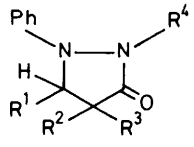
Electrochemical Oxidation of 1-Phenylpyrazolidin-3-ones. Part 3.[1] Reaction Mechanism

Anthony J. Bellamy * **and David I. Innes**
Chemistry Department, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ
Peter J. Hillson
Research Division, Kodak Ltd., Headstone Drive, Harrow HA1 4TY

A cyclic voltammetric study of 1-phenylpyrazolidin-3-one and some typical substituted analogues has shown that the chemical step following the initial electron transfer involves deprotonation of the cation-radical at position 2 (NH). In the absence of added base and at substrate concentration >2mM, the substrate itself deprotonates the cation-radical. In the presence of basic chloride ions oxidation occurs *via* the conjugate base of 1-phenylpyrazolidin-3-one. The lifetime of the cation-radical is relatively insensitive to the nature of the substituents at C(4) and C(5), but is increased markedly by substitution at N(2).

In Parts 1 [2] and 2 [1] of this series we reported results for the preparative electro-oxidation in aprotic solvents of some substituted 1-arylpyrazolidin-3-ones. Results for the unsubstituted 1-phenylpyrazolidin-3-one had previously been reported.[3,4] Those 1-phenylpyrazolidin-3-ones which possess a readily eliminated atom or group at C(4), *e.g.* H or CH_2OH, on oxidation in Et_4NBF_4–CH_3CN give a mixture of the corresponding pyrazolin-3-one (major product) and a 'dimer' (minor product), whilst oxidation in Et_4NCl–CH_3CN gives only the pyrazolin-3-one.[2-4] If however C(4) is blocked towards simple elimination as in 4,4-dimethyl derivatives, electro-oxidation in CH_3CN gives either an extremely complex mixture of products (Et_4NBF_4 electrolyte), or a product derived by reaction of the oxidised substrate with the solvent (Et_4NCl electrolyte).[1] Electro-oxidation of 1-phenylpyrazolidin-3-one in CH_2Cl_2 still gives the pyrazolin-3-one, but the C(4)-blocked systems give 'dimers' under the same conditions.[1] All the 'monomeric' products, and the 'dimers' formed from the C(4)-blocked pyrazolidin-3-ones can be accounted for by either elimination from [2,3] or nucleophilic addition to [1] a 3-oxopyrazolidin-5-yl cation (III), whereas the 'dimers' formed from the C(4)-unblocked pyrazolidin-3-ones can be accounted for by reaction of the isomeric cation (II) with the unoxidised substrate.[2]

In this paper we report an electroanalytical study of 2-, 4-, and 5-substituted 1-phenylpyrazolidin-3-ones (Ia—e) in CH_3CN (i) in the absence of chloride ion, and (ii) in the presence of chloride ion, and show how these results support the mechanisms previously proposed to account for the results of the preparative electrolyses.



(I)

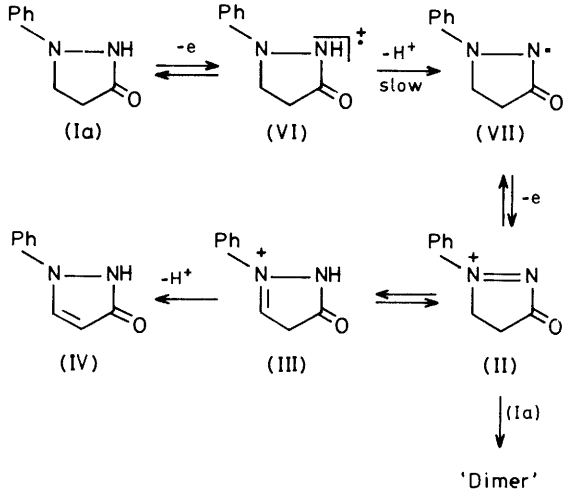
	R^1	R^2	R^3	R^4
a;	H	H	H	H
b;	H	H	H	Me
c;	Ph	H	H	Ph
d;	Ph	H	H	H
e;	H	Me	Me	H

Results and Discussion

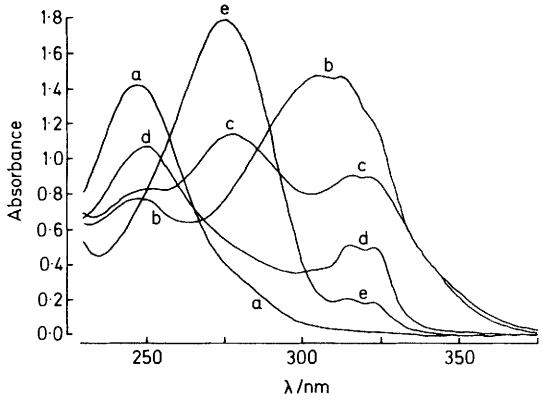
(i) *Behaviour in the Absence of Chloride Ion.*—An earlier paper on the electroanalytical behaviour of 1-phenylpyrazolidin-3-one (Ia) in Et_4NClO_4–CH_3CN reported that at 10mM-substrate and a sweep rate of 0.1 V s^{-1} a single, irreversible oxidation peak was observed in the cyclic voltammogram; this peak became reversible at v 10 V s^{-1}, and had a constant current function $i_p\, v^{-\frac{1}{2}}$ within the range v 0.01—0.2 V s^{-1}. At slow sweep rates, *e.g.* 0.03 V s^{-1}, a second oxidation peak was observed, 0.21 V anodic of the main peak, which increased in intensity with decreasing sweep rate. This second peak was attributed to oxidation of the protonated 1-phenylpyrazolidin-3-one. In an exploratory study at lower substrate concentrations we observed that at v 0.1 V s^{-1}, the second oxidation peak was absent at substrate concentrations <2mM, but above 2mM both oxidation peaks increased, the second peak more rapidly than the first. Therefore, in order to avoid the complication due to the second oxidation peak, our initial study used a substrate concentration of *ca.* 1mM.

For 1mM-(Ia) in 0.4M-Et_4NBF_4–CH_3CN and v 0.1 V s^{-1}, the cyclic voltammogram exhibited a single, irreversible, oxidation peak at $E_{p,a}$ 0.264 V (*versus* Ag–0.1M-$AgNO_3$–CH_3CN) ($E_{p/2}$ 0.180 V); there was no corresponding cathodic peak. However as v was increased, $E_{p,a}$ shifted anodically, the anodic current function $i_{p,a}v^{-\frac{1}{2}}$ decreased, and the cathodic current on the reverse sweep increased. By comparing $i_{p,a}$ for (Ia) at v 0.1 V s^{-1} with that for ferrocene, an established one-electron oxidation standard,[5] under the same conditions, the n value for (Ia) at this concentration was found to be 1.54. As the sweep rate was increased n approached a value of unity. Such behaviour is typical of an e.c.e. or disp 1 process.[6] For substrate concentrations <2mM, the plot of $E_{p,a}$ *versus* log C was linear (slope 39 mV $decade^{-1}$; v 0.1 V s^{-1}), but above 2mM there was no further change in $E_{p,a}$ and the second oxidation peak appeared at *ca.* 0.40 V. The plot of $i_{p,a}$ *versus* concentration was also linear up to C 2mM, but with the appearance of the second oxidation peak above 2mM the increase in $i_{p,a}$ for the first peak diminished.

The chemical reaction which seems most likely to follow the initial electron transfer is deprotonation of the cation-radical; this could occur at either position 2 (NH) or position 5 (CH) in the pyrazolidinone ring. In order to obtain further supportive evidence for this, the *N*(2)-methyl derivative (Ib) was prepared and its cyclic voltammetric behaviour was studied. Even at v 0.1 V s^{-1} the cyclic voltammogram showed chemical reversibility, with $E_{p,a}$ 0.53 V. This strongly suggests that deprotonation at position 2 normally follows electron transfer and a mechanistic interpretation of this and the other results is shown in the Scheme. This Scheme is similar to that originally proposed.[3]



Scheme



U.v. spectrum of (Ia) under various conditions: a, 0.15mM-(Ia) in CH_3CN; b, a after addition of Et_4NCl (320 equivalents); c, b after 3 h; d, b after addition of acetic acid (20 equivalents); e, c after addition of acetic acid (10 equivalents)

The base effecting deprotonation of the cation-radical (VI) is most probably (I) at the higher substrate concentrations (>2mM) since an oxidation peak for protonated (Ia) appears in the cyclic voltammogram at these concentrations, but at lower substrate concentration (<2mM) some other base appears to be involved, *e.g.* trace amounts of water or other basic impurities present in the CH_3CN. The second electron transfer, oxidising the radical (VII) to the cation (II), would occur either at the electrode if the initial deprotonation is fast (e.c.e. mechanism), or in solution, involving electron transfer from (VII) to (VI), if the deprotonation is slow (disp 1 mechanism). The cation (II) could then lead to both the 'dimeric' product [by reaction with (Ia); see Scheme 3, Part 1], and the pyrazolin-3-one (IV) *via* the isomeric cation (III). The step between (II) and (III) is shown as reversible since in the presence of basic chloride ion [7] (see later) all material is diverted to the pyrazolinone, but in the absence of base a mixture of the two products is obtained.

It had previously been reported [3] that electrolysis of (Ia) (0.1M) at a potential slightly anodic of the first oxidation peak caused a decrease in the first oxidation peak (as indicated by cyclic voltammograms run at intervals) at a rate corresponding to a one-electron oxidation, and an increase in the second oxidation peak. This can be interpreted as a two-electron oxidation of those molecules undergoing oxidation, with the remainder becoming electro-inactive at the potential used due to protonation. Electrolysis at a higher potential, sufficient to oxidise the protonated form of (Ia) also, gave an *n* value of 1.8. It was also reported that electrolysis at either potential gave the same products. Thus although the formation of the protonated pyrazolidin-3-one complicates the interpretation of the electroanalytical data, it does not affect the results from a preparative electrolysis.

We have found that on the cyclic voltammetric time scale (v 0.1 V s^{-1}), a solution which was 10mM in both (Ia) and perchloric acid exhibited a chemically reversible oxidation–reduction system for the protonated form of (Ia) at $E_{p,a}$ 0.49 V; no peak due to oxidation of unprotonated (Ia) was observed. Thus under these conditions the dication-radical formed by oxidation of the protonated substrate is much more stable towards deprotonation than is the cation-radical (VI). Undoubtedly this is due to the absence of a suitable base rather than an inherently greater stability of the dication-radical.

(ii) *Behaviour in the Presence of Chloride Ion.*—Previous workers had reported [4] that the cyclic voltammogram of (Ia) (10mM) in 0.1M-Et_4NCl–CH_3CN was significantly different from that observed in Et_4NClO_4–CH_3CN. Only one oxidation wave was now observed, 0.10 V cathodic of that previously reported,[3] which was chemically irreversible even at high sweep rates (100 V s^{-1}). An irreversible, ill defined cathodic peak on the reverse sweep was attributed to reduction of HCl, generated by chloride ion catalysed deprotonation on the forward sweep. Controlled potential coulometry gave an *n* value of 1.94 for 0—85% conversion. Since the presence of chloride ion did not affect the u.v. spectrum of (Ia) it was concluded that chloride ion in CH_3CN is not sufficiently basic to deprotonate (Ia) itself, but basic enough to rapidly deprotonate the electrogenerated cation-radical of (Ia), and that the initial electron transfer is therefore from (Ia) and not from its conjugate base, *i.e.* the overall mechanism is not very different from that operating in the absence of chloride ion. The results which we now present indicate that this conclusion is incorrect and that electron transfer occurs from the conjugate base of (Ia) when chloride ion is present in excess.

Contrary to the previous report [4] we found that the u.v. spectrum of (Ia) was significantly changed in the presence of chloride ion. Compound (Ia) in CH_3CN has $\lambda_{max.}$ 247 nm (ε 9 500) (Figure, curve a). The addition of a solution of anhydrous Et_4NCl in CH_3CN caused this peak to decrease in intensity and a new envelope of peaks to appear centred at *ca.* 310—315 nm. The latter reached its maximum intensity after 320 equivalents of Et_4NCl had been added (curve b); a good isosbestic point was observed at 266 nm throughout the addition. The new spectrum was not stable; during 3 h, the 310—315 nm peak decreased and shifted to slightly longer wavelength, and a new peak at 275—280 nm increased in intensity (curve c). The addition of acetic acid in CH_3CN (20 equivalents) immediately after the addition of 320 equivalents of Et_4NCl caused a large decrease in the 310—315 nm peak, leaving two peaks at 315 and 323 nm which were presumably responsible for the small bumps on the 310—315 nm peaks, and the appearance of a peak at 250 nm (curve d); the peaks at 315 and 323 nm slowly disappeared over a 2 h period. If however the addition of acetic acid was delayed for 3 h, the decrease in the 310—315 nm peak was accompanied by the appearance of a peak at 275 nm (curve e). An almost identical series of curves was observed when sodium hydride was used instead of Et_4NCl in the first stage. For comparison 1-phenylpyrazolin-3-one (IV) in CH_3CN has $\lambda_{max.}$ 269 nm (ε 21 000); the addition of Et_4NCl (320 equivalents) caused the spectrum to change to two peaks at 283

and 320 nm, while the subsequent addition of acetic acid (10 equivalents) gave a single peak at 275 nm.

We interpret these spectra as follows. The addition of Et_4NCl effects deprotonation (Cl^- is basic in CH_3CN; HCl is 99% associated [7]) of (Ia) and curve b is largely that of the corresponding anion. The immediate addition of acetic acid causes reprotonation and regeneration of most of the original (Ia) (curve d); the peaks at 315 and 323 nm, also present in curve b, must be due to some other unstable species. The changes which occur when the solution of the anion is left appear to involve oxidation of the anion of (Ia), by dissolved oxygen, to the anion of the pyrazolin-3-one (IV), since addition of acetic acid after a 3 h delay generates free pyrazolinone instead of pyrazolidinone. The inexact correspondence of the peak maxima between for example curves a and d (247 *versus* 250 nm), curve e and that for authentic 1-phenylpyrazolin-3-one (275 *versus* 269 nm), and those for authentic 1-phenylpyrazolin-3-one before and after the deprotonation–protonation sequence (269 *versus* 275 nm), are most probably due to medium effects since the maximum in curve e is at the same wavelength as that for authentic 1-phenylpyrazolin-3-one after the deprotonation–protonation sequence (275 nm).

The most likely cause of the difference between our results and those reported [4] is that in the latter work anhydrous Et_4NCl may not have been used. Anhydrous Et_4NCl is very hygroscopic and we have found that the addition of Et_4NCl, H_2O to a solution of (Ia) in CH_3CN has no effect on the u.v. spectrum.

The effect of chloride ion upon the linear sweep voltammogram of (Ia) was studied by adding increasing amounts of anhydrous Et_4NCl (0.1—10mM) to a 1.0mM solution of (Ia) in 0.4M-Et_4NBF_4–CH_3CN (v 0.1 V s^{-1}). Increasing chloride ion concentration caused a shift in $E_{p,a}$ from 0.265 (no Et_4NCl) to 0.10 V (10mM-Et_4NCl). Although no well defined pre-peak which could be attributed to the oxidation of the conjugate base of (Ia) was observed at any stage, a distinct broadening of the peak occurred at 2—5mM-Et_4NCl, and further addition of Et_4NCl caused the peak to sharpen and move cathodically. While a cathodic shift can be caused by an increase in the rate of the following chemical reaction,[4,8] in view of the spectroscopic evidence above we prefer to explain the peak broadening and cathodic shift in terms of the increasing importance of oxidation of the conjugate base, the latter being more easily oxidised than un-ionised (Ia). The oxidation of the conjugate base of (Ia) would give the radical (VII) directly (see Scheme).

The effect which chloride ion has upon the outcome of a preparative electrolysis *viz.* production of the pyrazolinone only, can be explained by a base catalysed perturbation of the equilibrating ions (II) and (III), with (III) being converted into (IV) much faster than (II) reacts to give 'dimer' (Scheme). Furthermore, since almost all (Ia) will be present as its conjugate base, 'dimerisation' of the type encountered in the absence of chloride ion may not be possible.

2,6-Lutidine was also observed to cause deprotonation of (Ia), and in this case a distinct pre-peak for the oxidation of the conjugate base was observed in the linear sweep voltammogram. A small oxidation peak at *ca.* 0.1 V appeared when *ca.* 0.5 equivalents of 2,6-lutidine was added to 1.67mM-(Ia) in 0.4M-Et_4NBF_4–CH_3CN (v 0.1 V s^{-1}), with the main oxidation peak being at 0.265 V. The new peak increased in size and shifted anodically with increasing concentrations of 2,6-lutidine, while the original peak shifted cathodically, and at 10 equivalents of 2,6-lutidine a single peak with $E_{p,a}$ 0.19 V was observed. This result supports our interpretation of the voltammetric data for (Ia) in the presence of chloride ion, and also supports the schemes proposed [1] to account for the formation of different 'dimers' when (Ie) is electrolysed in Bu_4NBF_4–CH_2Cl_2 in the presence of and in the absence of 2,6-lutidine.

(iii) *Stability of the Cation-radicals formed from* (Ia—e).—The efficacy of 1-phenylpyrazolidin-3-ones as superadditive developing agents in aqueous alkaline media is considered to be due in part to the stability of the initial oxidation product.[9] For these conditions this species, for the parent system, is the neutral radical (VII). It has been shown that this radical normally disappears by a second-order dismutation process, the rate of which is dependent upon substituents in the pyrazolidinone ring and/or the phenyl ring, and correlates with the degree of superadditivity.[10] For the electro-oxidation of 1-phenylpyrazolidin-3-ones in an aqueous alkaline medium, the lifetime of the initial oxidation product has been studied by cyclic voltammetry.[11]

When 1-phenylpyrazolidin-3-ones are electro-oxidised in neutral Et_4NBF_4–CH_3CN, the initial oxidation product is the cation-radical (VI), and its stability is dependent upon the rate at which a proton is lost from N(2) to produce the radical (VII). The rate of this step will depend upon the availability of a suitable base, and possibly upon substituent effects which may or may not differ from those affecting the stability of the radical (VII) in aqueous systems. We have briefly studied the stability of various cation-radical species by cyclic voltammetric experiments on the 1-phenylpyrazolidin-3-ones (Ia—e).

Since we have shown in (i) that the cyclic voltammetric behaviour of (Ia) in the absence of added base is dependent upon the concentration of the substrate, we chose to work at 5mM concentrations so that the results would not be dependent upon the presence of bases as trace impurities; at this concentration the substrate itself appears to function as the deprotonating agent. As a measure of the stability of the cation-radical we determined the voltage sweep rate at which $i_{p,c}/i_{p,a}$ was 0.75, this value of the peak current ratio lying on the steep part of the $i_{p,c}/i_{p,a}$ *versus* log $k_f\tau$ curve,[8] and therefore being most sensitive to changes in k_f, the rate constant for the chemical reaction following the electron transfer, and sweep rate v (and hence τ, the time taken to sweep from $E_{\frac{1}{2}}$ to the switching potential E_λ). For $i_{p,c}/i_{p,a} = 0.75$, $\log_{10} k_f\tau =$ *ca.* -0.5 and $k_f\tau =$ *ca.* 0.32. $E_p - E_\lambda$ was maintained constant at 300 mV for the whole series, and may be taken to approximate to $E_{\frac{1}{2}} - E_\lambda$ for the purpose of calculating τ and hence k_f. The $i_{p,c}/i_{p,a}$ ratios were calculated using Nicholson's semi-empirical procedure.[12] The results are reported in the Table.*

As described above, the replacement of NH by NR [R = Me or Ph; (Ib and c)] at position 2 causes the cyclic voltammogram of the pyrazolidinone to be chemically reversible even at slow sweep rates (v 0.1 V s^{-1}) with $E_{p,a}$ considerably anodic of that for (Ia). This indicates that their corresponding cation-radicals are stable on the cyclic voltammetric timescale ($k_f < 10^{-2}$ s^{-1}). For those systems with NH at position 2 *viz.* (Ia, d, and e), the cation-radicals are less stable and their life-times are relatively insensitive to the nature of the substituents at C(4) and C(5), the k_f values lying in the narrow range 1.7—3.5 s^{-1}. Clearly positions 4 and 5 are not directly involved in the oxidation mechanism until a later stage. Interestingly, these results for 1-phenylpyrazolidin-3-ones

* The system being studied is in fact not one in which the electrogenerated species is undergoing a first- or pseudo-first-order irreversible reaction; the rate-determining deprotonation step is second order, with the base (unoxidised substrate) concentration comparable to the concentration of the electrogenerated species. Consequently analysis as a simple e.c. system will give rate constants which are slightly different from their true values, but this does not invalidate the comparisons made here.

Compound	$E_{p,a}$/V [a]	v/V s^{-1} [b]
(Ia)	0.275	2.55
(Ib)	0.53	*c*
(Ic)	0.76	*c*
(Id)	*d*	3.3
(Ie)	*d*	1.65

Conditions: 5mM-pyrazolidinone in 0.4M-Et_4NBF_4–acetonitrile

[a] $E_{p,a}$ at sufficiently high sweep rate for the cyclic voltammogram to be chemically reversible; *versus* Ag—0.1M-$AgNO_3$—CH_3CN. [b] Sweep rate at which $i_{p,c}/i_{p,a} = 0.75$. [c] Reversible at $v = 0.1$ V s^{-1}. [d] Not determined with sufficient accuracy, but close to that for (Ia).

unsubstituted at position 2 (NH) parallel those observed for (Ia and e) in aqueous alkali.[10,11]

Experimental

Acetonitrile (Fisons SLR grade) was purified by treatment with potassium permanganate and sodium carbonate, followed by distillation.[13] The 1-phenylpyrazolidin-3-ones (Ia and e) were supplied by Eastman Kodak Ltd. Compound (Id) was prepared according to a literature procedure [14] and had m.p. 160—161 °C (lit.,[14] 159 °C). Tetraethylammonium chloride was supplied as the monohydrate; the anhydrous salt was obtained by storing over P_2O_5 *in vacuo* for 7 days.

1,2,5-*Triphenylpyrazolidin*-3-*one* (Ic).—Sodium (3.0 g) was dissolved in ethanol (100 ml), and 1,2-diphenylhydrazine (19.0 g, 0.1 mol) and ethyl cinnamate (16.6 ml, 0.1 mol) were added. The mixture was refluxed for 24 h, concentrated by rotary evaporation, and then poured into water (250 ml). After neutralisation with acetic acid, the product was extracted into ethyl acetate, and the solvent was then distilled off. Distillation under reduced pressure removed the by-product cinnamic acid (2.1 g), b.p. 120—125 °C at 2 mmHg, and the residue (13.5 g) was chromatographed on silica gel (60 g; grade III; 4 × 100 cm). Elution with light petroleum (b.p. 40—60 °C)–ethyl acetate (4 : 1) gave a yellow oil (7.0 g) which was distilled to give 1,2,5-*triphenylpyrazolidin*-3-*one*, (1.82 g), b.p. 250 °C at 0.1 mmHg as a resin (Found: C, 80.0, H, 5.65, N, 8.65. $C_{21}H_{18}N_2O$ requires C, 80.25, H, 5.75, N, 8.9%), δ(100 MHz; $CDCl_3$) 2.64 (d, *J* 8 Hz, C*H*HCO), 3.47 (dd, *J* 8 and 4 Hz, CH*H*CO), 4.97 (d, *J* 4 Hz, PhC*H*), and 6.88—7.89 (m, 3 Ph); $\nu_{max.}$ (Nujol) 1 720 cm^{-1}; *m/e* 314.142 891 (*P*). $C_{21}H_{18}N_2O$ requires 314.141 905.

2-*Methyl*-1-*phenylpyrazolidin*-3-*one* (Ib).—1-Phenylpyrazolidin-3-one (4.86 g, 0.03 mol) was added to potassium carbonate (8.28 g, 0.02 mol) in methyl iodide (4.5 g, 0.03 mol), and the mixture was stirred for 16 h. After pouring into water (200 ml), the product was extracted into ethyl acetate (6 × 50 ml). Distillation of the combined extracts gave a fraction (2.85 g), b.p. 95—110 °C at 0.1 mmHg, which was shown by h.p.l.c. to be largely (Ib). This was purified by chromatography on silica gel (grade III; 1 × 25 cm). Elution with CH_2Cl_2 gave a green oil (0.16 g) as the first fraction, and 2-methyl-1-phenylpyrazolidin-3-one (1.42 g, as an oil which crystallised on standing), m.p. 28 °C, as the second fraction. The latter had δ_H(100 MHz; $CDCl_3$) 2.53 (t, *J* 3.5 Hz, CH_2CO), 3.05 (s, NCH_3), 3.82 (t, *J* 3.5 Hz, N-CH_2), and 6.85—7.47 (m, Ph) (lit.,[15] δ_H 2.49, 3.02, 3.77, and 7.12); δ_C ([$^2H_6$]DMSO) 26.88, 30.53, 55.14, 118.23, 123.21, 129.30, 150.11, and 172.13 p.p.m.; $\nu_{max.}$ (film) 1 725 cm^{-1}; *m/e* 176 (*P*).

Voltammetry.—A single compartment cell was used. The working electrode was a platinum disc (diam. 0.64 mm) sealed in soft glass and polished with 3 μm alumina. The secondary electrode was a platinum gauze cylinder positioned symmetrically around the working electrode. The reference electrode, Ag–0.1M-$AgNO_3$ in CH_3CN, was connected *via* a cracked-glass seal [16] and a Luggin capillary to a point *ca.* 2 mm from the surface of the working electrode. Using the method of Saveant and his co-workers,[17] the uncompensated resistance in the above cell containing 1mM-ferrocene in 0.4M-Et_4NBF_4–CH_3CN was found to be 730 Ω. The experiments were controlled by either a potentiostatic sweep unit built from a design kindly supplied by Professor V. D. Parker (Trondheim, Norway), or a Chemical Electronics TR 70/2A potentiostat driven by a Chemical Electronics waveform generator type RB1. The voltammograms were recorded on either a Hewlett-Packard 7045A or a Bryans model 26 000 A4 *X–Y* recorder for slow sweep rates, and a Tektronix 5103N storage oscilloscope for fast (>1 V s^{-1}) sweep rates.

Acknowledgements

We thank the S.E.R.C. for the CASE award to D. I. I., and Drs. B. D. Baigrie and T. A. Joslin for helpful discussions.

References

1 Part 2, A. J. Bellamy, D. I. Innes, and P. J. Hillson, preceding paper.
2 Part 1, A. J. Bellamy, D. I. Innes, and P. J. Hillson, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1599.
3 H. H. Adam, B. D. Baigrie, and T. A. Joslin, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1287.
4 B. D. Baigrie and T. A. Joslin, *J. Electroanal. Chem.*, 1978, **87**, 405.
5 E. R. Brown and R. F. Large, in ' Techniques of Chemistry,' eds. A. Weissberger and B. W. Rossiter, Wiley-Interscience, New York, 1971, vol. I, Part IIA, p. 433.
6 L. Nadjo and J. M. Saveant, *J. Electroanal. Chem.*, 1973, **48**, 113.
7 I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, *J. Am. Chem. Soc.*, 1961, **83**, 3927; I. M. Kolthoff, IUPAC Symposium on Non-Aqueous Electrochemistry, Paris, 1970, Butterworths, London, p. 319.
8 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
9 J. F. Willems, *J. Photogr. Sci.*, 1972, **20**, 121.
10 W. E. Lee and D. W. Miller, *Photogr. Sci. Eng.*, 1966, **10**, 192.
11 H. H. Adam and T. A. Joslin, *J. Electroanal. Chem.*, 1975, **58**, 393; 1976, **72**, 197.
12 R. S. Nicholson, *Anal. Chem.*, 1966, **38**, 1406.
13 D. Clark, M. Fleischmann, and D. Pletcher, *J. Electroanal. Chem.*, 1972, **36**, 137.
14 J. D. Kendall, G. F. Duffin, and A. J. Axford, U.S.P., 2 688 024.
15 P. Bouchet, J. Elguero, and R. Jacquier, *Bull. Soc. Chim. Fr.*, 1967, 3502.
16 N. S. Moe, *Anal. Chem.*, 1974, **46**, 968.
17 J. C. Imbeaux and J. M. Saveant, *J. Electroanal. Chem.*, 1970, **28**, 325; D. Garreau and J. M. Saveant, *ibid.*, 1972, **35**, 309.

Received 14*th June* 1982; *Paper* 2/991