Anodic Reactions of Acetate Ion at Graphite Anodes

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MECHANISTIC investigations of anodic acetoxylation are made difficult by the occurrence of a competing reaction, oxidation of acetate ion to methyl radical, which in many cases accounts for most of the charge passed.[1,2] It has been demonstrated that the methyl radical derived from the oxidation of acetate ion is oxidized to methyl cation at carbon anodes.[3] We now compare results of anodic acetoxylation of aromatic compounds at platinum and graphite anodes and show how change in the nature of the competing reaction, acetate oxidation, affects the product distribution.

Electrolysis of solutions of sodium acetate in acetic acid containing benzene, at a platinum anode, produces phenylacetate as the only monosubstitution product.[4] We have verified this result at a platinum anode, but found that at a graphite anode methylation products predominate. Toluene could not be detected among the products at a platinum anode, but it is the major product at a graphite anode.

We have compared the product distribution at platinum and graphite anodes for the electrolysis of a number of aromatic compounds in acetic acid containing sodium acetate (Table 1). The electrolyses were conducted at constant current, a graphite (area 6·5 cm.^{2}) and a platinum electrode (6·5 cm.^{2}) being used. Solutions containing the aromatic compound (0·60M) and sodium acetate (1·0M) in glacial acetic acid were electrolyzed for a given time at 300 mA, the platinum electrode being used as the anode. An identical solution was then electrolyzed for the same time in the same cell with the polarity of the electrodes reversed. The products of the electrolysis were analyzed by g.l.c. and identified by comparison of their retention times and i.r. and mass spectra with those of authentic samples.

Two factors other than anode material appear to be important in controlling the relative amounts of methylation and acetoxylation; (*a*) ease of anodic oxidation of the aromatic substrate, and (*b*) reactivity toward electrophilic substitution. Anisole and naphthalene, both easily oxidized, give predominant acetoxylation. Benzene and chlorobenzene are very similar in ease of oxidation (Table 1). However, benzene is more than four times as reactive as chlorobenzene toward electrophilic alkylation.[5] Methylation predominates in the case of benzene while acetoxylation is slightly favoured with chlorobenzene. Methylation of naphthalene occurs at both graphite and platinum anodes but to a much greater extent on graphite.

Methylation at a platinum anode apparently involves attack on the aromatic substrate by methyl radical in the manner suggested for the anodic methylation of trinitrotoluene to trinitroxylene.[6] Methylation, at a graphite anode, of compounds that are not methylated at platinum anodes, most likely involves an electrophilic attack on the aromatic substrate by methyl cation. A competing reaction is the combination of methyl cation with acetate ion to form methyl acetate.[3]

TABLE 1

Effect of anode material on product distribution

	Half-wave potential[a] Ag/Ag+ (v)	Graphite		Platinum	
		Methylation	Acetoxylation	Methylation	Acetoxylation
Benzene	2·08[b]	89	11	0	100
Chlorobenzene	2·07[c]	34	66	0	100
Bromobenzene	1·98[c]	69	31	1	99
Anisole	1·35[c]	0	100	0	100
Naphthalene	1·34[c]	10·8	89·2	1·3	98·7

[a] Measured in acetonitrile. [b] Ref. 4. [c] Ref. 2.

Table 2 compares products obtained at platinum and graphite anodes for the anodic acetoxylation of mesitylene.

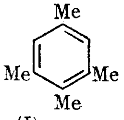
At a platinum anode, both nuclear and side-chain acetoxylation, as well as methylation, take place during the electrolysis of mesitylene (0·6M) and sodium acetate (1·0M) in glacial acetic acid. Changing the anode material to graphite almost completely suppresses side-chain substitution, and only nuclear substitution products are observed (Table 2).

TABLE 2

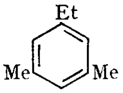
Effect of methyl radical concentration on product distribution

Product	Platinum[a]	Graphite[a,b]	Platinum (ref. 1)
(I)	2·4	7·8	4·8
(II)	3·8		13·6
(III)	25·9	Trace	23·2
(IV)	67·9	92·2	58·4

[a] Area = 6·5 cm.^{2}, NaOAc = 1·0M. [b] Spectrographic grade graphite rod. Mesitylene = 0·6M.



(I)



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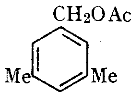

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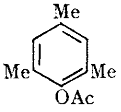
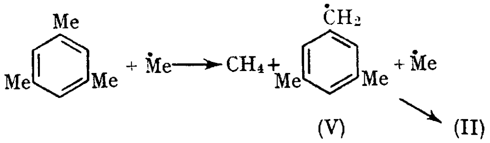


(IV)

The only conceivable route to the formation of 5-ethyl-*m*-xylene (II) is the combination of the appropriate benzyl radical (V) with methyl



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radical (Scheme). This compound is only observed at platinum anodes. The absence of (II) at graphite anodes may be a consequence of the diminished concentration of methyl radical due to the ready oxidation to methyl cation. Likewise, the acetate (III) is only observed at platinum anodes. The absence of both (II) and (III) at graphite anodes strongly suggests that the radical (V) is a precursor to the side-chain substituted acetate (III) as well as 5-ethyl-*m*-xylene (II).

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