Studies on the Possible Effects of Adsorption on the Product Distribution of Organic Electrode Reactions. A Reinterpretation of Mutual Interactions between Two Substrates in Anodic Acetoxylation

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The effect of the presence of trace amounts of polynuclear aromatics on the o/p product ratio of the acetoxylation of anisole has been reinvestigated. The previously reported increase of the o/p ratio, tentatively explained by assuming the existence of a charge-transfer complex adsorbate, could not be reproduced, even when notorious charge-transfer complex agents were added. The decreased o/p product ratio generally observed in the presence of additives is explained in terms of a co-adsorption model.

The classical method of nucleophilic aromatic substitution as a synthetic tool is limited in scope. Often substantial activation of the aromatic nucleus by strong electron-attracting groups such as nitro or chloro substituents and severe reaction conditions are required. Moreover, in most cases the attack of the nucleophile is rate-determining [1] and as a result only rather strong nucleophiles can be used. In this connection it is worth investigating to what extent electrochemical nucleophilic aromatic substitution can be regarded as an alternative to the classical synthesis routes.

Anodic acetoxylation of anisole, e.g., has been extensively studied by Eberson et al.[2-5] They found that the product distribution of this reaction is similar to that of the chemical electrophilic aromatic substitution. Eberson and Wilkinson [4,5] observed that it is possible to influence the o/p ratio by carrying out the anodic acetoxylation of anisole in the presence of trace amounts of polynuclear aromatics. Pyrene and naphthalene were found to decrease the o/p ratio from 2.2 to 1.3, whereas coronene and hexahelicene increased this ratio from 2.2 to about 4. The effect was discussed in terms of a preferentially adsorbed additive molecule being oxidized to a radical cation which then acts as an oxidant toward the main substrate. This implies that the oxidation should take place in a layer of charge-transfer complexed molecules adsorbed at the electrode, the electron-acceptor molecule acting as a type of conductor for the discharge of electrons from anisole to the electrode. If we assume the existence of such charge-transfer complexes adsorbed at the electrode surface, we can explain the change in o/p product ratio in terms of the nature of the complex. Verhoeven and Schroff [6] have shown that for charge-transfer interaction to be optimal the centers of the donor and acceptor molecules do not always have to lie directly above each other, but may be somewhat shifted in an asymmetric arrangement. In such a situation the accessibility of the *ortho* and *para* positions during the acetoxylation would depend on the nature of the complex. Since the observations of Eberson and Wilkinson [4] indicate the existence of an entirely new mechanism in electrocatalysis and in view of the afore-mentioned

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desirability to extend the scope of the nucleo-
philic aromatic substitution we decided to
study the charge-transfer complex model
in some more detail.

RESULTS

*Acetoxylation of anisole in the presence of
polynuclear aromatics.* Constant-current electrol-
ysis (40 mA cm^{-2}) in an undivided cell of
anisole (0.6 M) dissolved in acetic acid/sodium
acetate (1 M) yielded the expected *o*-, *m*- and
p-acetoxyanisoles (eqn. 1).

$$\text{(1)}$$
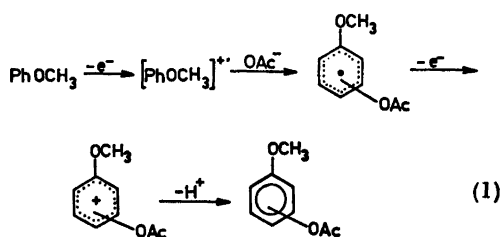
The observed *o/p* ratio (1.8) was lower than
that reported previously [4] (2.2) for slightly
different conditions (*e.g.*, 30 mA cm^{-2}, anisole
0.3 M). Addition of anthracene or coronene
gave rise to difficulties owing to their low
solubility in acetic acid. Electrolysis afforded
o/p ratios of 1.1 and 1.5 with naphthalene
and coronene, respectively, different from
those reported before (1.3 and 4.2, respectively).
Addition of a cosolvent, such as CH$_2$Cl$_2$,
to dissolve the polyaromatics decreased the
current density by a factor of 3 − 4 and had
virtually no effect on the *o/p* ratio. Using
0.2 M NaOAc in the mixed solvent system

CH$_3$CN/HOAc (4/1), which system had pre-
viously been used for kinetic studies, we found
an *o/p* ratio of 2.25, identical to that reported
for pure acetic acid/sodium acetate. Addition
of polyaromatics changed the *o/p* ratio only
little (see Table 1).

The data indicate that when the concentra-
tion of these additives is decreased the *o/p*
ratio approaches that obtained in the blank
experiment. Our data further show that the
current yield of acetoxyanisoles is lower if
polyaromatic compounds having a lower oxida-
tion potential than anisole are added. Ap-
parently, the polyaromatic nucleus is pref-
erentially acetoxylated. Experiments carried
out under controlled potential conditions
(+2.0 V *vs* SCE) gave essentially the same
results.

The above-mentioned data were obtained
by working in an argon atmosphere. To rule
out the possibility that traces of oxygen
present in the electrolyte would destroy the
small amount of coronene or hexahelicene or,
more likely, their electrogenerated radical
cations, we did several control experiments after
2 h of intensive argon purge (using argon with
less than 3 ppm of oxygen). No change in
current yield or in *o/p* product ratio could be
observed.

*Acetoxylation of anisole in the presence of
charge-transfer agents.* In order to assess the
validity of the charge-transfer hypothesis we
also investigated the effect of adding charge-
transfer agents on the acetoxylation of anisole.
The results, collected in Table 2, indicate
a slight decrease in *o/p* product ratio upon
addition of a strong electron donor, such as

Table 1. Effect of the presence of polyaromatic compounds on the acetoxylation of anisole;
solvent CH$_3$CN/HOAc (4/1), [NaOAc] 0.2 M, current density 40 mA cm^{-2}, conversion 5 %.

Additive	Oxidation [a] potential/V	Additive/ anisole ratio	Current [b] yield of acetoxylation products/%		*o/p* Ratio [b]	
None	1.76 [c]	0	55	(38)	2.25	(2.2)
Naphthalene	1.72	0.1	25	(25)	1.2	(1.3)
Anthracene	1.20	0.05	13	(26)	1.6	(1.6)
Coronene [d]	1.23	0.005	60	(16)	1.95	(4.2)
Hexahelicene	−	0.005	48	(19)	1.8	(4.0)
Pyrene	1.42	0.001	55	(38)	1.95	(2.4)

[a] *Versus* saturated calomel electrode (SCE). [b] In parentheses previous results. [c] Oxidation potential
of anisole. [d] Only partly dissolved.

Table 2. Effect of the presence of charge-transfer agents on the acetoxylation of anisole at 1.75 V.[a] Solvent HOAc, [NaOAc] 1.0 M, additive/anisole ratio 0.005.

Additive	Oxidation [a] potential/V	Current yield/%	Current density mA cm^{-2}	o/p Ratio
None	1.76 [d]	33	20	1.8
p-Dimethoxybenzene	1.45	27	34	1.8
p-bis(Dimethylamino)benzene	0.45	23	27	1.6
m-Dinitrobenzene [b]	2.00	27	27	1.7
N,N'-Dihexyl-1,8:4,5-naphthalenecarbodiimide [c]		30	10	1.5
Triphenylphosphine		27	25	1.6

[a] *Versus* saturated calomel electrode (SCE). [b] 2 % CH$_2$Cl$_2$ on acetic acid added. [c] 5 % CH$_2$Cl$_2$ on acetic acid added. [d] Oxidation potential of anisole.

p-dimethoxybenzene or p-bis(dimethylamino)-benzene. However, addition of electron acceptors, such as m-dinitrobenzene or N,N'-dihexyl-1,8:4,5-naphthalenecarbodiimide, results in comparable o/p product ratios. Hence the effect seems not to originate from adsorbed charge-transfer complexes, especially as addition of naphthalene, being a poorer electron acceptor, causes a far lower o/p product ratio (Table 1). A similar effect is observed upon addition of triphenylphosphine, a compound expected to adsorb strongly on the platinum electrode.

DISCUSSION

It has been suggested by Rozhkov that two reaction modes might be responsible for the anodic acetoxylation of anisole, *i.e*, electron transfer from the aromatic substrate molecule to the anode followed by attack of the nucleophile on the radical cation thus formed (*vide supra*) and, oxidation of the nucleophile to its corresponding acetoxy radical with subsequent coupling with the radical cation. The rate of decarboxylation of acyloxy radicals, however, is known [8] to be extremely fast (*ca* 2×10^9 s^{-1} at 60 °C) and chemically induced dynamic nuclear polarisation (CIDNP) studies [9] on the thermolysis of diacetyl peroxide (as well as on other diacyl peroxides) suggest that this decarboxylation rate is limited by the rate of diffusion of the alkyl radical and carbon dioxide out of the solvent cage.[10] CIDNP experiments carried out in aromatic solvents such as bromo-

benzene never gave any indication of the formation of acetoxylated aromatic products. As far as we know, up to now, nobody succeeded * in scavenging acetoxy radicals prior to their decarboxylation. We therefore think it unlikely that attack of acetoxy radicals on the aromatic nucleus constitutes a significant contribution to the formation of acetoxylated products in the anodic acetoxylation of anisole.

Instead, we favour a mechanism in which adsorption of the co-substrate influences the o/p ratio for the acetoxylation of anisole. In the absence of additives, the o/p ratio is almost statistical; the *meta* isomer constitutes less than 3 % of the product mixture. In the presence of additives, we observe a decrease in current yield and a decrease in o/p ratio. The latter effect approaches a limit with increasing additive concentrations, as observed previously for a number of additives [4] and as expected for an adsorption controlled phenomenon. The former effect is proportional to the amount of additive used. We therefore conclude that (1) the additive, possessing a lower oxidation potential than the anisole substrate, is the first species to be oxidized, and (2) that the oxidized species remains absorbed at the electrode surface. Indeed, this is in accord with the results of previous pulse experiments,

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* To our knowledge, only in one publication is the scavenging of acetoxy radicals by spin-trapping techniques reported.[11] In a personal communication to Dr. R. Kaptein at the University of Groningen, however, this claim has been withdrawn by one of the authors.

which had shown [4] that the additives exert their activity *via* adsorption effects. Attack of acetate anion on the anisole radical cation, obtained from anodic oxidation of anisole, appears to take place prior to diffusion of the latter into the bulk of the solution. However, owing to the charge of the anode, the positively charged part of the anisole radical cation is repelled from the electrode, whereas the oxygen atom (lone electron pair) remains adsorbed somewhat longer.* As a result, the *para* position of the semi-adsorbed anisole radical cation, surrounded to a lesser extent by the (partly oxidized) adsorbed additive molecules, can be approached more easily by the attacking species than the two *ortho* positions.
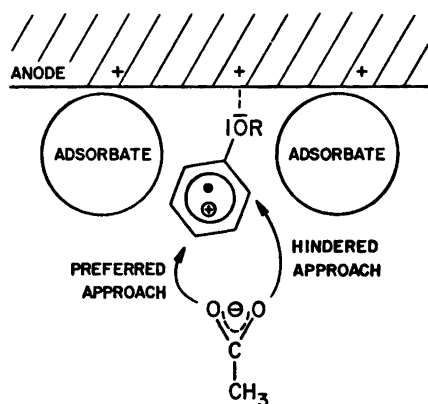
This model explains the "preference" for *para* substitution in the presence of foreign adsorbed species. We could not reproduce the result reported earlier,[4] *viz.* that the *o/p* ratio increases if the acetoxylation is carried out in the presence of coronene or hexahelicene (see Table 1). We therefore believe that the validity of the very attractive charge-transfer complex model is questionable. Finally, it should be noted that the same phenomenon, change of isomer distribution with addition of adsorbable compounds, has very recently been detected in two other electrode reactions.[12,13]

EXPERIMENTAL

Starting materials. Anisole, the polynuclear aromatics (except for hexahelicene) and the

* INDO calculations show that the positive change resides predominantly (∼70 %) in the ring [16] (*cf.* also Ref. 7).

charge-transfer agents (except for the naphthalenecarbodiimide) were commercially available products, which were used without purification. A sample of hexahelicene was obtained from Dr. W. H. Laarhoven, the University of Nijmegen. N,N'-Dihexyl-1,8:4,5-naphthalenecarbodiimide was prepared according to the method given by Schroff.[14] The identity of the products was checked by comparison with authentic samples.

Electrolysis and work-up. Anisole, dissolved in 60 ml of 0.2 M NaOAc in acetonitrile/acetic acid, (4/1) was electrolyzed in a one-compartment cell provided with two Pt electrodes (15 cm²), a Luggin capillary [15] with reference cell (SCE) for potential measurements or controlled potential electrolysis, a magnetic stirrer and a gas inlet tube. Before electrolysis, argon was bubbled through the solution for at least 10 min. Constant-current electrolyses were performed using a Delta Electronica D050-10 power supply. For controlled potential electrolysis a Wenking HP72 potentiostat was used. The amount of current passed was determined by means of a Tacussel IG5-N integrator. After electrolysis (0.1 F/mol), the acetonitrile solvent was evaporated, the residue dissolved in aqueous sodium bicarbonate solution and extracted three times with ether. After drying with MgSO₄ the ether was evaporated and the residue dissolved in a small amount of benzene containing a weighed amount of 1,3-dichloro-5-bromobenzene as GLC reference compound. The yield of the respective products was determined by GLC analysis (Hewlett Packard Model 5750, 12 ft 10 % UCCW on Chromosorb W).

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