Anode Potential Controlled Mechanisms of Oxidation of Aryl Olefins

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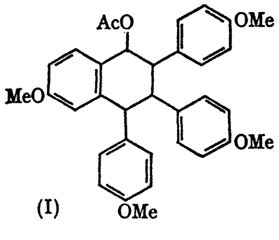
Summary Whether a 1e dimerization or a 2e oxidation occurs during the anodic oxidation of 4,4′-dimethoxystilbene depends on the anode potential used.

ANODIC substitutions involving nucleophilic attack on an aromatic nucleus are generally not amenable to study by quantitative electrochemical techniques since the products are frequently further oxidized and current efficiencies are low. In contrast the present study shows that products from anodic addition of nucleophiles to an olefinic linkage conjugated with an aromatic ring produces a product substantially more difficult to oxidize than the parent compound and thus quantitative electrochemical techniques are applicable to the study of these reactions. Furthermore, the reactions can be made to involve either the cation-radical or the dication by proper selection of the anode potential.

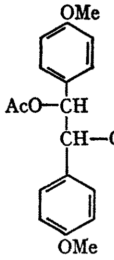
At a rotating platinum electrode, 4,4′-dimethoxystilbene shows two anodic waves in acetonitrile ([$LiClO_4$] = 0·1 M) with half-wave potentials of +0·90 v and 1·15 v together with a more poorly defined wave at more positive potentials. The number of electrons transferred at the first wave was 1·0, found by comparing the peak height of a voltammogram obtained with a stationary electrode with that for the oxidation of 9,10-diphenylanthracene which exhibits a reversible one-electron oxidation in acetonitrile.[1]

The results of controlled potential coulometry of the stilbene under various conditions are summarized in the Table.

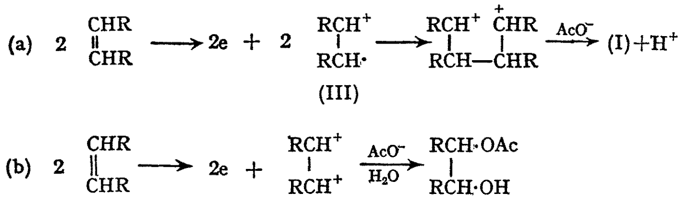
The results show that at low potentials (< 1·05 v) a one-electron oxidation of 4,4′-dimethoxystilbene is observed while at the higher potentials (> +1·20 v) a two-electron oxidation occurs. The 2e oxidation does not involve further oxidation of the 1e oxidation product since the voltammetric curve at a stationary electrode shows only a single 1e oxidation peak at +0·90 v and a much smaller peak at +1·12 v where the 2e oxidation occurs. A solution of 4,4′-dimethoxystilbene exhaustively electrolysed at +0·90 v, in which 1 equivalent of charge was passed (run 6) showed no anodic voltammetric peaks at potentials less than +1·50 v.



(I)



(IIa) R= Ac
(IIb) R= H



$$\text{(a)}\quad 2\ \overset{\text{CHR}}{\underset{\text{CHR}}{\Vert}} \longrightarrow 2e + 2\ \underset{\text{(III)}}{\begin{matrix}\text{RCH}^+\\ |\\ \text{RCH}\cdot\end{matrix}} \longrightarrow \begin{matrix}\text{RCH}^+ & \overset{+}{\text{CHR}}\\ | & |\\ \text{RCH} & \!\!-\!\!\text{CHR}\end{matrix} \xrightarrow{\text{AcO}^-} \text{(I)} + \text{H}^+$$

$$\text{(b)}\quad 2\ \overset{\text{CHR}}{\underset{\text{CHR}}{\Vert}} \longrightarrow 2e + \underset{\text{(IV)}}{\begin{matrix}\text{RCH}^+\\ |\\ \text{RCH}^+\end{matrix}} \xrightarrow[\text{H}_2\text{O}]{\text{AcO}^-} \begin{matrix}\text{RCH}\cdot\text{OAc}\\ |\\ \text{RCH}\cdot\text{OH}\end{matrix}$$

R=p-MeO·C_6H_4

SCHEME

On the basis of mass, n.m.r., and i.r. spectral evidence, the 1e oxidation product was assigned structure (I), which is analogous to that assigned to the oxidation product of 3,4-dimethoxypropenylbenzene.[2] The 2e oxidation product (a mono-acetate) after acetylation gave (IIa), and was thus assigned structure (IIb). The stereochemistry of the product was in accordance with that reported for acetoxylation of stilbene.[3]

The voltammetric and coulometric data as well as the nature of the products show that two independent mechanisms are operative at the low and high potentials (see scheme). Our results indicate that the cation-radical (III) undergoes dimerization more rapidly than the reaction with the acetate ion. This rules out an ECE mechanism for path b which involves 1e oxidation (E) to the cation-radical followed by rapid reaction (C) with acetate ion and further oxidation (E) of the resulting radical. Therefore, a direct 2e oxidation to the dication (IV) is implied for path (b). The fact that the presence or absence of a nucleophile does not affect the coulometry (Table) or voltammetry is indicative that the oxidation does not involve assistance by the nucleophile.

Controlled potential coulometry of 4,4′-*dimethoxystilbene* (*DMS*)

Run	Solvent[a]	E_a (v *vs.* SCE)	Nucleophile	n[c]
2	MeCN–HOAc[d]	+1·20	0·25M-NaOAc	2·2
3	" "	+1·05	" "	1·2
4	" "	+1·05	" "	1·3
5	" "	+1·20	" "	2·1
6	" "	+0·90	" "	1·1
7	MeCN	+0·90	None	0·9
8	"	+1·35	"	1·9
9	MeCN–HOAc[b]	+1·35	"	2·2
10	" "	+0·90	"	0·9
11	MeCN	+0·90	10mM-Pyridine	1·0
12	"	+1·35	" "	1·9
13[d]	MeCNH–OAc[b]	+0·90	0·25M-NaOAc	1·1
14[d]	" "	+1·35	" "	2·0

[a] $LiClO_4$ (0·1M) in all runs; [b] 3 parts MeCN, 1 part HOAc; [c] Determined by integration of the current-time curve; [d] For preparative purposes, [DMS] = 10mM, all other runs [DMS] = 1mM.

The voltammetric and coulometric behaviour of 3,4-dimethoxypropenylbenzene parallels that of 4,4′-dimethoxystilbene. Our results contradict those of O'Connor and Pearl[2] who reported that the former undergoes 2e voltammetric oxidation in the presence of pyridine.

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