Anodic Oxidation of Amines. Part III.[1] Cyclic Voltammetry and Controlled Potential Electrolysis of 4-Dimethylaminoantipyrine (4-Dimethylamino-2,3-dimethyl-1-phenyl-Δ^3-pyrazolin-5-one) in Acetonitrile

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The anodic oxidation of 4-dimethylamino-, 4-methylamino-, 4-amino-, and unsubstituted antipyrines has been investigated in acetonitrile at a glassy-carbon electrode. The first step in the anodic oxidation of 4-dimethylaminoantipyrine is a quasi-reversible electron transfer from the lone-pair electrons on the 4-dimethylamino-nitrogen atom to form the cation radical. The blue-violet cation radical decays in a second-order manner with a rate constant of 12·0 ± 0·4 l mol^{-1} s^{-1} at 25 °C as determined by reversal coulometry. The second-order rate constant determined by spectrophotometry increases with increase in concentration of 4-dimethylaminoantipyrine. A well resolved e.s.r. spectrum of the cation radical was obtained and interpreted on the basis of HMO calculation. A mechanism for the first wave of the anodic oxidation of 4-dimethylaminoantipyrine is suggested.

CHEMICAL and enzymatic oxidations of 4-dimethylaminoantipyrine (4-dimethylamine-2,3-dimethyl-1-phenyl-Δ^3-pyrazolin-5-one) (I) have been studied extensively. The oxidation of (I) by ferric chloride, potassium iodate, potassium bromate, or nitrous acid gave a transient blue-violet colour, which has been thought to be due to formation of the radical (II) or the quaternary ammonium ion (III).[2a–c] 1,2-Bis-(4-hydroxy-2-methyl-5-oxo-1-phenylpyrazolin-3-yl)-ethane (IV) was obtained together with the products of complete decomposition, phenol, formaldehyde, nitrogen, dimethylamine, acetic acid, and oxalic acid. Scheme 1 has been suggested.

On the other hand, Pechtold reported that the oxidation of (I) by oxygen and light gave diantipyrylamine (V) (Scheme 2).[2d]

The enzymatic oxidation of (I) has been reported to result in demethylation of the 4-dimethylamino-group to give 4-aminoantipyrine and formaldehyde.[2e]

To obtain more detailed information on the mechanism of oxidation of (I) we examined the cyclic voltammetry of 4-dimethylamino-, 4-methylamino-, 4-amino-, and unsubstituted antipyrine, and e.s.r. spectrum of a radical generated electrochemically from (I). Anodic voltammetry of (I) has been studied by Lugovoi and Ryazanov [3] at a rotating platinum electrode, but

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[1] Part II, M. Masui and H. Sayo, *J. Chem. Soc.* (*B*), 1971, 1593.

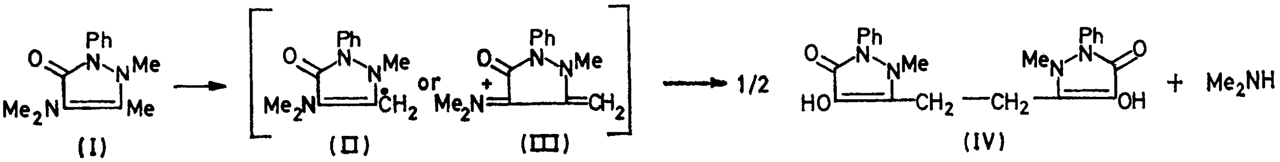
[2] (*a*) W. Awe and R. Buerhop, *Arch. Pharm.*, 1959, **292**, 749; (*b*) W. Awe, E. Stoy-Geilich, and R. Buerhop, *ibid.*, 1960, **293**, 462; (*c*) W. Awe, E. Stoy-Geilich, R. Buerhop, and H. Bammel, *Arzneim. Forsch.*, 1960, **10**, 796; (*d*) F. Pechtold, *ibid.*, 1964, **14**, 258; (*e*) B. N. La Du, L. Gaudette, N. Trousof, and B. B. Brodie, *J. Biol. Chem.*, 1955, **214**, 741.

[3] S. V. Lugovoi and I. P. Ryazanov, *Zhur. analyt. Khim.*, 1967, **22**, 1093.

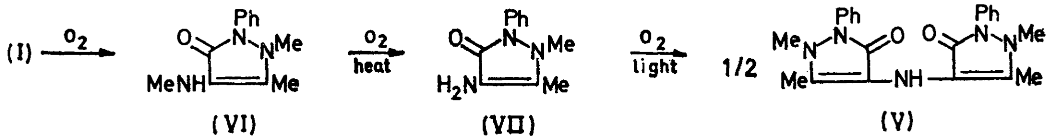
details of the oxidation mechanism have not been reported.

RESULTS

Cyclic Voltammetry.—4-Dimethylaminoantipyrine (I) showed three anodic waves, with peak potentials (E_p) of 0·34, 0·85, and 1·32 V, respectively at a potential scan rate (v) of 6 V min^{-1}. All potentials were measured against a saturated calomel electrode. Typical voltammograms are shown in Figure 1. Upon reversal of the scan direction, only the first wave gave a cathodic counterpart. Thus only the first wave had some reversibility. No extra wave was observed in a multiple sweep. The variation of the peak current (i_p) of the first wave as a function of v was measured at v 1·5—12 V min^{-1}. The value of $i_p/v^{\frac{1}{2}}$ slightly decreased with increasing v, whereas the ratio of the cathodic to anodic peak current remained constant, $i_{pc}/i_{pa} = 0{\cdot}91$. As the scan rate decreased from 12 to 1·5 V min^{-1}, the separation in peak potentials of anodic and cathodic waves decreased from 140 to 93 mV. This suggests that the first wave is quasi-reversible.



SCHEME 1



SCHEME 2

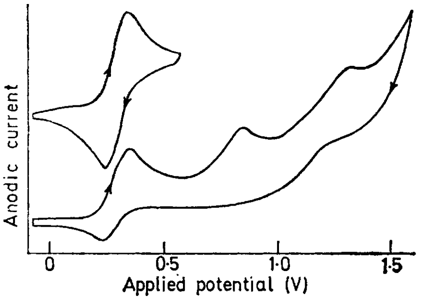


FIGURE 1 Cyclic voltammogram of 2mM-4-dimethylamino-antipyrine in acetonitrile: scan rate 6 V min^{-1}

Cyclic voltammetry of 4-methylaminoantipyrine (VI) and 4-aminoantipyrine (VII) showed three anodic waves, with peak potentials of 0·31, 0·60, and 1·19, and 0·40, 0·85, and 1·28 V, respectively at v 6 V min^{-1}. Upon reversal of the scan direction at a potential beyond the second wave, (VII) showed a small cathodic wave at 0·42 V, whereas (VI) showed no wave. It is interesting to note that the E_p value of the first wave of (VI) was less positive than that of (I), unlike those of aliphatic amines [4] and *N*-substituted anilines.[5]

Antipyrine showed two anodic waves, with peak potentials of 1·22 and 1·65 V at v 6 V min^{-1}. No cathodic wave corresponding to reversible reduction of the oxidation. product was observed upon reversal of the scan direction.

Controlled Potential Electrolysis.—Controlled potential electrolysis of (I) in acetonitrile at 0·45 V gave an n value of 0·88 ± 0·04. Voltammetry of the solution after electrolysis showed nearly complete disappearance of the first and second waves. On addition of pyridine (0·1 ml) to this solution, the voltammogram of (I) was restored, and the concentration of (I), determined from the i_p value of the first wave, was *ca.* 85% of the initial concentration. The perchlorate salt of (I) was obtained from the solution after electrolysis as white crystals in *ca.* 65% yield, and dimethylamine (*ca.* 2%) and formaldehyde (*ca.* 10%) were also detected (mole % of starting amine). Controlled potential electrolysis of (I) at 0·45 V in the presence of pyridine (1%) gave an n value of *ca.* 6, and dimethylamine (*ca.* 10%) and formaldehyde (*ca.* 40%) were produced. Controlled potential electrolysis of (I) at 0·95 V gave an n value of 1·3 ± 0·1 and the perchlorate salt of (I) was obtained as a main product in *ca.* 60% yield.

E.s.r. Spectrometry.—A 10^{-2}M solution of (I) in acetonitrile containing 0·1M-sodium perchlorate was subjected to electrolysis at a glassy-carbon anode at 0·45 V, and the solution was allowed to flow to a sample tube in the cavity of an e.s.r. spectrometer. The solution turned blue-violet immediately and the colour deepened with time. At the same time an e.s.r. signal with a g value of 2·0037 was observed, and its intensity increased with time and reached a maximum after *ca.* 1 h. When the flow of solution was stopped, the intensity of the e.s.r. signal showed a second-order decay. Since facilities for determining the radical concentration were not available, no attempt was made to determine the second-order rate constant of the decay. A similar, but weaker spectrum was observed on anodic oxidation of (I) at 0·45 V in an aqueous solution of pH 7. When the potential applied was increased to 0·9 V, the intensity of the e.s.r. signal decreased to a negligible level. The e.s.r. spectrum of the radical consisted of many fine splittings with a total spectral width of *ca.* 120 G (Figure 2). The spectrum was difficult to interpret owing to the large number of coupling constants. Hückel molecular orbital (HMO) calculations were applied to the cation radical of (I) in an attempt to interpret the spectrum.

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[4] M. Masui, H. Sayo, and Y. Tsuda, *J. Chem. Soc.* (*B*), 1968, 973; C. K. Mann, *Analyt. Chem.*, 1964, **36**, 2424.

[5] R. N. Adams, J. H. McClure, and J. B. Morris, *Analyt. Chem.*, 1958, **30**, 471; Yu. I. Beilis, *Zhur. obschchei. Khim.*, 1970, **40**, 1182.

An inductive model was used for the methyl group.[6] The results shown in Table 1 suggest a negligible, hyperfine coupling with the N(1) atom and the protons in the phenyl ring. A large number of spectra were computed from possible combinations of plausible coupling constants.

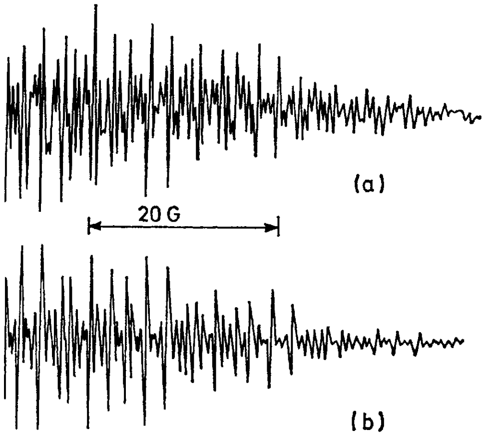

FIGURE 2 (a) E.s.r. spectrum (low field one-half) of 4-dimethylaminoantipyrine following controlled potential electrolysis at first wave; (b) Calculated spectrum using coupling constants given in Table 1 and line width of 0·3 G (Lorentzian line shape)

The spectrum could not be interpreted unequivocally, but the computed one best fitting the experimental data is shown in Figure 2, and the set of coupling constants used for the simulation is listed in Table 1. Differences between the calculated and experimental spectra may be due to some nonlinearity of the magnetic field sweep and to the fact that the spectrum arises from a large set of coupling constants of about the same magnitude.

TABLE 1

Results of HMO calculation for 4-dimethylamino-antipyrine

Position	Nucleus	ρ [a]	Coupling constant (G) Calc.[b]	Coupling constant (G) Found
1	N	0·000		
2	N	0·063	1·6	2·2
	H(Me)		1·6	2·2
3	C	0·082		
	H(Me)		3·3	5·9
4-amino	N	0·504	12·6	11·2
	H(Me$_2$)		13·1	13·4

[a] Calculated π electron spin density. [b] $a^{N} = 25\rho_{N}$, $a^{H}_{MeN} = 26\rho_{N}$, $a^{H}_{MeC} = 40\rho_{C}$ (P. Smejtek, J. Honzl, and V. Metalová, *Coll. Czech. Chem. Comm.*, 1965, **30**, 3875; E. T. Kaiser and L. Kevan, ' Radical Ions,' Interscience, New York, 1968, ch. 4).

Kinetics of Disappearance of the Intermediate in Anodic Oxidation of (I) *in Acetonitrile.*—(*a*) *Reversal coulometry.* The first electron-transfer step of (I) in acetonitrile was quasi-reversible, and the conditions needed for an accurate determination of the rate constant of the chemical reaction which follows from the theory of cyclic voltammetry were not satisfied.[7] Hence the rate of disappearance of the intermediate (VIII) (Scheme 3), formed on anodic oxidation of (I) at the first wave, was measured by reversal coulometry[8] at 25 °C.

During the forward electrolysis at 0·45 V a blue-violet colour developed and during reverse electrolysis at 0·0 V, which was a sufficiently negative potential for the cathodic wave, the colour faded away. The final solution was faint pink. The rate constant k_2 for a second-order decay of the intermediate was calculated from equation (1), where Q_f and $Q_b{}^0$ are the numbers of coulombs consumed in the forward and reverse electrolysis, respectively, p is the mass transfer constant, (C_i) is the initial concentration of (I), $\kappa = k_2(C_i)/p$, and I_m and K_m are modified Bessel functions of the first and second kind, respectively, of order m. [Note equation (50) in ref. 8 is incorrect.] Values of

$$Q_b{}^0/Q_f = \frac{\ln(Bx/2 + 1)}{\kappa(1 - e^{-pt})} \qquad (1)$$

$$B = \frac{\beta' K_1(x) - I_1(x)}{\beta' K_0(x) - I_0(x)}$$

$$\beta' = I_1(2\sqrt{\kappa})/K_1(2\sqrt{\kappa})$$

$$x = 2\sqrt{\kappa}\exp(-pt/2)$$

$Q_b{}^0/Q_f$ were computed as a function of k_2, *i.e.* the values of k_2 were estimated from the experimental values of $Q_b{}^0/Q_f$ and a computed table. The results are shown in Table 2. The value of k_2 obtained was almost independent of (C_i), whereas the rate constant obtained assuming first-order decay of (VIII), k_1, increased with increase in (C_i). The value of k_2 was rather insensitive to the presence of oxygen and a small amount of water (0·1%).

TABLE 2

Data for reversal coulometry of 4-dimethylamino-antipyrine in acetonitrile at 25 °C

(C_i)/ mM	t/ min	pt	$Q_b{}^0/Q_f$ [a]	10^3k_1/ s^{-1}	k_2/ l mol^{-1} s^{-1}	Remarks
1·1	3	0·484	0·458	2·4	12·6	
2·1	3	0·394	0·339	2·4	11·7	
2·0	4	0·481	0·270	2·5	12·8	O$_2$ Present
2·1	3	0·345	0·344	2·4	11·6	0·1% H$_2$O added
3·0	3	0·411	0·268	3·3	12·1	
3·0	3	0·423	0·260	3·3	12·3	O$_2$ Present
4·1	3	0·396	0·220	4·4	11·6	

[a] Oxidation potential, +0·45 V; reduction potential, 0·0 V.

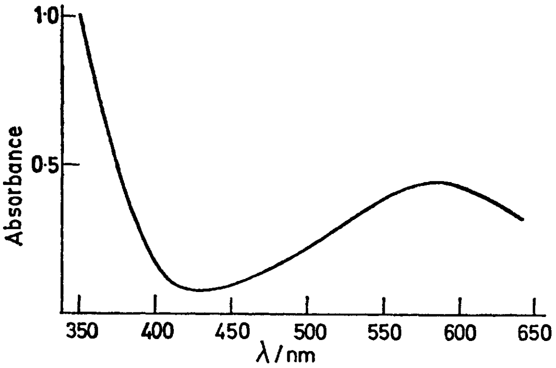

FIGURE 3 Visible spectrum of 4-dimethylaminoantipyrine following controlled potential electrolysis at first wave

(*b*) *Spectrophotometric measurements.* As (VIII) shows an absorption maximum at 580 nm, the variation of

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[6] A. Streitwieser, jun., ' Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, ch. 5.

[7] D. H. Evans, *J. Phys. Chem.*, 1972, **76**, 1160.

[8] A. J. Bard and S. V. Tatwawadi, *J. Phys. Chem.*, 1964, **68**, 2676.

absorbance (*A*) of the solution after electrolysis with time was measured at 580 nm just after stopping the electrolysis of (I) at 0·45 V. The electrolysis was carried out for only 30 or 60 s to minimize the effect of the chemical and electron-transfer reactions which follow. Plots of $1/A$ against time were linear up to 80% decay, characterizing disappearance of (VIII) as a second-order process. In runs with the same period of electrolysis, the slope obtained (k_2/ε) increased slightly with increase in (C_i), where ε is the molar absorption coefficient of (VIII). The presence of oxygen had little effect on the slope, but addition of a small amount of water (0·1%) to the solution slightly increased the value of the slope. The concentration of electrogenerated (VIII), (R_i), was estimated as follows: (*a*) the initial value of *A*, A^0, was calculated from the intercept of the plots; (*b*) the concentration of (VIII) to a first approximation was calculated from Q_f assuming that $n = 1$ and that there was no other reaction to follow: (*c*) the first approximation of k_2, $k_2{}^1$, was calculated from $k_2 = \text{slope} \cdot A/(R)$; (*d*) the second approximation of (*R*) was calculated from equation (43) in ref. 8 and $k_2{}^1$; and (*e*) procedures (*c*) and (*d*) were iterated until a consistent value of k_2 was obtained. The results are shown in Table 3. The values of k_2 obtained were nearly equal to those obtained from reversal coulometry. With 30 s electrolysis, the plot of k_2 against (C_i) was nearly linear with a slope of 905 $l^2\ mol^{-2}\ s^{-1}$, an intercept of 10·6 $l\ mol^{-1}\ s^{-1}$ and a correlation coefficient of 0·941.

TABLE 3

Data for decay of the intermediate (VIII) measured by spectrophotometry in acetonitrile containing 0·1M-$NaClO_4$ at 25 °C

(C_i)/mM	$10^3p/s^{-1}$	Time of electrolysis/s [a]	$10^3k_2\varepsilon^{-1}/s^{-1}$	(R_i)/mM	$\varepsilon/l\ mol^{-1}\ cm^{-1}$ [b]	$k_2/l\ mol^{-1}\ s^{-1}$	Remarks
0·95	2·92	30	4·90	0·079	2290	11·2	
1·56	2·46	30	5·14	0·107	2400	12·4	
2·01	2·69	30	5·42	0·149	2320	12·6	
3·52	2·46	30	5·63	0·240	2340	13·2	
4·09	2·15	30	5·75	0·244	2560	14·7	
1·32	3·42	60	5·30	0·230	2390	12·7	
2·08	2·96	60	5·58	0·308	2400	13·4	
2·23	2·57	60	5·71	0·290	2500	14·3	0·1% H_2O Added
2·38	3·00	60	5·65	0·352	2410	13·6	O_2 Present
2·64	2·87	60	5·50	0·373	2410	13·3	
3·03	2·30	60	5·51	0·349	2610	14·4	
3·10	2·73	60	5·85	0·407	2590	15·1	0·1% H_2O Added

[a] Potential applied, +0·45 V. [b] At 580 nm.

DISCUSSION

The fact that the $E_{\frac{1}{2}p}$ values of the first waves of (I), (VI), and (VII) are far less positive than that of antipyrine shows that it involves abstraction of an electron from the lone-pair of electrons on the 4-amino-nitrogen atom. The reason why 4-aminoantipyrines undergo anodic oxidation more readily than *N*-alkylanilines and *p*-toluidines[5] could be due to a contribution from the enamine structure, since enamines have been reported to be oxidized very readily.[9]

In contrast with results for aliphatic amines[4] and *N*-substituted anilines,[5] the $E_{\frac{1}{2}p}$ value of the first wave of (I), which is a tertiary amine, is more positive than that of (VI), which is a secondary amine. This contradiction can be explained in terms of a twisted π overlap between the lone-pair orbital on the 4-amino-nitrogen atom and the π orbital on the pyrazolinone ring. This effect was taken into account in HMO calculation by a reduction of the resonance integral between the 4-amino-nitrogen atom and the pyrazolinone ring, k_{CN}. Calculation of the highest filled molecular orbital (h.f.m.o.) energies are shown in Table 4. The coefficient of β in $\varepsilon_{h.f.m.o.} = \alpha + \chi\beta$, $\chi_{h.f.m.o.}$, increased with decrease in the value of k_{CN}, which means that the oxidation potential becomes more positive as the twist angle increases. The dimethylamino-group is the most bulky among the 4-amino-substituents tested, so a reduction of k_{CN} is quite reasonable.

It was concluded that the first step in anodic oxidation of (I) is a quasi-reversible, one-electron transfer to form the cation radical of (I) followed by chemical reactions, and the blue-violet intermediate is, in fact, the cation radical of (I). These conclusions are based on the following experimental results: (*a*) cyclic voltammetry of (I) showed a quasi-reversible first wave; (*b*) an e.s.r. signal was observed during controlled potential electrolysis of (I) at the first wave; (*c*) the appearance of the e.s.r. signal was paralleled by the development of the blue-violet colour; (*d*) the hyperfine structure of the e.s.r. signal was reasonably interpreted as that of the cation radical of (I) and consistent with the result of HMO calculation; (*e*) the intensity of the e.s.r. signal showed a second-order decay; (*f*) the results of reversal coulometry and spectrophotometric measurements showed a second-order decay of the intermediate (VIII); and (*g*) the second-order rate constants obtained using two methods were nearly the same.

TABLE 4

Dependence of $\chi_{h.f.m.o.}$ on the value of HMO parameters

	Position	(I)			(VI)		(VII)	
h_N [a]	4-amino	0·5	0·5	0·5	1·0	1·0	1·5	1·5
k_{CN} [b]	4-amino	0·4	0·6	0·8	0·6	0·8	0·8	1·0
$\chi_{h.f.m.o.}$ [c]		0·301	0·192	0·085	0·363	0·277	0·364	0·294

[a] $\alpha_N = \alpha_C + h_N\beta_{CC}$; α and β represent the coulomb and resonance integrals, respectively. [b] $\beta_{CN} = k_{CN}\beta_{CC}$. [c] $\varepsilon = \alpha_C + \chi\beta_{CC}$.

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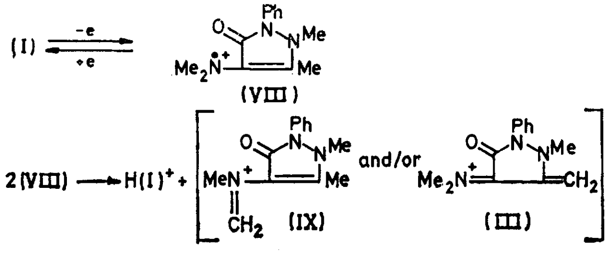
[9] J. M. Fritsh, H. Weingarten, and J. D. Wilson, *J. Amer. Chem. Soc.*, 1970, **92**, 4038.

The second wave of (I) is due to the oxidation of the cation radical (VIII) for the following reasons: (*a*) only a very weak e.s.r. signal was observed during controlled potential electrolysis of (I) at the potential of the second wave; (*b*) only a small cathodic counterpart of the first wave was observed on reversal of the scan direction beyond the potential of the second wave; and (*c*) after completion of electrolysis of (I) at the potential of the first wave neither the first or second wave was detectable in a voltammogram of the solution.

Disproportionation of (VIII) (Scheme 3) is considered to be a major process in chemical reactions which follow, since (VIII) decays in a second-order manner, and a large amount of the perchlorate salt of (I) was obtained from the solution after electrolysis. However, deprotonation of (VIII) and subsequent dimerization or disproportionation may compete with disproportionation of (VIII), because the value of k_2 increased with increase in concentration of (I). The decreased stability of (VIII) and increased *n* value observed on controlled potential electrolysis of (I) with added pyridine supports this possibility. As the acetonitrile used contained *ca.* 0·025% of water, (IX) and (III) will decompose to give formaldehyde and dimethylamine, respectively.



SCHEME 3

On large-scale, controlled-potential electrolysis, a relatively long duration of electrolysis and high concentration of (I) led to complete decomposition of (VIII) and further oxidation of the initial products before completion of electrolysis. Hence, on controlled potential electrolysis of (I) at the first wave >50% of (I) remained unchanged as the protonated form although the *n* value was 0·88. In the presence of pyridine protonation of pyridine predominates over that of (I), and hence all (I) is oxidized without formation of the inactive protonated form. However, the other final products have not yet been identified.

Controlled potential electrolysis of (I) at the first wave is accompanied by secondary, electron-transfer reactions, so there is inevitably some error in the second-order rate constant obtained. However, spectrophotometric measurement showed that the amount of cation radical decomposed during electrochemical generation for 30 s was <4% of (R_i), which corresponds to <0·2 mole % of the starting concentration of (I). Hence the amount of electricity consumed for the secondary, electron-transfer reactions during electrogeneration of (VIII) must be negligible, so that the value of k_2 obtained spectrophotometrically must be fairly reliable. On the other hand, the error in the value of k_2 obtained by reversal coulometry is somewhat larger owing to the longer time of electrolysis required for its estimation.

EXPERIMENTAL

Reagents.—4-Dimethylaminoantipyrine and 4-aminoantipyrine were obtained from commercial sources and recrystallized from ligroin and benzene, respectively. 4-Methylaminoantipyrine was prepared by the method of Chiti.[10] Acetonitrile was purified by the method of ref. 11 and its water content, determined by the Karl Fischer method, was <0·025%. The supporting electrolyte, sodium perchlorate, was recrystallized from ethanol–water and stored over phosphorus pentoxide under reduced pressure.

Apparatus.—Cyclic voltammetry was carried out in a one-compartment cell with an agar bridge (containing 0·1M-NaClO$_4$) separating the calomel reference electrode (s.c.e.) from the bulk of the solution. A glassy-carbon rod (Tokai Electrode GC-20; diameter 3 mm) was used as the working electrode. After recording each voltammogram the working electrode was rinsed in methanol and cleaned with filter paper. A Hokuto Denko LS-2 voltage scanner, PS-200 potentiostat, and Toa Dempa XYR-2A recorder were used throughout. All measurements were carried out at 25 ± 0·05 °C. E.s.r. spectra were recorded in a JEOL JES-P 10 spectrometer, with 100 kHz modulation and an X-band klystron. The value of *g* was measured by comparison with that of aqueous peroxylamine disulphonate ($g = 2{\cdot}0055 \pm 0{\cdot}0005$), the maximum uncertainty being $\pm 0{\cdot}0002$. The e.s.r. spectrum of the cation radical of (I) was obtained by external generation techniques using a glassy-carbon working electrode. The flow rate of solutions during electrolysis was 10—30 ml h^{-1}. Large-scale, controlled-potential electrolysis was performed with a Yanagimoto V-8 potentiostat. An H type cell was used. The anode compartment was separated with a methyl cellulose (350—500 c.p.s.) plug and a sintered glass disk. Nitrogen gas was introduced into the solution during pre-electrolysis and passed over the solution during electrolysis. The current was recorded on a Toa Dempa EPR-2T recorder, and the electricity consumed was estimated from the area below the current-time curve. A Hitachi spectrophotometer, model 139 equipped with a thermostatically controlled cell compartment was used for spectrophotometric measurements. The output of the photometer was connected to a Hitachi 056 recorder. The reaction cell was a standard spectrophotometric cell of 1·0 or 2·0 cm light path. HMO Calculations, simulation of the e.s.r. spectrum, and calculation of Q_b^0/Q_f as a function of k_2 were made on an NEAC 2200 model 700 computer at Osaka University using QCPE 70 and 83 programs, and the library subroutines for the modified Bessel functions.

Controlled Potential Electrolysis.—4-Dimethylaminoantipyrine (439·4 mg) was subjected to electrolysis in acetonitrile (100 ml) containing 0·1M-NaClO$_4$ at 0·45 V for 130 min at room temperature. The resulting red-violet solution showed essentially no first or second wave in the

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[10] W. Chiti, *Farm.* (*Pavia*), *Ed. Sci.*, 1960, **15**, 679.

[11] J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Analyt. Chem.*, 1965, **37**, 1161.

cyclic voltammogram and consumed 162 coulombs, which corresponds to *n* 0·86. The solution was evaporated to dryness under reduced pressure and the residue was extracted with $CHCl_3$. Evaporation of the extract gave a small amount of red-violet solid. A thin layer chromatogram of the solid showed several spots. The residue was extracted with $CHCl_3$ and washed with ethyl acetate to remove $NaClO_4$. The crystals obtained (403 mg) were recrystallized from ethanol, m.p. 235° (Found: C, 47·1; H, 5·4; N, 12·5. Calc. for $C_{13}H_{18}ClN_3O_5$: C, 47·1; H, 5·5; N, 12·7%). The i.r. spectrum of the crystals was in good agreement with that of authentic 4-dimethylaminoantipyrinium perchlorate. Formaldehyde and dimethylamine were determined as described previously.[1]

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