Electrochemical Oxidation of 1-Phenylpyrazolidin-3-one in Acetonitrile

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The electrochemical oxidation of 1-phenylpyrazolidin-3-one in acetonitrile has been studied. Two oxidation waves were observed using cyclic voltammetry and these were found to be due to the oxidation of the protonated and neutral compound. Controlled potential electrolyses resulted in the isolation of two main components which were 1-phenylpyrazolin-3-one (75%) and 3-anilino-*N*-[4-(3-oxopyrazolin-1-yl)phenyl]propionamide (20%). The oxidative mechanism which results in these two products is discussed.

1-PHENYLPYRAZOLIDIN-3-ONE (RH) and its derivatives are used as antioxidants [1] and photographic developers.[2] As a result of the role of pyrazolidinones in photography, the literature contains numerous references to their photographic and physical properties and to their chemical synthesis.[3] Because the reducing characteristic of the molecules is an important factor in the photographic process, the oxidation of pyrazolidinones has been studied in aqueous alkaline solutions by both

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[1] V. Tisler, *Nafta*, 1973, **24**, 485.

[2] C. E. K. Mees and T. H. James, ' The Theory of the Photographic Process,' Macmillan, New York, 1966, 3rd edn.

[3] J. Eggers, ' International Congress on Scientific Photography Symposium,' Zurich, 1961, Focal Press, London, 1963.

chemical and electrochemical methods.[4,5] The oxidative mechanism in aqueous alkaline solutions is generally accepted to be, in the absence of oxygen, an initial reversible one-electron transfer from the pyrazolidinone anion to give a free radical which then disproportionates to give 1-phenylpyrazolin-3-one (P),[4-7] and the original pyrazolidinone. In strong aqueous acid, the mechanism is more complicated; dimeric and polymeric species are formed.[8-10] The initial oxidative processes in aqueous solutions of varying pH are shown in Scheme 1.

$$R^- \overset{-e}{\rightleftharpoons} R^{\cdot}$$

$$RH \overset{-e}{\rightleftharpoons} R^{\cdot} + H^+$$

$$RH_2^+ \overset{-e}{\rightleftharpoons} RH^{+\cdot} + H^+$$

SCHEME 1

Few studies on the chemical or electrochemical oxidation of pyrazolidinones in non-aqueous solutions have been reported [11] and, because the environment is an important parameter governing electrochemical reactions,[12] a study of the electrochemical oxidation of 1-phenylpyrazolidin-3-one in acetonitrile was undertaken.

RESULTS AND DISCUSSION

Cyclic voltammograms were obtained from a 10^{-2}M solution of (RH) in acetonitrile containing 10^{-1}M-tetraethylammonium perchlorate as electrolyte. With a sweep rate of 0.1 V s^{-1} and a voltage range between -0.4 and 1.2 V, an initial oxidation wave was observed with a peak ($E_p{}^A$) at 0.61 V *versus* s.c.e. (saturated calomel electrode). The half-peak potential ($E_{p/2}{}^A$) was at 0.55 V giving a separation between the peak and half-peak potentials of 60 mV. A cathodic wave due to the reversible reduction of the initial oxidation product, which was reduced in magnitude when compared with the wave height of the oxidative process, was observed with a peak ($E_p{}^C$) at 0.55 V. The results suggested a reversible one-electron wave. The ratio of the oxidation to reduction peaks approached unity at 10 V s^{-1} suggesting that a chemical reaction was occurring after the oxidative electron transfer. A further reduction wave was observed at -0.2 V which corresponded to a similar wave previously observed during electrochemical studies on aniline in acetonitrile and which was attributed to proton reduction.[13]

Cyclic voltammograms were also obtained as a function of sweep rate (ν) between the scan rates of 0.2 and 0.01 V s^{-1}. A plot of the peak–current function $(i_p)/\nu^{\frac{1}{2}}$ against $\nu^{\frac{1}{2}}$ was linear and independent of sweep rate indicating a diffusion controlled process. The variation of peak potential as a function of sweep rate was examined. The peak potential shifted anodically with increasing sweep rate however the results were not sufficiently precise to allow characterisation of the oxidation mechanism and direct comparison with the previously reported mechanism for pyrazolidines in acetonitrile.[14-16]

At a slower rate ($\nu = 0.03$ V s^{-1}) a second oxidation became apparent with a peak ($E_p{}^A$) at *ca.* 0.82 V *versus* s.c.e. which became more obvious with decreasing sweep rate. This second oxidation also appeared to be reversible. A typical voltammogram showing both oxidations is given in Figure 1. Cyclic voltammograms were also performed with concentrations of RH varying from 10^{-3} to 10^{-1}M, and the peak height at 0.61 V was found to increase linearly with concentration.

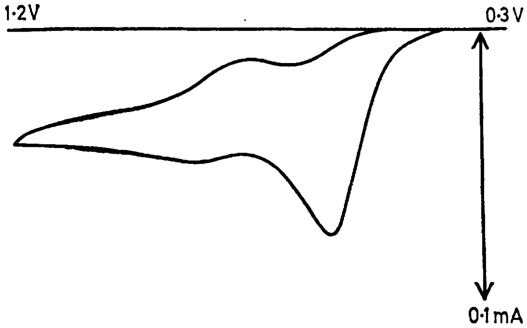

FIGURE 1 Electrolysis of 10^{-2}M-1-phenylpyrazolidin-3-one in acetonitrile containing 10^{-1}M-tetraethylammonium perchlorate: sweep rate 0.03 V s^{-1}; electrode area 0.031 4 cm^2; reference electrode s.c.e.

Rotating disc experiments again with 10^{-2}M solutions of RH and 10^{-1}M-electrolyte indicated a mass-transfer controlled limiting current using rotation speeds between 8.33 and 83.3 Hz. The half-wave potential for the initial oxidation wave was 0.59 V *versus* s.c.e. and the diffusion coefficient of 1-phenylpyrazolidin-3-one was determined from the Levich equation to be $2.07 \pm 0.07 \times 10^{-9}$ $m^2 s^{-1}$, taking the kinematic viscosity of acetonitrile to be 4.41×10^{-7} $m^2 s^{-1}$.[17] The limiting current was compared with the corresponding current obtained with a known one-electron system; that of ferrocene in acetonitrile. The comparison indicated that the oxidation wave of

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[4] C. J. Battaglia, W. E. Lee, D. W. Miller, E. S. Allen, and W. J. Glover, *Photogr. Sci. Engineering*, 1970, **14**, 397.

[5] H. H. Adam and T. A. Joslin, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1975, **14**, 393.

[6] W. E. Lee and D. W. Miller, *Photogr. Sci. Engineering*, 1966, **10**, 192.

[7] A. Castellan, L. Griggio, and E. Vianello, *Atti. Accad. naz. Lincei, Rend. Classe Sci.*, 1965, **39**, 510.

[8] D. Vogel and W. Jaenicke, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 1297.

[9] D. Vogel and W. Jaenicke, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 1302.

[10] J. A. Keiler, East Ger. P. 50,309/1966.

[11] B. R. J. Nicolaus, L. Mariani, E. Bellasio, and E. Testa, *Gazzetta*, 1964, **94**, 652.

[12] M. Fleischmann and D. Pletcher, *Adv. Phys. Org. Chem.*, 1973, **10**, 155.

[13] R. L. Hand and R. F. Nelson, *J. Amer. Chem. Soc.*, 1974, **96**, 850.

[14] I. Tavakovic, M. Lacan, and Sh. Damoni, *Electrochim. Acta*, 1976, **21**, 621.

[15] P. Carbon, G. Barbey, A. Dupre, and C. Caullet, *Bull. Soc. chim. France*, 1974, 768.

[16] F. Pragst and C. Bock, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1975, **61**, 47.

[17] L. S. Marcoux, R. N. Adams, and S. W. Feldberg, *J. Phys. Chem.*, 1969, **73**, 2611.

RH corresponded to a one-electron wave, the *n* value being 1.05 ± 0.05.

The second oxidation wave at 0.82 V observed by cyclic voltammetry could correspond to a further oxidation of a reactive intermediate ($RH^{+\cdot}$ or $R^{\cdot}$), or could represent the oxidation of the protonated pyrazolidinone (RH_2^+), since the latter has been shown to be electroactive.[8] Because the perchlorate anion is present in solution as the electrolyte and because perchloric acid has been shown to be completely dissociated in acetonitrile,[18] cyclic voltammograms were obtained in the presence of perchloric acid. The perchloric acid (60% in water) was added dropwise to the neutral 10^{-2}M solution of RH in acetonitrile. The effect of increasing acid concentrations is shown in Figure 2. The addition of perchloric acid clearly reduces the initial oxidation wave at 0.61 V and increases the more anodic wave. This result suggests that the second oxidation wave ($E_p{}^A$) at 0.82 V is due to the oxidation of the protonated pyrazolidinone. The peak potential of the oxidation wave for the acidic solution (1.92 × 10^{-2}M in concentrated perchloric acid) was 0.82 V with a half-peak potential at 0.74 V. The corresponding reduction peak was found to be at 0.74 V (ν 0.10 V s^{-1}). A plot of $i_p \nu^{-\frac{1}{2}}$ against $\nu^{\frac{1}{2}}$ showed a gradual increase with decreasing sweep rate, indicating that the electrochemical oxidation occurring was possibly an ECE process (electron transfer–chemical reaction–electron transfer). The effect of the water present in the concentrated perchloric acid was also examined with cyclic voltammetry. Varying quantities of distilled water were added to a 10^{-2}M solution of RH and the resulting voltammograms are shown in Figure 3. The results indicate that although water affects the oxidative processes, the effect of the water present in 1.9 × 10^{-2}M-perchloric acid is small; the major effect observed being due to the added protons. However, the effect of added water is to move the oxidation wave of the protonated pyrazolidinone cathodically. The cathodic movement of the wave can be explained in terms of the Nernst equation and the equilibrium processes in Scheme 2. The effect of the addition of water reflects the aprotic nature of acetonitrile and the fact that acetonitrile is a very weak base compared with water.[19]

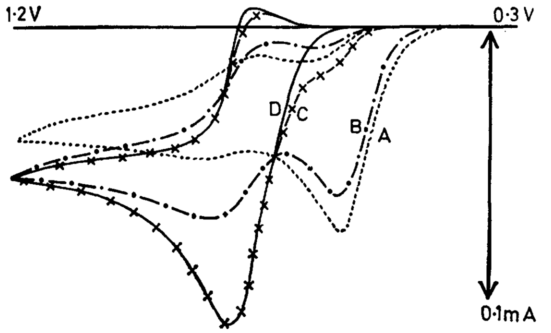

FIGURE 2 Electrolysis of 10^{-2}M-1-phenylpyrazolidin-3-one in acetonitrile containing 10^{-1}M-tetraethylammonium perchlorate: A, 0.0M; B, 3.9 × 10^{-3}M-perchloric acid; C, 1.52 × 10^{-2}M-perchloric acid; D, 1.9 × 10^{-2}M-perchloric acid. Sweep rate 0.03 V s^{-1}, electrode area 0.031 4 cm^2, reference electrode s.c.e.

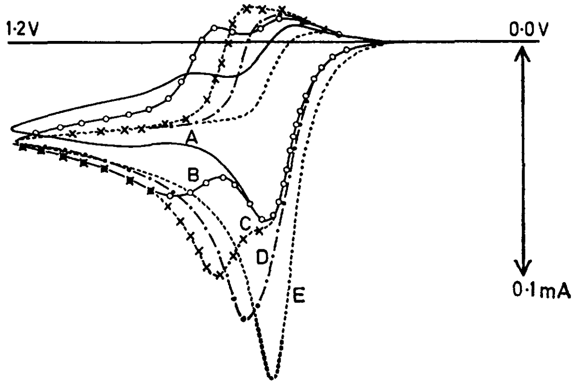

FIGURE 3 Electrolysis of 10^{-2}M-1-phenylpyrazolidin-3-one in acetonitrile containing 10^{-1}M-tetraethylammonium perchlorate: A, 0.0M; B, 2.8 × 10^{-2}M-water; C, 1.4 × 10^{-1}M-water; D, 2.8 × 10^{-1}M-water; E, 7.0 × 10^{-1}M-water. Sweep rate 0.03 V s^{-1}, electrode area 0.031 4 cm^2, reference electrode s.c.e.

$$\begin{tikzcd} RH + H_3^+O \arrow[r, rightleftharpoons] & RH_2^+ + H_2O \arrow[d, shift left, "-e"] \\ RH^{+\cdot} + H_3^+O \arrow[r, leftrightharpoons] & RH_2^{2+\cdot} + H_2O \arrow[u, shift left] \end{tikzcd}$$

SCHEME 2

Cyclic voltammograms were also obtained in the presence of pyridine and the results are shown in Figure 4.

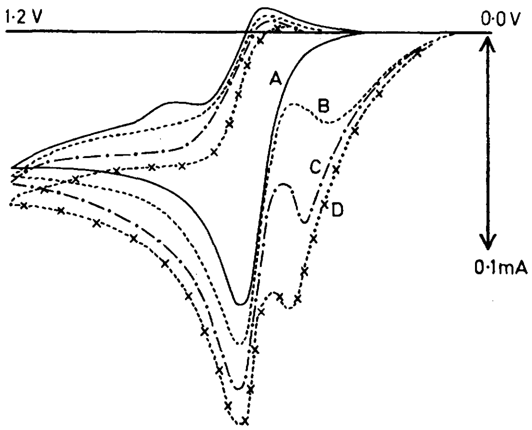

FIGURE 4 Electrolysis of 10^{-2}M-1-phenylpyrazolidin-3-one in acetonitrile containing 10^{-1}M-tetraethylammonium perchlorate: A, 0.0M; B, 3.1 × 10^{-3}M-pyridine; C, 6.2 × 10^{-3}M-pyridine; D, 9.3 × 10^{-3}M-pyridine. Sweep rate 0.1 V s^{-1}, electrode area 0.031 4 cm^2, reference electrode s.c.e.

The voltammograms show a pre-wave similar to that previously described for the oxidation of 9-phenylanthracene in the presence of pyridine.[20] No oxidation wave was observed at 0.82 V in the presence of pyridine,

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[18] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 3927.

[19] I. M. Kolthoff, ' IUPAC Symposium on Non-aqueous Electrochemistry, Paris,' Butterworths, London, 1970, p. 319.

[20] B. S. Jensen and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 665.

again suggesting that the initial wave at 0.61 V was due to the oxidation of the neutral pyrazolidinone and the more anodic wave was due to the protonated molecule. The fact that a pre-wave is observed supports the assertion that the wave of 0.61 V is due to the oxidation of un-ionised substrate. The pre-wave itself is probably the oxidation of the anion produced by reaction with pyridine. If the wave at 0.61 V were due to the anion it is difficult to see how a pre-wave could occur.

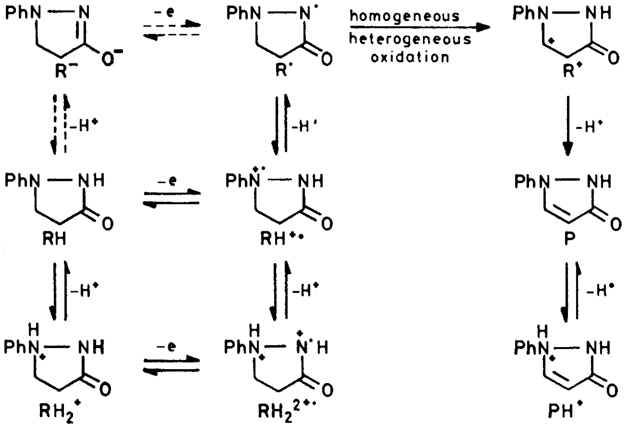
Coulometric experiments were performed with 10^{-1}M solutions of RH. Cyclic voltammograms with constant conditions were obtained as a function of the charge passed and the results indicated that for a constant potential electrolysis at 0.7 V, the initial wave at 0.61 V decreased at a rate corresponding to a one-electron oxidation. The more anodic wave at 0.82 V was found to increase relative to the wave at 0.61 V; the peak current at 0.82 V was found initially to remain relatively constant during the early part of the electrolysis and then decrease at a similar rate to the more cathodic wave. For an electrolysis at 0.82 V the coulometry suggested that 1.8 electrons were necessary to oxidise all the pyrazolidinone present.

Controlled potential electrolyses were performed at 0.7 and 0.84 V. At both potentials two oxidation products, 1-phenylpyrazolin-3-one (P) and 3-anilino-*N*-[4-(3-oxopyrazolin-1-yl)phenyl]propionamide were isolated. The major product was the monomer (P) (75% current yield) whereas in previous oxidative studies on other pyrazolidines in acetonitrile mainly dimers were formed.[14]

Mechanism.—The results indicate that at 0.7 and 0.84 V two distinct oxidative processes were occurring, both of which resulted in the same products. The most likely mechanism which would fit the observed electrochemical properties of 1-phenylpyrazolidin-3-one can best be described in the form of Scheme 3.[3,21]

In neutral acetonitrile solution the pyrazolidinone RH is initially oxidised *via* a reversible one-electron process to the radical-cation $RH^{+\cdot}$ which can undergo proton loss to give the neutral acylhydrazyl radical $R^{\cdot}$. In alkaline aqueous solution a further oxidation wave at a potential between the waves for the oxidation of the pyrazolidinone RH and the pyrazolinone (P) is observed. However, in acetonitrile no oxidation wave which could be attributed to the further oxidation of the radical $R^{\cdot}$ was observed between 0.6 and 1.2 V.

1-Phenylpyrazolin-3-one (P) was found to oxidise irreversibly in acetonitrile, with a half-peak potential of 1.08 V (10^{-3}M; ν 0.03 V s^{-1}). This would suggest that the radical was being oxidised at the same potential as RH. Results from experiments in the presence of excess of chloride, which acts as a strong base in acetonitrile, strongly supported this assertion.[22] These showed an irreversible two-electron wave using a 10^{-2}M solution of RH in the presence of excess of chloride for sweep rates up to 300 V s^{-1}, indicating that the radical-cation rapidly transfers a proton to the chloride anion giving a neutral radical which is further oxidised by heterogeneous electron transfer or by a rapid homogeneous reaction involving either the radical-cation or itself. Disproportionation reactions between acylhydrazyl radicals $R^{\cdot}$ are known.[23]



SCHEME 3

Steady-state experiments with a rotating disc electrode indicated that one electron is being transferred during the initial oxidative process (0.61 V). This result can be explained by the mechanism in Scheme 4.

$$\begin{tikzcd}
2RH \arrow[r, shift left, "-e"] & RH + RH^{+\cdot} \arrow[l, shift left] \arrow[r, shift left] & R^{\cdot} + RH_2^{+} \arrow[l, shift left] \arrow[d, "\text{homogeneous-heterogeneous oxidation}"] & \\
 & & R^{+} \arrow[r, "\text{rearrangement}"] & PH^{+}
\end{tikzcd}$$

SCHEME 4

In accord with Scheme 4 is the existence of the previously known 1-phenylpyrazolidin-3-one hydrochloride ($RH_2^+Cl^-$) and 1-phenylpyrazolin-3-one hydrochloride (PH^+Cl^-).[24] The overall reaction thus corresponds to a one-electron transfer per molecule of RH because the protonated pyrazolidinone RH_2^+ is not electroactive at 0.61 V. This mechanism is similar to that previously reported for aniline [13] and phenylhydrazine [25] in acetonitrile, where the number of electrons transferred per parent molecule was 0.66 and where protonated substrate was postulated, but where protonated product was not claimed.

Coulometric experiments indicated that at potentials where the protonated pyrazolidinone RH_2^+ was electroactive (0.82 V), the number of electrons transferred per molecule of substrate approached two, in agreement with our mechanism. Cyclic voltammetric results indicated an ECE process, suggesting that a chemical reaction was occurring during the oxidation. The slow

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[21] W. J. Albery and M. L. Hitchman, ' Ring Disc Electrodes,' Clarendon Press, Oxford, 1971.

[22] B. D. Baigrie and T. A. Joslin, unpublished work.

[23] W. C. Danen and F. A. Neugebauer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 783.

[24] C. Harries and G. Loth, *Ber.*, 1896, **29**, 513.

[25] G. Cauquis and M. Genies, *Tetrahedron Letters*, 1968, 3537.

step in acidic media is probably proton loss from the radical-cation to form the neutral intermediate. The addition of perchloric acid to a neutral solution of 1,1-diphenylhydrazine[26] gives electrochemical data analogous to our results. In neutral solution three oxidation waves were observed. The addition of perchloric acid resulted in the disappearance of the two more cathodic waves, leaving a two-electron wave which was attributed to the oxidation of protonated 1,1-diphenylhydrazine.

Results from cyclic voltammetry indicated that the oxidation wave at 0.82 V was due to the oxidation of protonated pyrazolidinone RH_2^+. That this species existed in acidic acetonitrile solution was confirmed by bubbling dry hydrogen chloride gas through a solution of the pyrazolidinone; solution i.r. measurements gave absorptions, $\nu_{max.}$ 3 200br and 2 500br cm^{-1}, compatible with an ammonium type salt. Potentiometric titrations carried out with a glass electrode system, which had previously been reported to work satisfactorily in acetonitrile,[27] indicated that protonation of (RH) was also occurring in acetonitrile containing perchloric acid.

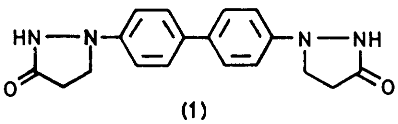
An alternative route for the formation of the pyrazolinone (P) is given in Scheme 5. There are two aspects of this mechanism which render it less acceptable than Scheme 4. No observation was made for a heterogeneous oxidation of the radical-cation whilst this mechanism implies an easy homogeneous oxidation. In acidic solution, the oxidation of the protonated substrate must lead to a radical-dication. As this process is more reversible the implication of Scheme 5 is that the radical-dication is more stable than the radical-cation.

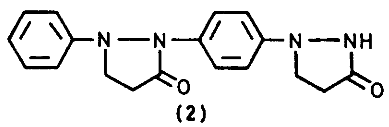
$$\mathrm{RH} \overset{-e}{\rightleftharpoons} \mathrm{RH}^{+\cdot}$$

$$\mathrm{RH}^{+\cdot} + \mathrm{RH}^{+\cdot} \rightleftharpoons \mathrm{RH}_2^{+} + \mathrm{R}^{+}$$

$$\mathrm{R}^{+} \xrightarrow{\text{rearrangement}} \mathrm{PH}^{+}$$

SCHEME 5


(1)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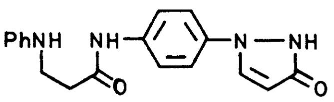
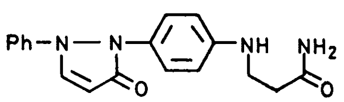

(3)


(4)

So far we have accounted for the main product, 1-phenylpyrazolin-3-one, as shown in Scheme 3. We were also able to isolate a dimeric species, which was not the expected product, (1)[8-10] nor the more usual product (2), formed *via* head-to-tail dimerisation; a mode of reaction which has been documented for acylhydrazyl radicals in which the lone electron is extensively delocalised.[23] Our dimer was identified as 3-anilino-*N*-[4-(3-oxopyrazolin-1-yl)phenyl]propionamide (3) on the basis of i.r., n.m.r., and mass spectral data. Thus while our product had elemental analysis and molecular weight (high resolution mass spectrometry) which suggested a dimer with molecular weight $C_{18}H_{18}N_4O_2$, the ^{1}H n.m.r. spectrum clearly identified the following characteristic features: (i) a monosubstituted phenyl ring and a *para*-disubstituted phenyl ring; (ii) a pyrazole nucleus, τ 1.90 (d, *J* 3 Hz) and 4.23 (d, *J* 3 Hz); (iii) two different exchangeable protons, τ 0.00br (s) and 4.45 (t); and (iv) two adjacent methylene groups, the signal for one of which (downfield) was coupled to the exchangeable proton signal at τ 4.45.

Structures (1) and (2) were clearly incompatible with this information, but two other structures (3) and (4) which incorporate all these features were possible. Detailed analysis of the mass spectrum confirmed that the compound had structure (3) (*m/e* 322, Scheme 6). The product fragmented as would be expected for a molecule with structure (3) to give a radical at *m/e* 229, thus indicating loss of aniline (C_6H_7N) from the parent radical ion. The subsequent fragmentation pattern as indicated in Scheme 6 was further confirmed by accurate mass measurement of the major fragments as shown in the Table. Finally, the i.r. spectrum indicated an absorption, $\nu_{max.}$ 3 400sh cm^{-1}, due to the N–H stretch of a secondary amine.

Accurate mass measurements

m/e	Expected formula	Measured mass	Calculated mass
322	$C_{18}H_{18}N_4O_2$	322.142 177	322.142 970
217	$C_{11}H_{11}N_3O_2$	217.084 612	217.085 112
202	$C_{10}H_8N_3O_2$	202.061 107	202.061 647
175	$C_9H_9N_3O_2$	175.074 291	175.074 558
105	C_7H_7N	105.057 496	105.057 848

The mode of formation of the two-electron oxidation product, (3), is not completely clear. It is possible however to rationalise the formation of this unusual product *via* the intermediary dimers (5) or (6) as shown in Scheme 7.

The current yields of the products were monitored as a function of coulombs passed during a controlled potential electrolysis at 0.7 V, by high presure liquid chromatography (h.p.l.c.). The results indicated that the yield of (3) was initially zero (up to 15% conversion) but rose to 20% current yield (at 75% conversion). Because the acidity of the medium increases with charge passed,

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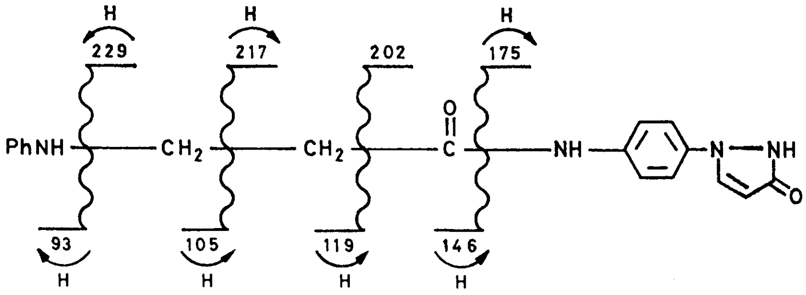
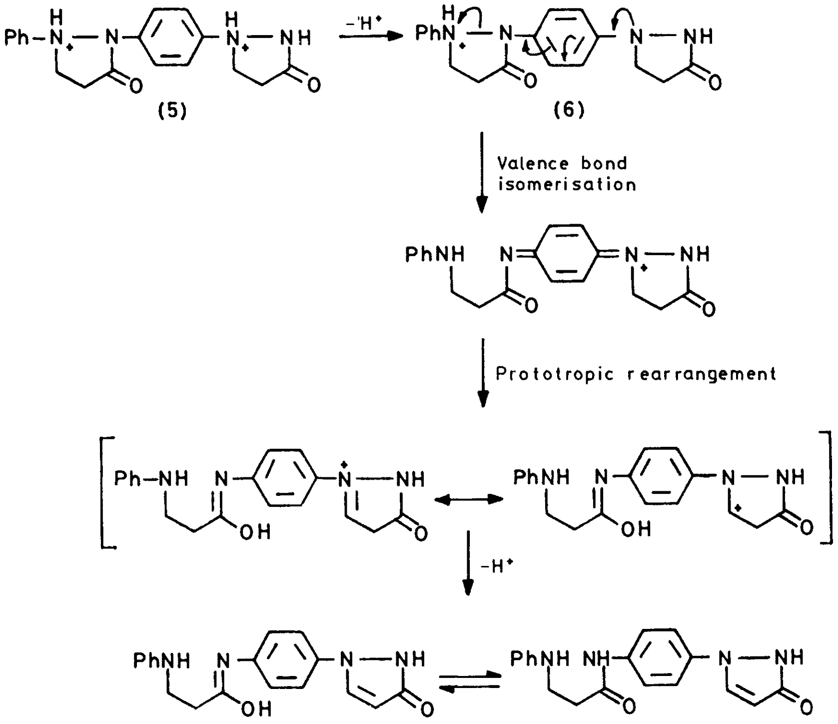
[26] G. Cauquis and M. Genies, *Tetrahedron Letters*, 1970, 2903.

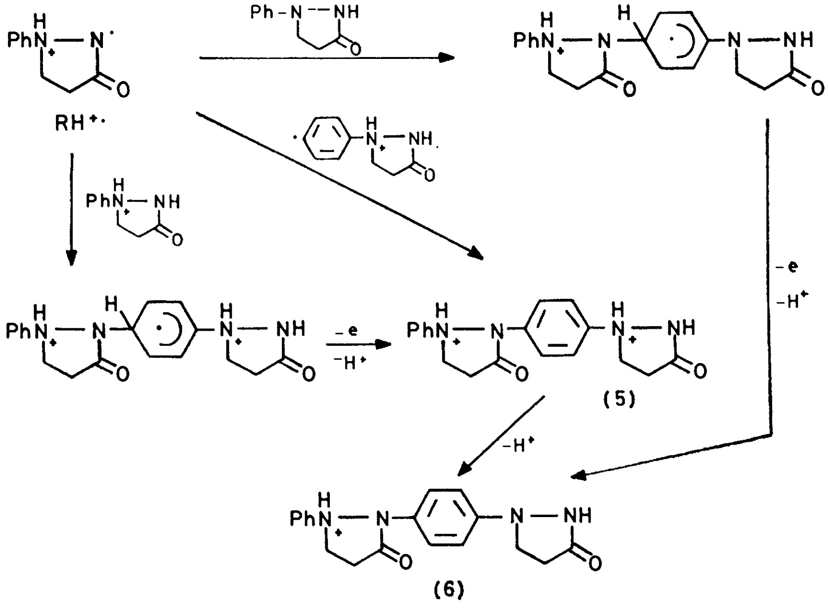
[27] J. F. Coetzee and G. P. Padmanabhan, *J. Phys. Chem.*, 1962, **66**, 1708.



Scheme 6



Scheme 7



Scheme 8

and because the radical-cation is kinetically more stable in acid medium as indicated by cyclic voltammetry, we believe that this intermediate plays a key role in the mechanism. Dimers (5) and (6) can be formed by a number of routes[28] involving the radical-cation $RH^{+\cdot}$ (Scheme 8).

Conclusion.—The mechanism of the electrochemical oxidation of 1-phenylpyrazolidin-3-one in acetonitrile is more complex than that observed in aqueous alkali. The nature of the oxidative processes undoubtedly result from the aprotic nature of the solvent which leads to the formation of protonated intermediates and products. The different mechanisms observed in both media can conveniently be related by an oxidative scheme of squares.

A further oxidation product was obtained in acetonitrile. The exact mechanism by which this product is formed is uncertain; however our evidence suggests that a key role is played by the 1-phenylpyrazolidin-3-one radical cation.

EXPERIMENTAL

Chemicals.—1-Phenylpyrazolidin-3-one was obtained from Eastman Kodak (photographic grade) and was used directly. Tetraethylammonium perchlorate was obtained from Eastman Kodak (polarography grade) and was used directly, after an initial drying period of 12 h at 80 °C under vacuum. Acetonitrile was obtained from Koch–Light and purified as previously reported.[29] An alternative procedure where anhydrous sodium sulphate was used instead of sodium carbonate was also used and found to give satisfactory results with a u.v. cut-off below 200 nm[30] (the results are very sensitive to the presence of certain impurities in untreated acetonitrile).

Electrochemical Equipment.—All electrochemical experiments were performed in glass three-component cells coupled to a Chemical Electronics transistorised potentiostat (70 V, 2 A). The cyclic voltammetry experiments also used a Chemical Electronics wave form generator, type RB2. The current voltage response was recorded on either a Hewlett-Packard 7035B X-Y recorder or a Tektronics 5103N storage oscilloscope. Rotating disc experiments were performed with a Tacussel rotating disc system connected to a platinum disc electrode (0.031 4 cm^2). This electrode was also used for cyclic voltammetry. During controlled potential electrolyses, a Chemical Electronics current integrator was used. Platinum gauze electrodes were used for preparative scale electrolyses.

The reference electrode system consisted of a commercially available calomel electrode (Radiometer K401) situated in a glass compartment separated from the working electrode by means of a glass tap and Luggin capillary.

Chromatography.—For analytical and quantitative h.p.l.c. investigations a Du Pont 830 liquid chromatography was used together with a Du Pont permaphase E.T.H. column (0.5 mm × 2.1 mm). A linear graded eluant 100% water to 100% methanol was used and product detection was achieved using a fixed wavelength (254 nm) u.v. detector.

Dry column chromatography was carried out after the method of Loev and Goodman.[31] The columns were made up in C gauge nylon tubing supplied by Walter Coles and Co. Ltd., London. After development, the columns were sliced and the products washed off with ether or methanol. P.l.c. was carried out using Merck preparative glass plates coated with Silica gel 60 F_{254}.

Controlled Potential Electrolyses.—A controlled potential electrolysis was performed at 0.7 V *versus* s.c.e. with a divided glass cell containing tetraethylammonium perchlorate (11.5 g, 0.05M) in acetonitrile (500 cm^3) with a working electrode compartment containing 1-phenylpyrazolidin-3-one (3.0 g, 0.018M). After 90% conversion, the oxidised solution from the working compartment was reduced in volume (40 cm^3), poured into water (200 cm^3) with stirring, and the yellow solution was carefully neutralised with sodium carbonate. The aqueous solution was extracted with ethyl acetate (6 × 25 cm^3) and the organic phase was dried (Na_2SO_4) and evaporated to give an orange gum (3.3 g). This was chromatographed on a silica gel dry column (5 × 65 cm), developed with ether to give two fractions. The first fraction, a pale yellow solid, was recrystallised from chloroform to give 1-phenylpyrazolin-3-one (1.0 g; 75.4% current yield) as needles, m.p. 156° (lit.,[32] 155 °C) (Found: C, 67.8; H, 5.2; N, 17.6%; *m/e* 160. Calc. for $C_9H_8N_2O$: C, 67.5; H, 5.0; N, 17.5%; *M*, 160), τ ($CDCl_3$) 2.35 (1 H, d, *J* 3 Hz), 2.40—3.00 (5 H, m, aromatic), 4.13 (1 H, d, *J* 3 Hz); i.r. spectrum identical with that previously reported.[32] The second fraction, a cream-coloured solid (0.45 g), was further purified by p.l.c. to give, after recrystallisation from methanol, *3-anilino-*N*-[4-(3-oxopyrazolin-1-yl)phenyl]propionamide* (0.2 g), current yield 7.5%, m.p. 191° (Found: C, 66.7; H, 5.7; N, 17.3. $C_{18}H_{18}N_4O_2$ requires C, 67.1; H, 5.6; N, 17.4%). The mass spectrum showed the parent ion at *m/e* 322 (Found: M^+, 322.142 177. $C_{18}H_{18}N_4O_2$ requires M^+, 322.142 970), τ ([$^2H_6$]DMSO) 0.00 (1 H, s, exchangeable with D_2O), 1.90 (1 H, d, *J* 3 Hz), 2.35 (4 H, s, aromatic), 2.70—3.60 (5 H, m, aromatic), 4.23 (1 H, d, *J* 3 Hz), 4.45br (1 H, exchangeable with D_2O, NH), 6.40—6.80 (2 H, t, $NHCH_2$), and 7.30—7.50 (2 H, t, CH_2), $\nu_{max.}$ (KBr) 3 400 (N–H) and 1 645 cm^{-1} (CONH), $\lambda_{max.}$ 208 (log ε 4.35), 247 (3.93), and 286 nm (4.40).

A controlled potential electrolysis was also performed at 0.84 V *versus* s.c.e. on a 10^{-1}M solution of 1-phenylpyrazolidin-3-one in acetonitrile containing 2 × 10^{-1}M-perchloric acid. The products isolated were identical to those obtained from the electrolysis at 0.7 V. The current yields of both products were the same as previously obtained with controlled potential electrolyses at 0.7 V (70% current yield of monomer and 20% current yield of dimer using h.p.l.c.). The current yield of dimer was however increased at lower conversions, 15% yield at 20% conversion.

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