Studies on the Possible Effects of Adsorption on the Product Distribution of Organic Electrode Reactions. III.* Competition Processes and Mutual Interactions Between Two Substrates in Anodic Acetoxylation

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Electrochemical reactions in which two substrates compete for the active sites at the electrode surface have been studied, using anodic acetoxylation of aromatic compounds as a model reaction and anisole as a reference system. It has been found that the competition factors (= ratios between product(s) formed from each substrate) change only by a small factor for different compounds exhibiting $E_{1/2}$ values over a fairly wide range. The most interesting observation is that the o/p ratio for acetoxylation of anisole is changed appreciably when certain other substrates are present, such as naphthalene, pentamethylbenzene, and pyrene. This effect is observed even for very small concentrations of additive and shows a saturation effect at higher concentrations. In one case it was shown that the interaction between two substrates produces changes in the product distributions from both. This behavior is probably linked with the adsorption properties of the substrates, since compounds (biphenyl, t-butylbenzene) which would be expected to adsorb weakly do not affect the product distribution at all. Pulse electrolysis shows promise to be a suitable technique for studying competition reactions.

It has become increasingly well recognized during the last few years that the heterogeneity of electrode processes in many cases has a profound influence on the product distribution from the electrolysis of organic compounds. This effect may reflect itself in various ways, *e.g.*, in anomalous stereochemistry,[1–3] in an anomalous nucleophilicity order between nucleophiles in anodic oxidation [4–7] and proton donating ability between proton donors in cathodic reduction,[8–10] in the absence of an expected product,[11] or an

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unexpectedly strong influence of an added compound. To quote just one prominent example of the last-mentioned effect, it has been qualitatively known since long ago [12] that foreign anions inhibit the formation of dimer in the Kolbe oxidation of carboxylates. Recently, this was put on a quantitative basis in a study [13] showing that as little as 0.5 % of added sodium perchlorate to electrolyzing sodium phenylacetate completely suppresses dimer formation with a concomitant switch-over to the carbonium ion pathway. It is obvious that such effects, if capable of being systematized and rationalized in a satisfactory manner, could be of great importance in preparative and mechanistic organic electrochemistry. Actually, the term electrocatalysis should be applied to many of these phenomena since the critical additive is not consumed during electrolysis.

In this paper we wish to report a study of electrolytic competition processes, *i.e.*, reactions in which two organic substrates compete for the active sites at the electrode surface. In the light of previous experience, one would expect interactions between the two types of molecules that might possibly influence the product distribution from one or both substrates. Also, we were interested in studying competition reactions *per se*, since such experiments have only seldom been used in electrochemistry and hence their value for mechanistic inference is not very well established.[14-16]

<div align="center">RESULTS</div>

The standard technique for performing competition experiments [17] in homogeneous solution requires that two compounds are allowed to compete for a small amount of reagent, the reagent concentration being typically of the order of 5 % of the total substrate concentration. This in turn calls for accurate analytical methods in order to obtain the desired competition factors by analysis of the product mixture. Therefore the reaction to be studied should give as high a current yield as possible of known product(s), and, since many experiments are required, the reaction mixture should preferably be analyzable by GLPC. With regard to reaction conditions, the competition experiments must be run at low conversions in order to satisfy both the requirements of the competition method in itself and to avoid further reactions of primary products at the electrode. Moreover, the possibility of mass transfer being of critical importance in determining the competition factor [15] must be eliminated by running the experiments at fairly high substrate concentrations and low current densities, *i.e.*, at the foot of the voltammetric curve.

Anodic acetoxylation in acetic acid-sodium acetate,[18-20] using aromatic compounds as substrates, fulfills these requirements reasonably well. Even if current yields of monoacetoxy products have been reported to be low or moderate due to the competing Kolbe oxidation of acetate ion,[18,20] the reaction is known to give cleanly monoacetoxylation products at low conversion.[19] The main side-products are those resulting from Kolbe oxidation of acetate ion, carbon dioxide and ethane.[20] Analyses can readily be performed using GLPC.

Preliminary experiments in HOAc/1.0 M NaOAc at a platinum electrode using a 1:1 mixture of anisole and naphthalene (total concentration 0.6 M)

at different current densities, 3, 30, and 75 mA/cm², demonstrated these assumptions to be essentially correct. Table 1 shows that current yields are very nearly the same at these low current densities, and that the total current yield is between 35 and 40 %. This is an admittedly low yield, but it is difficult to find another electrode process that gives a better compromise between the features mentioned above.

Table 1. Competition experiments between anisole [a] (0.3 M) and naphthalene [b] (0.3 M) at a Pt anode in HOAc/1.0 M NaOAc at different current densities. Conversion 10 % of theoretical (2e-process).

| Current density, mA/cm² | Current yield, % | | | Competition factor (naphthalene/anisole) |
	o- and p-anisyl acetate	1-naphthyl acetate [c]	Total	
3	7.8[d]	28.0	35.8	3.6
30	9.3[d]	26.2	35.5	2.9
75	8.5[d]	29.5	38.0	3.4

[a] Current yield when run alone under the same conditions, 38 %.
[b] Current yield when run alone under the same conditions, 34 %.
[c] Contains 3 − 4 % of the 2-isomer.
[d] Ratio between o- and p-isomer, 1.0.

From the current yields of Table 1 it is seen that naphthalene is oxidized approximately 3 times faster at the electrode than anisole, in spite of the fact that half-wave potentials indicate that anisole should be slightly easier to oxidize ($E_{1/2}$ of naphthalene and anisole have been reported [18] to be 1.72 and 1.67 V vs. SCE in HOAc/0.5 M NaOAc, respectively). The most important finding of Table 1 is, however, the fact that the ratio between o- and p-anisyl acetates has changed from 2.2, found when anisole is electrolyzed alone,[19] to 1.0, obtained when an equimolar amount of naphthalene is present. This change was well reproducible over a large number of experiments, and

Table 2. Competition between anisole (0.3 M) and naphthalene (0.3 M) at a Pt anode in HOAc/1.0 M NaOAc at different conversions. C.d. 30 mA/cm².

Conversion,[a] % (calc. for a 2e-process)	Competition factor (naphthalene/anisole)	Ratio between o- and p-anisyl acetates
2	2.6	1.0
5	2.7	1.1
10	2.9	1.0
25	2.7	1.1
60	2.7	1.2

[a] Total current yield in all cases is approximately 35 %.

was subjected to further studies (see below) using different concentration ratios between anisole and naphthalene and other additives as well.

A second series of experiments (Table 2) established that the competition factor and ratio between o- och p-anisyl acetate is not significantly dependent on the degree of conversion. Only at higher conversions (60 %) is there a slight tendency toward an increase in the o/p ratio, as would be expected if preferential further oxidation of the p-isomer takes place.[18]

Next we studied the competition factor as a function of the naphthalene/anisole ratio, careful analyses of the o/p ratio being performed at the same time. If the change in this ratio is due to an adsorption effect (e.g., that adsorbed naphthalene molecules would somehow change the reaction conditions for acetoxylation of anisole at or near the electrode surface) one would expect to observe an increasing o/p ratio with decreasing naphthalene/anisole ratio, and a saturation effect at higher ratios. Table 3 shows that these expectations

Table 3. Competition between naphthalene and anisole at different ratios between substrate concentrations at a platinum anode in HOAc/1.0 M NaOAc. C.d. 30 mA/cm², conversion 10 % of theoretical.

[Naphthalene]/ [anisole][a]	Current yield, %			Competition factor	o/p Ratio, anisyl acetates
	Anisyl acetates	Naphthyl acetate	Total		
10	1.1	41.8	42.9	3.8	1.0
3	4.2	34.5	38.7	2.7	1.1
1	9.3	6.2	35.5	2.9	1.0
0.33	18.0	17.7	35.7	2.9	1.
0.167	25.2	0.6	35.8	2.5	1.1
0.10	4.6	7.3	1.9	3.0	1.3
0	37.7	—	37.7	—	2.2

[a] Total substrate concentration, 0.3 — 0.6 M.

were fulfilled; as little as 10 mol % of added naphthalene has a significant effect on the o/p ratio but the ratio never becomes lower than 1.0 at high naphthalene/anisole ratios. The competition factor does not change with a change in the naphthalene/anisole ratio of 100 (keeping in mind that analyses at the highest ratio are not very accurate).

Competition factors between anisole and a few other compounds were then determined (Table 4). The most noticeable trend in this series of experiments is that competition factors change to a relatively small extent with changing $E_{1/2}$ of the additive; a change of a factor of 6 is observed in the range of 1.72 − 1.91 V. For the much more difficultly oxidizable substrate, t-butylbenzene, the competition factor decreases by a factor of 50 − 100, though. It should be added that the competition factors are internally consistent in that, e.g., a competition experiment between naphthalene and biphenyl

Table 4. Competition between different compounds and anisole at a Pt anode in HOAc/1.0 M NaOAc. C.d. 30 mA/cm², [substrate] = 0.3 M each.

Compound	Competition factor (compound/anisole)	$E_{1/2}{}^a$	o/p Ratio, anisyl acetates
t-Butylbenzene	0.01 − 0.02	2.23[b]	2.2
Biphenyl	0.5	1.91	2.7
Pentamethylbenzene	1.1	1.62	1.0
Naphthalene	3.0	1.72	1.0

[a] Ref. 18.
[b] Extrapolated value.

under identical conditions gave a competition factor of 5 (*vs.* 6 calculated from the values of Table 3).

The naphthalene/anisole competition experiments did not answer the question of whether there is a *mutual* influence between the two electroactive species due to the difficulty in analyzing the small percentage (*ca.* 3 %) of 2-naphthyl acetate besides the 1-isomer. Competition experiments between pentamethylbenzene (PMB) and anisole (see Table 5) were therefore performed,

Table 5. Mutual influence between anisole and pentamethylbenzene (PMB) during acetoxylation at a Pt anode in HOAc/1.0 M NaOAc. C.d. 30 mA/cm², conversion 10 % of theoretical.

[Anisole]/ [PMB]	Current yield, %			Ratio	
	Anisyl acetates	Acetates from TMB[a]	Total	o/p Ratio, anisyl acetates	Acetates from TMB[b]
0.5	12.8	21.3	34.1	1.0	0.41
1.0	19.3	20.4	39.7	1.0	0.43
3.0	32.0	18.7	50.7	1.1	0.42
∞	37.7	−	−	2.2	−
0	−	27.2	−	−	0.52

[a] 2,3,4,5- and 2,3,4,6-tetramethylbenzyl acetate.
[b] Ratio between 2,3,4,5- and 2,3,4,6-isomer.

and it was found that in this case a significant mutual influence exists. The o/p ratio for acetoxylation of anisole changes from 2.2 to 1.0, as in the naphthalene case (Tables 2 and 3), whereas the ratio between the two tetramethylbenzyl acetates changes from 0.52 to 0.42. The latter change is not large, but of enough significance to demonstrate the mutual influence between the two substrates. A different situation exists for the pair biphenyl/anisole, where both o/p ratios are only little changed in the same type of experiments (Table 6).

Table 6. Mutual influence between anisole and biphenyl during acetoxylation at a Pt anode in HOAc/1.0 M NaOAc. C.d. 30 mA/cm², conversion 10 % of theoretical.

[Anisole]/ [biphenyl]	Current yield, %			Ratio	
	Anisyl acetates	Biphenylyl acetates	Total	*o/p* Ratio, anisyl acetates	*o/p* Ratio, biphenylyl acetates
1	25.7	15.5	41.2	2.7	0.35
3	42.7	9.2	51.9	2.6	0.41
0	35.8	2.1	37.9	2.3	0.53[a]
∞	37.7	—	—	2.2	—
0	—	43.5	—	—	0.42

[a] Less accurate value due to the low current yield.

At this stage of the investigation it was obvious that adsorption must play an important role in determining the change in the *o/p* ratio for acetoxylation of anisole. Pentamethylbenzene and naphthalene, both relatively strong π-donors and hence by inference from the π-donor-acceptor model of aromatic adsorption at the Pt electrode strongly adsorbing molecules,[21-23] change the *o/p* ratio by a factor of about 2, whereas biphenyl and *t*-butylbenzene, both relatively weak as π-donors, do not change it significantly. From these considerations one would expect pyrene to be an even more efficient molecule than PMB and naphthalene in changing the *o/p* ratio. Table 7 shows that this is indeed the case; the *o/p* ratio is not restored to its value in the absence of additive until a ratio of anisole/[pyrene] of 1 : 100 is reached. Table 7 also shows the effect of adding coronene and hexahelicene, two large aromatic ring systems, in the acetoxylation of anisole. Here an increase in the *o/p* ratio is observed.

Two additives of the ether type, phenetole and diphenyl ether, had no influence on the *o/p* ratio of anisyl acetates when co-electrolyzed with anisole

Table 7. Acetoxylation of anisole in the presence of aromatic additives at a Pt anode in HOAc/1.0 M NaOAc. C.d. 30 mA/cm², conversion 10 % of theoretical.

Additive	[Additive]/[anisole]	Current yield, % anisyl acetates	*o/p* Ratio, anisyl acetates
Naphthalene	1 : 10	24.6	1.3
Pyrene	1 : 10	9.2	1.3
Pyrene	1 : 20	18	1.3
Pyrene	1 : 30	20	1.4
Pyrene	1 : 100	21	1.9
Pyrene	1 : 1000	38	2.4
Anthracene	1 : 20	26	1.6
Coronene	1 : 200	16	4.2
Hexahelicene	1 : 200	19	4.0

(concentration ratios 1 : 1). Finally, it should be mentioned that some experiments have been performed using carbon anodes in that the series of experiments shown in Table 2 was run also at carbon with similar results; *i.e.* giving a competition factor of about 3 and a change in the o/p ratio from 2.2 to 1.0.

The importance of adsorption for the phenomena observed in the experiments described above can also be shown using pulse electrolysis. It is usually assumed that adsorption is maximal at potentials around the potential of zero charge and gradually decreases at positive or negative potentials. This means that a competition pulse electrolysis conducted from a low to a high potential ought to favor the more strongly adsorbing compound since this should accumulate during the low-potential period and therefore be selectively oxidized during the high-potential period. A gradual change should be observable as the pulse frequency increases. Table 8 shows the results from pulse

Table 8. Pulse electrolysis of naphthalene (0.04 M) and anisole (0.04 M) at a Pt anode in 20 % HOAc/80 % CH₃CN/0.2 M NaOAc.

Pulse conditions, msec at 0.2 V/ msec at 1.8 V	Current yield, %		Competition factor	o/p Ratio, anisyl acetates
	Anisyl acetates	Naphthyl acetates		
100/300	5.2	20.5	4.0	1.3
10/30	3.2	20.1	6.4	1.3
1/3	1.0	20.6	21	1.5

a Analysis uncertain due to the low yield.

electrolysis experiments conducted between 0.2 and 1.8 V *vs.* SCE in an electrolyte of anisole and naphthalene in 20 % HOAc/80 % CH₃CN/0.2 M NaOAc. A significant increase in favor of oxidation of naphthalene is observed as the pulse frequency increases, whereas the o/p ratio remains largely unchanged.

DISCUSSION

The trends in the competition factors and the o/p ratios for acetoxylation of anisole in the presence of different additives are in qualitative accordance with a mechanism involving adsorption as an important factor. Compounds that would be expected to adsorb strongly have a maximal influence on the o/p ratio, the phenomenon shows a saturation effect as the concentration of the additive is increased beyond a certain value, and the behavior upon pulse electrolysis using high pulse frequencies is the expected one. Exactly how this influence shall be formulated in a detailed reaction mechanism is, however, not clear at all. One might for example envisage a mechanism in which the adsorption of one type of molecule influences the reactions of the second type of molecule by something which resembles a solvent effect: A non-polar hydrocarbon adsorbed at the anode surface provides a less polar environment

for the reaction under study than when it is not present. Another possibility is that the preferentially adsorbed molecule is oxidized to a cation radical which then acts as an oxidant toward the second substrate. In effect this amounts to saying that the less strongly adsorbing molecule is discharged on top of a layer of the more strongly adsorbing one, at least in the very reactive systems studied here.

Whatever the mechanism may be, we feel that we have provided evidence that competition reactions should be of limited value for mechanistic studies for reasons outlined above. Moreover, it has been shown that electrode processes mutually influence each other to a certain extent and that adsorption probably is the controlling factor. Finally, preliminary runs indicate that preparative pulse electrolysis should be a valuable technique for studying these phenomena.

EXPERIMENTAL

All reagents used were either of commercial analytical grade quality or carefully purified samples of lower grade quality. Electrolyses were carried out in a thermostated cell (20.0°) using a Pt anode (2 × 1 cm) and a carbon rod cathode. The volume of the electrolyte was 50 ml in each experiment. Constant current experiments were performed using a Radiak (Stocksund, Sweden) power supply, whereas the pulse electrolyses were performed using a Waveform Generator Type RB1 connected to a Potentiostat Type TR70/2A (both from Chemical Electronics, Durham, England).

After electrolysis the reaction mixture was poured into water (150 ml). After ether extraction (3 × 30 ml) the ether solution was washed three times with water and once with sodium hydrogen carbonate solution. The ether layer was dried over anhydrous $MgSO_4$ and the volume of the solution was then adjusted to a final volume of 50.0 ml. A suitable quantity of durene (as internal standard) was then weighed into a 5 ml graduated flask made up to volume with the ether solution. Analysis were then performed using a Perkin-Elmer Model 880 gas chromatograph, equipped with a disc integrator. A 2 m × 0.3 mm column containing 5 % neopentylglycol succinate on Chromosorb W was used with a temperature program from 100 to 200° at a rate of 6°/min. The detector was calibrated relative to durene for all the acetates and substrates used in the study. The identity of all acetates was checked by gas chromatographic and mass spectral (LKB A-9000 system) comparison with authentic samples.

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