

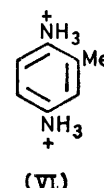
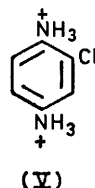
The Anodic Oxidation of 1,4-Diaminobenzene: an Electron Spin Resonance and Electrochemical Study

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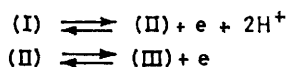
The electrochemical e.s.r. of 1,4-diaminobenzene, 1,4-diamino-2-chlorobenzene, and 1,4-diamino-2-methylbenzene has been studied in aqueous methanol using an apparatus in which a tube electrode is linked to the e.s.r. cavity. Laminar flow transports species from the electrode into the cavity. The distribution of species in the cavity can be described theoretically and from the variation of e.s.r. signal with current, flow rate, concentration, and pH the protonation and kinetic stability of the 1,4-diaminobenzene cation radical is established. From the electrochemistry, the protonation of the unstable benzoquinone di-imide is deduced. The kinetics and the mechanism of its substitution reaction with water leading to benzoquinone are deduced from the behaviour of the e.s.r. signal from the radical cation with which the benzoquinone di-imide is in equilibrium.

We have shown that, when one links a tube electrode to an e.s.r. cavity, the equations describing the transport of electrogenerated radicals from the electrode through the cavity can be solved.¹⁻⁴ The transport is by laminar flow and the equations describe the e.s.r. signal strength as a function of the generating current, the flow rate, and rate constants for any homogeneous decomposition. We have verified the theory by experiment for the following cases: a stable radical, a radical decomposing by first- or second-order kinetics, and a radical in thermodynamic equilibrium within a disproportionation reaction, *e.g.* semiquinone in the presence of quinone and hydroquinone. In this paper we apply the technique to study the electrochemical and homogeneous behaviour of the 1,4-diaminobenzene (I) system.

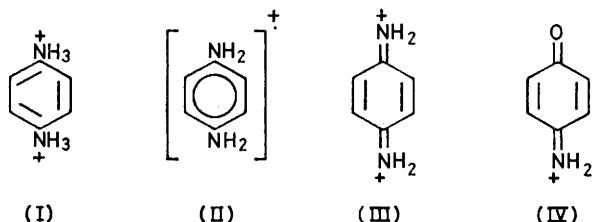
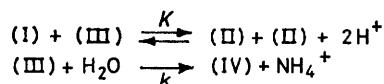
proportionation equilibrium constant K and its pH dependence have been measured from the e.s.r. signal from (II). The variation of this signal with flow rate allows us to measure the first-order rate constant k and its pH dependence. This rate constant describes the substitution reaction of (III) with water. Besides (I) we have also studied the substituted precursors (V) and (VI).



Electrochemistry



Homogeneous



SCHEME 1

We have studied the system in a 50% v/v methanol water mixture in the pH range 0–1.5. We shall show that the system obeys Scheme 1 which is similar to that found in water.^{5,6} In our experiments (III) and a much smaller amount of the radical (II) are generated electrochemically from the precursor (I). Values of the dis-

EXPERIMENTAL

Apparatus.—The tube electrode assembly has been described previously.^{3,4} The e.s.r. spectrometer used in this work was a Bruker ER 200tt. This instrument possesses a dual cavity (TE₁₀₄) so that by placing a standard sample (Mn-doped MgO) in the second cavity the response and sensitivity of the instrument can be measured for each reading, and the signals corrected for machine drift. The spectrometer was calibrated from time to time by measuring the signal from a solution containing a known concentration of galvinoxyl or 1,1-diphenyl-2-picrylhydrazyl (DPPH) in the tube electrode assembly. By using a small crystal of DPPH we confirmed that the cavity sensitivity varied in the expected \cos^2 fashion. The results of the calibration experiments agreed to within $\pm 10\%$. The geometric parameters for the tube electrode assembly are as follows: radius of tube, $r_0/\text{cm} = 0.045$; length of electrode, $r_e/\text{cm} = 0.29$; length of electrode + cavity, $l/\text{cm} = 2.4$.

Chemicals and Solutions.—All water was doubly distilled and all chemicals were of AnalaR grade except for (I), (V), and (VI) which were supplied by B.D.H. In each case the m.p. was found to be within 1° of the published values, and the compounds were therefore used without further purification.

RESULTS AND DISCUSSION

The e.s.r. spectrum of (II) was found to be similar to that obtained by Adams⁷ in aqueous solution (pH 4.8) and in acetonitrile. In particular the spectrum was con-

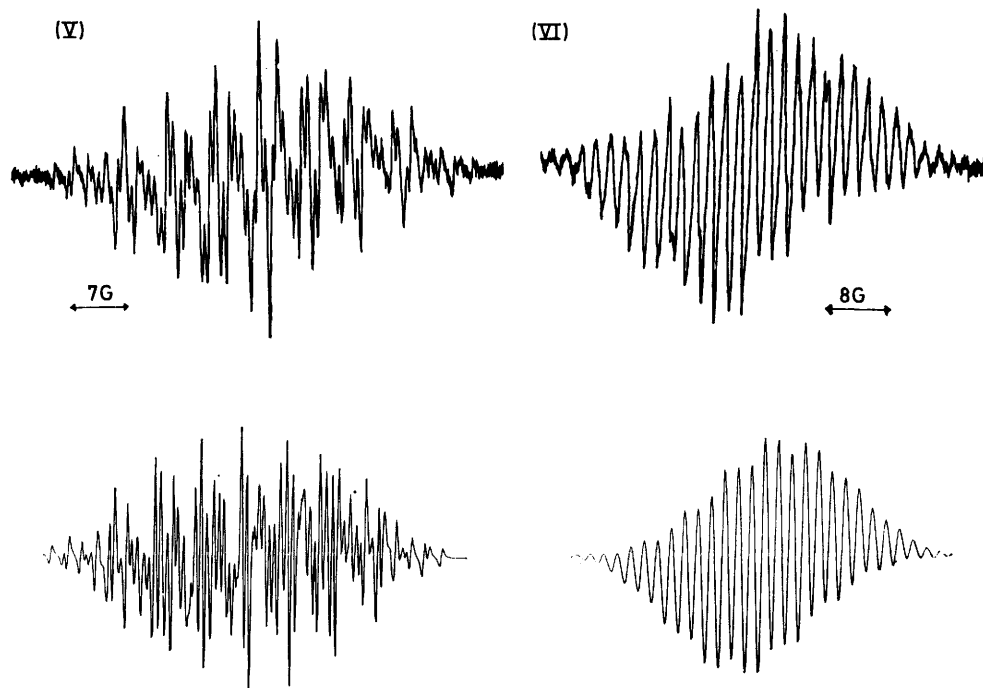


FIGURE 1 Spectra of the radical ions from the oxidation of (V) and (VI). In each case the upper diagram shows the observed e.s.r. spectrum and the lower the simulated spectrum

sistent with the degree of protonation of the radical cation given in (II). The splitting constants are given in Table 1. Figure (1) shows spectra obtained from the

fine splitting constants given in Table 1. The spectra were simulated assuming that the radicals have the same degree of protonation as (II). The good agreement between the observed and simulated spectra shows that this is correct.

Next we turn to the electrode kinetics. In Figure 2

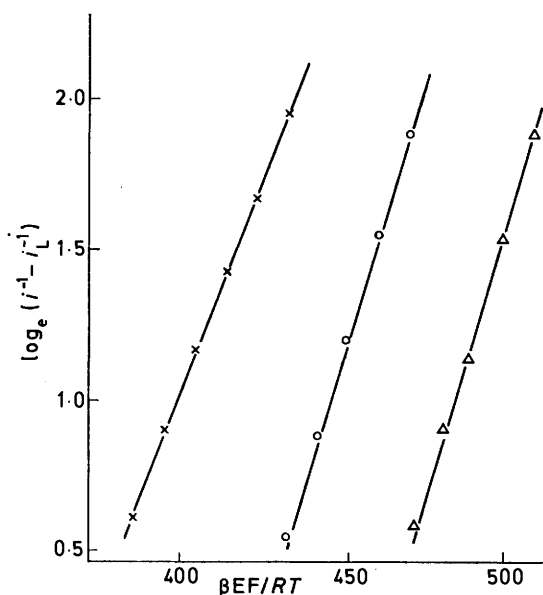


FIGURE 2 Tafel plots (corrected for concentration polarisation) as given in equation (1): \circ , (I); Δ , (V); \times , (VI). Systems (I) and (V) are reversible two-electron systems. For (VI) the system is irreversible with β 1.57

radical cations derived from (V) and (VI). E.s.r. spectra from these radicals have not been previously observed. We also show, in Figure 1, simulated spectra calculated using Lorentzian lineshapes and the hyper-

TABLE 1
Coupling constants (in Gauss)

	a_N	a_{HN}	a_{C-H}
(II)			
50% MeOH-H ₂ O (7)	5.11	5.78	2.08
MeCN	5.24	5.88	2.13
AcOH-AcO ⁻ (7)	5.12	5.67	2.10
(V)	5.22	5.91	2.28
	4.98	5.84	2.24
			1.64
(VI)	5.32	5.60	3×1.82
	5.18	5.45	3×1.68

we show concentration-polarization-corrected Tafel plots⁸ for (I) and for (V) and (VI) plotted according to equation (1) where i_L is the limiting current.

$$\log_e(i^{-1} - i_L^{-1}) = \text{constant} - \beta EF/RT \quad (1)$$

For (I) [and for (V)], $\beta = 2$, showing that the system is reversible with fast electrode kinetics and a transfer of two electrons. For (VI) on the other hand we find β 1.57. For (I), since it is a reversible system, the half-wave potential measures E° and in Figure 3 we show how E° varies with pH. The gradient of 59 mV per pH unit shows that for the two-electron transfer between (I) and (III), two protons are transferred as well. This confirms the degree of protonation of (III). For (VI), from

β 1.57 and the results in Figure 3 we can deduce that the transition state for the rate-limiting electron transfer has the degree of protonation shown in (VII) and this

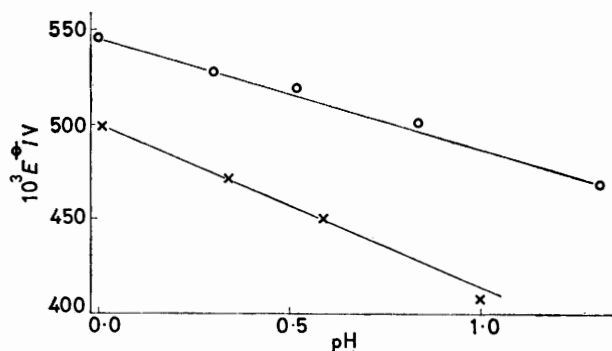
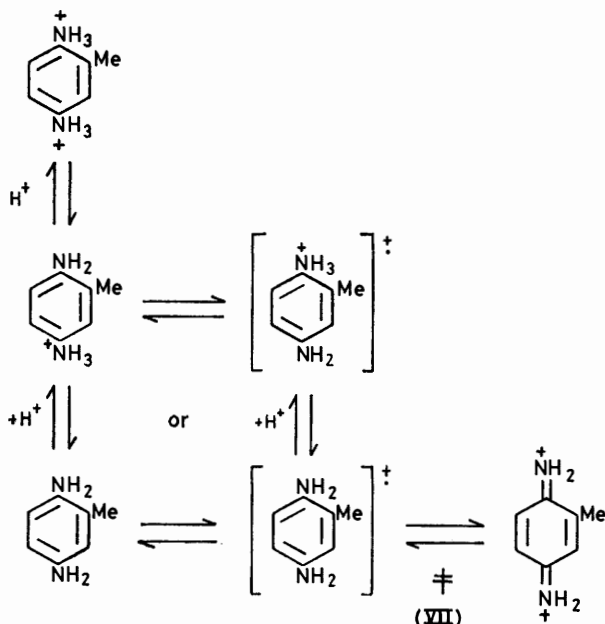


FIGURE 3 Variation of the half-wave potentials with pH for (I) (O) and (VI) (X). For (I) the system is reversible and $E_1 \approx E_0$; the gradient shows, besides two electrons (Figure 3), two protons are also involved in the equilibrium. For (VI) the system is irreversible and the gradient shows that two protons have been lost in the transition state (see Scheme 2)

suggests that the electrochemical mechanism proceeds by the scheme of squares⁹ shown in Scheme 2.

The protonation of (I)—(III) is further confirmed by the variation of the concentration of (II) with pH. Typical results for the variation of e.s.r. signal with flow rate are shown in Figure 4. At high velocities of flow,



SCHEME 2

v_f , kinetic decomposition is unimportant and the normalized e.s.r. signal strength (S/i^{\ddagger}) for a system such as Scheme 1 varies with $v_f^{-\ddagger}$; this has been confirmed for the quinone system.² The signal decreases with flow rate because the radicals are swept more rapidly through

the cavity. Values of K' can be calculated from the e.s.r. signal strength at high values of v_f according to equation (2). In equation (2) S^* is the signal from one

$$(K')^{\ddagger} = \frac{0.76F^{\ddagger}}{(l - x_e)r_0^2 S^*} \cdot \frac{S/i^{\ddagger}}{v_f^{-\ddagger}} \quad (2)$$

mole of spins at the centre of the cavity found by calibrating the spectrometer and the second term is found for

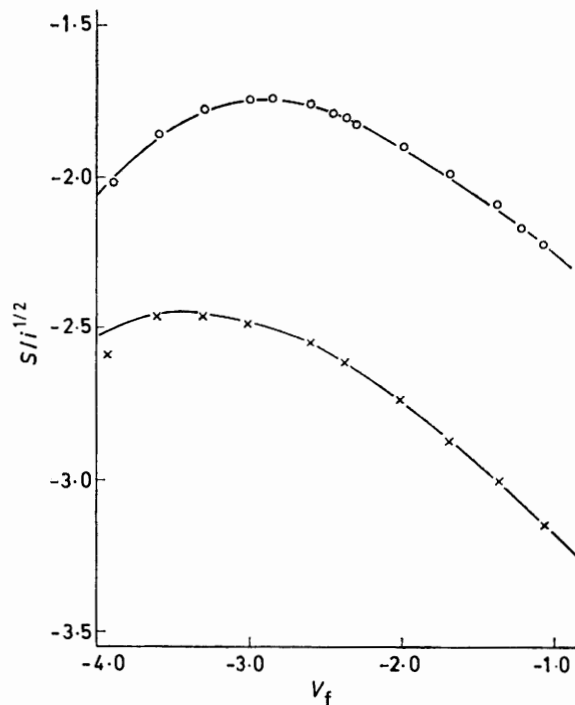


FIGURE 4 Typical plots for the normalised e.s.r. signal strength (S/i^{\ddagger}) (from I as precursor) as a function of flow rate, v_f , at pH = 0 (X) and 1 (O)

each pH from the asymptotic lines at high v_f , such as those shown in Figure 4; the equilibrium constant $K' = [(II)]^2/[I][III]$.

Figure 5 shows the variation of $\log K'$ with pH. The gradient of 2 confirms both the protonation of (I)—(III) deduced independently above and also the interpretation of the electrochemical e.s.r. experiment; the value of K in Scheme 1 is $3.5 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$. Values for K' for (V) and (VI) are also displayed in Figure 6.

Turning to the homogeneous kinetics, the maxima in e.s.r. signal with flow rate (see Figure 4) are caused by the decomposition of (III). At slow flow rates (III), and with it (II), have largely decomposed before they reach the centre of the cavity. A good estimate of the value of k can be found from the value of the flow rate at the maximum signal strength, $(v_f)_{\text{max}}$, by using equation (3).⁴ From the values of the limiting current of (I) we

$$k = 2.23D^{\ddagger}(v_f)_{\text{max}}^{\ddagger} l^{-\ddagger} \gamma_0^{-2} \quad (3)$$

estimate $D/\text{cm}^2 \text{ mol l}^{-1} \text{ s}^{-1}$ to be 3.6. More precise values for k can be found by using the procedure described previously.⁴ As displayed in Figure 4 for each set of

data a value of k can be found which fits the data at all flow rates. When the concentration of (I) is varied by a factor of 5 the value of k does not change. This shows that (III) rather than (II) is reacting by first order kinetics, and thereby confirms Scheme 1. Results for k are shown in Figure 6.

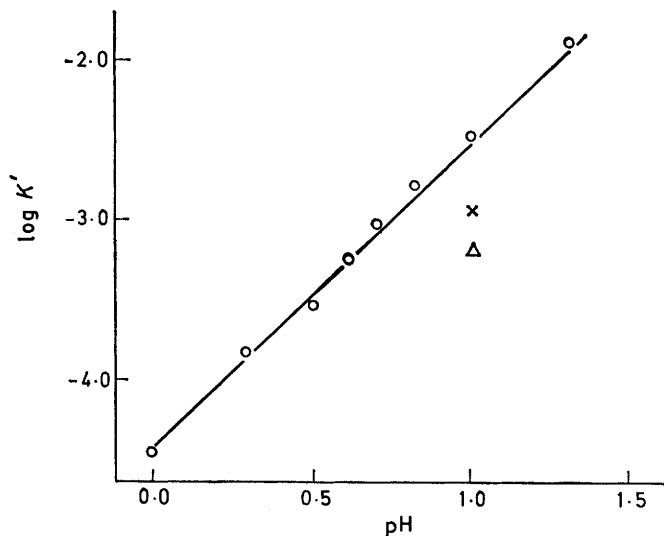


FIGURE 5 Plot of $\log K'$ calculated from equation (2) against pH for (I) (O). The gradient corresponds to a change of two protons, and K in Scheme 1 = $3.5 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$; the points Δ and \times are values of K' for (V) and (VI), respectively

For 1,4-diaminobenzene the value of k passes through a maximum as the pH is varied. This type of curve could conceivably be caused by a change in the protonation of the reactant, (III), but this is disproved by the good straight line in Figure 5. Hence the maximum in the pH profile must be caused by two transition states with different degrees of protonation. The fact that the

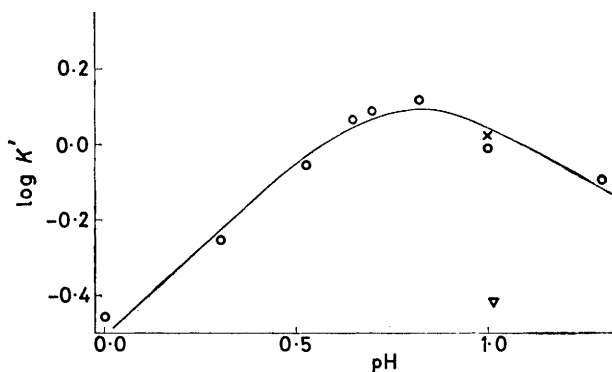
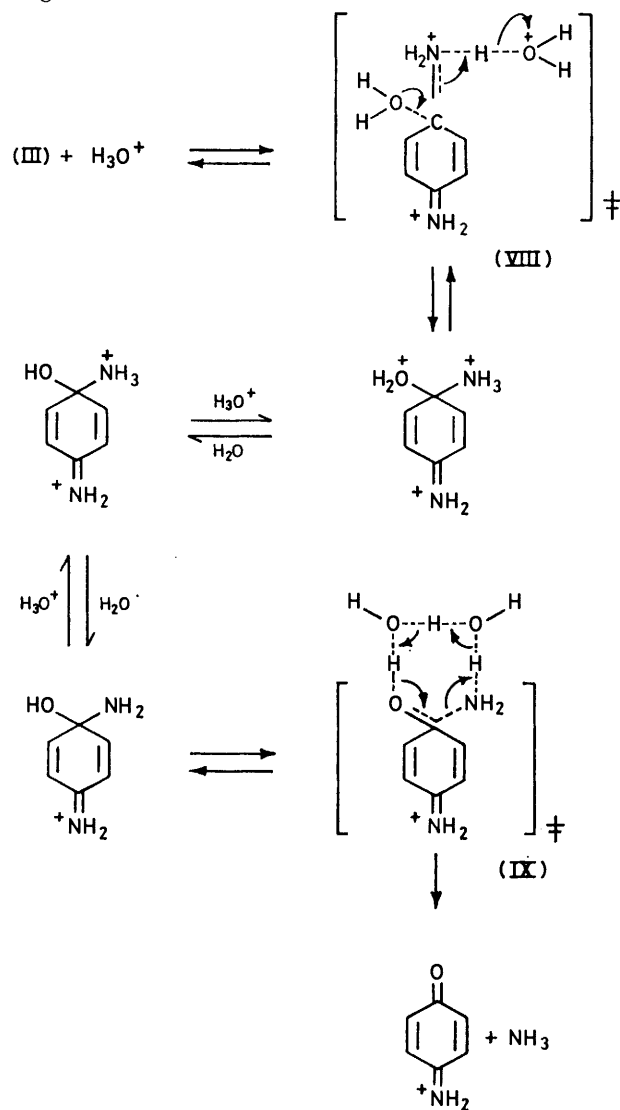


FIGURE 6 Variation with pH of $\log k'$ [calculated from equation (3)] for (III). The curve is calculated for Scheme 3. The points ∇ and \times are values for (V) and (VI), respectively

curvature of the profile is concave downwards means that the mechanism requires two consecutive transition states along the same reaction path. As shown by the good fit of the curve to the points in Figure 6 the data can be explained reasonably well if one of these transition

states has one proton less than (III) and the other one proton more than (III).

The reaction of (III) with water eventually produces benzoquinone.⁶ However the first stage is the conversion of (III) to (IV), followed by the slower reaction of (IV) to benzoquinone.⁶ The loss of the first nitrogen is irreversible and hence the two transition states responsible for the pH profile must be rate-limiting in the conversion of (III) to (IV). The same type of profile has been found for the solvolysis of a series of benzoquinone bis-*N*-phenylimides.¹⁰ Following Jencks¹⁰ we suggest that the two transition states are (VIII) and (IX) in Scheme 3 where in (VIII) the oxygen-carbon bond is being formed and in (IX) the nitrogen-carbon bond is being broken.



SCHEME 3

The solvent isotope effect was measured by repeating the experiment in D₂O and the results are reported in Table 2. In agreement with Jencks¹¹ we find that the rate is approximately halved. Assuming that the same

mechanism holds, we can then calculate the limiting values at low and high pH reported in Table 2, where the value for $[\text{DCl}] = 0$ corresponds to transition state (VIII) and that for $[\text{DCl}] > 1$ to transition state (IX). The result for transition state (VIII) suggests that the

TABLE 2
Solvent isotope effects

$[\text{DCl}]/\text{mol dm}^{-3}$ $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$	Experimental values		Limiting values	
	0.09 0.78	0.27 0.52	0 1.0	>1 0.45

oxygen-carbon bond is only loosely formed since the development of positive charge on the oxygen would lead to fractionation factors for the adjacent hydrogen sites of less than unity. The fractionation factor for the proton in flight between the oxygen and nitrogen must be compensated by the reversion of the fractionation for the two secondary sites from 0.69 for L_3O^+ to 1.0 for L_2O . In going from the reactants to transition state (IX) there is a net release of one H_3O^+ which will account for fractionation of $(0.69)^3 = 0.33$. This means that for the sites shown in transition state (IX) the fractionation would be 1.36. This value suggests first that the protons transferring in transition state (IX) must be very reactant-like with fractionation factors close to unity. Secondly the factors of 1.36 must arise from either a medium effect or from reactant fractionation in (III).

Finally it is interesting that by combining the electrochemical and e.s.r. information we can deduce the nature of the four different species (II), (III), (VIII), and (IX), all of which have limited lifetimes.

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