Anodic Oxidation of Schiff Bases. Part I. Oxidation of *N*-Benzylidene-*p*-anisidines in Acetonitrile

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The anodic oxidations of several *N*-benzylidene-*p*-anisidines have been investigated by cyclic voltammetry and controlled potential electrolysis at a glassy-carbon electrode in acetonitrile. All the compounds tested were oxidized irreversibly. *N*-Benzylidene-*p*-anisidines showed two anodic waves. The relationship between the peak potentials of their first wave and the σ^+ values of the substituents on the benzylidene group was linear, whereas that for the second wave was not. On controlled potential electrolysis at the first wave, protonated benzylidene-*p*-anisidines were identified, and on electrolysis at the potential of the second wave, *p*-benzoquinone imine and the corresponding benzaldehyde were identified as the main products. When water was added to the solution, the second wave shifted to a lower potential, whereas the potential of the first wave remained unchanged. Hence a combined wave was observed in the presence of sufficient water. On controlled potential electrolysis in the presence of 5% water, *p*-benzoquinone and the corresponding benzaldehyde were formed as the main products. Analysis of the minor product suggested that the *p*-anisidine radical cation was formed as an intermediate. A possible reaction mechanism is suggested.

ELECTROCHEMICAL reduction of azomethine compounds at a dropping mercury electrode has been studied extensively.[1] Photochemical [2] and chemical [3] oxidations of azomethine compounds have also been studied, but little attention has been paid to the anodic oxidations of these compounds. Hampson *et al.*[4] suggested that an imine intermediate was formed which was then oxidized to a nitrile on oxidation of primary amines at silver electrode. They also investigated the oxidation of some Schiff bases in alkaline media at silver electrodes and identified various nitriles as one of the oxidation products.[4] These seem to be the only studies reported on electrochemical oxidation of azomethine compounds. Therefore, we examined the anodic oxidations of several aromatic Schiff bases using a glassy-carbon electrode [5] in acetonitrile. This electrode has been used by us for cyclic voltammetry of aliphatic amines and its utility is well established.[6]

Cyclic voltammetry of several benzylideneanilines with *meta*- or *para*-substituents on the aniline group was examined, but except for *p*-methoxy-derivatives severe electrode filming and poor reproducibility were observed. Therefore, we used substituted *N*-benzylidene-*p*-anisidines as substrates.

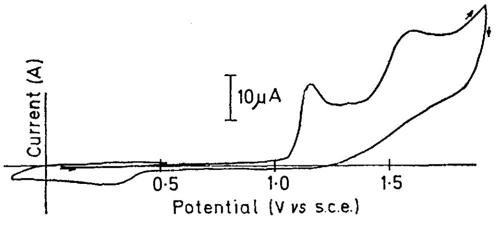

FIGURE 1 Cyclic voltammogram of *N*-benzylidene-*p*-anisidine (1 mM) in acetonitrile; 0·1M-NaClO$_4$, 47 mV s^{-1}

RESULTS

Cyclic Voltammetry of N-*Benzylidene*-p-*anisidines*.—*N*-Benzylidene-*p*-anisidines showed two anodic peaks in acetonitrile containing 0·1M-sodium perchlorate. A typical example is shown in Figure 1. The values of the peak currents and the peak potentials are summarized in Table 1. When the peak potentials of the first wave were plotted against the σ^+ values of the substituent in the benzylidene ring, good linearity was obtained (Figure 2). However, the plot for the second wave did not give a linear relationship (Figure 2). A linear relationship between the i_p value of the first wave and the square root of the scan rate was obtained at scan rates of 11—192 mV s^{-1}. There was no evidence of a reversible process at any rate examined.

TABLE 1

Results of cyclic voltammetry of substituted *N*-benzylidene-*p*-anisidines in acetonitrile containing 0·1M-NaClO$_4$; voltage scan rate 47 mV s^{-1}, concentration of Schiff base 1 mM, geometric electrode area 0·071 cm^2

	First wave		Second wave
Substituent	E_{p_1}/V *vs.* s.c.e.	i_p/μA	E_{p_2}/V *vs.* s.c.e.
None	1·16	17·7	1·61
p-OMe	1·08	16·5	1·52
p-Me	1·13	17·3	1·60
p-Cl	1·19	18·3	1·54
m-Cl	1·21	19·3	1·52
o-Cl	1·20	20·1	1·41
p-NO$_2$	1·25	20·7	1·42

The height of the first wave of *N*-benzylidene-*p*-anisidines decreased with increase in the concentration of perchloric acid added and almost disappeared in the presence of an equimolar amount of perchloric acid. On the other hand, the height of the second wave increased slightly with the concentration of acid and the peak potential shifted to slightly less positive potentials (*ca.* 30—50 mV). This shift in the peak potential seems to be due to the effect of the water added together with the perchloric acid (see below).

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[1] H. Lund, *Acta Chem. Scand.*, 1959, **13**, 249, and references therein; P. Zuman and O. Exner, *Coll. Czech. Chem. Comm.*, 1965, **30**, 1832; B. Fleet and P. Zuman, *ibid.*, 1967, **32**, 2066; H. Lund, *Tetrahedron Letters*, 1968, 3651, and references therein.

[2] R. L. Furey and R. O. Kan, *Tetrahedron*, 1968, **24**, 3085; D. A. Nelson, R. L. Atkins, and G. L. Clifton, *Chem. Comm.*, 1968, 399; T. Oine and T. Mukai, *Tetrahedron Letters*, 1969, 157; F. C. Schaefer and W. D. Zimmermann, *J. Org. Chem.*, 1970, **35**, 2165; N. Toshima and H. Hirai, *Tetrahedron Letters*, 1970, 433; and references therein.

[3] R. N. Butler, *Chem. and Ind.*, 1968, **6**, 437; R. E. Erikson, P. J. Andrulis, jun., J. C. Collins, M. L. Lungle, and G. D. Mercer, *J. Org. Chem.*, 1969, **34**, 2961; J. W. Bird and D. G. M. Diaper, *Canad. J. Chem.*, 1969, **47**, 145; V. Madan and L. B. Clapp, *J. Amer. Chem. Soc.*, 1969, **91**, 6078; 1970, **92**, 4902; D. H. R. Barton, J. F. McGhie, and P. L. Batten, *J. Chem. Soc.* (*C*), 1970, 1033; J. B. Ayward, *ibid.*, p, 1494; A. Stojilikovic, N. Orbovic, S. Sredojevic, and M. Lj. Mihailovic, *Tetrahedron*, 1970, **26**, 1101; A. Pross and S. Sternhell, *Austral. J. Chem.*, 1970, **23**, 989; E. G. E. Hawkins, *J. Chem. Soc.* (*C*), 1971, 160, and references therein.

[4] N. A. Hampson, J. B. Lee, J. R. Morley, and B. Scanlon, *Canad. J. Chem.*, 1969, **47**, 3729; N. A. Hampson, J. B. Lee, J. R. Morley, K. I. MacDonald, and B. Scanlon, *Tetrahedron*, 1970, **26**, 1109; N. A. Hampson, J. B. Lee, K. I. MacDonald, and M. J. Shaw, *J. Chem. Soc.* (*B*), 1970, 1766.

[5] H. E. Zittel and F. J. Miller, *Analyt. Chem.*, 1965, **37**, 200.

[6] M. Masui, H. Sayo, and Y. Tsuda, *J. Chem. Soc.* (*B*), 1968, 973.

The peak potential of the second wave shifted towards a less positive potential on addition of water, whereas that of the first wave remained unchanged. Hence the two waves combined at a higher concentration of water (Figure 3 and Table 2).

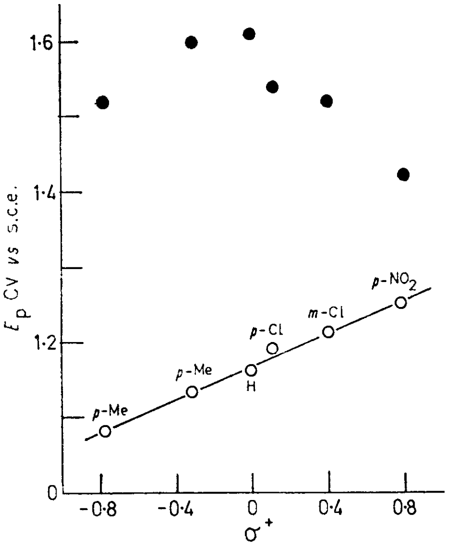


FIGURE 2 Effect of substituents on peak potential. ○, First wave; ●, second wave

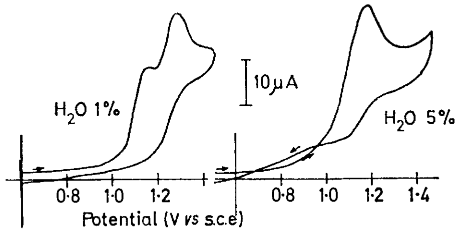


FIGURE 3 Effect of added water on the cyclic voltammogram of N-benzylidene-p-anisidine (1 mM) in acetonitrile (cf. Figure 1); 0·1M-$\mathrm{NaClO_4}$, 47 mV s^{-1}

The effect of oxygen in cyclic voltammetry was examined by comparing the above results with those obtained in solution from which air had been removed with a stream of nitrogen, but no appreciable difference was detected either in the presence or absence of added water.

TABLE 2

Effect of added water on the second wave of substituted N-benzylidene-p-anisidines in acetonitrile containing 0·1M-$\mathrm{NaClO_4}$; voltage scan rate 47 mV s^{-1}, concentration of Schiff base 1 mM

	E_{p_2}/V vs. s.c.e. Water content (%)					
Substituent	0·5	1·0	2·0	3·0	4·0	5·0
None	1·31	1·28	1·25	1·22	1·21 *	1·18 *
p-OMe		1·33	1·24			1·18
p-$\mathrm{NO_2}$		1·29	1·26 *			1·24 *

* Combined wave.

N-p-Methoxybenzylidene-p-anisidine was subjected to potential step cyclic voltammetry.[7] On stepping up the potential to 1·1 V (a potential just above the E_p of the first wave) for 60 s, no peak was observed on the subsequent cathodic sweep down to −0·4 V. On stepping up the potential to +1·6 V (a potential well above the E_p of the second wave) for 60 s, two reduction peaks were observed at +0·35 and +0·15 V on the cathodic sweep and a new oxidation peak at +0·29 V was seen on the subsequent anodic sweep. p-Aminophenol is reported to be oxidized to p-benzoquinone imine in acetonitrile.[8] On cyclic voltammetry it showed two peaks at +0·29 and ca. +0·5 V on the anodic sweep and two peaks at +0·35 and +0·15 V on the subsequent cathodic sweep. These results strongly suggest that the second wave of N-p-methoxybenzylidene-p-anisidine corresponds to the formation of p-benzoquinone imine.

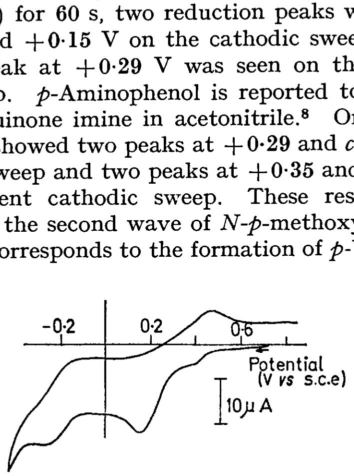
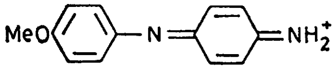


FIGURE 4 A typical cyclic voltammogram of N-benzylidene-p-anisidines (ca. 1 mM) after electrolysis in acetonitrile containing 5% water. The small cathodic peak at +0·4 V, which soon disappeared on standing, may be due to p-benzoquinone imine

Controlled Potential Electrolysis.—Table 3 summarizes results on controlled potential electrolysis. The results were the same in the presence and absence of oxygen. The main products of electrolysis in the presence of 5% water were the corresponding benzaldehyde and p-benzoquinone. On electrolysis all the N-benzylidene-p-anisidines examined exhibited essentially the same cyclic voltammogram though the peak height differed somewhat from one another (Figure 4). However, a violet colour with absorption maxima at 562 and ca. 360 nm (shoulder) developed. The same colouration was also observed when p-anisidine was subjected to electrolysis under the same conditions. The degree of colouration and the cyclic voltammogram of the resulting solution were essentially the same as those observed in the case of N-benzylidene-p-anisidines if the same potential was applied (Figure 4 and Table 4). The main product was p-benzoquinone (Table 3).



(I)

The evidence strongly suggests that the violet colour, which gradually disappeared on standing, is attributable to the oxidized form of 4-amino-4′-methoxydiphenylamine (I) formed as a minor product. Bacon and Adams reported that in the controlled potential electrolysis of p-anisidine in aqueous acid solution, one electron per molecule was consumed and a purple colour developed.[9] They ascribed the colour to the ion (I) with absorption maxima at 332 and 540 nm at pH 3·5. They also reported that p-anisidine at pH 2 yielded the ion (I) on electrolysis at +0·75 V and p-benzoquinone and/or p-benzoquinone imine at +1·0 V.[7] When p-anisidine (10^{-3}M) was submitted to electrolysis at +0·7 V in acetonitrile containing 5% water, one electron per molecule was consumed and a deep violet colour developed. When the solution was diluted five-fold with acetonitrile, the resulting solution exhibited absorption maxima at 360 and 566 nm (log ε 1·18). When the solution from electrolysis was diluted five-fold with Britton–Robinson buffer (pH 3·4), the absorption maxima shifted to 331 and 535 nm. These findings suggest that the ion (I) was

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[7] L. Papouchado, J. Bacon, and R. N. Adams, *J. Electroanalyt. Chem.*, 1970, **24**, App. 1—5.

[8] F. P. Knobloch, *Coll. Czech. Chem. Comm.*, 1971, **36**, 1644.

[9] J. Bacon and R. N. Adams, *J. Amer. Chem. Soc.*, 1968, **90**, 6596.

TABLE 3

Results of controlled potential electrolysis [a]

Compounds	Amount of water added [b] (w/v %)	Applied potential (V *vs.* s.c.e.)	*n* Value	Products identified	Amount of sample (mg)
N-Benzylidene-*p*-anisidine	0	1·10	0·75	*c*	22·3
N-Benzylidene-*p*-anisidine	0	1·18	0·80	*c*	23·7
N-Benzylidene-*p*-anisidine	0	1·62	2·42	QI, BzA	24·2
N-Benzylidene-*p*-anisidine	1	1·15	1·91	Q, QI [d,e]	22·2
N-Benzylidene-*p*-anisidine	2	1·15	2·03	Q, QI [d,e]	22·5
N-Benzylidene-*p*-anisidine	5	1·15	2·19	Q, BzA [d]	23·0
N-Benzylidene-*p*-anisidine	5	1·15	2·10	Q, BzA [d]	21·7
N-*p*-Methoxybenzylidene-*p*-anisidine	0	1·10	0·77	*c*	25·0
N-*p*-Methoxybenzylidene-*p*-anisidine	0	1·10	0·77	AAP	270·0
N-*p*-Methoxybenzylidene-*p*-anisidine	0	1·12	0·81	AAP	465·0
N-*p*-Methoxybenzylidene-*p*-anisidine	0	1·50	2·24	QI, AnisA	26·4
N-*p*-Methoxybenzylidene-*p*-anisidine	0	1·58	2·48	QI [e]	27·0
N-*p*-Methoxybenzylidene-*p*-anisidine	5	1·10	2·15	Q, AnisA [d]	25·4
N-*p*-Methoxybenzylidene-*p*-anisidine	5	1·10	2·04	Q [d,e]	25·7
N-*p*-Methoxybenzylidene-*p*-anisidine	5	1·25	2·16	Q [d,e]	24·5
N-*p*-Nitrobenzylidene-*p*-anisidine	0	1·25	1·06	*c*	27·4
N-*p*-Nitrobenzylidene-*p*-anisidine	0	1·42	2·16	QI [e]	28·3
N-*p*-Nitrobenzylidene-*p*-anisidine	5	1·25	2·25	Q, NitBzA [d]	26·9
N-*p*-Nitrobenzylidene-*p*-anisidine	5	1·25	2·24	Q [d,e]	25·3
N-*p*-Chlorobenzylidene-*p*-anisidine	5	1·20	2·18	Q [d,e]	25·6
N-*p*-Chlorobenzylidene-*p*-anisidine	5	1·20	2·19	Q [d,e]	24·7
AAP	0	1·52	2·10	QI, AnisA	36·3
p-Anisidine	0	1·10	1·06	*f*	12·5
p-Anisidine	2	1·15	2·20	Q, QI [d]	12·9
p-Anisidine	5	1·25	2·27	Q [d]	12·8
p-Anisidine	5	1·10	2·13	Q [d]	12·7
p-Anisidine	5	1·10	2·03	Q [d]	12·7
p-Anisidine	5	1·10	1·60	*d*, *f*	123·2
p-Anisidine	5	0·90	1·36	*d*	12·8
p-Anisidine	5	0·70	1·14	*d*	12·1

[a] The volume of anolyte was 100 ml in all cases. 0·1M-NaClO$_4$ was used as supporting electrolyte. Q, *p*-Benzoquinone; QI, *p*-benzoquinone imine; BzA, benzaldehyde; AnisA, *p*-anisaldehyde; NitBzA, *p*-nitrobenzaldehyde; AAP, *N*-*p*-methoxybenzylidene-*p*-anisidinium perchlorate. [b] Hydrolysis of the original *N*-benzylidene-*p*-anisidines during the period of electrolysis was found to be negligible. [c] A cyclic voltammogram of the solution from electrolysis coincided with that of the original *N*-benzylidene-*p*-anisidine in acetonitrile containing an equimolar amount of perchloric acid. [d] A violet colour developed, though it varied in intensity in each case (see text). [e] Analysis for aldehyde was not carried out. [f] Products were not identified, because anisidine itself acted as a base and hence on electrolysis the nature of the solution was very complex.

TABLE 4

Relative amount of oxidized form of 4-amino-4′-methoxydiphenylamine (I) formed on electrolysis in acetonitrile containing 5% water and 0·1M-NaClO$_4$,[a,b] concentration of original substrate *ca.* 1 mM[c]

X-Substituted *N*-*p*-benzylidene-*p*-anisidine	Applied potential (V *vs.* s.c.e.)	Found (%)
X = *p*-NO$_2$	1·25	3·9
X = *p*-Cl	1·20	7·0
X = H	1·15	10·9
X = *p*-OMe	1·10	20·2
X = *p*-OMe	1·25	2·8
p-Anisidine	1·25	3·8
p-Anisidine	1·10	18·5
p-Anisidine	0·90	83·1
p-Anisidine	0·70	(100)

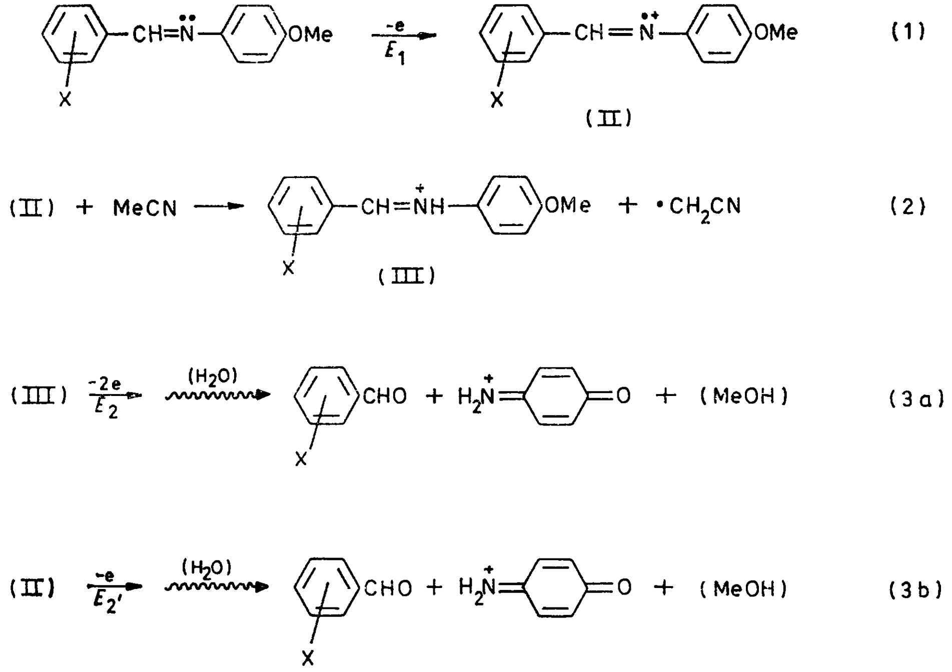
[a] Based on the absorbance at 562 nm. The value was corrected for the increase in absorbance caused by *p*-benzoquinone. The amount of (I) from the run for *p*-anisidine at 0·70 V was assumed to be 100%. [b] Electrolyses were allowed to continue for 120 min at room temperature: the oxidation were essentially complete in all cases. [c] The yield of (I) increased with increase in the concentration of the original substrate.

formed as a main product under the experimental conditions. Small differences in wave length of the absorption maxima from the reported values [9] may be caused from the difference in medium composition. The absorption spectrum of the ion (I) was affected by *p*-benzoquinone. For example, when the solution was diluted with acetonitrile containing 10^{-3}M-*p*-benzoquinone, the absorbance increased by *ca.* 12%. The violet colour produced on electrolysis of *p*-anisidine and *N*-benzylidene-*p*-anisidines showed acid–base indicator properties as described by Bacon and Adams.[9] The amounts of (I) formed on electrolysis are summarized in Table 4.

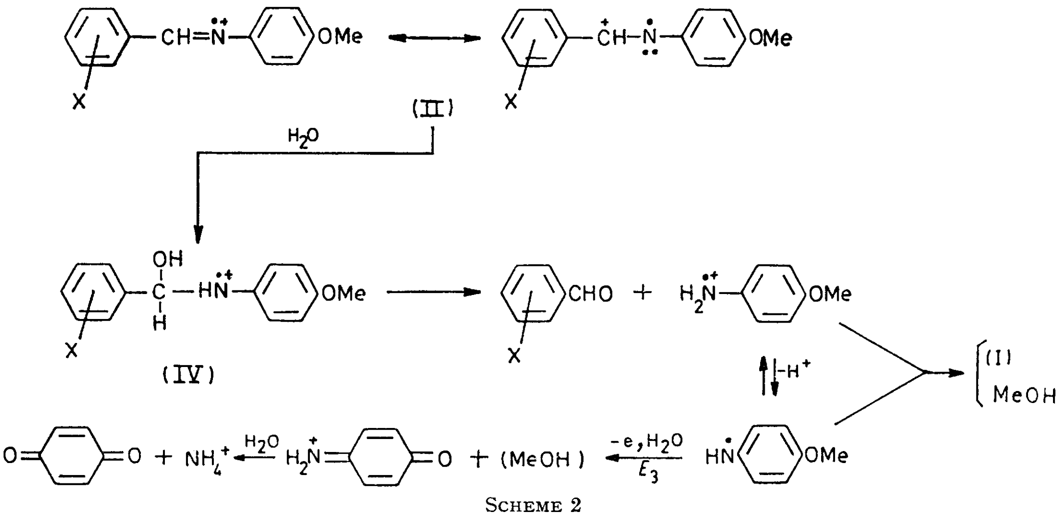
DISCUSSION

From the present results the anodic reaction of *N*-benzylidene-*p*-anisidines in acetonitrile without added water may be described by Scheme 1 where reactions (1) and (3) represent the first wave and the second wave, respectively.

A large body of evidence favours Scheme 1. (*a*) The peak potential of the first wave was linearly related to the σ^+ value (Figure 2), indicating that the stability of the cation radical (II) determines the ease of electron transfer (1). (*b*) In controlled potential electrolysis of *N*-benzylidene-*p*-anisidines at the peak potential of the first wave, 0·8—1·0 electron per molecule was consumed, and on electrolysis the cyclic voltammogram of the solution coincided with those of *N*-benzylidene-*p*-anisidines in acetonitrile containing an equimolar amount of perchloric acid. In the case of *N*-*p*-methoxybenzylidene-*p*-anisidine, *N*-*p*-methoxybenzylidene-*p*-anisidinium perchlorate was isolated as the main product and the cyclic voltammogram of the salt also coincided with that of *N*-*p*-methoxybenzylidene-*p*-anisidine in the presence of an equimolar amount of perchloric acid (see Experimental section). Similar pathways to reactions (1) and (2) have been suggested in the anodic oxidation of aliphatic amines[10] and amides[11] in acetonitrile. In both cases $\cdot CH_2CN$ has been suggested to dimerize to give succinonitrile and in the case of amides the occurrence of the nitrile has been proved.[11] (*c*) In controlled potential electrolysis of *N*-*p*-methoxybenzylidene-*p*-anisidinium perchlorate (II), two electrons per molecule were consumed, and anisaldehyde and *p*-benzoquinone imine were identified in the resulting solution. In controlled potential electrolysis of *N*-benzylidene-*p*-anisidines at the peak potential of the second wave, two electrons per molecule were consumed, and the corresponding aldehyde and *p*-benzoquinone imine were identified as the products. It cannot be decided from these results alone whether reaction (3a) or (3b) is actually operative in the cyclic voltammetry of *N*-benzylidene-*p*-anisidines at their second wave. Both pathways may be equally possible. The downward curvature observed in the plot of the peak potential of the second wave against the σ^+ value (Figure 2) suggests[12] that a third reaction pathway differing from (3a) or (3b) must be considered for *N*-benzylidene-*p*-anisidines with an electron-attracting substituent on the benzylidene ring. Table 2 shows the effect of water on the second wave of *N*-benzylidene-*p*-anisidines increases with increase in the electron-attracting effect of the substituent. The acetonitrile used was unavoidably contaminated



SCHEME 1



SCHEME 2

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[10] R. F. Dapo and C. K. Mann, *Analyt. Chem.*, 1963, **35**, 677; C. D. Russell, *ibid.*, p. 1291.

[11] J. F. O'Donell and C. K. Mann, *J. Electroanalyt. Chem.*, 1967, **13**, 157.

[12] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York and London, 1963, pp. 189—190. A change in the mechanism is demonstrated when a minimum is observed in the Hammett type plot. In the plot of E_p *vs.* σ^+ in Figure 2 the maximum observed corresponds to the minimum in a usual Hammett type plot.

with water (see Experimental section), so a path in which water participates in the electron-transfer process (see below) may predominate at the potential of the second wave of *N*-benzylidene-*p*-anisidines with electron-attracting substituents.

In the presence of added water the reaction at the electrode became more complicated. The exact mechanism is still uncertain, but Scheme 2 explains all the experimental results. Thus on controlled potential electrolysis of *N*-benzylidene-*p*-anisidines in the presence of 5% water, about two electrons per molecule were consumed, and *p*-benzoquinone and the corresponding benzaldehyde were identified as the main products. However, 4-amino-4′-methoxydiphenylamine in its oxidized form (I) was also found, though as a minor product. This compound has been reported to be produced *via* head-to-tail coupling of the anisidine radical cation.[7] The coupling reaction is second order in the radical, while further oxidation of the radical producing *p*-benzoquinone imine and/or *p*-benzoquinone should be first order. The relative amount of (I) formed on electrolysis will thus increase with increase in the concentration of the original substrate when the other conditions are held constant. On the other hand, the yield of (I) will decrease with increase in the applied potential, because the rate of further oxidation of the radical should increase. The latter expectation was found to be the case in electrolysis of *p*-anisidine and *N*-benzylidene-*p*-anisidines in acetonitrile containing 5% water (Table 4). The former could not be proved quantitatively, because *p*-anisidine itself acted as a base at higher concentration and hence on electrolysis the nature of the solution was very complex (Table 3). It was noticed, however, that the relative amount of the ion (I) increased with the concentration of original substrate.

On cyclic voltammetry of *N*-benzylidene-*p*-anisidines in the presence of a sufficient amount of water, the current potential curve on the reverse sweep crosses that on the first anodic sweep (Figure 3). This suggests that a more easily oxidized species than the starting Schiff base was formed in the follow-up chemical reaction. Hence the value of E_3 in Scheme 2 is less positive than that of E_1 in Scheme 1.

The tetrahedral addition intermediate (IV) is assumed to be formed by analogy with that usually demonstrated on hydrolysis of Schiff bases.[13] In the anodic oxidation of *N*-phenyl-*p*-anisidines [14] and *p*-methoxyphenol.[15] formation of quinonoid compounds by the rapid ejection of the methoxy-group as methanol has been reported. In the present study methanol is considered to be formed by a similar process.

Hydrolysis of *N*-benzylidene-*p*-anisidines in acetonitrile containing 5% water was negligible during the period of electrolysis (*ca.* 2 h). However, hydrolysis of *N*-benzylidene-*p*-anisidinium ions (II) was quite rapid under these conditions. Hence a reaction pathway involving hydrolysis of (II) must be considered. Thus the *N*-benzylidene-*p*-anisidinium ion formed first as shown in Scheme 1 is hydrolysed to produce *p*-anisidine, which is further oxidized at the applied potential. If this was the case, the number of electrons consumed per molecule of the Schiff base should be three, that is, one electron to produce *N*-benzylidene-*p*-anisidinium ion, and two electrons to oxidize *p*-anisidine. The observed value was, however, comparable to that found on electrolysis of *p*-anisidine under the same conditions, *i.e.*, about two electrons per molecule (Table 3). The contribution of such reaction, therefore, is believed to be small. In any case the overall results of electrolysis in the presence of added water can be regarded as an electrolytic promotion of hydrolysis of *N*-benzylidene-*p*-anisidines.

In the presence of a base, such as pyridine, the reaction of *N*-benzylidene-*p*-anisidines at the electrode is quite different from the present case. Detailed studies on this are now in progress.

EXPERIMENTAL

Materials.—*N*-Benzylidene-*p*-anisidines were prepared by a known method [16] and gave the following values on analysis: $XC_6H_4{\cdot}CH{=}N{\cdot}C_6H_4OMe$-(*p*) (X, m.p., N% found, N% calc.) H, 72°, 6·7, 6·65; *p*-NO_2, 134°, 10·95, 10·95; *p*-Cl, 123°, 5·4, 5·7; *m*-Cl, 71·5—72°, 5·75, 5·7; *o*-Cl, 62·5°, 6·1, 5·7; *p*-OMe, 146°, 5·6, 5·8; and *p*-Me, 85·5—86°, 6·3, 6·2. Other organic compounds were commercial; *p*-anisidine was recrystallized from ethanol, *p*-aminophenol was recrystallized from ethanol under nitrogen just before use, *p*-benzoquinone was purified by sublimation, and the various benzaldehydes were distilled or recrystallized before use. Sodium perchlorate, used as supporting electrolyte, was recrystallized from ethanol–water and stored over phosphorus pentoxide under reduced pressure. Acetonitrile was purified as described by Mann *et al.*[17] and its water content, determined by the Karl Fischer method, was less than 0·025%. Inorganic reagents were of reagent grade and were used without further purification.

Apparatus.—Cyclic voltammograms were obtained essentially as described previously.[6] All potentials were measured against a saturated calomel electrode. All measurements were carried out at 25 ± 0·05°. A Toa–Dempa XYR-2A type X–Y recorder was used throughout the study. The working electrode was prepared from a glassy-carbon rod (Tokai Electrode GC-20, diameter 3 mm) as described previously.[6] Before each measurement the working electrode was rinsed twice in methanol and once in water. Then the blank current–potential curve was measured in 0·07M-borate buffer (pH 9, containing 0·015M-Na_2SO_4) between −0·3 and +1·3 V. Then the electrode was washed with distilled water and immersed in the test solution. This procedure confirmed the reproducibility of the cyclic voltammogram. Polarographic measurements were carried out with a Yokogawa type POL-11 polarograph, as described previously.[18] A Shimazu spectrophotometer, type QV-50, was used for spectroscopy. I.r.

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spectra were obtained using a Hitachi EPI-2 spectrophotometer. Controlled potential electrolysis was performed with a Yanagimoto V-8 potentiostat. Current was recorded on a Toa–Dempa EPR-10A recorder and the electricity consumed was estimated from the area below the current–time curve. An H-type electrolysis cell was used. On electrolysis in acetonitrile, the anode compartment was separated with methyl cellulose plug (350—500 cps) and a sintered glass disk. Other details of the procedure were described previously.[19] The concentration of reactants was *ca.* 10^{-3}M and the supporting electrolyte was 0·1M-$NaClO_4$, unless otherwise noted.

Analysis of Products obtained on Controlled Potential Electrolysis.—Typical examples of the procedure are described.

(a) N-p-*Methoxybenzylidene*-p-*anisidinium perchlorate*. *N*-*p*-Methoxybenzylidene-*p*-anisidine (465 mg) was subjected to electrolysis in acetonitrile (100 ml) at +1·12 V for 130 min at room temperature. The resulting deep brown solution showed essentially no first wave in the cyclic voltammogram and consumed 150 coulombs, which corresponds to n = 0·81. The solution was evaporated to dryness under reduced pressure and the residue was washed with ethyl acetate (100 ml) to remove $NaClO_4$. The brown crystals obtained (310 mg) were recrystallized from Ac_2O–EtOAc to give yellowish green needles, m.p. 239—242° (decomp.) (Found: C, 52·7; H, 4·75; N, 4·2; Cl, 10·5. $C_{15}H_{16}ClO_6$ requires C, 52·7; H, 4·7; N, 4·1; Cl, 10·35%), $\nu_{max.}$ (Nujol) 3176, 1657 (C=NH),[20] and *ca.* 1100 cm^{-1} (ClO_4). A cyclic voltammogram of this compound in acetonitrile coincided with that of *N*-*p*-methoxybenzylidene-*p*-anisidine in acetonitrile in the presence of an equimolar amount of perchloric acid.

(b) p-*Benzoquinone and benzaldehyde*. *N*-Benzylidene-*p*-anisidine (23 mg) was subjected to electrolysis in acetonitrile (100 ml) containing 5% water at +1·15 V. The cyclic voltammogram of the solution from electrolysis is shown in Figure 4. The solution was mixed with an equal amount of 0·075M-borate buffer, pH 9, containing 0·15M-Na_2SO_4; the cyclic voltammogram of the mixture coincided with that of authentic *p*-benzoquinone (5 × 10^{-4}M) obtained under the same conditions (E_p cathodic = −0·19 V, E_p anodic = −0·08 V) and the polarogram of the mixture coincided with that of an authentic mixture of *p*-benzoquinone and benzaldehyde (5 × 10^{-4}M each) ($E_{\frac{1}{2}}$ of benzaldehyde = −1·667 V). After the solution from electrolysis was diluted fifty-fold with acetonitrile, the u.v. spectrum was compared with that of a mixture of authentic samples of *p*-benzoquinone and benzaldehyde (2·2 × 10^{-5}M each) in acetonitrile.

(c) p-*Benzoquinone imine and benzaldehyde*. *N*-Benzylidene-*p*-anisidine (24·2 mg) was subjected to electrolysis in acetonitrile (100 ml) at 1·62 V. The cyclic voltammogram of the solution from electrolysis was very similar to that of *p*-aminophenol obtained in acetonitrile containing an equimolar amount of perchloric acid. *p*-Aminophenol is reported to be oxidized to *p*-benzoquinone imine in acetonitrile.[8] The resulting solution was mixed with an equal amount of borate buffer, pH 9, and tested for the presence of *p*-benzoquinone. After electrolysis another portion of the solution was mixed with a small amount of water and stood overnight. *p*-Benzoquinone and benzaldehyde were detected in the mixture by u.v. spectroscopy.

The results in Table 3 were all obtained by similar treatments to those described above.

[2/667 *Received*, 21*st March*, 1972]

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