodic Oxidation of PMT. The medium used for anodic oxidation of PMT was made by adding 2% acetic anhydride to acetic acid–sodium acetate solution and refluxing the solution overnight.

Manganic Acetate Oxidations. These were performed in stoppered flasks (100-ml volume), containing 80-ml samples 0.125 *M* in $Mn(OAc)_3 \cdot 2H_2O$ and 0.125 *M* in PMT with glacial acetic acid (Table VII) or glacial acetic acid containing 2.5% of water (Table VIII) as solvent. In the third case (Table IX) the manganic acetate solution was first made 5% with respect to acetic anhydride and kept at 70° for 20 hr before addition of PMT. Samples were withdrawn at suitable intervals, worked up, and analyzed as described above. Vpc was carried out using column B (see Table XI). At a column temperature of 130° and a nitrogen flow rate of 30 cc/min, retention times (minutes) of products were: *p*-methoxybenzaldehyde, 14.6; 2-acetoxy-4-methylanisole, 16.8; 3-acetoxy-4-methylanisole, 20.0; *p*-methoxybenzyl acetate, 28.0; unknown peak I (molecular weight 194), 30.5; and unknown peak II (molecular weight 194), 38.2.

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The Transition State for Base-Catalyzed Cleavage of the Silicon–Oxygen Bond[1]

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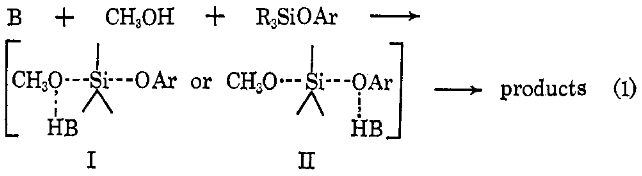
Abstract: Substituent correlations and solvent isotope effects have been examined for the general base catalyzed methanolysis of aryloxytriphenysilanes, previously shown to follow a protolytic mechanism. The solvent isotope effects for *p*-chlorophenoxytriphenylsilane are $k_H/k_D = 1.25 \pm 0.06$ (acetate ion catalysis) and 1.35 ± 0.06 (methoxide ion catalysis), consistent with "solvation-rule" behavior. Curvature in the free-energy relations for leaving-group structural variation is analyzed and is tentatively interpreted in terms of π bonding of the leaving group to silicon in the activated complex or of a change in mechanism with substituent.

Our earlier observation[1] that the methanolysis of phenoxytriphenylsilane is subject to general base catalysis by phenoxide ion, leading to the conclusion that the reaction follows a protolytic pathway (eq 1), further substantiates a general resemblance of these reactions to the cleavage of carboxylic and phosphate esters. We have therefore undertaken a more detailed characterization of the transition state for base-catalyzed solvolysis of silicon–oxygen compounds, by use of isotope and substituent effects.



Results

Observed rate constants for methanolysis of five aryloxytriphenylsilanes in acetic acid–acetate ion buffers in methanol and methanol-d_1 (CH_3OD) and in phenol–phenoxide ion buffers in methanol are given in Table I. The results may be summarized by the kinetic law of eq 2, where S represents the substrate organosilicon compound and the summation is over all bases, B_i, in the solution. The values of the catalytic constants of eq 2 are shown in Table II. From corresponding rate constants in methanol and methanol-*d*, the isotope effects for methanolysis of *p*-chlorophenoxytriphenylsilane, catalyzed by acetate and methoxide ions, can be calculated.

$$(k_H/k_D)_{CH_3CO_2^-} = 1.25 \pm 0.06$$

$$(k_H/k_D)_{CH_3O^-} = 1.35 \pm 0.06$$

$$v = [S]\left\{k_0 + \sum_i k_i[B_i]\right\} \qquad (2)$$

Discussion

Solvent Isotope Effects. The activated complex drawn in eq 1 for the reaction under study depicts a proton undergoing transfer from or to the catalyst. If such a transfer were part of the primary activation process, so that the proton would be in an unstable potential at the activated complex, a primary isotope effect of about 7.8, corresponding to the Brønsted β value[1] of about 0.7, would have been expected.[2] The observed isotope effects are much smaller than the predicted ones, and it therefore appears likely that the proton is not in an unstable potential at the activated complex; the BH moiety is presumably stabilizing the activated complex by a hydrogen-bonding interaction, as postulated by Swain and his co-workers[3] for other examples of general catalysis in protic solvents. The methanolysis of aryloxysilanes appears to conform to the "solvation rule" classification[3] as do carbonyl derivative reactions in which the leaving group is an oxyanion.[2]

These isotope effects present an interesting contrast to the striking observation of Menger[4] that methoxide ion attack on *p*-nitrophenyl acetate proceeds 2.6 times more rapidly in methanol-*d* than in methanol at −78°. If a completely exponential temperature dependence with unit preexponential factor is assumed ($k_H/k_D = \exp(-a/T)$ the inverse isotope effect is still 1.9 at 25°, equal to the effect reported by Menger[4] for methoxide attack on phenyl benzoate at 25°. The regular effects

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(1) Catalysis in Organosilicon Chemistry. II. For part I, see R. L. Schowen and K. S. Latham, Jr., *J. Am. Chem. Soc.*, **88**, 3795 (1966). For further details, see K. S. Latham, Jr., Ph.D. Thesis, University of Kansas, Oct 1966. This work was supported by the National Science Foundation under Research Grant No. GP 3539 and by the National Institutes of Health under Research Grant No. GM 12477-02 and was carried out in part at the Computation Center of the University of Kansas.

(2) The primary isotope effect prediction is made with the aid of Figure 1 of R. L. Schowen, H. Jayaraman, L. Kershner, and G. W. Zuorick, *J. Am. Chem. Soc.*, **88**, 4008 (1966).

(3) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *ibid.*, **87**, 1553 (1965).

(4) F. M. Menger, *ibid.*, **88**, 5356 (1966).