The Kinetics and Mechanism of the Anodic Coupling of 4,4'-Dimethoxystilbene. Evidence for the Radical — Substrate Coupling Mechanism

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The cation radical formed upon oxidation of 4,4'-dimethoxystilbene in acetonitrile is short-lived, undergoing a rapid coupling reaction with the substrate. The intermediate dimeric cation radical is then oxidized to the dimeric dication by substrate cation radical. The dimer dication can dissociate to give substrate cation radical. The product forming reactions involve nucleophilic attack by water or methanol, when present, to give dimeric products. This complex reaction scheme was studied by a combination of electrochemical techniques including linear sweep voltammetry, linear current potential wave form analysis, derivative cyclic voltammetry as well as phase selective second harmonic a.c. voltammetry. Variable temperature studies confirmed the complex nature of the reactions.

Coupling reactions are among the most synthetically useful electrode processes. A variety of mechanisms is possible involving either initial dimerization of the electrode generated intermediates (eqn. 1) or reaction of the intermediate with substrate (eqn. 2). This paper deals with anodic coupling reactions but it should be kept in mind that the primary distinction between the anodic and cathodic processes is simply one of charge type.

$$2A^{\cdot +} \rightarrow A^{+} - A^{+} \qquad (1)$$

$$A^{\cdot +} + A \rightarrow A^{+} - A^{\cdot} \qquad (2)$$

Voltammetric data along with preparative studies were reported on a series of methoxy-substituted arylolefins several years ago.[1,2] 4,4'-Dimethoxystilbene, which was among the compounds studied, has been scrutinized in more detail lately, both by spectroelectrochemical[3] and rotating ring disc electrode voltammetry.[4] These studies resulted in the conclusion that the reaction is of the EC(dim) type with the rate determining step, analogous to (1) having a rate constant equal to 1.6×10^{4} M^{-1} s^{-1} at 25 °C. This relatively slow second order process aroused our curiosity since the earlier studies[1,2] had indicated that the coupling reaction is so rapid that it takes place even in the presence of high concentrations of acetate ion which would be expected to react very rapidly with the cation radical. It was also thought that the mechanism of this reaction could have bearing on those observed in related work[5-7] and perhaps serve a model for the more simple aryl ethers, such as anisole,[8] which are more difficult to study quantitatively.

In this paper we give the details of a mechanistic investigation which show that the coupling reaction is of the radical — substrate type (2) rather than the previously proposed[3,4] radical — radical process (1).

RESULTS

Structures and identifying symbols. The structures of the substrate and the reaction intermediates are identified by letters below, where An refers to *p*-anisyl.

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Structure	Symbol
An−CH=CH−An	D
(An−CH=CH−An)$^{·+}$	D$^{·+}$
(An−CH=CH−An)$^{2+}$	D^{2+}

An−CH−CH−CH−CH−An   D$^+$−D$^·$

An−CH−CH−CH−CH−An   D$^+$−D$^+$

Cyclic voltammetry. Previous studies[3,4] have shown that the reduction of D$^{+·}$ can be observed during cyclic voltammetry of D in acetonitrile at sweep rates as low as 320 mVs^{-1}. This leads to the prediction that at high voltage sweep rate, v, the peak current ratio (I^p_{red}/I^p_{ox}) for reaction (3) should approach 1.0. Furthermore, the peak current ratio for the first and second consecutive charge transfers (I^{p1}_{ox}/I^{p2}_{ox}) should approach unity as well. An oxidation

$$D - e^- \rightleftarrows D^{·+} \qquad (3)$$

$$D^{·+} - e^- \rightleftarrows D^{2+} \qquad (4)$$

peak, about 200 mV more positive than that due to (3) has previously been observed[1,3] and assigned to reaction (4).[1] The cyclic voltammogram shown in Fig. 1a, recorded at 100 Vs^{-1} in acetonitrile containing Bu$_4$NBF$_4$ (0.1 M), does not conform to these predictions. Processes (3) and (4) are observed as expected but the peak current ratios are far from unity which suggests some kinetic complications not reflected by the simple charge transfer reactions. This is further confirmed by the derivative linear sweep voltammogram[9] shown in Fig. 1b. The derivative peak current ratio I'_1/I'_2 indicates that the current due to (4) is considerably less than that due to (3). It should be pointed out that the voltammograms were recorded in the presence of alumina to eliminate the effects of residual water[10] which was a problem in previous studies.[3,4] This explains the stability of the dication D^{2+} under the reaction conditions.

The complexity of the system was confirmed by low temperature voltammetry. At 25 °C, the derivative cyclic voltammogram shows the oxidation of D (O'_1) and the reduction of D$^{·+}$ (R'_1) (Fig. 2a) while at −30 °C only a small current due to R'_1 is observed (Fig. 2b) and a new reduction peak (R'_2) is the major process on the reverse scan. The voltammograms were recorded at v equal to 100 V s^{-1}
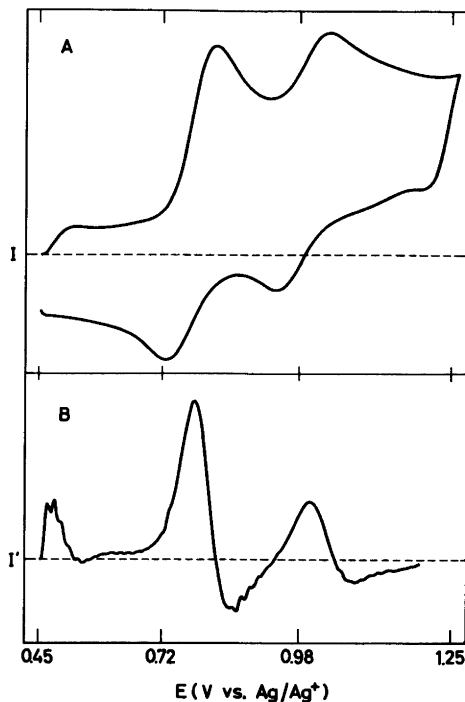

Fig. 1. Voltammograms for the oxidation of 4,4'-dimethoxystilbene in acetonitrile at 100 V s^{-1} measured in the presence of neutral alumina.

which indicates that even at −30 °C, the primary reaction is very rapid producing an intermediate which is in equilibrium with D$^{·+}$.

Linear sweep voltammetry (LSV). Providing that charge transfer is rapid, the location of the peak potential during LSV is linearly related to the logarithm of v and $C°$ (substrate concentration) during rapid second order reactions[11,12] following charge transfer. The numerical values of d E^p/d log v and d E^p/d log $C°$ are then characteristic of the electrode mechanism. For example, the EC(dim) mechanism previously proposed for the anodic oxidation of D[3,4] predicts that both of the slopes should equal 19.7 mV/decade at 298 K. The data in Table 1 were obtained by derivative LSV during the oxidation of D in acetonitrile containing Bu$_4$NBF$_4$ (0.1 M). The measurements were restricted to v equal to or less than 1 V s^{-1} in order to avoid complications due to interference of the charge transfer rate. This restriction results in the data being obtained over a narrow region of v and thus requires a very high degree of precision in the peak potential measure-
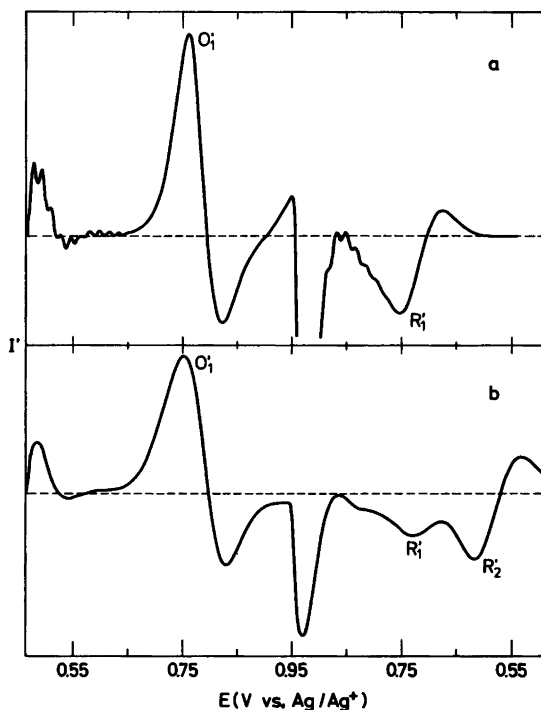
Fig. 2. Derivative cyclic voltammograms for the oxidation of 4,4'-dimethoxystilbene in acetonitrile at 25 (a) and $-30\,^\circ$C. Voltage sweep rate $= 100$ V s^{-1}, $(Bu_4NBF_4) = 0.1$ M.

ments in order to obtain meaningful slopes. That the required precision is achieved by analog differentiation[9] of the LSV waves is shown by the standard deviations listed in parentheses in Table 1. The average standard deviation in five measurements ± 0.4 mV.

The observed slopes d E^p/d log $v = 19.1 \pm 0.5$ mV/

decade and d E^p/d log $C^\circ = 37.4 \pm 1.1$ mV/decade at 293 K immediately rule out the EC(dim) mechanism. Both slopes are predicted to equal 19.4 mV/decade at 293 K. While the sweep rate dependence conforms to the prediction the substrate concentration dependence is double that predicted by the EC(dim) mechanism. Calculations have been carried out

Table 1. Linear sweep voltammetric analysis of the oxidation of 4,4'-dimethoxystilbene in acetonitrile.[a]

[D]/mM	E^p/mV				d E/d log v
	0.100[b]	0.200[b]	0.400[b]	1.000[b]	
0.20	296.4(3)	304.0(3)	310.0(4)	316.3(4)	19.7
0.50	276.6(2)	281.4(2)	287.2(3)	295.0(7)	18.5
1.00	269.5(0)	274.6(3)	280.6(6)	288.5(7)	19.1
2.00	259.6(6)	264.5(4)	270.8(6)	278.5(9)	19.1
d E/d log C°	-36.1	-38.5	-38.2	-36.8	

[a] Measurements at a platinum electrode at 20 °C, supporting electrolyte Bu_4NBF_4 (0.1 M). The peak potentials listed are relative to a bias setting of $+0.450$ V *vs.* Ag/Ag$^+$ in acetonitrile. The numbers in parentheses are the standard deviation in five measurements. [b] v/V s^{-1} and refer to the digit after the decimal point.

for the radical—substrate mechanism (eqn. 2)[13] and the slopes predicted at 293 K are 29.1 mV/decade for both d E^p/d log v and d E^p/d log C^o, providing that the radical—substrate reaction is rate determining.[13] However, if the rate determining step is electron transfer reaction (5), the slopes become 19.4 and 38.8 mV/decade for d E^p/d log v and

$$A^+ - A^\cdot + A^{\cdot +} \rightarrow A^+ - A^+ + A \qquad (5)$$
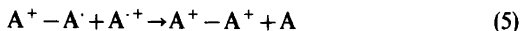
d E^p/d log C^o, respectively.[13] Thus, the LSV results are consistent with the radical—substrate coupling mechanism providing that oxidation of the initial adduct by cation radical is rate determining.

Linear current potential (LCP) waveform analysis. The shape of the purely kinetic LSV wave is characteristic of the mechanism of the electrode reaction. A very nearly linear segment of the wave exists where I_N, the normalized current equal to I/I^p, is equal to 0.50 to 0.75.[14] The slope in this region equal to 52.6 mV for a second order process and 68.9 mV for a first order reaction following Nernstian charge transfer.[14] This analysis not only gives support for the mechanism assignment based upon LSV slopes but also verifies the purely kinetic nature of the LSV wave. The slopes are obtained by measuring E relative to $E^{p/2}$ at six values of I_N equal to 0.50, 0.55, 0.60 0.65, 0.70 and 0.75. Results of the analysis of five different voltammograms recorded at v equal to 237 mV s^{-1} are summarized in Table 2. The correlation coefficients are 1.0000 in all cases and the mean value of the slopes, excluding the first entry which deviates from the others, is 53.6±0.3 which is in excellent agreement with the theoretical value expected for the second order mechanism.

Table 2. Linear current potential waveform analysis of the oxidation of 4,4'-dimethoxystilbene in acetonitrile.[a]

Voltammogram	dE/dI_N[b]	Correlation coefficient
1	55.8	0.99999
2	53.6	0.99998
3	53.3	0.99997
4	53.5	0.99999
5	54.0	0.99999

[a] Measurements at 25 °C at a platinum electrode in solvent containing Bu$_4$NBF$_4$ (0.1 M) at 237 mV s^{-1}. [b] Correlations at I_N values of 0.50, 0.55, 0.60, 0.65, 0.70 and 0.75.
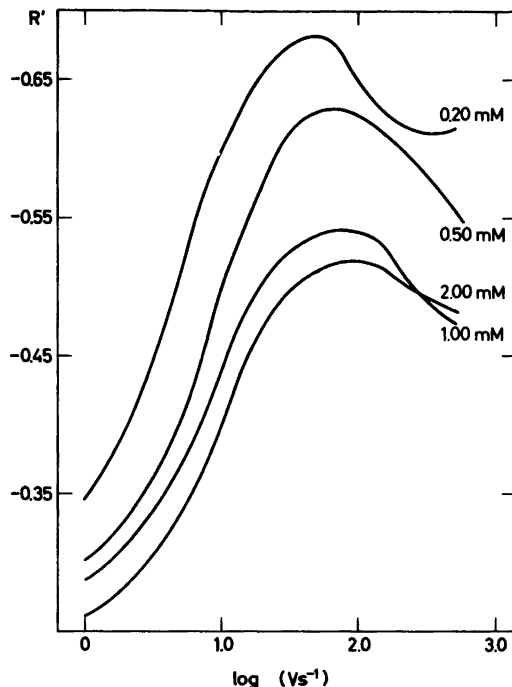

Fig. 3. Dependence of the derivative peak current ratios on voltage sweep rate and substrate concentration.

This analysis does not distinguish between the radical—radical and the radical—substrate with rate determining further oxidation mechanisms. The purely kinetic nature of the LSV waveform for the oxidation of D is confirmed by the data in Table 2.

Derivative cyclic voltammetry kinetic measurements. The derivative peak current ratio of a cyclic voltammogram is a direct measure of the rate of the reaction coupled to charge transfer.[15,16] The data in Fig. 3 show the effect of changes in v and C^o on $I'_{red}/I'_{ox}(=R')$ corresponding to reaction (3). For a second order mechanism the ratio R' at a given value of v is expected to decrease with increasing substrate concentration reflecting the increase in the reaction rate. Likewise, increasing v at a given value of C^o is expected to bring about an increase in R' which is a reflection of the shorter time gate and hence less reaction. The concentration dependence is qualitatively that expected according to the remarks above. However, the simple relationship between R' and v expected for the second order process was not observed. At all four concentrations, R' increased with increasing sweep rate and reached
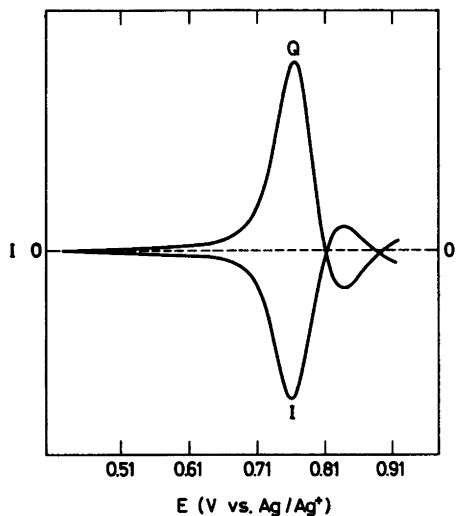
Fig. 4. Phase selective second harmonic AC voltammograms for the oxidation of 4,4'-dimethoxystilbene in acetonitrile containing Bu_4NBF_4 (0.1 M). Voltage sweep rate equal 50 mV s^{-1} and frequency equal 300 Hz, substrate concentration equal 0.20 M.

a maximum value at $v \sim 50$ V s^{-1} and then decreased at higher values of v. At v greater than 500 V s^{-1} R' once again increases but does not reach unity under any of the conditions studied. For example, at 3,000

Table 3. Second harmonic AC zero current crossing potentials measured during the oxidation of 4,4'-dimethoxystilbene in acetonitrile.[a]

		E_{zc}/mV[c]	
$C°$/mM	f/Hz[b]	Q	I
0.20	100	362.6(4)	361.3(2)
0.20	300	362.4(3)	361.8(7)
0.20	1000	362.9(3)	363.4(6)
2.00	100	344.5(5)	363.9(3)
2.00	300	351.3(2)	360.0(3)
2.00	1000	353.8(0)	361.4(5)

[a] Measured at a Pt electrode in solvent containing Bu_4NBF_4 (0.1 M) at a voltage sweep rate of 50.0 mV s^{-1}. [b] Applied *a.c.* frequency. [c] The zero current crossing potentials. Q refers to the quadrature component and I the in phase component. The numbers are the average of five determinations and the numbers in parentheses are the standard deviations. Measurements in the same solutions of E^p during LSV resulted in values of 334.3 mV at 2.00 mM and 372.2 mV at 0.20 mM with v equal to 1.00 V s^{-1}. All potentials are *vs.* a potentiostat bias setting of +0.45 V. *vs.* Ag/Ag$^+$ in acetonitrile.

V s^{-1} the reduction peak observed at low temperature R'_2 is observed along with R'_1 as in Fig. 2. The data at the higher sweep rates are not included in Fig. 3 since a higher switching potential was necessary rendering a direct comparison impossible. The data shown is for $E_{sw} - E_{rev} = 200$ mV.

Phase selective second harmonic AC voltammetry. The method of choice for the measurement of reversible electrode potentials in rapidly reacting redox systems is phase selective second harmonic a.c. voltammetry. The theoretical predictions[17,18] of the applicability in rapidly reacting systems has recently been experimentally verified.[19] The criteria necessary for verification of the reversible potential measurement are that the quadrature (Q) and in phase (I) components of the *a.c.* current intersect at zero current and that the intersection is frequency independent. The measurement of the reversible potential during the oxidation of D in acetonitrile is demonstrated in Fig. 4 which shows the near zero crossing of the I and Q components at a frequency of 300 Hz and a substrate concentration of 0.2 mM. The data in Table 3 demonstrate the frequency independence at 0.2 mM and also point out that it was not possible to measure E^{rev} at a substrate concentration of 2.0 mM where the reaction rate is higher. The value of the reversible potential was determined to be equal to 812.4 ± 0.8 mV *vs.* the Ag/Ag$^+$ reference electrode in acetonitrile.*

Linear sweep voltammetric analysis of the oxidation of D in acetonitrile containing methanol. Previous work[3] included kinetic studies of the oxidation of D in the presence of methanol and it was concluded that even at low methanol concentrations (2–10 mM), nucleophilic attack competes favorably with the radical dimerization. The data in Table 4 were obtained to test for the kinetic involvement of methanol in the coupling reaction. The value of d E^p/ d log v obtained, $21.4(\pm 1.5)$ mV/decade, is once again only consistent with a second order reaction. This observation is inconsistent with a mechanism involving rate determining nucleophilic attack of CH_3OH on D$^{\cdot +}$ under the conditions of the measurements which involved methanol concentrations as great as 31 mM. The slight lowering of the potentials in the presence of methanol is most likely due

* The LSV peak potentials measured at 1.000 V s^{-1}, using the same reference electrode and in the same solutions as the *a.c.* data were obtained, are given in Table 3, note c. The reference electrode was not the same as that used to obtained the data in Table 1.

Table 4. Linear sweep voltammetric analysis of the oxidation of 4,4'dimethoxystilbene in acetonitrile containing methanol.[a]

| (MeOH)/mM | E^p/mV | | | | dE/d log v |
	0.100[b]	0.200[b]	0.400[b]	1.000[b]	
0	356.8(2)	363.5(3)	369.2(1)	377.6(2)	20.6
7.7	352.9(1)	358.0(1)	364.6(2)	373.9(4)	21.2
15.4	349.1(1)	355.5(0)	362.5(2)	372.6(4)	23.6
30.8	349.2(1)	354.3(1)	360.1(2)	369.4(5)	20.2
Mean					21.4(15)

[a] Measurements at a platinum electrode at 23 °C, supporting electrolyte Bu_4NBF_4 (0.1 M). Peak potentials are relative to a bias setting of $+0.400$ V vs. Ag/Ag^+ in acetonitrile. The numbers in parentheses are the standard deviations in five measurements. [b] v/V s^{-1}.

to a reference electrode effect. The change of ~ 4 mV in going from 0 to 7.7 mM in methanol is too small to be considered as a kinetic effect.

Since the concentration dependence is especially sensitive to the particular coupling mechanism followed, it was of interest to apply the analysis to the reaction in the presence of methanol. The data in Table 6 confirm that there is no change in mechanism in the presence of methanol. The slopes observed, -36.7 and -36.3 mV/decade, are within experimental error of the expected values for the radical – substrate coupling mechanism. It should be noted that this concentration dependence study (Table 5) differs from that in the absence of methanol (Table 1) in that the two replicates were each carried out on single solutions with the substrate added incrementally to the acetonitrile solution containing methanol (25 mM). Conducting the experiments

in this way reduces possible experimental error associated with electrode placement and small potential changes which can take place when the potentiostat is turned on and off. Such small errors are apparent in the data in Table 1 in which case the sweep rate correlations, carried out on single solutions without any electrode configuration changes, are considerably better than those for the concentrations. The error in potentials resulting from the changes mentioned above is demonstrated by Fig. 5 which shows that the duplicate concentration dependence studies are internally consistent but follow different correlation lines.

Temperature dependence of the reaction rates. It has recently been pointed out that unusual temperature effects are often observed in complex ion radical reactions involving equilibria before the product forming steps.[20] A convenient method to

Table 5. Concentration dependence during LSV mechanism analysis of the oxidation of D in acetonitrile containing methanol.[a]

(D)/mM	E^p/mV Solutions 1[b]	E^p/mV Solution 2[b]
0.10	383.6(4)	385.6(10)
0.20	373.6(2)	373.8(8)
0.40	361.2(4)	363.2(4)
0.60	354.9(8)	357.9(6)
0.80	350.2(7)	353.8(8)
1.00	347.9(5)	347.7(3)
d E^p/d log C° (mV/decade)	-36.7	-36.3
Correlation coeff.[c]	0.999	0.998

[a] Measurements at a platinum electrode at 22 °C in solvent containing Bu_4NBF_4 (0.1 M) and methanol (25 mM). Voltage sweep rate $= 1.00$ V s^{-1}. [b] Substrate was added incrementally to the two solutions. The numbers in parentheses are the standard deviations in 5 measurements. [c] Data treated by linear regressions analysis.

Table 6. Effect of temperature on the rate of reactions following oxidation of D in acetonitrile.[a]

$T/°C$	R'	$v/V \, s^{-1}$	k_{rel}[b]
53.4	0.384	50.0	1.00
45.3	0.387	52.0	1.04
40.1	0.387	51.0	1.02
36.1	0.384	50.0	1.00
33.1	0.390	50.0	1.00
22.1	0.386	50.0	1.00
6.0	0.384	52.0	1.04
−4.4	0.383	70.0	1.40

[a] The value of R' was adjusted to 0.385 by fine-tuning of the sweep rate and the values recorded are the average of 10 determinations with an average standard deviation of 0.002. [b] relative rate constants calculated from the sweep rates necessary to hold R' constant according to Ref. 20. The units of the rate constants are unknown.

determine the apparent activation energies of electrode reactions without the necessity of having access to the rate constants has also been described.[21] The method involved, in the present case holding the peak ratio (R'_1) during derivative cyclic voltammetry constant by varying v as the tempera-

ture, was changed. The relative values of the apparent rate constants at the various temperatures are then simply related to the changes in the variable, v. The data in Table 6 show that the apparent rate constants of the reaction are essentially independent of the temperature in the range 53 to 6 °C and then begin to increase at lower temperature. This apparent inverse temperature effect must, at least in part, be connected with the fact that a new intermediate is observed at even lower temperatures (Fig. 2b). In any case, these observations support the other data that require a complex reaction mechanism.

Kinetic analysis of the coupling reaction. The results presented in the previous sections suggest that the anodic coupling of D is complex, involving a number of equilibria. A sequence of reactions consistent with all of the kinetic data are illustrated by eqns. (6) to (9).
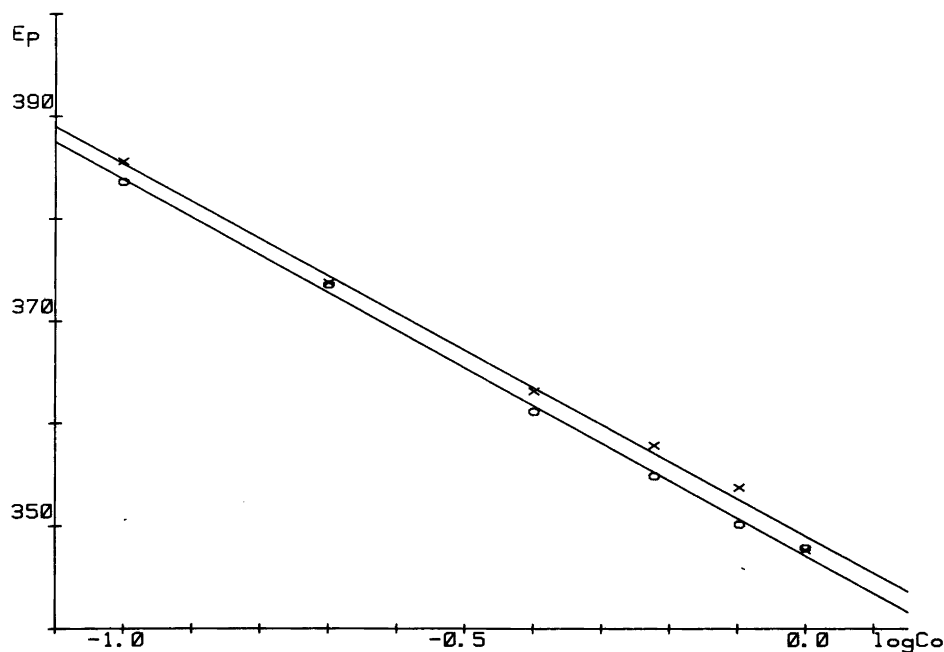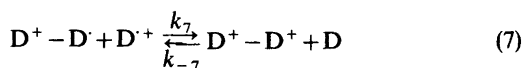
$$D^{\cdot+} + D \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} D^+ - D^{\cdot} \qquad (6)$$

$$D^+ - D^{\cdot} + D^{\cdot+} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} D^+ - D^+ + D \qquad (7)$$

$$D^+ - D^+ \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} 2D^{\cdot+} \qquad (8)$$

Fig. 5. Correlation of E^p vs. log $C°$ for the LSV analysis of the oxidation of D in acetonitrile containing methanol (25 mM) at 22 °C and a voltage sweep rate of 1.00 V s^{-1}

$$D^+ - D^+ \xrightarrow{k_9} \text{products} \tag{9}$$

The LSV results as well as the near independence of the reaction rate on temperature can be accounted for by considering reaction (6) to be in equilibrium and that electron transfer reaction (7) is rate determining resulting in rate law (10) where $k_{app} = k_7 K_6$. However, this simple explanation fails to account for the derivative cyclic voltammetry sweep rate

$$\text{Rate} = k_{app}(D^{\cdot +})^2(D) \tag{10}$$

dependence and the observation of the new reduction peak (R'_2) at low temperatures.

The latter two observations can be explained by incorporating equilibrium (8) in the mechanism. The reduction peak (R'_2) can then be assigned to the reduction of $D^+ - D^+$. The peculiar sweep rate dependence (Fig. 3) could arise when the sweep rate becomes high enough so that equilibrium conditions no longer hold for reaction (8).

A rate law incorporating all four reactions (6) to (9) can be derived by application of the steady state approximation on $D^+ - D^+$ giving rate law (11) and finally (12) if reaction (6) is considered to be in

$$\text{Rate} = k_9(k_7[D^+ - D^{\cdot}][D^{\cdot +}] + k_{-8}[D^{\cdot +}]^2)/(k_9 + k_8 + k_{-7}[D]) \tag{11}$$

$$\text{Rate} = k_9[D^{\cdot +}]^2(k_7 K_6[D] + k_{-8})/(k_9 + k_8 + k_{-7}[D]) \tag{12}$$

equilibrium. First, if $(k_9 + k_8) \gg k_{-7}[D]$ and $k_7 K_6[D] \gg k_{-8}$, the rate is described by eqn. (13) and k_{app} is equal to $k_9 k_7 K_6/(k_8 + k_9)$. On the other and if K_6 and K_7 are large and K_8 is small and the

$$\text{Rate} = k_9 k_7 K_6[D^{\cdot +}]^2[D]/(k_8 + k_9) \tag{13}$$

rate of reaction (9) is low compared to reaction (7), the latter can be considered to be essentially irreversible and rate determining. Under these conditions, the rate of the reaction is described by eqn. (14).

$$\text{Rate} = k_7 K_6[D^{\cdot +}]^2[D] \tag{14}$$

Kinetic behaviour predicted by previous mechanism proposals. Competing mechanisms were suggested[3] for the reactions of $D^{\cdot +}$ in acetonitrile containing methanol. Partitioning of the cation radical between reactions (15) and (16) was proposed

to give rise to rate law (17) with $k_{15} = 2k_{16}$. We can estimate the fraction of the reaction going by way
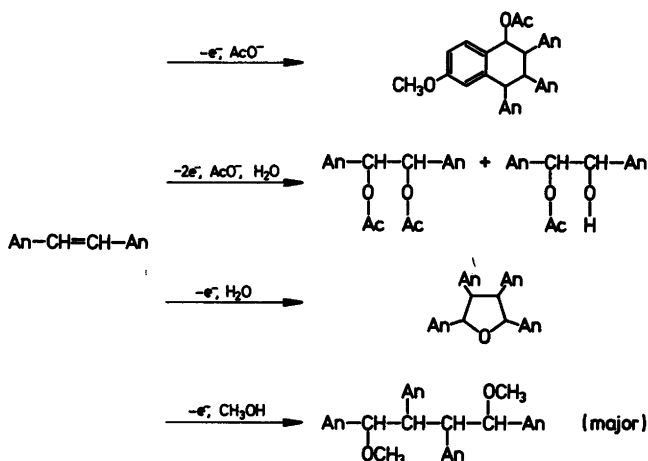
$$2D^{\cdot +} \xrightarrow{k_{15}} D^+ - D^+ \tag{15}$$

$$D^{\cdot +} + CH_3OH \xrightarrow{k_{16}} D\overset{+}{\underset{H}{O}}CH_3 \tag{16}$$
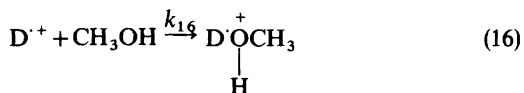
$$\text{Rate} = 2 k_{15}[D^{\cdot +}]^2 + k_{16}[D^{\cdot +}][CH_3OH] \tag{17}$$

$$v_{15}/v_{16} = 2 k_{15}[D^{\cdot +}]^2/k_{16}[D^{\cdot +}][CH_3OH] = 4[D^{\cdot +}]/[CH_3OH] \tag{18}$$

of the two pathways, v_{15}/v_{16}, from eqn. (18). When the substrate concentration is 10^{-3} M, the maximum concentration of $D^{\cdot +}$ at the electrode surface by any technique is considerably less than 10^{-3} M. However, we will take this as the maximum value, and assuming a linear decay in concentration of $D^{\cdot +}$ over the diffusion layer (which is also an over-estimation) we arrive at an absolute maximum estimate of the average value of $[D^{\cdot +}]$ in the reaction layer to be 5×10^{-4} M. When the methanol concentration is 25 mM, as for the data in Table 5, we then arrive at a maximum estimate of v_{15}/v_{16} to be 0.08. That is the competing mechanisms (15) and (16) with rate law (17) predicts that more than 92 % of the reaction would take place by the first order (in $D^{\cdot +}$) pathway. This is clearly inconsistent with all of the data obtained in this study.

DISCUSSION

The products of the anodic oxidation of 4,4'-dimethoxystilbene (D) in acetonitrile depend upon the reaction conditions as shown in Scheme 1. At a potential where only charge transfer reaction (3) takes place, the product observed was a tetrahydronaphthalene derivative derived from a coupling reaction in spite of the fact that sodium acetate, a strong nucleophile, was present in high concentration.[1,2] At a more positive potential, where charge transfer reaction (4) occurs as well, D^{2+} reacts with acetate ion and residual water to give the two adducts shown.[1,2] In less nucleophilic media, *i.e.* acetonitrile containing low concentrations of water, 2,3,4,5-tetraanisyltetrahydrofuran was isolated in high yield.[3] The mechanism for formation of the dimeric product in the former case was suggested to be initial dimerization of the cation radical, $D^{\cdot +}$,

$$-e^-, AcO^-$$

$$-2e^-, AcO^-, H_2O$$

$$An-CH=CH-An$$

$$-e^-, H_2O$$

$$-e^-, CH_3OH$$

An—CH—CH—An + An—CH—CH—An
| | | |
O   O   O   O
| | | |
Ac   Ac   Ac   H

An—CH—CH—CH—CH—An   (major)
| | | |
OCH_3   An   OCH_3   An

Scheme 1.

cyclization and reaction with acetate ion.[1] At that time no kinetic data were available to support the mechanism assignment. The more recent studies, conducted under conditions where the tetrahydrofuran derivative is the product, kinetic studies[3,4] led to the conclusion that the initial step in the reaction involves dimerization of the anodically generated $D^{\cdot+}$. The aspect of the more recent work which attracted our attention was the fact that the overall reaction was reported to be relatively slow, with the lifetime of $D^{\cdot+}$ such that observation was possible by cyclic voltammetry at voltage sweep rates as low as 320 mVs^{-1}. The latter appeared remarkable in that cation radicals are known to be very reactive toward nucleophiles such as water,[22] acetate ion[23] and even acetonitrile.[22] Another observation,[3] that the adduct formed upon the reaction of $D^{\cdot+}$ with methanol is more difficultly oxidized than the substrate, appeared to contradict the expected behaviour. The reaction of $D^{\cdot+}$ with methanol would be expected to produce the benzylic radical (eqn. 19), the highest occupied molecular orbital of which is non-bonding and expected to be at relatively high energy. In fact, the reduction of a number of benzylic cations to the alternant radicals has been reported to take place at potentials considerably less positive than the oxidation potential of D.[24]

$$An-\underset{\cdot}{C}H-\underset{+}{C}H-An+CH_3OH \rightarrow$$

$$An-\underset{\cdot}{C}H-\underset{\underset{OCH_3}{|}}{C}H-An+H^+ \qquad (19)$$
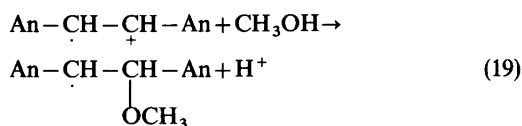
The points discussed in the previous paragraph concerning the proposed mechanism of the anodic coupling of D appeared to be inconsistent enough to warrant a re-investigation of the mechanism of the reaction.

The most illuminating mechanistic evidence was obtained from the data in Tables 1, 4 and 5. The fact that d E^p/d log v and d E^p/log C° conform to a mechanism consisting of equilibrium (6) followed by essentially irreversible (7) provides strong evidence for the radical—substrate coupling mechanism. We have been unable to find a reasonable alternative mechanism giving a rate law of the form of (14) which is required by the concentration dependence of the peak potential.

That the overall reaction is more complex than indicated by the LSV data alone is shown by the fact that the expected relationship between the derivative peak current ratio and v was not observed, as indicated by the data in Fig. 3. This complexity is also indicated by the derivative cyclic voltammogram in Fig. 2. which gives strong evidence for the formation of an intermediate very rapidly even at $-30\,^\circ$C. The most reasonable interpretation is that this intermediate is in equilibrium with $D^{\cdot+}$ and at low temperature the formation of $D^{\cdot+}$ from the intermediate becomes slower. Equilibrium (8) accommodates the latter requirement. Furthermore, the observation of R_2' (Fig. 2b) at less positive potentials than required for the oxidation of D is consistent with the benzylic cation type structure, D^+-D^+, for one of the primary intermediates of the reaction.

In our opinion, our data can only be interpreted

to indicate that the coupling mechanism of D^{+} is very complex. Under the conditions of the LSV studies, the very close fit of the sweep rate and concentration dependences to the theoretical values for the radical – substrate mechanism indicate that this is the dominant mechanism under those conditions. Thus, the primary reaction appears to be the attack of the cation radical on the substrate. The question arises as to why this reaction is fast relative to the radical – radical dimerization. In considering this question it is necessary to think in terms of rates rather than rate constants. It is possible that the rate constant for the dimerization (k_{-8}) is greater than that for reaction (6), k_6. The electrochemical techniques used to study the reactions involve generating D^{+} at the electrode surface where $[D]$ is low. However, since the gradient of $[D^{+}]$ near the surface is quite steep, the average concentration ratio, $[D]/[D^{+}]$, in the reaction layer can be quite large and the radical – substrate mechanism can predominate even though the rate constant for the dimerization of $[D^{+}]$ is greater.

The next question that arises is why the previous studies[3,4] produced data that could be interpreted to indicate a relatively simple mechanism differing from the one that we propose. In this respect, it has recently been emphasized that electrochemical response to complex mechanisms can fit theoretical working curves for rather simple mechanisms, at least within experimental error.[20] This is a consequence of the fact that the working curves for different mechanisms can be very similar and experimentally indistinguishable. Methods for detecting complexities, especially variable temperature and concentration studies, were outlined and methods for analyzing the complex schemes were discussed.[20] For example, the temperature study (Table 6) of this reaction gives a very definitive indication that the mechanism is complex.

In conclusion, we would like to point out that a number of electrode reactions for which simple mechanisms had previously been proposed have recently been shown to take place by rather complex mechanisms having some similarity to the scheme proposed for the oxidation of D (eqns. 6 – 9). Among these reactions are the deprotonation of hexamethylbenzene cation radicals,[25] the reduction of 9-diazofluorene[26] and the dehalodimerization of p-halo-N,N-dimethylanilines.[27] It seems likely that many more examples of complex mechanisms will emerge with the increasing availability of better measurement methods.

EXPERIMENTAL

Reagents, electrodes and cells. 4,4′-Dimethoxystilbene was reagent grade and purified by recrystallization from ethanol. Acetonitrile was allowed to reflux over phosphorus pentoxide for several hours before slowly distilling. Tetrabutylammonium tetrafluoroborate was prepared by ion exchange from the hydrogen sulfate (Hässle, Gothenburg), precipitated from dichloromethane with diethyl ether and dried. Solutions of supporting electrolyte in acetonitrile were passed through a column of neutral alumina immediately before voltammetric measurements were conducted. Under these conditions, the water content of the solvent – electrolyte system was estimated to be of the order of 1.0 mM. Reagent grade methanol was used as received.

The working electrodes were prepared by sealing small diameter platinum wire in glass and polishing to a planar surface. Reference electrodes were Ag/AgNO$_3$ (0.01 M) in acetonitrile separated from the voltammetry solutions by porous glass. Leakage from the reference electrodes was neglible as was the current flow using the small electrodes which allowed the use of a single compartment cell consisting of a cylindrical tube (25 ml volume) fitted with a joint to accomodate a teflon electrode holder equipped with a tube for the inlet of purified nitrogen.

Instrumentation. The potentiostats were PAR model 173D driven by either a PAR 175 or HITEK PPR1 signal generator. Data were digitized either using a Nicolet 1090 AR digital oscilloscope interfaced to a Hewlett Packard 9825A desk computer or a Hewlett Packard 59313A analog to digital converter interfaced to a Hewlett Packard 9825A desk computer. A PAR 5203 lock-in amplifier was used for second harmonic a.c. voltammetry and a PAR 189 selective amplifier was used for differentiation of the cyclic voltammograms.

Electrode potentials. It should be pointed out that the potentials of reference electrodes used in this study vary by as much as 50 – 100 mV depending upon the construction. We have made no particular effort to standardize the measurements since each set of measurements were with the same electrode and are thus self-consistent.

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