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Radical-anions of dinitrophenols in aqueous solution: intramolecular electron exchange and acid–base equilibria

João P. Telo and M. Cândida B. L. Shohoji *

Instituto Superior Técnico, Lab. Química Orgânica, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal

The radical-anions of three symmetrical dinitrophenols (3,5-dinitrophenol, 2,6-dinitrophenol and 4,6-dinitrobenzene-1,3-diol) in aqueous solution have been studied by EPR spectroscopy in the range of pH values from 6.5 to 13. EPR spectra of radical-anions of 3,5- and 2,6-dinitrophenol show line-broadening effects due to intramolecular electron exchange induced by asymmetric solvation of the two nitro groups. The position of the OH group is a decisive factor in the variation of the rate constant with the deprotonation of the radical-anion. This variation is larger when the OH group is in the *ortho* position to one nitro group. The activation parameters for the intramolecular electron exchange reaction have been determined by using the Marcus theory and the Rips–Jortner equation for the rate constant of a uniform and adiabatic reaction. ΔG^* values range from 12.6 kJ mol^{-1} for radical-dianion of 2,6-dinitrophenol to 46.0 kJ mol^{-1} for radical-dianion of 3,5-dinitrophenol. The EPR spectra of the radicals derived from 4,6-dinitrobenzene-1,3-diol show no line-broadening effects in the experimental range of temperatures. In the radical-anion and radical-dianion, the electron is localised mainly in one nitro group, while in the radical-trianion the spin density is evenly distributed over the two nitro groups. The pK_a values of the radical-anions are in the range 8–11.

Introduction

Radical-anions of 2,6-[1,2] and 3,5-dinitrophenol[3] were generated by electrolysis in aprotic solvents and studied by EPR a long time ago. In these radicals the distribution of the spin densities is symmetric and mainly concentrated on the two nitrogen atoms. More recently, radicals derived from 2,4-dinitrophenol were generated in aqueous solution using a flow technique. The localisation of the spin density was found to change from the *ortho* nitro group to the *para* nitro group on changing from the radical-anion to the radical-dianion.[4]

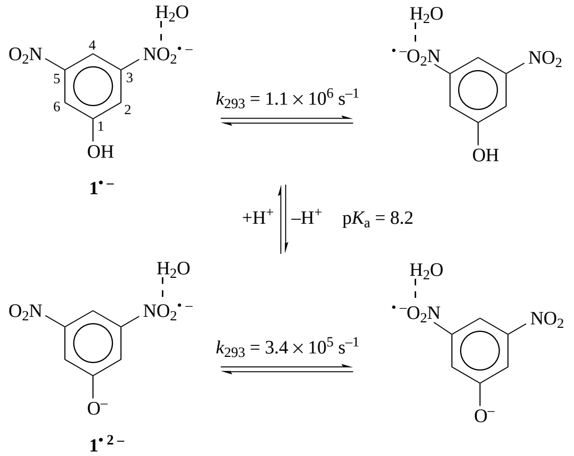
A significant change in the electronic structure of the radical-anions may occur in the transition from aprotic to protic media, as a result of change in the character of solvation. In radical-anions of symmetric 1,3-dinitrobenzenes[5,6] and 2,7-dinitronaphthalene[7] in protic solvents, the strong solvation of one nitro group through hydrogen bonding causes an asymmetric distribution of the spin densities on the nitrogen atoms, inducing slow intramolecular electron exchange between the two nitro groups. The rate constants determined by the analysis of the line broadening effects of the EPR spectra are in the fast region range ($k \sim 10^9$ s^{-1}) in aprotic solvents while in alcohols the exchange is slow ($k \sim 10^6$ s^{-1}) on the EPR timescale.[5–7]

With the aim of investigating the effects of the solvent and of the intramolecular hydrogen bonding on the rates of electron exchange, we generated in aqueous solution and studied by EPR spectroscopy the radical-anions of three symmetric dinitrophenols: 3,5-dinitrophenol **1**, 2,6-dinitrophenol **2** and 4,6-dinitrobenzene-1,3-diol **3**. The present work reports the distribution of the spin densities and the kinetics of the intramolecular electron exchange reaction, together with the pK_a values of the radicals.

Results and discussion

3,5-Dinitrophenol 1

The reduction of this compound at pH values in the range 6.7–8.2 yielded a radical whose EPR spectrum [Fig. 1(*a*)] showed two different nitrogen coupling constants and broadening of the corresponding lines. Above pH 8.2 another EPR spectrum became predominant [Fig. 1(*b*)], showing not only broadening of the lines due to the two nitrogens but also of those due to hydrogens in positions 2 and 4. The first spectrum was assigned to the radical-anion, $\mathbf{1}^{\bullet -}$, and the second one to its deprotonated form $\mathbf{1}^{\bullet 2-}$. Table 1 shows the values of *g*, those of the experimental hyperfine coupling constants of both radicals and the values of the constants of radical dianion $\mathbf{1}^{\bullet 2-}$ calculated by using the McLachlan method. The line broadening effects were interpreted as being caused by intramolecular electron exchange between the two nitro groups induced by the strong asymmetric solvation of one of them at a time. The existence of two different nitrogen coupling constants in both radicals (Table 1) indicates that the rate of the dynamic process in water (Scheme 1) is in the slow range of the EPR timescale whereas in acetonitrile it was found to be in the fast range ($k_{293} = 1.4 \times 10^9$ s^{-1} for $\mathbf{1}^{\bullet 2-}$).[8]



Scheme 1

At 293 K the reaction was found to be three times faster for the radical-anion $\mathbf{1}^{\bullet -}$ ($k = 1.1 \times 10^6$ s^{-1}) than for the radical dianion $\mathbf{1}^{\bullet 2-}$ ($k = 3.4 \times 10^5$ s^{-1}), as exhibited in Table 2. This fact agrees with the results obtained for radical-anions of 5-substituted 1,3-dinitrobenzenes in acetonitrile,[8] for which a

Table 1 Experimental and calculated EPR parameters and pK_a values of the radicals derived from dinitrophenols in aqueous solution at 293 K

			Hyperfine coupling constants/mT						
Radical	pK_a	g Value		a (N)		a (H)			
$\mathbf{1}^{\bullet -}$	8.2	2.00 454	exp.	1.290 N(3)	0.025 N(5)	0.348 H(2,6)		0.315 H(4)	
$\mathbf{1}^{\bullet 2-}$	—	2.00 456	exp.	1.402 N(3)	0.022 N(5)	0.320 H(2,6)		0.304 H(4)	
			calc.[a]	1.420 N(3)	0.039 N(5)	0.361 H(2)	0.311 H(6)	0.181 H(4)	
$\mathbf{2}^{\bullet -}$	10.7	2.00 455	exp.	1.373 N(2)	0.025 N(6)	0.413 H(3,5)		0.119 H(4)	0.048 H(OH)
			calc.[a]	1.428 N(2)	0.040 N(6)	0.355 H(3)	0.350 H(5)	0.116 H(4)	
$\mathbf{2}^{\bullet 2-}$	—	2.00 459	exp.	0.730 N(2,6)		0.436 H(3,5)		0.142 H(4)	
			calc.[a,b]	0.704 N(2,6)[c]		0.433 H(3,5)[d]		0.153 H(4)	
$\mathbf{3}^{\bullet -}$	9.9	2.00 464	exp.	1.278 N(4)	0.181 N(6)	0.612 H(5)	0.059 H(2)		
$\mathbf{3}^{\bullet 2-}$	11.0	2.00 494	exp.	1.658 N(4)	0.125 N(6)	0.352 H(5)	0.057 H(2)		
$\mathbf{3}^{\bullet 3-}$	—	2.00 473	exp.	0.707 N(4,6)		0.735 H(5)	0.030 H(2)		
			calc.[a]	0.690 N(4,6)[e]		0.670 H(5)	0.071 H(2)		

[a] McLachlan calculations[22] with $\gamma_{CN} = 1.0$, $\gamma_{NO} = 1.67$, $\gamma_{CO} = 1.0$, $\delta_N = 2.2$, $\delta_{O^-} = 2.0$, $\delta_O = 1.4$ (less solvated nitro group), $\delta_O = 1.84$ (more solvated nitro group); $Q^H{}_{CH} = -2.37$ mT, $Q^N = 8.9$ mT and $Q^N{}_{NO} = -4.2$ mT. [b] $\gamma_{C1\text{-}C2} = \gamma_{C1\text{-}C6} = 0.7$. [c] Mean value from $a_{N(2)} = 1.327$ and $a_{N(6)} = 0.082$ mT. [d] Mean value from $a_{H(3)} = 0.476$ and $a_{H(5)} = 0.390$ mT. [e] Mean value from $a_{N(4)} = 1.241$ and $a_{N(6)} = 0.138$ mT.

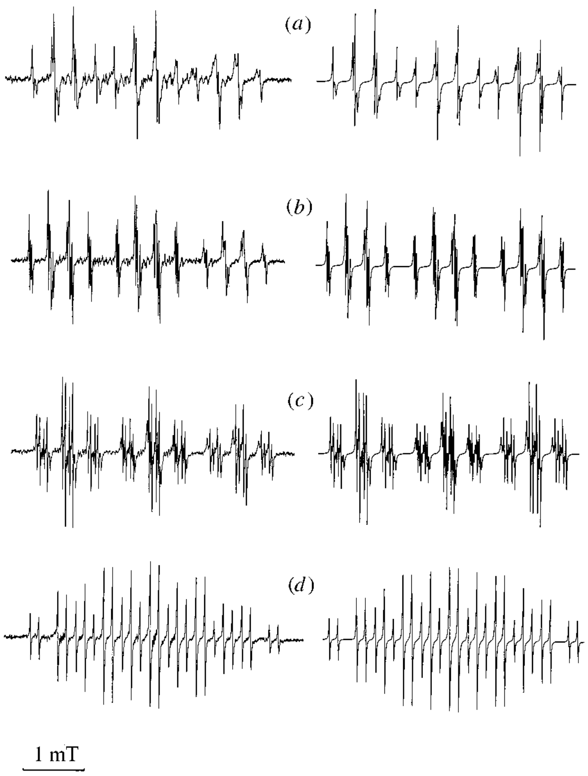


Fig. 1 Experimental EPR spectra obtained upon reduction of **1** and **2** in aqueous solution at 293 K (left-hand side) and corresponding simulations (right-hand side) with parameters shown in Tables 1 and 2. Spectra show asymmetric line-broadening which was not included in the simulations. (*a*) Spectrum assigned to $\mathbf{1}^{\bullet -}$, at pH = 6.4. (*b*) Spectrum assigned to $\mathbf{1}^{\bullet 2-}$, at pH = 11.6. (*c*) Spectrum assigned to $\mathbf{2}^{\bullet -}$, at pH = 7.8 (*d*) Spectrum assigned to $\mathbf{2}^{\bullet 2-}$, at pH = 12.9.

Table 2 Rate constants at 293 K and activation parameters for the intramolecular electron exchange reaction in radical anions and dianions of **1** and **2**

Radical	$k_{293\ K}$/s^{-1}	ΔG^*/kJ mol^{-1}	ln A
$\mathbf{1}^{\bullet -}$	1.1×10^6	42.9 ± 1.0	28.7
$\mathbf{1}^{\bullet 2-}$	3.4×10^5	46.0 ± 2.4	28.8
$\mathbf{2}^{\bullet -}$	9.9×10^5	36.1 ± 1.5	25.8
$\mathbf{2}^{\bullet 2-}$	4.9×10^{10}	12.6 ± 0.6	27.0

positive value of the Hammett constant was found for this reaction. Since the –O$^-$ group ($\sigma_m = -0.708$) is a stronger electron donor than the –OH group ($\sigma_m = 0.35$), the rate constant decreases when the radical anion is deprotonated.

The pK_a value of $\mathbf{1}^{\bullet -}$ was estimated as 8.2 from the pH dependence of the relative concentrations of the radical anion and radical-dianion. The value of the pK_a found for the radical-anion is, as expected, higher than that reported for the parent compound **1** (pK_a = 6.73),[9] showing the less acidic character of the more reduced species, and it is lower than the pK_a = 9.7 of 3-nitrophenol radical-anion[10] due to the presence of a second nitro group.

The line broadening effects depended on the temperature. Therefore, the rate constants at various temperatures were extracted from the computer simulations of the experimental EPR spectra (Fig. 1). The activation parameters were calculated by using the Marcus equation[11–13] and the Rip–Jortner approach[14] for a uniform and adiabatic reaction. As discussed in previous work[5,6] the expression of the rate constant for this type of reaction can be reduced to eqn. (1), with ΔG^* being

$$k = AT^{\frac{1}{2}}\exp(-\Delta G^*/RT) \qquad (1)$$

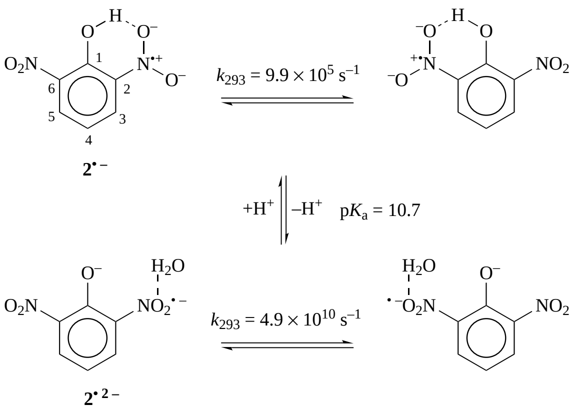
given by eqn. (2), where λ_i and λ_o are the inner-sphere and

$$\Delta G^* = \frac{\lambda_i + \lambda_o}{4} - H_{12} \qquad (2)$$

outer-sphere reorganisation energies and H_{12} is the resonance energy coupling. The pre-exponential factor, which depends only on the solvent parameters, was found to change very slightly within the range of temperatures used. Therefore, linear plots of ln($kT^{\frac{1}{2}}$) *vs.* T^{-1} allowed the estimation of the activation parameters ln$A$ and ΔG^*, shown in Table 2. The higher activation energy value estimated for $\mathbf{1}^{\bullet 2-}$ as compared with that for $\mathbf{1}^{\bullet -}$ agrees with our results on 5-substituted 1,3-dinitrobenzene radical-anions.[8]

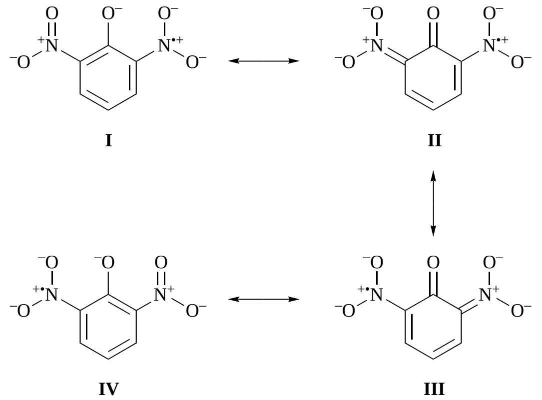
2,6-Dinitrophenol 2

On the reduction of this compound in the pH = 7–10 range, an EPR spectrum [Fig. 1(*c*)] was recorded which showed coupling constants of two non-equivalent nitrogens, a pair of equivalent hydrogens and another two non-equivalent hydrogens. This spectrum was assigned to the radical anion $\mathbf{2}^{\bullet -}$. The assignment of the hyperfine coupling constants shown in Table 1 raises no doubt. The value of 0.048 mT measured for the protonic constant of the hydroxyl agrees with that reported for the radical anion of 2-nitrophenol,[15] $a_{H(OH)} = 0.038$ mT. At room temperature the spectrum of $\mathbf{2}^{\bullet -}$ shows broadening of the lines corresponding to the two different nitrogen nuclei. A value of $k = 9.9 \times 10^5$ s^{-1} was estimated for the rate constant of intramolecular electron exchange in this radical.



Scheme 2

Above pH = 11.5 a totally different spectrum was obtained [Fig. 1(*d*)] with constants of a pair of equivalent nitrogens, a pair of equivalent hydrogens and another hydrogen. This radical was assigned to $\mathbf{2}^{\bullet 2-}$. Table 1 shows the experimental and calculated hyperfine coupling constants. In the spectra of $\mathbf{2}^{\bullet 2-}$ the nitrogen coupling constants are averaged and the broadening effects are very small. Since the values of the interchangeable nitrogen constants are unknown it is impossible to calculate accurately the rate constant of the intramolecular electron exchange reaction (Scheme 2). In spite of that, an estimation of the rate constants can be carried out by assuming a value of $\Delta a_N = 1.25$ mT based on the results of the HMO calculations for $\mathbf{2}^{\bullet 2-}$. This value of the fluctuation of the nitrogen coupling constants agrees with the value measured for $\mathbf{2}^{\bullet -}$ ($\Delta a_N = 1.35$ mT). With this approximation a value of $k = 4.9 \times 10^{10}$ s^{-1} was determined for the rate constant of the intramolecular electron exchange on $\mathbf{2}^{\bullet 2-}$ at 298 K. This value is unusually high and out of the range of the rate constants found for the same reaction on radical-anions of 1,3-dinitrobenzenes in protic solvents ($k = 10^5$–10^6 s^{-1}).[6,7] It is even higher than the rate constant measured for the radical-anion of 1,3-dinitrobenzene in acetonitrile ($k_{293} = 3.7 \times 10^9$ s^{-1}).[8] In contrast, the rate constant for the same reaction in $\mathbf{2}^{\bullet -}$ ($k = 9.9 \times 10^5$ s^{-1} at 293 K) is in the usual range found before for radical anions of 1,3-dinitrobenzenes in protic solvents (for instance, $k = 6.4 \times 10^5$ s^{-1} for 1,3-dinitrobenzene radical-anion in water, at 293 K).[16] The enormous increase of four orders of magnitude of the rate constant of intramolecular electron exchange on deprotonation of $\mathbf{2}^{\bullet -}$ to yield $\mathbf{2}^{\bullet 2-}$ cannot be explained exclusively by the disruption of the intramolecular hydrogen bond. The contribution of resonance structures **II** and **III** showing a delocalisation of the unpaired electron over the two nitro groups of $\mathbf{2}^{\bullet 2-}$ has to be taken into account.



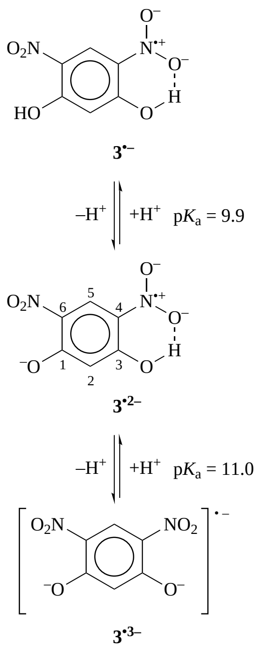
The importance of the contribution of the structures **II** and **III** to the resonance hybrid can be found in the interatomic distances determined by X-ray diffraction studies on crystals of potassium 2,6-dinitrophenolate.[17] According to the authors, the C1–C2 and the C6–C1 bonds ($d = 1.452$ Å) are the longest bonds found in benzenoid rings. In contrast, the other C–C bonds ($d = 1.385$ Å) are shorter than the typical bonds in benzene ($d = 1.395$ Å). This distortion of the benzenoid ring was taken into account in the HMO-McLachlan calculations. In the parent phenol **2**, the difference between the two types of bonds is not so pronounced.

The activation parameters ln*A* and ΔG^* shown in Table 2 were estimated for $\mathbf{2}^{\bullet -}$ and $\mathbf{2}^{\bullet 2-}$ in the same way as for $\mathbf{1}^{\bullet -}$ and $\mathbf{1}^{\bullet 2-}$. It is worth mentioning that although the accuracy of the rate constants in the radical dianion $\mathbf{2}^{\bullet 2-}$ depends on the assumed Δa_N value, the same does not apply to the activation energy ΔG^*, whose value is not affected by the uncertainty of Δa_N value, since parallel lines are obtained in the plot of $\ln(kT^{\frac{1}{2}})$ *vs.* $1/T$ for different values of Δa_N.[18,19] The values of the activation energy ΔG^* for the radicals derived from **2** are lower than for those originating from **1**. A justification may reside on the higher value of the resonance energy coupling H_{12} due to the delocalisation of the unpaired electron on the two nitro groups of $\mathbf{2}^{\bullet 2-}$ through structures **II** and **III**, as pointed out before. This type of delocalisation still exists in $\mathbf{2}^{\bullet -}$, although is much weaker.

The pK_a value of 10.7 determined for $\mathbf{2}^{\bullet -}$ is higher than the value of the pK_a of $\mathbf{1}^{\bullet -}$ due to the stabilisation of the former by intramolecular hydrogen bonding as it was found previously for the radical-anions of 2-nitrophenol (pK_a = 12.7) as compared with the radical-anion of 3-nitrophenol (pK_a = 9.7).[15]

4,6-Dinitrobenzene-1,3-diol 3

At pH = 8.5 the reduction of this compound yielded two radicals. The EPR spectrum of the dominant radical was characteristic of two non-equivalent nitrogens and two non-equivalent hydrogens [Fig. 2(*a*)]. There was no evidence of line broadening effects. Therefore, there was no intramolecular electron exchange on the EPR timescale. The spectrum was assigned to the radical-anion $\mathbf{3}^{\bullet -}$, which has the spin density localised mainly on one nitro group. The weakest spectrum, whose intensity increased with pH, was assigned to radical dianion $\mathbf{3}^{\bullet 2-}$.



Scheme 3

In strongly basic solutions (pH > 12.0) two overlapping spectra were observed [Fig. 2(*c*)]. The stronger one, which belongs to a radical in which the unpaired electron interacts with two non-equivalent hydrogens and a pair of equivalent

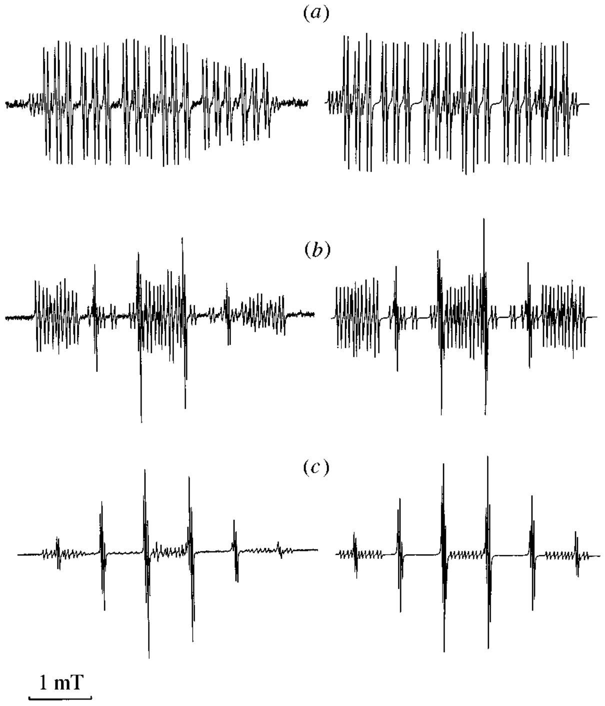


Fig. 2 Experimental EPR spectra obtained upon reduction of **3** in aqueous solution at 293 K (left-hand side) and corresponding simulations (right-hand side) with coupling constants shown in Table 1. (*a*) Spectrum at pH = 9.1 and simulation with 84% of **3**$^{\bullet -}$ and 16% of **3**$^{\bullet 2-}$. (*b*) Spectrum at pH = 10.6 and simulation with 14% of **3**$^{\bullet -}$, 55% of **3**$^{\bullet 2-}$ and 31% of **3**$^{\bullet 3-}$. (*c*) Spectrum at pH = 12.2 and simulation with 8% of **3**$^{\bullet 2-}$ and 92% of **3**$^{\bullet 3-}$.

nitrogen nuclei, was assigned to the radical trianion **3**$^{\bullet 3-}$, whereas the weak features belong to **3**$^{\bullet 2-}$.

In the intermediate range of pH values, the overlapping spectra of the three radicals were recorded [Fig. 2(*b*)]. Fig. 2 shows the spectra at different pH values together with their simulations for various relative abundances of the three radicals. The values of the experimental coupling constants are reported in Table 1, which includes the calculated constants for **3**$^{\bullet 3-}$.

In both radical-anion **3**$^{\bullet -}$ and radical-dianion **3**$^{\bullet 2-}$, where an intramolecular hydrogen bond exists (Scheme 3), the electron is localised mainly on one nitro group. In the radical trianion **3**$^{\bullet 3-}$, where the intramolecular hydrogen bonding is absent, the two nitro groups are equivalent and no line broadening effects are detected. In this radical, either the rate of electron exchange is too fast to be detected by EPR or the unpaired electron is symmetrically delocalised over the two nitro groups. The reason for this change in behaviour is the same as that found for **2**$^{\bullet 2-}$.

The pK_a values determined for **3**$^{\bullet -}$ and **3**$^{\bullet 2-}$ are 9.9 and 11.0, respectively. Since the two values are so close and three species are in equilibrium, the error in the determination of the pK_a values is considerable.

Experimental

Commercial 2,6-dinitrophenol **2** (Aldrich) was used without further purification. 3,5-Dinitrophenol[20] **1** and 4,6-dinitrobenzene-1,3-diol[21] **3** were prepared as described in the literature. All the inorganic chemicals were analytical grade.

Solutions were prepared in water purified by a Millipore Milli-Q50 system and contained typically 0.3–0.5 mM of the parent compound, 5% propan-2-ol and 5% acetone (v/v). Sodium hydrogen phosphate was used as a buffer. The solutions were previously deaerated with argon, thermostatted at constant temperature between 273 K and *ca*. 320 K, and allowed to flow through a quartz flat cell placed in the EPR cavity. Reductions were accomplished by *in situ* photolysis of the acetone–propan-2-ol system using an optically focused high pressure Hg-Xe lamp. EPR spectra were recorded by using a Bruker 200 D X-band spectrometer.

Computer simulations of EPR spectra were carried out by using our own program which solves the relevant Bloch equations for a two-jump model. Concentrations and lifetimes of the two asymmetrically solvated radicals in equilibrium were considered to be equal. Rate constants were determined by fitting the experimental spectra with the computer simulations for different rate constant inputs. For the pK_a determinations the relative concentrations of the radicals were estimated from the computer simulations of the overlapping spectra of the acid and basic forms.

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