Studies on Electrolytic Substitution Reactions. I. Anodic Acetoxylation

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Abstract: In order to elucidate the mechanism of anodic acetoxylation, a number of organic compounds, most of them aromatic, have been studied polarographically at a rotating platinum anode in acetic acid–0.5 *M* sodium acetate solution. Half-wave potentials thus obtained demonstrate that the organic substrate participates in an electrochemical process which takes place at a potential considerably lower than the discharge potential of the acetate ion. Controlled potential electrolysis of naphthalene, biphenyl, anisole, phenyl acetate, mesitylene, durene, and hexamethylbenzene confirms that acetates are formed at low anode potentials. For the polymethylbenzenes side-chain acetoxylation is observed, mesitylene being a borderline case. 1,1-Diphenylethylene and N,N-dimethylformamide, which previously have been shown to give acetoxylation products on electrolysis in acetic acid–sodium acetate, give the same products on controlled potential electrolysis. A mechanism involving an initial two-electron transfer from the organic substrate to the anode to form a dicationic intermediate, followed by reaction with acetate ion and loss of a proton, is proposed for anodic oxidation of aromatic compounds. The side-chain substitution products can be accounted for by assuming that the intermediate loses a proton from one methyl group to form a benzyl cation. A number of other anodic substitution processes probably conform to a similar mechanism.

Anodic substitution reactions are well documented in the chemical literature.[2] Thus, fluorinations, chlorinations, brominations, iodinations, cyanations, thiocyanations, nitrations, alkoxylations, formoxylations, and acetoxylations have been carried out by electrolyzing an organic substrate in the presence of the appropriate anion in a suitable solvent. The over-all reaction has generally been formulated as a one-electron transfer (eq 1), and the mechanism has been

$$RH + A^- \longrightarrow RA + H\cdot + e^- \qquad (1)$$

assumed to be an attack of an anodically generated radical on the organic substrate, followed by abstraction of a hydrogen atom. In some cases, notably halogenations, it has been suggested that molecular A_2 is the attacking species in a purely chemical step.

Closely connected with the mechanism of anodic substitution are a number of polarographic studies on aromatic compounds.[3–7] These have been run with a rotating platinum anode in the solvent system acetonitrile–sodium perchlorate, and it has been demonstrated that these reactions are two-electron processes[3] and that the half-wave potentials generally are well correlated with various parameters calculated from simple molecular orbital theory.[4,5,7,8]

The anodic acetoxylation reaction has been studied in a number of cases,[9–11] mainly with the purpose of demonstrating that the Kolbe electrolysis of acetic acid proceeds *via* an intermediate acetoxy radical. By electrolyzing acetic acid–sodium acetate in the presence of an aromatic compound, such as naphthalene[9] or anisole,[10,11] it was possible to isolate acetoxy compounds from the reaction mixture, and this was taken as evidence for a mechanism involving discharge of acetate ion to form the acetoxy radical, which then would attack the aromatic compound by a radical mechanism. Considering the fact that the Kolbe electrolysis of acetic acid requires a very high anode potential[12] ($>+2.0$ v *vs.* the saturated calomel electrode), that the oxidation half-wave potentials for anisole and naphthalene in acetonitrile are considerably lower than this potential,[3] and that the acetoxy radical is known to be extremely short lived,[13] it was proposed[14] that the formation of acetoxy compounds might instead occur by oxidation of the organic substrate followed by reaction of a cationic intermediate with acetate ion. In a preliminary communication[15] evidence was presented that this was actually the case. The system glacial acetic acid–acetate ion was a suitable medium for polarographic studies at the rotating platinum electrode, and it was found that a number of aromatic compounds, among them anisole and naphthalene, gave oxidation waves at considerably lower anode potentials than that required for the Kolbe electrolysis of acetic acid. Controlled potential electrolysis then confirmed that acetates were formed from anisole and naphthalene at a potential at which the contribution from the Kolbe process was almost negligible.

The correctness of this mechanism has independently

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[2] For review articles see M. J. Allen, "Organic Electrode Processes," Chapman and Hall Ltd., London, 1958, pp 142–163; A. P. Tomilov, *Russ. Chem. Rev.* (English Transl.), **30**, 639 (1961); on the technically important subject of anodic fluorination: M. Stacey, J. L. Tatlow, and A. G. Sharpe, *Advan. Fluorine Chem.*, **1**, 129 (1960).

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

[4] E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

[5] W. C. Neikam and M. M. Desmond, *ibid.*, **86**, 4811 (1964); W. C. Neikam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, **111**, 1190 (1964).

[6] F. J. Vermillion, Jr., and I. A. Pearl, *ibid.*, **111**, 1392 (1964).

[7] A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4124 (1964); A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *ibid.*, **86**, 4130 (1964); A. Zweig and J. E. Lehnsen, *ibid.*, **87**, 2647 (1965).

[8] G. J. Hoijtink, *Rec. Trav. Chim.*, **77**, 555 (1958).

[9] R. P. Linstead, J. C. Bunt, B. C. L. Weedon, and B. R. Shephard, *J. Chem. Soc.*, 3624 (1952).

[10] C. L. Wilson and W. T. Lippincott, *J. Am. Chem. Soc.*, 78, 4291 (1956); *J. Electrochem. Soc.*, 103, 672 (1956).

[11] D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 4860 (1964).

[12] For references see, G. E. Svadkovskaya and S. A. Voitkevich, *Russ. Chem. Rev.* (English Transl.), **29**, 161 (1959); see also B. E. Conway and M. Dzieciuch, *Can. J. Chem.*, **41**, 21, 38, 55 (1963).

[13] W. Braun, L. Rajkenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

[14] L. Eberson, *Acta Chem. Scand.*, **17**, 2004 (1963).

[15] L. Eberson and K. Nyberg, *ibid.*, **18**, 1568 (1964).

been demonstrated by Salzberg and co-workers,[16] who studied voltage–current density curves for the system acetic acid–acetate ion with and without added organic substrate and found that the oxidation potential was lowered sharply in the presence of the organic substrate. The same observation was made by Ross, Finkelstein, and Petersen,[17] who also found that addition of naphthalene decreased the amount of evolved Kolbe anode gas ($C_2H_6 + CO_2$) to about 5% of the theoretical value. Less easily oxidized compounds also lowered the rate of gas evolution at the anode, though not so drastically. An analogous mechanism was proposed by Mango and Bonner[18] in order to account for the formation of acetoxylation products by co-electrolyzing different diphenylethylenes and acetic acid–acetate ion. The latter two investigations were not, however, done under controlled anode potential conditions.

This paper is a full report of our work on the acetoxylation reaction, with special reference to systems which have been studied previously. In all cases studied a mechanism involving oxidation of the organic substrate as the electrochemical step appears to be valid.

Results

Half-wave potentials for a number of organic compounds in HOAc–0.5 *M* NaOAc are given in Table I.

Table I. Half-Wave Potentials for the Oxidation of Organic Compounds in HOAc–0.5 *M* NaOAc at the Rotating Pt Electrode

No.	Compound	$E_{1/2}$(ox), v *vs.* sce	Prep anode potential
1	Mesitylene	1.90	1.65
2	Durene	1.62	1.70
3	Pentamethylbenzene	1.62	
4	Hexamethylbenzene	1.52	1.50
5	Naphthalene	1.72	1.50
6	1-Methylnaphthalene	1.53	
7	2-Methylnaphthalene	1.55	
8	Biphenyl	1.91	1.60
9	Biphenylene	1.30	
10	Acenaphthene	1.36	
11	Acenaphthylene	1.53	
12	Fluorene	1.65	
13	Anthracene	1.20	
14	Phenanthrene	1.68	
15	Pyrene	1.20	
16	Triphenylene	1.74	
17	Perylene	1.00	
18	Fluoranthene	1.64	
19	Anisole	1.67	1.50
20	Phenyl acetate	1.30	1.60
21	*trans*-Stilbene	1.51	
22	1,1-Diphenylethylene	1.52	1.60
23	2-Biphenyl-COOH	1.71	1.75
24	Azulene	0.91	
25	Cyclooctatetraene	1.42	
26	Thiophene	1.91	
27	Furan	1.70	
28	2,5-Dimethylfuran	1.20	
29	Dimethylformamide	1.90	1.50

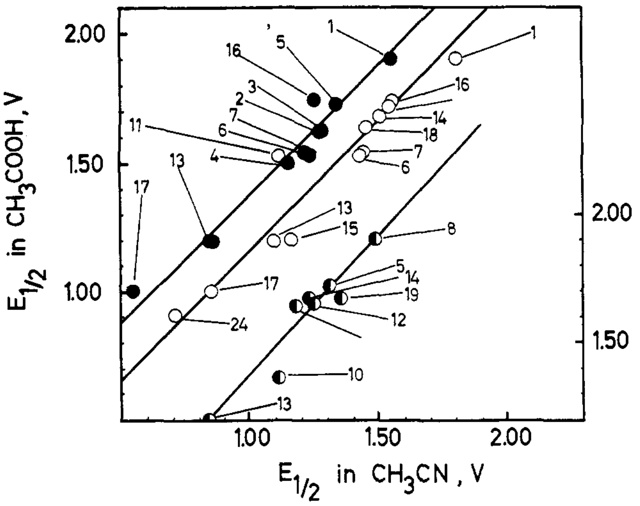

Figure 1. Plots of $E_{1/2}$(ox) in HOAc–0.5 *M* NaOAc against $E_{1/2}$(ox) in CH_3CN–$NaClO_4$. Filled circles correspond to data given by Neikam and Desmond;[5] semifilled circles to data given by Lund[3] (for clarity, the ordinate axis has been moved downwards by 0.7 v in this plot); empty circles to data given by Pysh and Yang.[4]

The compounds have partly been chosen to allow a comparison with previous investigations on polarographic oxidation potentials of aromatic hydrocarbons and partly to provide guidance in the preparative work. Therefore, compounds with half-wave potentials higher than +2.0 v have been omitted, since in this region preparative results would be inconclusive with regard to the mechanism of acetate formation. Also, the interference from the acetate discharge reaction becomes serious in this region, resulting in low accuracy in the half-wave potentials.

In Figure 1, our data have been plotted against those of Lund,[3] Pysh and Yang,[4] and Neikam and Desmond.[5] Satisfactory linear relationships are obtained with slopes very close to unity. The difference between the intercepts on the ordinate axis is about 0.24 v, in reasonable agreement with the difference between the potentials of the silver–silver ion (0.1 *N*) electrode and the saturated calomel electrode, 0.30 v.[4]

The preparative runs have all been run at anode potentials well below +2.0 v, as is seen from Table I. Generally, a potential close to the appropriate half-wave potential was chosen in order to keep the electrolysis time within reasonable limits, but it must be emphasized that the anode potentials could be lowered further by 0.3–0.4 v with an improvement in the yield of acetoxylated compounds. The electrolyses were run until 75% of the charge calculated for a two-electron process had passed through the electrolyte (except in the case of N,N-dimethylformamide). This was considered to be the best compromise for the entire series of compounds investigated. Since the main objective was to determine the mechanism by isolating and identifying products of monoacetoxylation, no effort was made to maximize the yields. Some of the low yields obtained were probably due to the fact that the monoacetoxylated products have half-wave potentials close to that of the starting material, resulting in a further oxidation to a diacetoxy compound, which in turn can be oxidized, etc., resulting in considerable tar formation. This is demonstrated by the data in Table II, which

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(16) M. Leung, J. Herz, and H. W. Salzberg, *J. Org. Chem.*, 30, 310 (1965); H. W. Salzberg and M. Leung, *ibid.*, 30, 2873 (1965).

(17) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 4139 (1964).

(18) F. D. Mango and W. H. Bonner, *J. Org. Chem.*, **29**, 1367 (1964).

gives half-wave potentials for monoacetoxy compounds derived from naphthalene, biphenyl, anisole, and phenyl acetate. In most cases the acetoxy compound has a half-wave potential close to or even lower than that of the starting material. Also, the difference in half-wave potential between isomeric acetoxy derivatives suggests that too much importance should not be attached to the isomer distributions obtained, since one isomer might well be enriched because of its higher oxidation potential.

Table II. Half-Wave Potentials for the Oxidation of Some Aromatic Compounds and the Corresponding Monoacetates, in HOAc–0.5 *M* NaOAc

No.	Compound	$E_{1/2}$(ox), v *vs.* sce
5	Naphthalene	1.72
	1-Acetoxynaphthalene	1.67
	2-Acetoxynaphthalene	1.86
8	Biphenyl	1.91
	2-Acetoxybiphenyl	2.04
	4-Acetoxybiphenyl	1.90
19	Anisole	1.67
	2-Acetoxyanisole	1.74
	3-Acetoxyanisole	1.25
	4-Acetoxyanisole	1.12
20	Phenyl acetate	1.30
	1,2-Diacetoxybenzene	~2.5
	1,3-Diacetoxybenzene	1.46
	1,4-Diacetoxybenzene	~2.5

On anodic oxidation of naphthalene in acetic acid–0.35 *M* sodium acetate at a potential of 1.50 v there was obtained a 22% yield of 1-acetoxynaphthalene in addition to a 1.0% yield of a mixture of 1- and 2-methylnaphthalene. The formation of methylnaphthalenes (and generally, of methylated products from the anodic oxidations of certain aromatic compounds in HOAc–NaOAc) has also been observed by Ross, Finkelstein, and Petersen[17] and was explained as a result of the homolytic methylation of naphthalene by anodically generated methyl radicals (eq 2). Their

$$CH_3COO^- \longrightarrow CH_3\cdot + CO_2 + e^- \qquad (2)$$

experiment was not done under controlled potential conditions. However, our run at 1.50 v shows that the Kolbe process is not completely excluded even at this rather low potential. To show this competition unequivocally, the oxidation was carried out at 1.0 v, in which case 24% of 1-acetoxynaphthalene and less than 0.4% of methylnaphthalenes were obtained, and at 1.7 v, in which case the yield of the acetate was 16% and of methylnaphthalenes, 4%. The increase in acetate yield and decrease in yield of methylated products with decreasing anode potential is a good indication that two anode processes are competitive in this system and that the formation of the acetoxy derivative occurs *via* an initial electrochemical oxidation of naphthalene.

Linstead, *et al.*,[9] reported a 24% yield of 1-acetoxynaphthalene, whereas Ross, *et al.*,[17] obtained 21% of the acetate and a total yield of methylnaphthalenes of 5.7%. In addition, they found a 4% yield of the 2 isomer, which we have failed to detect. The relatively high proportion of methylnaphthalenes indicates that the anode potential has been rather high in their experiment, allowing both the naphthalene oxidation and the Kolbe process to occur simultaneously.

Anodic oxidation of biphenyl produced a 37% yield of a mixture of 2- and 4-acetoxybiphenyl in the proportions 2:3 with no *meta* derivative nor any methylated products being detectable.

From anisole, 27% of a mixture of 2- and 4-acetoxyanisole was isolated, the distribution between the isomers being 9:1. By running the electrolysis under identical conditions, but with only 50% of the theoretically calculated current,[15] the yield of acetate was 40% and the *ortho*:*para* ratio 6:1, which nicely illustrates the importance of considering half-wave potentials of starting material and monoacetoxy derivatives (Table II) when trying to optimize the yields. The *para* compound has a half-wave potential which is about 0.6 v lower than that of the *ortho* compound and will be consumed at the anode at a higher rate. Previous investigators[10,11] have reported an *ortho*:*para* ratio of about 7:3.

Phenyl acetate gave a 17% yield of a 9:11 mixture of 1,2- and 1,4-diacetoxybenzene, respectively, whereas Ross, *et al.*,[17] working under somewhat differing conditions, obtained a 37% yield of an 11:9 mixture.

Mesitylene afforded an 18% yield of 2,4,6-trimethylphenyl acetate and 2% 3,5-dimethylbenzyl acetate, *e.g.*, a product resulting from side-chain acetoxylation. Previous investigators,[17] using a threefold excess of current over the theoretically calculated amount, isolated 29% of the 2,4,6-trimethylphenyl acetate and 11.5% 3,5-dimethylbenzyl acetate.

From durene, a 46% yield of the side-chain acetoxylation product, 2,4,5-trimethylbenzyl acetate, was isolated. Hexamethylbenzene gave 57% pentamethylbenzyl acetate.

Mango and Bonner[18] have electrolyzed 1,1-diphenylethylene in the presence of acetic acid–acetate ion and isolated 1,2-di-O-acetyl-1,1-diphenylethylene glycol (10%) and 2-O-acetyl-1,1-diphenylethylene glycol (30%). At an anode potential of 1.50 v, we obtained the same products in yields of 15 and 59%, respectively.

Ross and co-workers[19] have shown that N,N-dimethylformamide (DMF) can be formoxylated or acetoxylated in one methyl group anodically by electrolysis of a mixture of DMF and the appropriate acid and its anion. We have repeated the acetoxylation experiment at an anode potential of 1.50 v and isolated the same product, N-acetoxymethyl-N-methylformamide. In addition, we have tried to use a similar technique to elucidate the formoxylation mechanism but have not been successful as yet, since formic acid–formate has a much lower discharge potential. We do obtain the same compounds as reported, but the results are inconclusive as regards the mechanism.

Finally, biphenyl-2-carboxylic acid was electrolyzed at 1.75 v, giving a 36% yield of the lactone of 2′-hydroxybiphenyl-2-carboxylic acid. This conversion has been done previously by chemical agents (chromium trioxide, hydrogen peroxide) and by electrolysis (sodium salt, aqueous solution).[20]

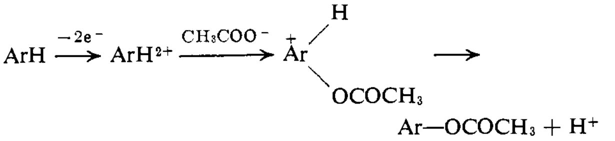
Discussion

We have previously[15] proposed that anodic acetoxylation of an aromatic compound proceeds *via* a two-

[19] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 2745 (1964).

[20] G. W. Kenner, M. A. Murray, and C. M. B. Tayler, *Tetrahedron*, **1**, 259 (1957).

electron transfer from the organic substrate to the anode followed or assisted by reaction with acetate ion to form the same type of intermediate as in normal electrophilic substitution in homogeneous solution (eq 3). This should be contrasted with the earlier proposal



$$\mathrm{ArH} \xrightarrow{-2e^-} \mathrm{ArH}^{2+} \xrightarrow{\mathrm{CH_3COO^-}} \overset{+}{\mathrm{Ar}}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OCOCH_3}\end{smallmatrix} \longrightarrow \mathrm{Ar{-}OCOCH_3} + \mathrm{H^+} \qquad (3)$$

that an acetoxy radical would be formed in the initial step by discharge of an acetate ion and subsequently react with the substrate by a radical mechanism.[9–11] To compare the merits of these two mechanisms it appeared to be a suitable starting point to see if there was a counterpart to anodic acetoxylation in homogeneous systems.

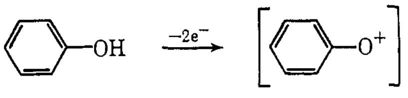
No instance of a direct acetoxylation by an acetoxy radical of a simple benzene derivative has been unambiguously established.[21] Acetoxy radicals generated by thermal decomposition of diacetyl peroxide decarboxylate to give methyl radicals, which then react with the aromate in different ways. This is the chemical basis for the well-known methyl affinity scale[22] developed by Szwarc. In some cases, acetoxylation has been accomplished by treating aromatic compounds, notably polynuclear hydrocarbons, with lead tetraacetate, but it has recently been demonstrated that this type of acetoxylation probably is an electrophilic process, occurring *via* the normal Wheland-type intermediate.[11] At temperatures below 80°, there was no evidence for the participation of radicals in the initial reaction between lead tetraacetate and the aromatics investigated. In this reaction naphthalene undergoes 1 substitution,[23] and anisole is attacked predominantly in the *para* position.[11]

In contrast to acetoxylation, homolytic benzoyloxylation[24] has been reported in a number of cases, which is not surprising since the benzoyloxy radical decarboxylates with an estimated rate constant[14] of about 1 sec^{-1} as compared to that of the acetoxy radical, 10^9 sec^{-1}. Naphthalene gives a mixture of 1- and 2-naphthyl benzoates in the proportion 73:27,[25] anisole a mixture of *o*- and *p*-benzoyloxyanisole in the approximate proportions 7:3,[26] and biphenyl an undefined mixture of 2-, 3-, and 4-benzoyloxybiphenyl.[27]

Finally, homolytic hydroxylations in homogeneous solution have been studied extensively.[28] As regards isomer distribution this type of substitution appears to discriminate very little between *ortho*, *meta*, and *para* positions in simple aromatic compounds.

Thus, there does not appear to be any homolytic analog in homogeneous solution to the anodic acetoxylation process, but instead an electrophilic one.[11] Unfortunately, we cannot compare the anodic isomer distribution data with those for the corresponding homogeneous electrophilic reaction, because of the possibility of selective anodic oxidation of one isomer. The preponderance of *ortho–para* substitution is, however, an indication of a polar process, although we do not want to stress this argument too much.

Therefore, polarographic and preparative electrochemical results will be needed as evidence for a polar mechanism. All of the compounds investigated have half-wave potentials well below that prevailing during Kolbe electrolysis of acetic acid and give acetates at potentials 0.5–1.0 v lower than this potential. The anodic oxidation of aromatic hydrocarbons has been shown to be a two-electron transfer[3] in agreement with what is required for mechanism 3. Also, anodic oxidation of nonionized phenolic compounds[6] has been shown to be a two-electron transfer and here a phenoxonium ion has been invoked as an intermediate (eq 4).



(4)

There are some cases reported of what appear to be one-electron transfers in anodic oxidations of aromatic compounds.[29,30] In these cases coupled products are formed, *e.g.*, bianthrone from the electrolytic oxidation of anthracene in acetonitrile.[29] In contrast to this, a two-electron oxidation of anthracene in acetonitrile–pyridine–perchlorate gives 9,10-dihydroanthranyldipyridinium diperchlorate.[3] We never isolated any coupled products in our systems, and therefore assume that the presence of the nucleophilic acetate ion may actually assist the electron transfer process, as is indeed indicated for pyridine by polarographic data.[3] Although acetonitrile behaves as a nucleophile toward the intermediate generated in anodic oxidation,[31] it is probably weak enough to allow one-electron transfers, especially for compounds like anthracene which in nonnucleophilic solvents display two anodic waves corresponding to the transfer of the first and second electron, respectively.[32]

At the potentials used in the preparative runs, discharge of acetate ion occurs to a small extent in addition to the anodic acetoxylation process. This results in the formation of small amounts of methylated compounds, and for naphthalene it was demonstrated that this side reaction can be almost eliminated at a sufficiently low anode potential. Naphthalene has a much higher methyl affinity than the other aromatics studied, which explains why methylation is not observed for other substrates. Ross, Finkelstein, and Petersen[17] found methylated products also from ethylbenzene and mesitylene, probably because a higher anode potential

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(21) H. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Ltd., London, 1960, p 118.

(22) See ref 21, p 99.

(23) L. F. Fieser, R. Clapp, and W. Daudt, *J. Am. Chem. Soc.*, **64**, 2052 (1942).

(24) See ref 21, p 116.

(25) D. I. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1878 (1958).

(26) B. M. Lynch and R. B. Moore, *Can. J. Chem.*, 40, 1461 (1962).

(27) D. J. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 562 (1961).

(28) See ref 21, p 110.

(29) K. E. Friend and W. E. Ohnesorge, *J. Org. Chem.*, 28, 2435 (1963).

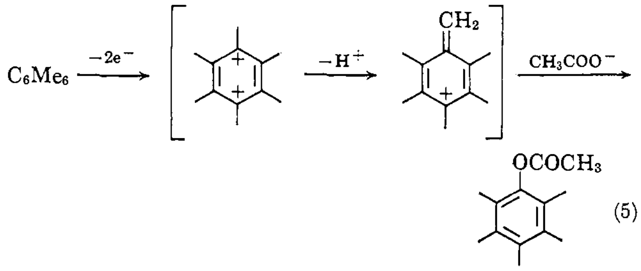
(30) J. F. K. Wilshire, *Australian J. Chem.*, **16**, 432 (1963); for further references see A. P. Tomilov and M. Ya. Fioshin, *Russ. Chem. Rev.* (English Transl.), **32**, 30 (1963), and A. I. Scott, *Quart. Rev.* (London), **19**, 1 (1965).

(31) Anodic side-chain acetamidation can be accomplished by electrolysis of durene and hexamethylbenzene in acetonitrile–water–sodium perchlorate: *cf.* L. Eberson and K. Nyberg, *Acta Chem. Scand.*, **18**, 1567 (1964).

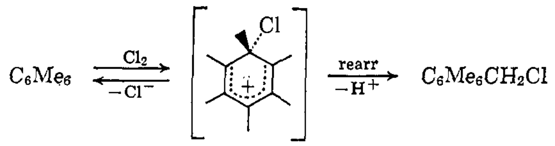
(32) Thus, two anodic waves are displayed in polarograms of aromatic hydrocarbons using dimethyl sulfate as a solvent and tetrabutylammonium perchlorate as a supporting electrolyte: G. J. Hoijtink, private communication.

was maintained allowing a better competition from the acetate discharge reaction.

Interestingly enough, side-chain acetoxylation appears to be the dominant process in the anodic oxidation of polymethylbenzenes in HOAc–NaOAc, mesitylene being a borderline case.[17] Only the homolytic attack of an acetoxy radical in the side-chain was considered probable in this case by previous investigators.[17] In view of the polarographic data and the preparative results from the controlled potential oxidation of mesitylene, durene, and hexamethylbenzene it seems highly probable that the mechanism is instead an initial two-electron transfer from the π-electron system to form a dicationic intermediate, which loses a proton from one methyl group to form a benzyl cation. This mechanism is exemplified for hexamethylbenzene in eq 5.



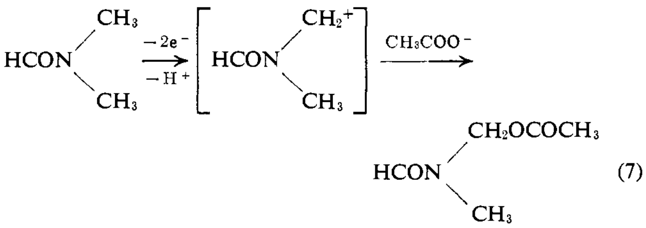
A similar substitution reaction, chlorination of hexamethylbenzene to form pentamethylbenzyl chloride, has been reported in homogeneous system. This reaction has been demonstrated to be an electrophilic process[33] (eq 6).



(6)

Mango and Bonner[18] studied the electrolysis of 1,1-diphenylethylene and stilbene in HOAc–NaOAc and found evidence for a mechanism involving a two-electron transfer from the alkene with the formation of an intermediate acetoxonium ion. The characteristic stereoselectivity of such an ion toward attack by water and acetic acid was observed in the stilbene experiment. Again, polarographic data and controlled potential electrolysis demonstrate the correctness of this mechanism.

Finally, the electrochemical data show that the acetoxylation of DMF[19] also proceeds according to a polar mechanism (eq 7). It is tempting to interpret



the formoxylation reaction in an analogous way, but it must be stressed that this cannot be demonstrated unequivocally by the methods used in this investigation. The electrochemical behavior of the formic acid–formate system is quite different from that of the acetic acid–acetate system, and, therefore, the same technique cannot be applied. The formation of N-(triphenylacetoxymethyl)-N-methylformamide[34] by electrolysis of triphenylacetic acid in DMF is, however, also best interpreted according to mechanism 7 and not as an attack by triphenylacetoxy radicals on DMF.

Some other anodic substitution processes have been examined briefly, and mechanisms analogous to (3) have been proposed in some cases. Recently, Tsutsumi and co-workers[35] obtained a mixture of 2- and 4-cyanoanisole by electrolysis of methanol–anisole–sodium cyanide, which was interpreted as an attack by cyano radicals on the aromatic compound. However, Parker and Burgert[36] demonstrated that no cyanoanisole was formed at an anode potential of 1.2 v, in spite of the fact that cyanide ions were actually discharged. At 2.0 v, cyanoanisoles were formed, indicating that the electrochemical process is an electron transfer from anisole. Thus, for anodic cyanation the same mechanism as for acetoxylation seems to be valid.

The technically important anodic fluorination process in liquid hydrofluoric acid is an interesting case of anodic substitution.[1] The reaction is applicable to virtually all kinds of organic compounds and usually leads to polyfluorination. No elemental fluorine is evolved during the reaction and it has been assumed that it occurs *via* adsorbed fluorine atoms. Schmidt and co-workers[37,38] studied anodic fluorination by co-electrolyzing olefins with an inorganic fluoride in a nonaqueous solvent. As an example, from 1,1-diphenylethylene in acetonitrile–silver fluoride there was isolated 1,2-difluoro-1,1-diphenylethylene,[38] quite analogous to what is obtained in the acetoxylation reaction. A mechanism involving an initial two-electron transfer from the alkene to form a dicationic intermediate was proposed. It is not clear, however, whether this experiment was done under controlled anode potential conditions.

Anodic methoxylation reactions have been studied in some detail[39–41] and it has been proposed that they proceed *via* anodically generated methoxyl radicals. No controlled potential experiments have been reported, but since the preparative results are partly different from other anodic substitution processes, this mechanism cannot be excluded. Yet, the formation of quinone ketals by anodic oxidation of dimethoxybenzenes[42] as well as the formation of dihydrobenzoin dimethyl ethers from stilbene[39] might well be interpreted similarly to eq 3.

There are many other anodic substitution processes, all of which have been known for many years. There has been very little mechanistic exploration, but we feel that a polar mechanism similar to eq 3 in many cases is an attractive alternative to other, more speculative ones.

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Investigations on anodic substitution processes in general are in progress.

Experimental Section

Materials. Analytical grade acetic acid was frozen out three times before use in the polarographic experiments. In the preparative runs, analytical grade acetic acid was used directly. Analytical grade sodium bicarbonate and acetic anhydride were used to make up the solution used in the polarographic runs.

Compounds **1**, **2**, **6**, **7**, **11**, **15–18**, **21**, **22**, **24**, **25**, **27**, and **29** were purchased from Fluka AG, Buchs, Switzerland; compound **19** was Eastman White Label quality; compounds **5**, **8**, **10**, **12**, and **13** were purchased from Kebo AB, Stockholm, Sweden; **26** was obtained from Merck AG, Darmstadt, Germany; and **28** was obtained from Light & Co., Colnbrook, England. Penta- and hexamethylbenzene,[43] biphenylene,[44] phenyl acetate,[45] and biphenyl-2-carboxylic acid[46] were prepared according to well-known procedures. The following standard substances were prepared according to known methods: 1- and 2-naphthyl acetate,[45] 2-acetoxyanisole,[47] 3-acetoxyanisole,[48] 4-acetoxyanisole,[49] 2- and 4-acetoxybiphenyl,[50] 3-acetoxybiphenyl,[51] 1,2- and 1,4-diacetoxybenzene,[52] 1,3-diacetoxybenzene,[53] 2-O-acetyl-1,1-diphenylethylene glycol,[18] and 2,4,6-trimethylphenyl acetate.[54] All compounds were purified by sublimation, distillation, and/or recrystallization and the purity checked by vapor phase chromatography and/or comparison of physical constants with literature values.

Procedures. For the polarographic investigations, the Type PO-4 "Polariter" polarograph equipped with the SMP 11/D 131/P 141 rotating Pt electrode from Radiometer, Copenhagen, was used. The preparation of solutions has been described elsewhere.[15] All half-wave potentials given in Tables I and II are corrected for *iR* drop.

The preparative experiments were run according to the following standard procedure (except for DMF). The electrolyte was made up of 0.025 mole of the organic compound, 0.05 mole of anhydrous sodium acetate, and 100–150 ml of glacial acetic acid. The electrolysis cell was a water-jacketed 250-ml beaker, fitted with a platinum wire anode (surface area about 2 cm^2) and a platinum foil cathode (area about 10 cm^2). The reference electrode was a saturated calomel electrode (Radiometer, Type K 101), brought into close contact with the anode. The anode potential was measured by means of a Senior VoltOhmyst WV-98C voltmeter. The potential was adjusted to the appropriate anode potential (Table I) and kept there with aid of an automatically controlled potential device, constructed by the Electronics Service Department, University of Lund, Sweden. Normally, this allowed for a current of 0.05–0.1 amp to pass through the electrolyte, which was stirred magnetically and kept around room temperature by passing water through the water jacket. The reaction was then run until 0.037 coulomb had passed through the electrolyte.

After terminating the reaction, most of the acetic acid was evaporated in a rotating film evaporator at 40°. The residue was treated with water and the organic material was extracted with ether. The ether solution was washed thoroughly with sodium bicarbonate solution and water. After drying with anhydrous magnesium sulfate, the ether was removed by distillation and the residue was worked up using column chromatography on silica gel, preparative vapor phase chromatography, or a combination of these methods. In addition to the compounds isolated, considerable amounts of tars were present in the reaction mixture in most cases.

All compounds mentioned in the Results and Experimental Section have been isolated in pure state and compared with authentic samples by means of melting point and/or infrared spectra or identified by comparison with literature data in combination with nmr spectral data. All yields given are based on unrecovered starting material.

Analytical gas chromatographic work was done using a Perkin-Elmer Model 800 or Perkin-Elmer "Fraktometer" gas chromatograph. The preparative separations were done using an Autoprep Model A-700. The following columns were used: for the analytical work, column A, 2 m × 0.6 cm 20% silicone oil DC-200 on Chromosorb P, or column B, 2 m × 0.6 cm 10% apiezon on Kieselguhr 60–100; for the preparative work, column C, 6 m × 1.0 cm 20% silicone gum rubber SE-30 on Chromosorb P.

Naphthalene. The reaction product was subjected to chromatography on silica gel using chloroform as an eluent. A mixture of naphthalene and 1- and 2-methylnaphthalene was eluted first and analyzed on column B. The next fraction was 1-acetoxynaphthalene, which was checked for the 2 isomer using vpc on column A.

Biphenyl. The reaction product was chromatographed on silica gel using benzene as an eluent. Unreacted biphenyl was eluted first, followed by a mixture of 2- and 4-acetoxybiphenyl. The isomers were separated by preparative vpc on column C.

Anisole. The reaction product was distilled and a fraction with boiling point up to 70° (0.5 mm) was collected. Analytical vpc on column A demonstrated it to be a mixture of 2- and 4-acetoxyanisole, which were then separated by preparative vpc on column C.

Phenyl Acetate. The reaction product was chromatographed on silica gel using benzene as an eluent. The first fraction contained unreacted phenyl acetate. Then, a mixture of 1,2- and 1,4-diacetoxybenzene was eluted with ether and separated by preparative vpc on column C.

Mesitylene. The reaction product was chromatographed on silica gel using benzene containing 10% ligroin as an eluent. This procedure gave a liquid fraction, which was distilled before being subjected to preparative vpc on column C. The liquid contained mesityl acetate as the major component, contaminated by a small proportion of 3,5-dimethylbenzyl acetate.

Durene. The reaction product was chromatographed on silica gel using benzene as an eluent. Unreacted durene was first eluted, followed by 2,4,5-trimethylbenzyl acetate, identified by hydrolysis (boiling with 10% ethanolic potassium hydroxide for 4 hr) to 2,4,5-trimethylbenzyl alcohol, mp 86–89° (lit[55] mp 83–83.5°).

Hexamethylbenzene. The reaction product was chromatographed on silica gel using benzene as an eluent. Hexamethylbenzene was eluted first, followed by pentamethylbenzyl acetate, mp 81.5–83.5° (lit[56] mp 83–85°), which was hydrolyzed to pentamethylbenzyl alcohol, mp 157.5–160° (lit[56] mp 155–158°).

1,1-Diphenylethylene. The work-up and separation procedure was essentially the same as that used by Mango and Bonner.[18] 2-O-Acetyl-1,1-diphenylethylene glycol had mp 90–91° (lit[18] mp 91–92.5°) and 1,2-di-O-acetyl-1,1-diphenylethylene glycol, mp 140–146° (lit[18] mp 145–148°).

N,N-Dimethylformamide. The electrolyte in this case consisted of DMF (75 ml), glacial acetic acid (75 ml), and anhydrous sodium acetate (4.2 g). It was electrolyzed for 42 hr at an anode potential of 1.50 v, which allowed for a current of 0.75 amp to pass through the solution. Then, most of the acetic acid and DMF was distilled off at 15 mm through a Glass-helix packed column of five theoretical plates. The residue was dissolved in water and the water solution was extracted continuously with ether for 24 hr. The ether solution was dried with anhydrous magnesium sulfate, and the ether was distilled off. The residual liquid was distilled at 0.5 mm and a fraction, bp 50–60°, collected. Accordingly to analytical vpc on column A, this material contained one major component, contaminated by acetic acid and DMF. The product was purified by preparative vpc on column C. Elemental analyses, and infrared and nmr spectra were in excellent agreement with the structure of N-acetoxymethyl-N-methylformamide.[19]

Biphenyl-2-carboxylic Acid. The ether solution containing the reaction products was extracted with sodium bicarbonate solution in order to remove unreacted starting material. The remaining material was chromatographed on alumina using chloroform as an eluent. The lactone of 2′-hydroxybiphenyl-2-carboxylic acid, mp 92–93° (lit[20] mp 86–88°), was obtained pure by this procedure.

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