A small sample of the methyl ester was hydrolyzed by boiling with an excess of ethanolic potassium hydroxide over night. The ethanol was distilled off and the residue acidified with 10 % hydrochloric acid. The solid was filtered off, dried, and recrystallized from ethyl acetate. According to analyses and infra-red spectrum it was N-acetyl-2,2,3,3-tetramethyl-β-alanine, m.p. 180–183°. (Analysis: Found: C 57.4; H 9.0; N 7.5; O 25.8. Calc. for $C_9H_{17}NO_3$: C 57.7; H 9.2; N 7.5; O 25.6).

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Studies on the Kolbe Electrolytic Synthesis

VI. On the Mechanism of Anodic Acetoxylation

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In paper IV of this series,[1] it was suggested that the formation of acetoxy compounds during electrolysis of sodium acetate in acetic acid in the presence of aromatic substrates (*e.g. o-* and *p*-acetoxyanisole from anisole [2] and 1-acetoxynaphthalene from naphthalene [3]) might occur by way of anodic oxidation of the aromatic substrate followed or assisted by reaction with acetate ion. The mechanism proposed earlier,[2] involving a homolytic reaction of electrolytically generated acetoxy radicals with the aromatic compounds, seems less attractive in view of the extremely short life-time of the acetoxy radical.

Table 1. Oxidation half-wave potentials for some aromatic compounds in acetic acid containing 0.5 M sodium acetate.

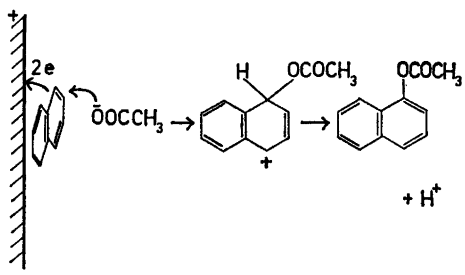
Compound	$E_{1/2}$ in acetic acid *versus* s.c.e., corrected for IR-drop in the solution	$E_{1/2}$ in acetonitrile [4] (0.5 M in $NaClO_4$) *versus* Ag^+/Ag
Anthracene	1.20	0.84
Acenaphthene	1.36	1.11
Trans-stilbene	1.51	
1,1-Diphenyl ethylene	1.52	
Retene	1.64	1.18
Fluorene	1.65	1.25
Anisole	1.67	1.35
Phenanthrene	1.68	1.23
Naphthalene	1.72	1.31
Diphenyl	1.91	1.48

We now wish to report some preliminary results which show that the first mechanism must be the correct one. Lund [4] and Pysh and Yang [5] have determined the oxidation half-wave potentials in acetonitrile for a large number of aromatic compounds at a rotating platinum anode. It was found that acetic acid containing 0.5 M sodium acetate was also suitable as a medium for this type of oxidation polarography. In Table 1 values of $E_{1/2}$ (ox) *versus* the saturated calomel electrode (s.c.e.) for some compounds of interest are given, together with Lund's values in acetonitrile. There is a reasonably good linear correlation between these two sets of values.

Now the main point of interest in Table 1 is the value of $E_{1/2}$ for anisole and naphthalene, both of which are known to give acetoxy compounds when co-electrolyzed with acetate-acetic acid. Since the Kolbe process *starts* at potentials above 2.0 V *vs.* s.c.e.[6] and does not occur at lower potentials, it is apparent that these two compounds are involved in an oxidation process at considerably lower potentials than

that demanded by the Kolbe reaction. This could be shown preparatively by running the electrolysis of anisole or naphthalene in acetate-acetic acid at a constant anode potential of 1.5 V (in fact, the reaction could be run even at an anode potential as low as 1.1 V), *i.e.* far below the potential region where the Kolbe reaction starts. The formation of *o*- and *p*-acetoxyanisole and 1-acetoxynaphthalene, respectively, shows that the electrode process must involve oxidation of the aromatic compound, not the acetate ion.

Recently, Bonner and Mango [7] arrived at similar conclusions from a study of the anodic acetoxylation of 1,1-diphenylethylene and *trans*-stilbene. They suggested that two electrons are removed from the diarylethylene molecule at the anode surface followed or assisted by acetate ion. In order to explain the steric course of the reaction in the case of *trans*-stilbene a cyclic acetoxonium intermediate was postulated. The low value of $E_{1/2}$ for 1,1-diphenylethylene and trans-stilbene given in Table 1 is entirely in accordance with this hypothesis. Thus we favor the following mechanism for the anodic acetoxylation of aromatic compounds (here exemplified by naphthalene):



We also suggest that a number of other oxidative electrolytic reactions should be interpreted along similar lines, *e.g.* certain anodic substitution reactions,[8] the formation of a spirodienone from 3-(*p*-hydroxyphenyl)-propionic acid,[9] the formation of phenyl cinnamate, phenyl 3-acetoxy-3-phenylpropionate and 3-phenyl-3,4-dihydrocoumarin from 3,3-diphenylpropionic acid,[10] the formation of meso- and DL-hydrobenzoindimethyl ether from *trans*-stilbene [11] and the formation of acetoxylated compounds from butadiene.[12] In all these cases there is reason to assume (as judged from the values of the energy coefficients of the highest occupied MO:s and the good linear correlation of these with the oxidation potentials [5]) that the oxidation of the unsaturated compound must take place at lower potentials than that required to discharge the anion present. Also certain purely chemical oxidations, *e.g.* the intramolecular oxidative coupling of 4′-hydroxybiphenyl-2-carboxylic acid with manganese dioxide,[13] may preferably be interpreted as an oxidation of the aromatic π-electron system instead of the carboxylate ion. Studies on some of these reactions are in progress.

Experimental. For the polarographic investigations a Radiometer Type PO3 h polarograph was used. The acetate-acetic acid solution was prepared by refluxing 500 ml of glacial acetic acid (*p.a.*, frozen out three times), 13.3 g of anhydrous sodium carbonate (*p.a.*) and 5 ml of acetic anhydride (*p.a.*) for half an hour. Measurements were carried out on solutions containing the oxidizable compound in a concentration of about 10^{-3} M.

The preparative experiments were made in an electrolysis cell fitted with two electrodes of platinum wire and a saturated calomel electrode as a reference electrode. The reference electrode was adjusted to obtain good contact with the anode. The electrolyte consisted of 150 ml of acetic acid containing 0.5 M sodium acetate and 2—3 % of water in order to decrease the resistance of the electrolyte. The aromatic compound (0.025 mole) was added to the solution and the electrolysis was run at a constant anode potential of 1.5 V *versus* s.c.e., which was controlled automatically by means of a potentiostat. This arrangement usually allowed for a current of about 0.2 A to pass through the solution. The temperature of the solution was 50—60°. When about half the theoretical amount of current had passed, the electrolysis was stopped and the reaction mixture freed from acetic acid in *vacuo*. The residue was treated with water, the organic layer taken up in ether, the ether solution washed with water and finally the ether evaporated in *vacuo*. The products were then analyzed by gas chromatography on a silicone oil DC-200 column. The yield of 1-acetoxynaphthalene was about 30 % (calculated on the basis of naphthalene used), whereas from anisole there was obtained a 40 % yield of a mixture of *o*- and *p*-acetoxyanisole in the proportions 6:1 (calculated on the basis of anisole used).

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On the Fractionation of Polymers by Membrane-Diffusion

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In a recent article by Almin [1] the concentration change in a membrane-diffusion unit was considered and an exact solution for special boundary conditions was derived. In addition an approximate solution was presented and its use in connection with multi-stage fractionation was indicated. In the present note some complementary remarks on the subject are made. Especially, a comparison between Almin's formula and an earlier approximate formula by the author [2] is made, and it is shown that for small values of the exponent $2bDl/v$ (*i.e.* for most cases of practical interest) the two formulae are nearly equal.

Using Almin's symbols and writing $2bDl/v = \alpha$ eqns. (14) and (15) in Ref.[2] give for small α

$$\frac{c(t)}{c(0)} = \exp\left(-\tfrac{1}{2}y\,\frac{\alpha\gamma}{1+\gamma-(\alpha\gamma/4)}\right) \quad (1)$$

On the other hand, the variable r in Ref.[1] is defined by

$$\tfrac{1}{2}(1+\mathrm{e}^{-\alpha})\gamma\mathrm{e}^{\gamma} = r\mathrm{e}^{r} \quad (2)$$

which gives for small α

$$r = \gamma - \tfrac{1}{2}\,\frac{\alpha\gamma}{1+\gamma} \quad (3)$$

With (3) eqn. (8) in Ref.[1] becomes

$$\frac{c(t)}{c_1(0)} = \frac{1}{1+\gamma-\tfrac{1}{2}[\alpha\gamma/(1+\gamma)]} \times \left(\exp-\tfrac{1}{2}y\,\frac{\alpha\gamma}{1+\gamma}\right) \quad (4)$$

Comparing (1) with (4) we must keep in mind that in the two cases different boundary conditions are used. Eqn. (1) is a steady state solution with $c(0)$ being the steady state concentration at $t = 0$. In Almin's paper the exact formula (eqn. (7) in Ref.[1]) refers to boundary conditions with solution of concentration $c_1(0)$ in the container A and pure solvent in the diffusion cell. The same boundary conditions are retained in the approximate formula (4), but the approximation requires that t is large, *i.e.* that steady state conditions are established. Thus, the initial (extrapolated) steady state concentration is according to (4)

$$c(0) = \frac{c_1(0)}{1+\gamma-\tfrac{1}{2}[\alpha\gamma/(1+\gamma)]} \quad (5)$$

With (5) in mind we see that for small α (1) and (4) are essentially the same. However, in multi-stage experiments (eqns. (16)–(23), Ref.[2]) the steady state concentration $c(0)$ has to be used in the interconnected fractionation units. Therefore, in this connection it is essential that a formula of the form of (1) is used.

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