

Short Communication

## The Effect of the Substitution Pattern on the Protonation Pathways of Dinitrobenzene Dianions in *N,N*-Dimethylformamide Solution

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The protonation reactions of radical anions of aromatic compounds have been studied extensively.<sup>1</sup> Although reactive dianions have occasionally been implicated as intermediates, via disproportionation of radical anions, in some cases<sup>2</sup> little is known about the reactions of these reactive intermediates. Qualitatively, it is well known that dianions react much more readily with proton donors than the corresponding radical anions.<sup>3</sup> In fact, dianions of most aromatic compounds cannot be observed by cyclic voltammetry unless residual proton donors are scrupulously removed from electrochemical solvent–electrolyte systems.<sup>4</sup>

The greater reactivity of the dianions is, at least in part, a consequence of a much greater thermodynamic basicity. We have shown, using electrode potentials in thermochemical cycles, that the  $pK_a$  of the conjugate acid of the anthracene dianion in DMSO is of the order of 53 while that of the conjugate acid of the corresponding radical anion is 30  $pK_a$  units lower.<sup>5</sup> The  $pK_a$  of 9,10-dihydroanthracene under these conditions is of the order of 27. The relative basicities of the dianion ( $AN^{2-}$ ), radical anion ( $AN^{\cdot-}$ ) and monoanion ( $ANH^-$ ) in the anthracene system allows for the observation of the protonation of the dianion by cyclic voltammetry in the presence of weak

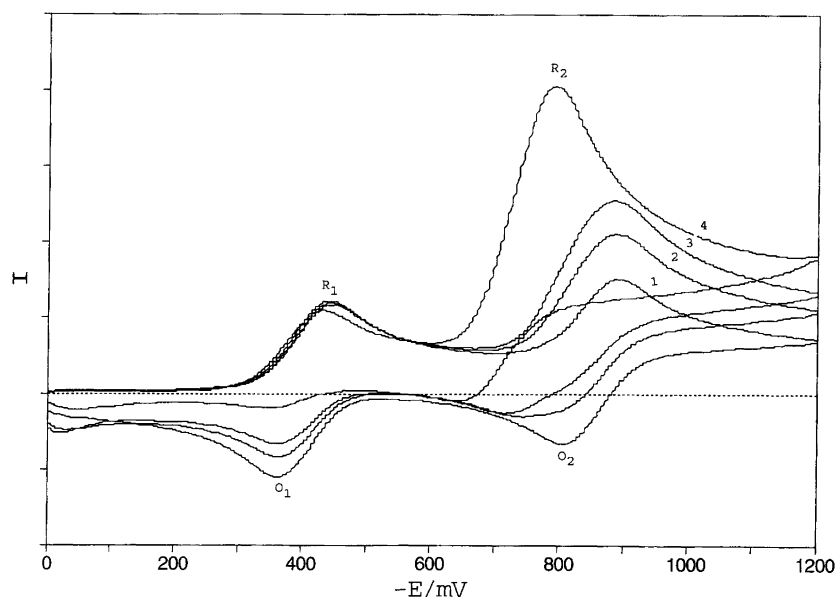


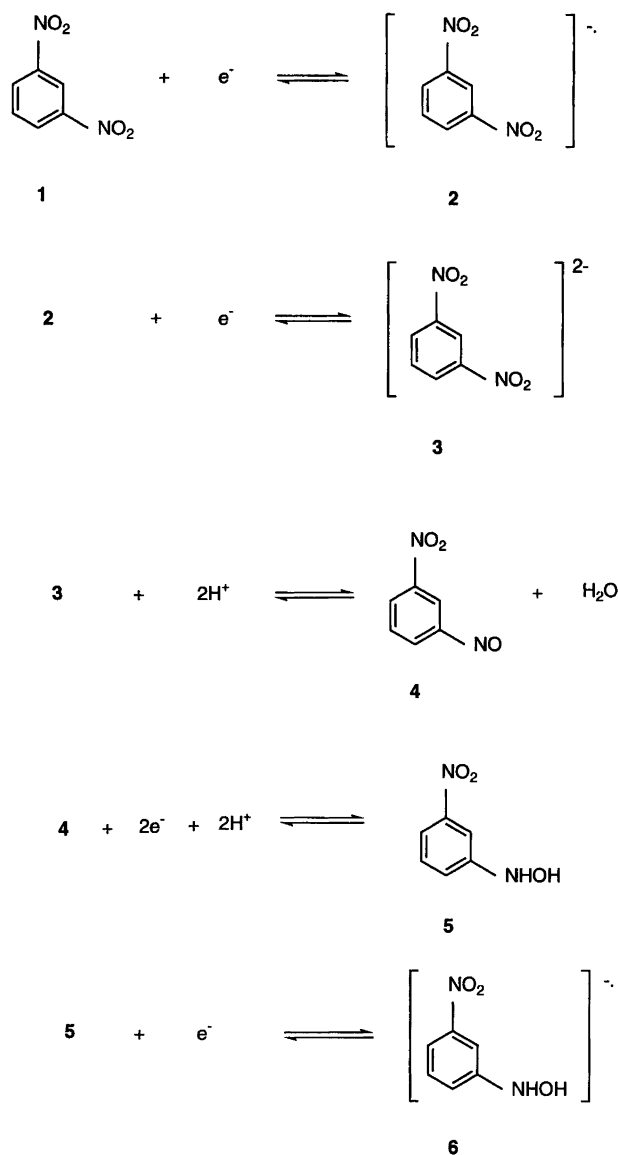
Fig. 1. Cyclic voltammograms for the reduction of 1,3-dinitrobenzene (2 mM) in the presence of phenol in DMF– $Bu_4NPF_6$  (0.1 M) at a mercury film electrode at 23°C. Phenol concentrations were 0 (1), 4 mM (2), 8 mM (3) and 100 mM (4).

Table 1. Charge ratios for potential steps beyond the first and second charge transfers to 1,3-dinitrobenzene (2 mM) in DMF–Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) in the presence of phenol (100 mM).

Pulse time/ms	$Q_2/Q_1$
2.0	2.0
5.0	3.0
10.0	4.3
20.0	5.1
50.0	4.9

proton donors under conditions where AN<sup>•-</sup> and ANH<sup>-</sup> do not react.<sup>5</sup>

Nitro-substituted aromatic compounds have served as prototype substrates for electrochemical studies of radical anions and dianions. The dianion of the parent compound in this series of substrates, nitrobenzene, can be



Scheme 1.

observed in *N,N*-dimethylformamide (DMF) in the presence of activated alumina<sup>6</sup> as well as in liquid ammonia.<sup>7</sup> A recent study of the reduction of 4-nitrobenzophenone in the presence of a number of proton donors in tetrahydrofuran revealed that the dianion reacts slowly with water while the anion radical does not.<sup>8</sup>

We have now carried out an electrochemical study of the protonation of the three isomeric dinitrobenzene dianions in DMF–Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M). Our objective was to attempt to observe the primary intermediates of the protonation of the dianions under conditions where the corresponding radical anions do not react. The results show an interesting dependence upon the substitution pattern of the dinitrobenzenes.

The reduction of 1,3-dinitrobenzene in the absence and the presence of increasing concentrations of phenol is illustrated by the cyclic voltammograms in Fig. 1. On the first scan (1) the cyclic voltammogram shows two reversible one-electron charge transfers, R<sub>1</sub>/O<sub>1</sub> and R<sub>2</sub>/O<sub>2</sub>, recorded in the absence of phenol. Scans (2)–(4) were recorded in the presence of 4, 8 and 100 mM phenol, respectively. As the phenol concentration is increased, R<sub>2</sub> increases in height and shifts to less cathodic potential while R<sub>1</sub> remains unchanged. Significantly, the peak current at O<sub>2</sub> remains constant while that at R<sub>2</sub> increases by a factor of nearly 4. Scans not shown in which the direction of potential sweep was changed at potentials intermediate between R<sub>1</sub> and R<sub>2</sub> confirm that R<sub>1</sub>/O<sub>1</sub> remains reversible as the phenol concentration is increased.

The number of electrons transferred at R<sub>2</sub> was confirmed by a chronoamperometry study of the reduction of 1,3-dinitrobenzene (2 mM) in DMF–Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) in the presence of phenol (100 mM) as described in the previous paragraph. The number of electrons transferred upon a step to a potential negative of R<sub>2</sub> was determined by comparing the charge ( $Q_2$ ), i.e., the integrated current–time curve, to that ( $Q_1$ ) for the one-electron transfer taking place upon stepping to a potential intermediate between R<sub>1</sub> and R<sub>2</sub>. The charge ratios ( $Q_2/Q_1$ ) as a function of pulse width are summarized in Table 1. The results confirm that during cyclic voltammetry at low sweep rates R<sub>2</sub> corresponds to the transfer of 4 electrons as suggested by Scheme 1.

The fact that O<sub>2</sub> corresponds to a one-electron oxidation even in the presence of the highest phenol concentration indicates that an intermediate which is stable to the reaction conditions is formed. We interpret these results to indicate the reaction pathway shown in Scheme 1.

The radical anion (2) does not react during the time-scale of the experiment. The dianion (3) reacts rapidly with phenol (abbreviated here as H<sup>+</sup> for simplicity) to form 4 which is reduced to 5 at potentials where 3 is formed. The radical anion 6, like 2, does not react with phenol under the reaction conditions. Reduction stops at this stage due to the stability of 6. This interpretation was confirmed by voltammetry studies of the reduction of 5<sup>9</sup>

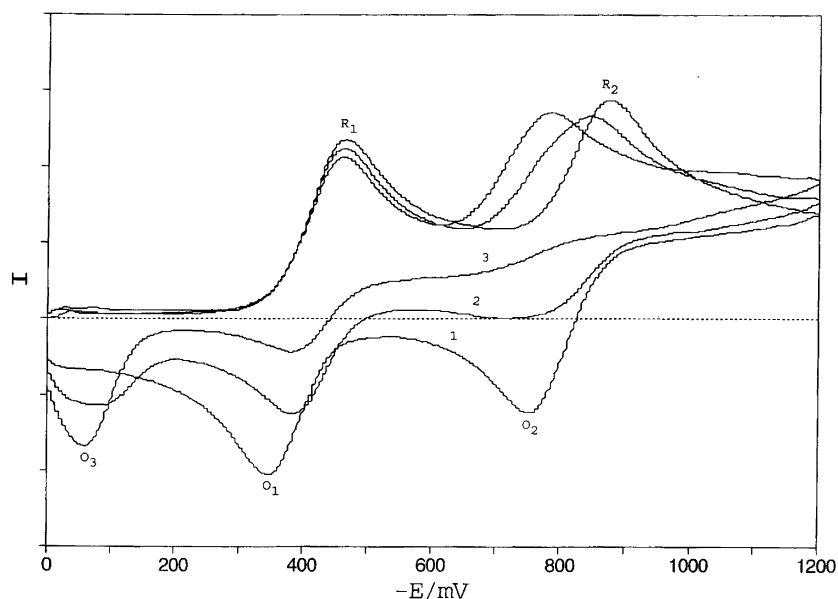


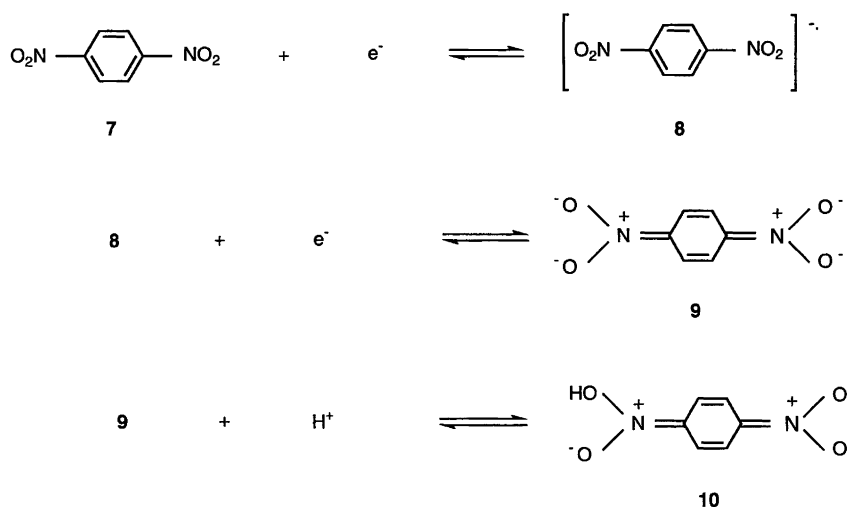
Fig. 2. Cyclic voltammograms for the reduction of 1,2-dinitrobenzene (2 mM) in the presence of phenol in DMF-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) at a mercury film electrode at 23°C. Phenol concentrations were 0 (1), 2 mM (2) and 8 mM (3).

in DMF in the presence of phenol (0.1 M). In the absence of phenol **5** is reduced reversibly with a peak potential 340 mV more negative than that for **1**. In the presence of phenol, the redox couple, **5** + e<sup>-</sup> ⇌ **6**, remains reversible but is shifted 33 mV in the positive direction. The potential shift in the presence of phenol is presumably due to hydrogen bonding between the radical anion and phenol.

The situation is quite different for the reduction of 1,2- and 1,4-dinitrobenzene. The reduction behaviour of these two compounds in DMF-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) is illustrated by the cyclic voltammograms for 1,2-dinitrobenzene in the absence and presence of phenol. In the absence of phenol the voltammogram consists, again, of two con-

secutive reversible charge transfers, R<sub>1</sub>/O<sub>1</sub> and R<sub>2</sub>/O<sub>2</sub>. In the presence of phenol, R<sub>1</sub>/O<sub>1</sub> remains reversible while the dianion formed at R<sub>2</sub> reacts (Fig. 2). However, in this case R<sub>2</sub> corresponds to the transfer of a single electron under all conditions. Furthermore, a new oxidation peak, O<sub>3</sub>, due to the oxidation of a product of the reaction of the dianion appears at less negative potentials. In scan (3) reaction of the dianion is essentially complete and O<sub>3</sub> corresponds to the transfer of one electron.

The results described in the previous paragraph indicate that protonation of the dianions of 1,2- and 1,4-dinitrobenzene gives rise to stable anionic intermediates. We interpret these results by the sequence of reactions in Scheme 2. Protonation of the dianion (**9**), in which the



Scheme 2.

two nitro functions are conjugated, leads to the highly delocalized anion (**10**). Due to the low reactivity of **10** toward proton donors, reduction stops at this stage after the overall transfer of two electrons.

The difference in substitution patterns of the dinitrobenzenes which gives rise to the two different reaction pathways of the dianions is that the two nitro groups are not conjugated in the first case (1,3-dinitrobenzene) while they are in the second (1,2- and 1,4-dinitrobenzene). As shown in Scheme 1, reduction of an unconjugated nitro group proceeds to the formation of the hydroxylamine (**5**) at the potential where the dianion of the substrate is formed. Further one-electron reduction of **5** is then reversible due to the low reactivity of the radical anion, **6**. The dianions of dinitrobenzenes with conjugated nitro groups are protonated by phenol to give delocalized anions which are not protonated under the reaction conditions.

In general, the products formed during protonation of dianions of aromatic compounds can only be expected to differ from those from the corresponding radical anion when it is possible to carry out the reduction of the dianion on a timescale where the radical anion does not react since the latter is expected to be the least reactive intermediate in the cascade of reactions that take place in going to neutral product. Under conditions where both the radical anion and the dianion react, the two reaction

pathways share a common intermediate which is the protonated dianion.

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