Anodic Oxidation of Carboxamides. Part I. Anodic Oxidation and Pyridination of 4- and 4′-Substituted Benzanilides

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Anodic oxidations of several 4- and 4′-substituted benzanilides were investigated by cyclic voltammetry and controlled potential electrolysis at a glassy-carbon electrode in aqueous buffer solution and also in dry acetonitrile in the absence and presence of pyridines. 4′-Methoxybenzanilide (MBA) showed two anodic peaks between pH 9·5 and 11·5. and a single anodic peak at higher and lower pH values. On electrolysis of MBA in weakly acidic or neutral solution. *N*-benzoyl-*p*-benzoquinone imine was formed, and on electrolysis in alkaline and strongly acidic solution. *p*-benzoquinone and benzamide were the main products. Anodic oxidation of MBA in acetonitrile containing excess of pyridine gave the pyridinated MBA. 1-(2-benzamido-5-methoxyphenyl)pyridinium perchlorate.

ANODIC oxidation of aliphatic carboxamides has been studied extensively by many workers,[1] but no systematic study has been made on aromatic carboxamides. Mann and O'Donnell reported that an *N*-phenylcarboxamide was easily oxidized with a coulometric *n*-value of more than one.[1a]

Recently, during studies on anodic oxidation of Schiff's bases, we found a new anodic pyridination reaction and discussed the reaction process and products.[2] Therefore, it seemed of interest to investigate anodic oxidation of benzanilides and attempt to find new examples of anodic pyridination.

This paper reports results on cyclic voltammetry and controlled potential electrolysis of 4- and 4′-substituted benzanilides in aqueous buffer solution and in dry acetonitrile. and the anodic oxidation process is discussed in some detail.

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[1] (*a*) C. K. Mann and J. F. O'Donnell, *J. Electroanal. Chem.*, 1967, **13**, 157, 162; (*b*) S. D. Ross and M. Finkelstein, *J. Org. Chem.*, 1966, **31**, 128; (*c*) E. J. Rudd, M. Finkelstein, and S. D. Ross, *ibid.*, 1972, **37**, 1763; (*d*) M. Finkelstein and S. D. Ross, *Tetrahedron*, 1972, **28**, 4497; (*e*) V. H. Scneider, *Ber.*, 1923, **56**, 2640; (*f*) D. E. Couch, *Electrochim. Acta*, 1964, **9**, 327.

[2] M. Masui and H. Ohmori, *J.C.S. Perkin II*, 1973, 1112.

RESULTS

Cyclic Voltammetry.—First, cyclic voltammetry of 4′-methoxybenzanilide (MBA) and 4′-hydroxybenzanilide (HBA) was studied in aqueous buffer solution of pH 0·7—12·5 containing 50% acetonitrile. MBA (1mM) showed a single anodic peak below pH 9·5 and above 11·5, and two peaks in the range pH 9·5—11·5. Typical voltammograms are shown in Figure 1. All potentials were measured against an aqueous saturated calomel electrode (s.c.e.). Upon reversal of the scan direction, MBA showed two cathodic peaks at pH 0·7 and one above pH 4. On subsequent anodic scan a small extra anodic peak was observed at a less positive potential than that of the original anodic peak over the entire pH range studied. As shown in Figure 2, plots of the peak potentials (E_p) of the anodic peaks against pH gave two separated lines, which suggests that a molecular form of MBA which is oxidized at the peak below pH 9·5 (peak A) is different from that at the peak above pH 11·5 (peak B). The peak current (i_p) of peak A decreased with increase in pH above 10, whereas that of peak B increased. The i_p value of peak B (i_{pB}) remained nearly constant with increase in the concentration of MBA at pH 10·6. That is, the value of i_{pB}/i_{pA} decreased and the pH range where two anodic peaks were observed shifted to a higher pH with increase in the concentration of MBA. The variation of i_p as a function of the potential scan rate (v) was measured at v = 10—200 mV s^{-1}. The values of $i_p v^{-\frac{1}{2}}$ of peaks A and B were nearly constant below pH 9·5 and above 11·5, whereas between these pH values that of peak B (the first peak) decreased with increase in the value of v.

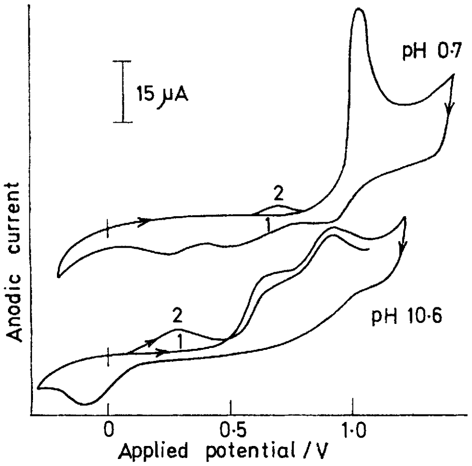

FIGURE 1 Cyclic voltammograms of 4′-methoxybenzanilide (1mM) in 50% aqueous acetonitrile; numbers 1 and 2 denote the first and second cycles, respectively, at a sweep rate of 50 mV s^{-1}

HBA showed a single anodic peak over the entire pH range. Least square analysis of the shift of peak potential with pH resulted in the following equation:

$$E_p = 0{\cdot}70 - 0{\cdot}039 \text{ pH} \quad (\text{V } vs. \text{ s.c.e.})$$

The E_p value of HBA nearly coincided with that of the extra anodic peak of MBA. Upon reversal of the scan direction, HBA showed two cathodic peaks at pH 0·7 and a broad cathodic peak above pH 4. On subsequent anodic scan, a small extra anodic peak was observed at 0·55 V, only below pH 1·0.

In dry acetonitrile containing 0·1M-sodium perchlorate MBA showed a single anodic peak at 1·20 V, and on reversing the direction of the scan, two cathodic peaks were observed at 0·70 and 0·15 V. On subsequent anodic scan a small extra anodic peak was observed at 0·96 V. The value of $i_p v^{-\frac{1}{2}}$ for the anodic peak at 1·2 V was independent of the scan rate.

TABLE 1

Results of cyclic voltammetry of 4- and 4′-substituted benzanilides (1mM) in acetonitrile containing 0·1M-NaClO$_4$, at 50 mV s^{-1}

Substituent	Peak potential E_p (V)	βn_a *	$i_p/cv^{\frac{1}{2}}A$ † (A cm mol^{-1} s$^{\frac{1}{2}}$ V$^{-\frac{1}{2}}$)
4-OMe, 4′-OMe	1·13	0·51	2090
4-Me, 4′-OMe	1·13	0·44	2800
4-Cl, 4′-OMe	1·16	0·48	2770
4-NO$_2$, 4′-OMe	1·17	0·60	2600
4-OMe	1·48	0·40	2940
4-Cl	1·50	0·44	3000
4-NO$_2$	1·58	0·40	3350
None	1·55	0·48	3600
4′-Me	1·41	0·44	2890
4′-OMe	1·20	0·60	2550
4′-OH	0·97	0·80	2650
4′-Br	1·52	0·32	4370
4′-Cl	1·51	0·37	4940
4′-F	1·49	0·40	3790
4′-NO$_2$	1·75	0·37	3690
4′-COMe	1·61	0·41	3110

* β = Anodic transfer coefficient, n_a = no. of electrons in the charge transfer (or rate-determining charge transfer) step. † i_p = Peak current, c = concentration (M), v = potential scan rate, A = area.

In acetonitrile HBA showed a single anodic peak at 0·97 V and two cathodic peaks at 0·73 and 0·18 V on reverse scan. No extra peak was observed on a multiple sweep. The E_p value of the anodic peak of HBA coincided with that of the extra anodic peak observed in MBA. Voltammetric data on 4- and 4′-substituted benzanilides are shown in Table 1. The E_p value of the anodic peaks shifted to a more positive potential with increase in the

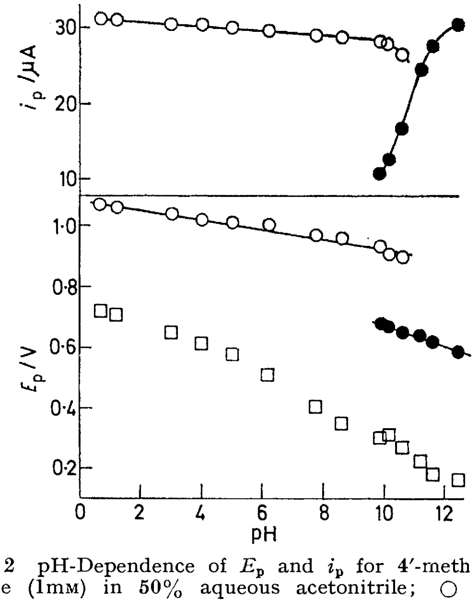

FIGURE 2 pH-Dependence of E_p and i_p for 4′-methoxybenzanilide (1mM) in 50% aqueous acetonitrile; ○ peak A, ● peak B, □ extra anodic peak

Hammett value, σ, of the 4′-substituent. However, a plot of E_p against σ showed a break at σ = 0.

Controlled Potential Electrolysis.—Table 2 summarizes results on controlled potential electrolysis of MBA in 50% aqueous acetonitrile solution. The results were the same in the presence and absence of oxygen. Electrolysis of MBA in buffer solution of pH 0·7 at 1·1 V resulted in consumption of 2 Faradays per mole of substrate, and formation of *p*-benzoquinone and benzamide. The voltammogram of the resulting solution showed a single peak at 0·22 V on a cathodic sweep and a single peak at 0·57 V on a subsequent anodic sweep, which was in good agreement with that of *p*-benzoquinone under the same conditions. The u.v. spectrum of the resulting solution had $\lambda_{max.}$ 242 nm, which also agreed well with that of *p*-benzoquinone containing an equimolar amount of benzamide.

TABLE 2

Results of controlled potential electrolysis of 4′-methoxybenzanilide (MBA) (*ca.* 1mM) in 50% aqueous acetonitrile

pH	Applied potential (V)	*n*-Value	Voltammetric data on the resulting solution, at 50 mV s^{-1}	
			E_p (cathodic) (V)	E_p (anodic) (V)
0·7	1·10	1·97	0·22	0·57
1·1	1·10	2·11	0·21	0·54
2·9	1·10	2·20	0·10	0·41, 0·57
3·7	1·10	1·92	0·03	0·36, 0·56
4·7	1·10	1·95	0·00	0·52
5·9	1·10	2·00	−0·01	0·47
6·5	1·10	2·00	−0·04	0·44
7·4	1·05	1·97	−0·09	0·41
8·0	1·05	2·00	−0·10	0·38
9·7	1·05	2·30	−0·10, −0·21	−0·10, 0·27
10·6	0·70	1·91	−0·11, −0·21	−0·10, 0·28
10·6	0·95	2·20	−0·11, −0·22	−0·12, 0·26

Electrolysis of MBA at pH 3·7 gave a coulometric *n*-value of two, and *p*-benzoquinone and benzamide were identified as the final products. However, the voltammogram and absorption spectrum of the resulting solution were very different from those of *p*-benzoquinone in contrast to results at pH 0·7. Immediately after electrolysis the solution showed a broad cathodic peak at 0·03 V, two anodic peaks at 0·36 and 0·56 V on reverse scan, and absorption maxima at 242 and 268 nm. The anodic peak at 0·56 V coincided with that of HBA. Its peak height and absorbance at 268 nm decreased with time, whereas those at 0·36 V and 242 nm increased, and the cathodic peak became sharper.

Electrolysis of MBA at pH 5·9 also gave an *n*-value of two, and *p*-benzoquinone and benzamide were the final products. Immediately after the electrolysis the solution showed a single cathodic peak and a single anodic peak on voltammetry, and an absorption maximum at 268 nm. However, after standing for 24 h the solution showed the same voltammogram and u.v. maximum as those of *p*-benzoquinone containing an equimolar amount of benzamide. The above results suggested that the initial product of electrolysis was fairly stable in weakly acidic solution, but gradually decomposed to give *p*-benzoquinone and benzamide.

Electrolysis of MBA in buffer solution of pH 10·6 at the potential of the first peak required more than 5 h and gave an *n*-value of two, and *p*-benzoquinone and benzamide were produced. During the electrolysis the solution turned reddish brown and the colour deepened with time, and the first and second peaks both decreased and disappeared by the end of electrolysis. The reddish brown colour could be ascribed to decomposition of some of the *p*-benzoquinone produced in alkaline solution. A voltammogram of the resulting solution was in good agreement with that of *p*-benzoquinone. Electrolysis of MBA at the potential of the second peak gave the same result as that at the potential of the first peak except for the shorter time required to complete the electrolysis. Electrolysis of HBA in buffer solution of pH 3·7 containing 50% acetonitrile gave an *n*-value of two, and *p*-benzoquinone and benzamide were identified.

Electrolysis of MBA in dry acetonitrile containing 0·1M-sodium perchlorate gave an *n*-value of two, and *p*-benzoquinone, benzamide, and methanol were identified. The resulting solution gave a voltammogram with a single cathodic peak at 0·1 V and a single anodic peak at 0·8 V on reverse scan,[3] and an absorption maximum at 242 nm. The findings were in good agreement with those for *p*-benzoquinone containing an equimolar amount of benzamide under the same conditions.

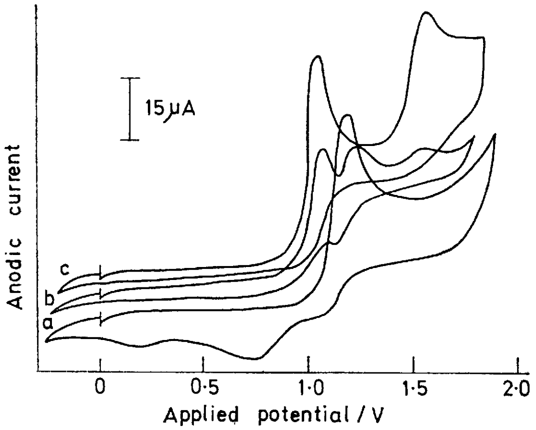

FIGURE 3 Cyclic voltammograms of 4′-methoxybenzanilide (1mM) in acetonitrile containing various concentrations of pyridine; 0·1M-$NaClO_4$, 50 mV s^{-1}, (a) in the absence of pyridine, (b) with pyridine 0·8mM, (c) with pryidine 10mM

Electrolysis of HBA in acetonitrile gave the same result as that of MBA except for the absence of methanol in the resulting solution.

The results of electrolyses of 4- and 4′-substituted benzanilides in acetonitrile are summarized in Table 3.

TABLE 3

Results of controlled potential electrolysis of 4- and 4′-substituted benzanilides (*ca.* 1mM) in acetonitrile containing 0·1M-$NaClO_4$

Substituent	Applied potential (V)	*n*-Value	Voltammetric data on the resulting solution, at 50 mV s^{-1}	
			E_p (cathodic) (V)	E_p (anodic) (V)
4′-OMe	1·20	2·00	0·10	0·80
4-OMe, 4′-OMe	1·20	2·20	0·15	0·78
4-Cl, 4′-OMe	1·20	2·20	0·18	0·82
4′-OH	1·00	2·05	0·11	0·77
4-Me, 4′-OMe	1·20	1·83	0·15	0·78

Effects of Pyridines on Anodic Oxidation of Benzanilides.—Figure 3 shows typical voltammograms of MBA in acetonitrile containing various concentrations of pyridine. Two

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[3] V. D. Parker, *Chem. Comm.*, 1969, 716.

anodic peaks appeared at 1·00 (peak B) and 1·60 V (peak C) in addition to the anodic peak at 1·20 V (peak A) which was present in the absence of pyridine. The $i_{\rm p}$ values of peaks B and C increase with increasing concentration of pyridine, whereas that of peak A decreased. In the presence of excess of pyridine the value of $i_{\rm p}v^{-\frac{1}{2}}$ of peak B was nearly constant, whereas that of peak C decreased with increase in the scan rate from 10 to 200 mV s^{-1}.

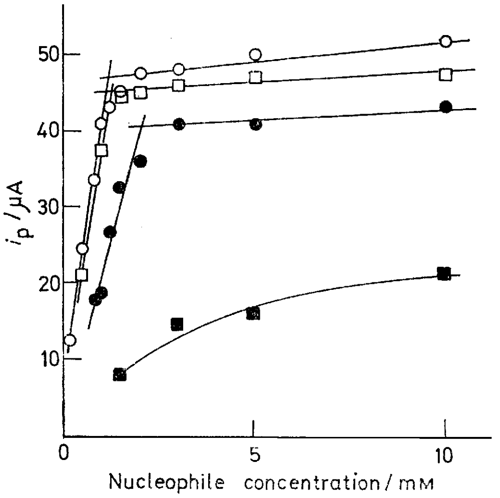


FIGURE 4 Dependence of peak current on nucleophile concentration in the voltammetric oxidation of 4′-methoxybenzanilide in acetonitrile, 1mM, 50 mV s^{-1}; ○ pyridine, peak B; ● pyridine, peak C; □ 2,6-lutidine, peak B; ■ 2,6-lutidine, peak C

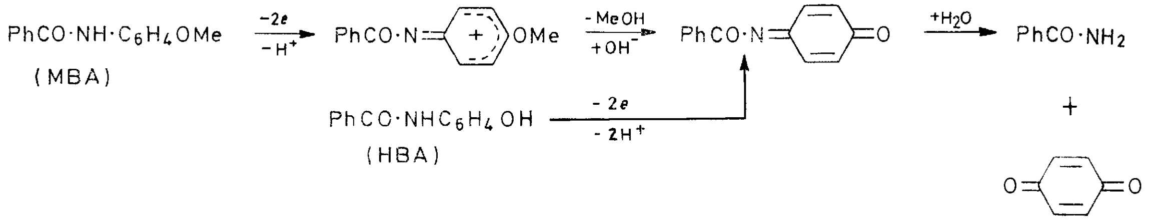
A plot of the peak currents against the concentration of nucleophiles (Figure 4) showed that the $i_{\rm p}$ value of peak B first increased linearly with the concentration of nucleophiles and then gradually reached a limiting value. Extrapolation of the straight line drawn through the initial part of the plot intersected the limiting line near a concentration of the nucleophile equivalent to 1·2M of MBA. On the other hand, plots of values for peak C of unhindered nucleophiles, such as pyridine and 3,5-lutidine, intersected the limiting line at concentrations near 2·1M of MBA, whereas those of hindered nucleophiles, such as 2,6-lutidine, did not attain a limiting value.

Electrolysis of MBA in acetonitrile containing excess of pyridine at the potential of peak B gave an n-value of two, and the pyridinated MBA, 1-(2-benzamido-5-methoxyphenyl)pyridinium perchlorate, was isolated. Details of the procedures used to identify the product are described in the Experimental section. A voltammogram of the solution after the electrolysis showed the disappearance of peak B and presence of peak C. A similar voltammogram was obtained when pyridinated MBA was subjected to cyclic voltammetry under the same conditions. Electrolysis of MBA in acetonitrile containing excess of 2,6-lutidine at the potential of peak B gave an n-value of two, but substituted MBA was not found and only p-benzoquinone was identified; the voltammogram of the resulting solution was in good agreement with that of p-benzoquinone under the same conditions. Methanol was not detected in the solution.

DISCUSSION

The present results indicate that the process of anodic oxidation of MBA in 50% aqueous acetonitrile solution is a two-electron oxidation leading to an intermediate, which is unstable in acidic or alkaline solution and is rapidly hydrolysed to p-benzoquinone and benzamide. An attempt to isolate the intermediate from the solution was not successful. However, it was rather stable in weakly acidic or neutral solution, and immediately after electrolysis its decomposition was not detected by voltammetry or spectrophotometry. The $E_{\rm p}$ value of the extra anodic peak of MBA coincided with that of the anodic peak of HBA, so the intermediate may be common in both. The intermediate is thought to be N-benzoyl-p-benzoquinone imine, since its $\lambda_{\rm max.}$ 268 nm (ε 30,000) is very close to that of N-phenyl-p-benzoquinone imine, at 264 nm.[4] Though the latter compound also has fairly strong absorption at 436 nm (ε 3200), the intermediate formed was almost colourless (pale yellow). In the case of N-phenyl-p-benzoquinone imine both phenyl rings will be conjugated with each other to exhibit the violet colour. The carbonyl group in N-benzoyl-p-benzoquinone imine seems to prevent the conjugation of both rings. The instability of the quinone imine in acidic or alkaline solution can be explained in terms of acid- or alkali-catalysed hydrolysis.

The following scheme is proposed for the reaction:



A similar oxidation process was suggested for the anodic oxidation of p-hydroxy- and p-methoxy-diphenylamines.[5]

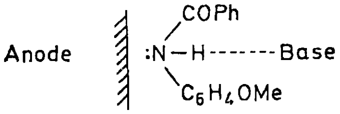
The anodic oxidation in acetonitrile under present conditions can be considered analogous with that in strongly acidic solution. Thus the observed results of cyclic voltammetry of MBA and HBA in acetonitrile indicate the intermediate formation of N-benzoyl-p-benzoquinone imine as in aqueous solution. Upon controlled potential electrolysis, however, only the formation of p-benzoquinone and benzamide was observed. In acetonitrile the solution is not buffered, and hence will become fairly acidic due to liberation of protons

[4] G. Cauquis and D. Serve, *Analyt. Chem.*, 1972, **44**, 2222.

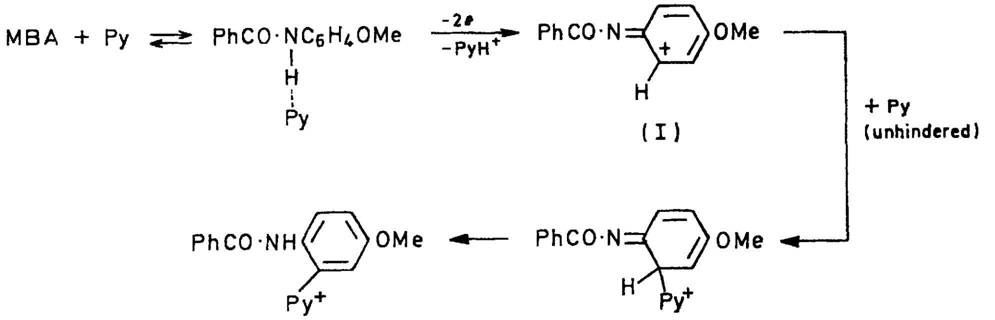
[5] D. W. Leedy and R. N. Adams, *J. Amer. Chem. Soc.*, 1970, **92**, 1646.

during oxidation.* The acetonitrile used was unavoidably contaminated with a little water, so the quinoneimine formed would be hydrolysed by acidic catalysis within the time scale of controlled potential electrolysis (*ca.* 120 min).

The presence of two anodic peaks in the range of pH 9·5—11·5 was first thought to be due to deprotonation of MBA. However, assignment of the first peak (peak B) to oxidation of the anionic form of MBA was found to be unreasonable, because the pK_a of MBA must be larger than 16 (the pK_a of benzanilide was reported to be 16·53[6]), and because to supply sufficient of the anionic form by deprotonation of MBA to produce peak B in the pH region, the rate constant must be extremely large[7] (much larger than that of a diffusion-controlled reaction). Furthermore in acetonitrile, addition of weak bases, such as pyridines, had the same effect on the anodic peaks (peak A and B) as that observed in aqueous alkaline solution. Therefore, although the dissociation of MBA is negligible in the bulk of the solution, partial deprotonation of MBA or formation of a complex of MBA with bases which produces an easily oxidizable form may occur at the surface of the anode. The facts that the intersection for peak B in Figure 4 was observed at a concentration near 1·2M of the pyridine, and that the anodic peak of *N*-phenyl-*p*-benzanisidide did not split into two peaks in the alkaline region[8] substantiate the above consideration.



The following scheme is suggested for the anodic oxidation of MBA in dry acetonitrile containing excess of the pyridine (Py). The fact that the intersection for peak C in Figure 4 was observed at a concentration near 2M for the unhindered pyridine suggests that one molecule of pyridine acts as a base and the other as a nucleophile in the pyridination process. Even when a sterically hindered pyridine, such as 2,6-lutidine is used, the anodic process for the formation of the intermediate (I) will be the same because 2,6-lutidine is almost as effective as unhindered pyridines in increasing peak B (Figure 4). It has been reported that 2,6-lutidine was *ca.* 30 times less reactive toward the anthracene cation radical than 3,5-lutidine when acting as a nucleophile, while as a base its reactivity is similar to that of the latter.[9] Similar effects have been observed in the anodic pyridination of *N*-benzylidene-*p*-anisidines in acetonitrile.[2] In the case of 2,6-lutidine, however, the fate of the intermediate (I) is still uncertain, since no lutidinated product was obtained but almost quantitative formation of *p*-benzoquinone was identified from the cyclic voltammogram on the solution from controlled potential electrolysis.



An alternative mechanism for the formation of the intermediate (I) could be considered. Thus initial one-electron transfer from the lone pair of the amide nitrogen to form a cation radical, base assisted proton transfer from the nitrogen to form a neutral radical, and a further one-electron transfer to form (I). This type of anodic substitution has been reported for anodic pyridination of *N*-benzylidene-*p*-anisidines[2] and for anodic acetoxylation of aliphatic amides.[1b] Similar stepwise electron transfer has been discussed in the anodic pyridination of anthracene derivatives.[9] In this mechanism, however, since the initial electron-transfer step will be the same as in the absence of bases, the peak potential for the step will not shift toward a less positive potential on addition of base. In the anodic pyridination of *N*-benzylidene-*p*-anisidines the peak potential of the corresponding step is essentially the same as that in the absence of a pyridine, the peak height is nearly doubled in the presence of sufficient pyridine, and the value of $i_p v^{-\frac{1}{2}}$ decreased with increase in the scan rate from 11 to 192 mV s^{-1}[2] On the other hand the peak potential of MBA shifted towards a less positive potential by *ca.* 200 mV in the presence of pyridines, the peak height was almost unchanged [*cf.* Figure 3, curves a and c], and the value of $i_p v^{-\frac{1}{2}}$ was nearly constant. These findings are incompatible with the stepwise e.c.e. mechanism. The behaviour in cyclic voltammetry described above, together with the technique developed

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* When MBA (*ca.* 1mM) was subjected to electrolysis in unbuffered 50% aqueous acetonitrile (100 ml) at 1·05 V, the pH value of the resulting solution was almost two, and *p*-benzoquinone and benzamide were identified.

[6] K. Bowden, *Chem. Rev.*, 1966, **66**, 119.

[7] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[8] M. Masui, in preparation.

[9] V. D. Parker and L. Eberson, *Acta Chem. Scand.*, 1970, **24**, 3542.

by Parker and Eberson,[9] may be used for a diagnosis of the mechanism of anodic pyridinations.

EXPERIMENTAL

Materials.—4- and 4′-Substituted benzanilides were prepared from the corresponding benzoyl chlorides and anilines by known methods [10] and recrystallized from ethanol: $XC_6H_4CO{\cdot}NHC_6H_4Y$ (X, Y, m.p.); OMe, OMe, 202—203°; Me, OMe, 168—169°; H, OMe, 155—156°; Cl, OMe, 208—209°; NO_2, OMe, 196—197°; OMe, H, 171—172°; Cl, H, 192—194°; NO_2, H, 211—212°; H, OH, 213—214°; H, H, 161—162°; H, Me, 157—158°; H, Br, 203—204°; H, Cl, 191—192°; H, F, 184—185°; H, NO_2, 196—197°; and H, COMe, 204—205°. The buffers used in this study were prepared from: $HClO_4$ (pH 0·7—1·0), 0·05M-H_3PO_4–NaH_2PO_4 (pH 2—3), 0·05M-HOAc–NaOAc (pH 4—5), 0·05M-NaH_2PO_4–Na_2HPO_4 (pH 6—8), 0·05M-H_3BO_3–NaOH (pH 9—10), and 0·05M-Na_2HPO_4–NaOH (pH 11—12·5). Sodium sulphate (0·1M) was added to the buffers as the supporting electrolyte. The pH values of the solutions were determined with a Toa Dempa HM-5 pH meter after voltammetric measurement. Acetonitrile and sodium perchlorate were purified as described previously.[11] Pyridine, 3,5-, 2,5-, and 2,6-lutidine, and α-picoline were obtained from commercial sources and purified by distillation.

Apparatus.—Cyclic voltammetry and controlled potential electrolysis were carried out as described previously.[11] The base line for peak C was measured by stopping the scan and allowing the current to decay at constant potential.[12] U.v., i.r., and n.m.r. spectra were obtained using Hitachi 139, EPI-2, and R-20A spectrometers, respectively. All measurements were carried out at 25 ± 0·05°. A JEOL JGC-750 gas chromatograph with a flame ionization detector was used to detect methanol. The packing material was 25% dioctyl phthalate on Celite (40—60 mesh).

Analysis and Isolation of Products Obtained by Controlled Potential Electrolysis.—Typical examples of the procedure are described.

(a) *Electrolysis in aqueous acetonitrile*. (i) 4′-Methoxybenzanilide (23·2 mg, *ca*. 10^{-4} mol) was subjected to electrolysis in 50% aqueous acetonitrile buffer of pH 0·7 (100 ml) at 1·1 V at room temperature until the value of current became less than 2% of the initial value (*ca*. 120 min). From the current–time curve 19·5 C, which corresponded to $n = 1{\cdot}97$, was found to be consumed. The cyclic voltammogram of the solution from electrolysis coincided with that of authentic *p*-benzoquinone (10^{-3}M) obtained under the same conditions. After the solution from electrolysis was diluted 25-fold with the buffer, the u.v. spectrum was compared with that of a mixture of authentic samples of *p*-benzoquinone and benzamide (4×10^{-5}M each) in the same buffer. Good agreement was observed. Each solution from electrolysis cited in Tables 2 and 3 was treated in similar fashion.

(ii) 4′-Methoxybenzanilide (250 mg) was subjected to electrolysis in 50% aqueous acetonitrile buffer of pH 0·7 (100 ml) at 1·1 V at *ca*. 5°. The resulting solution was extracted with ether (100 ml). The ether layer was washed three times with 10% sodium carbonate solution and evaporated to dryness to give white crystals of benzamide, m.p. 130°, identified by i.r. and t.l.c. The sodium carbonate solutions were combined, acidified with hydrochloric acid, and extracted with ether. Evaporation of the ether layer gave *p*-benzoquinone as yellow crystalline material, m.p. 115°, identified by i.r. and t.l.c.

(b) *Electrolysis in acetonitrile*. 4′-Methoxybenzanilide (100·7 mg) was subjected to electrolysis in acetonitrile (100 ml) containing 0·1M-$NaClO_4$ at 1·20 V. A little of the resulting solution was used for determination of methanol by g.l.c. The remainder was evaporated to dryness under reduced pressure and extracted with benzene (100 ml). Evaporation of the benzene extract gave *p*-benzoquinone (i.r.). The residue was extracted with ether (100 ml), and the ether layer was washed with 10% NaOH and evaporated to dryness to give white crystals of benzamide (*ca*. 30 mg).

(c) *Electrolysis in acetonitrile containing excess of pyridine*. 4′-Methoxybenzanilide (290 mg) was subjected to electrolysis in acetonitrile (100 ml) containing 1% pyridine and 0·1M-$NaClO_4$ at 1·1 V. The resulting solution was evaporated to dryness under reduced pressure and the residue was washed with ethyl acetate (100 ml) to remove $NaClO_4$. The residue was subjected to column chromatography on neutral alumina using acetonitrile as eluant. Evaporation of the first fraction gave pale yellow crystals (420 mg) which were recrystallized from methanol, m.p. 235° (Found: C, 55·95; H, 4·2; N, 6·85. $C_{19}H_{17}ClN_2O_6$ requires C, 56·35; H, 4·2; N, 6·9), $\nu_{max.}$ (KBr) 3330 (NH), 1665 (C=O), 1623 (amide I), and 1513 cm^{-1} (amide II). The n.m.r. spectrum of the crystalline material [δ (MeCN; Me_4Si standard) 3·92 (s, 3H), 7·3—7·8 (m, 8H), and 7·9—9·0 (m, 5H)] was compared with that of MBA. The signals at δ 7·9—9·0 were assigned to the protons of the pyridinium group.[2] The signal at δ 3·92 was assigned to the protons of the methoxy-group, and was very close to the signal of the methoxy-group in MBA (δ 3·80). On the other hand, the signals of the 3′- and 5′-protons, which were present at δ 6·84 and 7·00 in the spectrum of MBA, were shifted to 7·3—7·8. The results of elemental analysis and the i.r. and n.m.r. spectra of the crystals were in reasonable agreement with the product being 1-(2-benzamido-5-methoxyphenyl)pyridinium perchlorate.

4′-Methoxybenzanilide (298 mg) was also subjected to electrolysis in acetonitrile (100 ml) containing 1% 2,6-lutidine and 0·1M-$NaClO_4$ at 1·1 V. In this case, however, no lutidinated product was found. The cyclic voltammogram of the solution from electrolysis showed almost quantitative formation of *p*-benzoquinone, which was confirmed by comparing the cyclic voltammogram with that of authentic sample.

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