Acidity of Two Dialkylhydrazine Radical Cations

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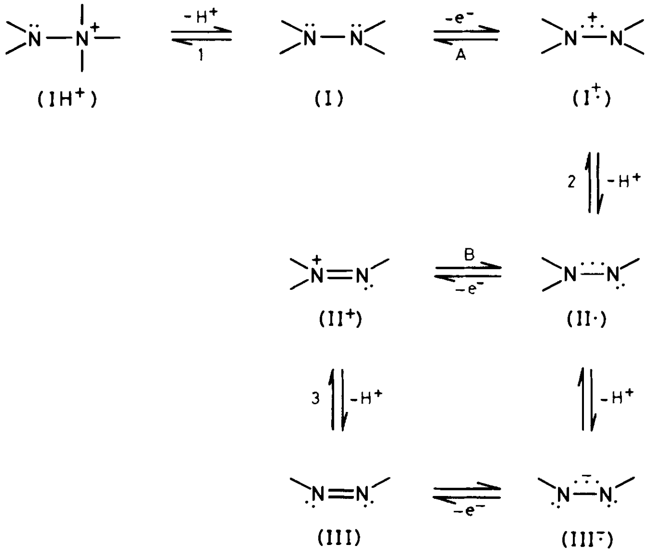
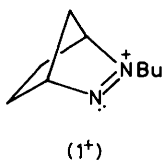
Pulse radiolysis reduction of 2,3-diazabicyclo[2.2.1]hept-2-ene (pK_a 7.93) and 2,3-diazabicyclo[2.2.2]-oct-2-ene in water was used to determine the pK_a values for the related dialkylhydrazine radical cations as 5.3 and 5.5 (± 0.5) respectively.

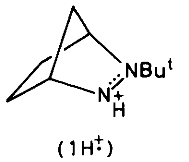
The oxidation of hydrazine derivatives to azo-compounds is a complex multistep process, shown as a network of electron- and proton-transfer steps in the Scheme. Considerable progress has been made in understanding both the thermodynamics and the kinetics of the first electron-transfer equilibrium A in non-aqueous solvents for tetra-alkyl derivatives (I).[1] Although neither (II$^\cdot$) nor (II$^+$) is usually long-lived, electron-transfer equilibrium B has been explored by employing long-lived trialkyl derivatives in which all α-hydrogens are held near the nodal plane of the *p* orbital at nitrogen.[2]



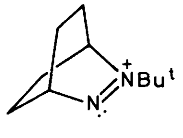
Scheme.



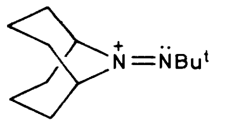
(1$^+$)



(1H$^{+\cdot}$)



(2$^+$)



(3$^+$)

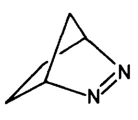
Less work has been done on the proton transfers. The (I)—(IH$^+$) equilibrium (1 in the Scheme) is only indirectly involved in the oxidation, because (IH$^+$) is far more difficult to oxidize than is (I), and only the latter is attacked under most conditions. No special measurement problems are involved, and the pK_a values of many hydrazines are known.[3] Evans and his co-workers have devised an electrochemical technique [4] which allows rate measurements to be made on equilibrium 1 in dimethyl sulphoxide, revealing significant conformational effects on the kinetics of proton transfer.[5] Equilibrium 3 is not very important for hydrazine oxidations either, because azo-compounds are such weak bases that they are not significantly protonated until very high acid concentrations are reached.[6]

In contrast, equilibrium 2 is obviously directly involved in NH-containing hydrazine oxidations, and its study is difficult. Not only are both (I$^{+\cdot}$) and (II$^\cdot$) paramagnetic and hence inherently reactive, but the electron-transfer equilibria A and B have unfavourable formal potentials for the study of the reaction. Species (I$^{+\cdot}$) is rapidly reduced at potentials where (II$^\cdot$) is formed from (II$^+$), and (II$^\cdot$) is rapidly oxidized at potentials where (I$^{+\cdot}$) is formed from (I). Electrochemical studies therefore show only multistep irreversible processes, from which essentially nothing is learned about the intermediate proton transfer, equilibrium 2.

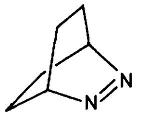
The technique of pulse radiolysis, in which a burst of accelerated electrons impinges upon a water sample, rapidly producing (*inter alia*) known concentrations of hydroxyl radicals and solvated electrons, provides a solution to the relative redox-potential problem. Hayon and Simic [7] used hydroxyl radical oxidation of hydrazine and 1,1-dimethylhydrazine to measure pK_a values of their radical cations using optical absorption changes to monitor the reaction. The reactivity of hydroxyl radicals toward CH bonds and the fact that several absorbing species are produced make interpretation of such experiments difficult for substituted hydrazines. We previously employed reduction of trialkyldiazenium cations by solvated electrons to generate hydrazine radical cations I$^{+\cdot}$ by sequence (i). A large excess of (II$^+$) over e_{aq}^-

$$(\mathrm{II}^+) \xrightarrow{e_{aq}^-} (\mathrm{II}^\cdot) \overset{\mathrm{H}^+}{\rightleftharpoons} (\mathrm{I}^{+\cdot}) \qquad \text{(i)}$$

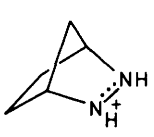
ensures that the electrons are scavenged by (II$^+$) and not available for reduction of (I$^{+\cdot}$). The (II$^\cdot$)-(I$^{+\cdot}$) equilibrium (equilibrium 2) has been shown to be rapidly established relative to destruction of these species by other processes, allowing pK_a (I$^{+\cdot}$) to be measured by observing conductivity changes after the pulse as a function of pH. This method was applied to (1$^+$)-(1H$^{+\cdot}$) as well as (2$^+$)-(2H$^\cdot$) and (3$^+$)-(3H$^\cdot$).[8] This experiment requires that (II$^+$) be stable in aqueous acid and base, which proves only to be true for compounds with special alkyl groups, known examples of which all bear a t-



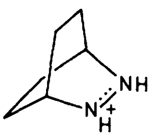
(4)



(5)



$(4\mathrm{H}_2^{+\cdot})$



$(5\mathrm{H}_2^{+\cdot})$

butyl substituent at nitrogen. To determine how important the effect of the bulky t-alkyl substituent actually is in determining the pK_a of the hydrazine radical cations ($\mathrm{I}^{+\cdot}$), we desired a way of generating less highly substituted examples from acid- and base-stable precursors, which requires that a different approach be used. This paper reports a pulse radiolysis study on bicyclic azo-compounds (4) and (5), from which we generated the related dialkylhydrazine radical cations ($4\mathrm{H}_2^{+\cdot}$) and ($5\mathrm{H}_2^{+\cdot}$) *via* sequence (ii). This method of generation could in principle also measure pK_a ($\mathrm{II}^{\cdot}$), but in practice this pK_a was too high for measurement.

$$(\mathrm{III}) \xrightarrow{e_{aq}^-} (\mathrm{III}^{-\cdot}) \overset{\mathrm{H}^+}{\rightleftharpoons} (\mathrm{II}^{\cdot}) \overset{\mathrm{H}^+}{\rightleftharpoons} (\mathrm{I}^{+\cdot}) \qquad \text{(ii)}$$

Results

Our experiments were carried out on 10^{-4}M solutions of (4) and (5) in water, and the initial pH was changed by adding aqueous $HClO_4$ or NaOH solutions. The pulse of fast electrons generates species, as shown in equation (iii) (all species are understood to be solvated by water under our conditions). Although hydrogen and hydrogen peroxide are far too unreactive to cause problems, and relatively few hydrogen atoms are formed above pH 5, it is necessary to remove the very reactive hydroxyl radical to preclude it from reacting with the azo-compound. This was accomplished by adding 0.1M-t-butyl or isopropyl alcohol to the solution. Hydroxyl radicals abstract a hydrogen atom from the alcohol, generating a carbon-centred radical as illustrated for t-butyl alcohol in equation (iv). These reactions are known to be rapid enough that the hydroxyl radical is efficiently scavenged. Although the radicals generated are quite reactive with themselves, they neither reduce the azo-compound nor are they rapidly reduced by solvated electrons, so they do not interfere with the conductivity measurements (see below).

$$\mathrm{H_2O} \longrightarrow e_{aq}^- + \mathrm{H}^+ + \mathrm{OH}^{\cdot} + \mathrm{H}^{\cdot} + \mathrm{H_2} + \mathrm{H_2O_2} \qquad \text{(iii)}$$

$$\mathrm{HO}^{\cdot} + \mathrm{(CH_3)_3COH} \xrightarrow{k_{iv}} \mathrm{H_2O} + {}^{\cdot}\mathrm{CH_2(CH_3)_2COH} \qquad \text{(iv)}$$

The first requirement for using azo-compounds as hydrazine radical cation precursors is that they react rapidly enough with solvated electrons so that the electrons are effectively scavenged, allowing the concentration of ($\mathrm{III}^{-\cdot}$), ($R_2N_2^{-\cdot}$), and its protonation products to be determined from the known concentration of solvated electrons produced by the pulse. This was established by monitoring the disappearance of the solvated electron absorption at 650 nm in the presence of an excess of azo-compound. The 650 nm absorption proved to decrease exponentially with the half-life decreasing linearly with the azo-compound concentration ([R_2N_2] *ca.* 10^{-5}—10^{-4}M, pH *ca.* 6) [equation (v)], and the k_v values thus determined were 2.3×10^{10} l mol^{-1} s^{-1} for (4) and 2.0×10^{10} l mol^{-1} s^{-1} for (5).

$$e_{aq}^- + \mathrm{R_2N_2} \xrightarrow{k_v} \mathrm{R_2N_2}^{-\cdot} \qquad \text{(v)}$$

It would be possible to try to measure the amounts of hydrazyl and hydrazine radical cations produced by protonation of $R_2N_2^{-\cdot}$ by using optical absorption, but these species should have very similar absorption spectra, as has already been established for their trialkyl analogues ($1\mathrm{H}^{+\cdot}$)-($1^{\cdot}$) and ($2\mathrm{H}^{+\cdot}$)-($2^{\cdot}$).[8] Absorption peaking at about 260 nm was observed after the pulse, indicating that hydrazyls and/or hydrazine radical cations are indeed produced. The azo-radical anions $R_2N_2^{-\cdot}$ should have longer-wavelength absorption, but a peak attributable to such species was never observed in our experiments, which is consistent with the conductivity results discussed below.

Because of the similarity of $R_2N_2H^{\cdot}$ and $R_2N_2H_2^{+\cdot}$ absorption spectra, conductivity changes give a far better way of measuring the ratio of these two species as a function of pH. The reactions necessary for considering the conductivity changes at pH > 7 are (iii) and (v)—(viii). In base, the proton produced in the radiolysis is very rapidly consumed by equation (vi), and the electron by equation (v), so if the azo-radical anion were not protonated, one would observe the sum of equations (iii), (v), and (vi), and $\Delta\Lambda$ would be $-\Lambda(\mathrm{OH}^-) + \Lambda(\mathrm{R_2N_2}^{-\cdot})$, a negative number because hydroxide has a higher specific conductivity than an organic anion. Experimentally, however, $\Delta\Lambda$ is zero in the entire range 7.5—10.5 (the conductivity-change measurement becomes difficult at pH > 10.5) implying that pK_a ($R_2N_2H^{\cdot}$) is greater than 11, because $\Delta\Lambda = 0$ is expected if equation (vii) lies entirely to the right, but equation (viii) lies to the left.

$$\mathrm{H}^+ + \mathrm{OH}^- \rightleftharpoons \mathrm{H_2O} \qquad \text{(vi)}$$

$$\mathrm{R_2N_2}^{-\cdot} + \mathrm{H_2O} \rightleftharpoons \mathrm{R_2N_2H}^{\cdot} + \mathrm{OH}^- \qquad \text{(vii)}$$

$$\mathrm{R_2N_2H}^{\cdot} + \mathrm{H_2O} \rightleftharpoons \mathrm{R_2N_2H_2}^{+\cdot} + \mathrm{OH}^- \qquad \text{(viii)}$$

The observed conductivity change becomes negative as the pH is lowered below 7, as expected if $R_2N_2H^{\cdot}$ protonates in acidic solutions. Below pH 7, the protonations will be by H^+, so equations (vii) and (viii) should be replaced by (viia) and (viiia). At a low enough pH for equation (viiia) to lie entirely to the right, $\Delta\Lambda$ will be $-\Lambda(\mathrm{H}^+) + \Lambda(\mathrm{R_2N_2H_2}^{+\cdot})$, or -315 Ω^{-1} cm^2 + *ca.* 40 Ω^{-1} cm^2, so a limiting value of *ca.* -275 Ω^{-1} cm^2 is predicted. This would produce a simple titration curve, with $\Delta\Lambda$ ranging from -275 at low pH, where only $R_2N_2H_2^{+\cdot}$ is present, to 0 at higher pH, where only $R_2N_2H^{\cdot}$ is present, and pK_a ($R_2N_2H_2^{+\cdot}$) would be the pH at the point of inflection of this curve.

$$\mathrm{R_2N_2}^{-\cdot} + \mathrm{H}^+ \rightleftharpoons \mathrm{R_2N_2H}^{\cdot} \qquad \text{(viia)}$$

$$\mathrm{R_2N_2H}^{\cdot} + \mathrm{H}^+ \rightleftharpoons \mathrm{R_2N_2H_2}^{+\cdot} \qquad \text{(viiia)}$$

Using the above equilibrium equations for conductivity requires that the reaction mixtures be at equilibrium. Even with rapid reaction rate constants this requires a significant period of time because the pulse generates *ca.* 10^{-6}M protons and electrons. Illustrating this, and the competition between H^+ and R_2N_2 for e^- as a function of pH, Figure 1 shows a plot of simulated $\Delta\Lambda$ *versus* pH for the 10^{-4}M-R_2N_2 employed in these experiments, using the known rate constants for equations (vi) and (ix),[9] forward rate constants of 10^{10}

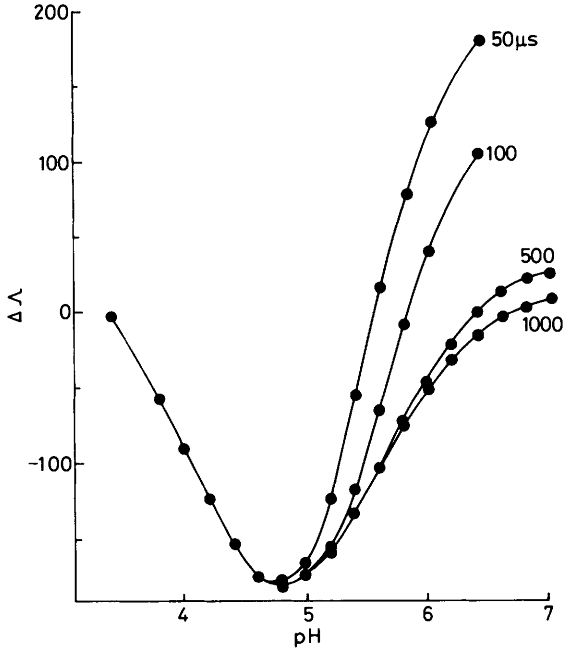


Figure 1. Calculated ΔΛ *versus* pH curve for a 10^{-4}M-R_2N_2 sample with pK_a ($R_2N_2H^\cdot$) 11 and pK_a ($R_2N_2H_2^{+\cdot}$) 5.5 for time intervals of 50, 100, 500, and 1 000 μs after the pulse (see text for rate constants employed) (ΔΛ in Ω^{-1} cm^2)

(diffusion controlled) for equations (viia) and (viiia), and backward rate constants to make pK_a ($R_2N_2H_2^{+\cdot}$) 5.5 and pK_a ($R_2N_2H^\cdot$) 11 (this pK_a is probably greater than 11, but its value does not affect ΔΛ below pH 7). The simulation is given for various time delays after the pulse, and it is seen that hundreds of microseconds are required for the system to reach equilibrium; the experimental plots of ΔΛ *versus* delay time show the same trend, ΔΛ changing rapidly at first, but levelling out after *ca.* 500 μs and becomes constant on a 10 ms timescale plot. Values obtained after 1 ms were used in our estimates of pK_a ($R_2N_2H_2^{+\cdot}$).

The observed ΔΛ *versus* pH curve, however, decreases only to *ca.* −150 as the pH is lowered, and then increases again as the pH is lowered further. One of the reasons for the observed increase in ΔΛ at lower pH could be associated with a competing process, namely the conversion of hydrated electrons into hydrogen atoms *via* reaction (ix). Assuming that H$^\cdot$ atoms

$$H^+ + e_{aq}^- \xrightarrow{k_{ix}} H^\cdot \qquad \text{(ix)}$$

do either not react with the azo-compound or in case of a reaction produce only non-conducting products (*e.g.* in a hydrogen-atom-abstraction process) theoretical curves of ΔΛ *versus* pH (shown as solid lines in the Figures) could be calculated on the basis of a competition between reactions (v) and (ix) (k_{ix} 2.4 × 10^{10} l mol^{-1} s^{-1} [9]).

Figure 2 shows the experimental ΔΛ *versus* pH points for radiolysis of (4) using both t-butyl alcohol (triangles) and isopropyl alcohol (squares) as hydroxyl-radical scavenger. Data from four separate experiments are shown in Figure 2, and it will be seen that irreproducibility is a problem. The solid line is in this case a simulation employing k_v 2.3 × 10^{10} l mol^{-1} s^{-1} and pK_a ($4H_2^{+\cdot}$) 5.3. The points above pH 5 fit this curve reasonably well, but the low-pH points show tremendous scatter in ΔΛ.

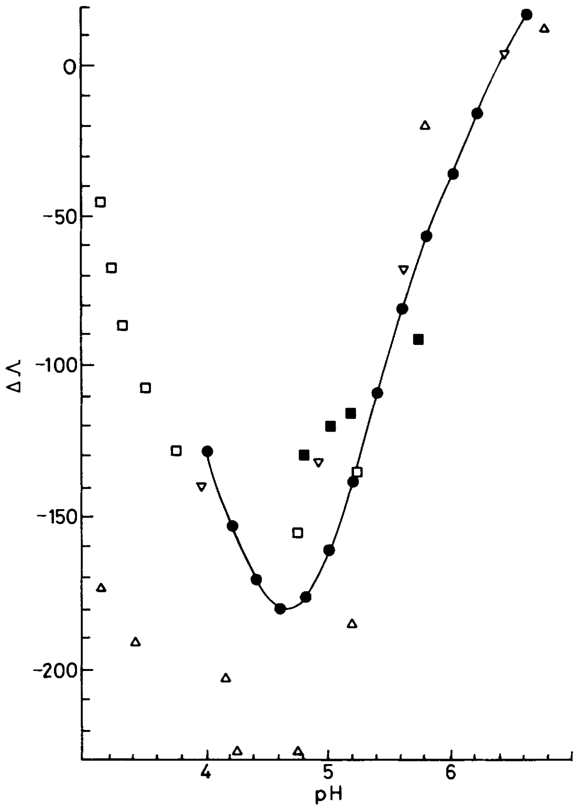


Figure 2. ΔΛ *versus* pH plot for pulse radiolysis of 10^{-4}M-(4) in water containing isopropyl alcohol (squares) or t-butyl alcohol (triangles), displayed along with the curve calculated (—●—) as in Figure 1 for pK_a ($4H_2^{+\cdot}$) 5.3, k_v 2.3 × 10^{10} l mol^{-1} s^{-1} (ΔΛ in Ω^{-1} cm^2)

Corresponding data for compound (5) are shown in Figure 3. Again, a good fit between the experimental data and the curve calculated with k_v 2.0 × 10^{10} l mol^{-1} s^{-1} and pK_a ($5H_2^+$) 5.5 is obtained only at the high-pH side. At the low-pH side the observed decrease in conductivity (relative to the prepulse zero value) is found to be considerably smaller than predicted on the basis of the competition scheme discussed above. A possible explanation would be provided by a protonation equilibrium of the parent azo-compound ($R_2N_2 + H^+ \rightleftharpoons R_2N_2H^+$) and the fact that the resulting reaction sequence $R_2N_2H^+ + e_{aq}^- \longrightarrow R_2N_2H^\cdot$ followed by $R_2N_2H^\cdot + H^+ \longrightarrow R_2N_2H_2^{+\cdot}$ would not result in any significant change of conductivity. Although it seems that protonation of such azo-compounds requires rather high proton concentrations [6] it can on the other hand be expected that the rate for $e_{aq}^- + R_2N_2H^+$ is faster than for $e_{aq}^- + R_2N_2$. The former reaction may therefore already come into play at a pH *ca.* 2 units above the pK of the azo-compound. In addition, the buffer capacity of such an acid–base system would further reduce the measurable conductivity changes near the pK of the parent compound.[10] A more positive conductivity signal than expected could, of course, also result from the formation of some free, *i.e.* highly conducting, protons in a possible reaction of compound (5) with hydrogen atoms or from a, however, still only small yield (at the time of measurement) of decay products from the radicals.

In conclusion, it is not possible at present to quantify the low-pH part of the ΔΛ *versus* pH curves. It seems justified, however, to consider the high-pH side a true measure of the protonation equilibria according to equation (viiia). From the theoretical halfpoints at ΔΛ = 0.5 × (−275) = −137.5 Ω^{-1} cm^2 we estimate pK_a 5.3 ± 0.5 and 5.5 ± 0.5 for ($4H_2^{+\cdot}$) and ($5H_2^{+\cdot}$), respectively.

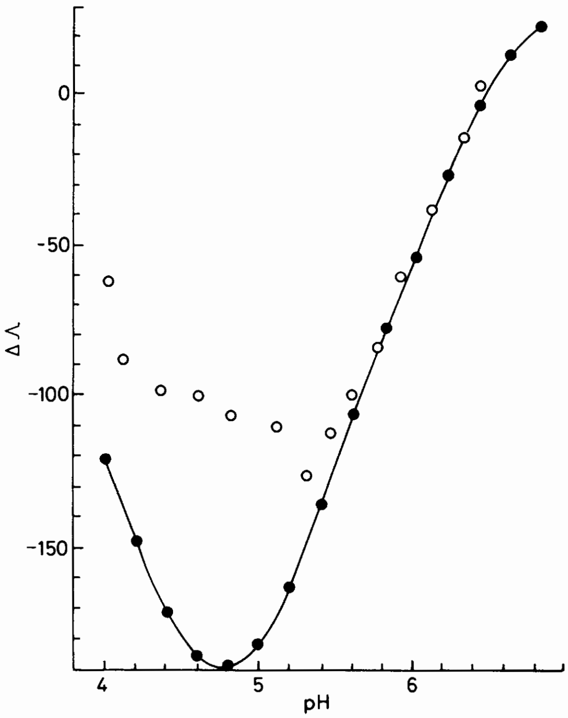


Figure 3. ΔΛ *versus* pH plot for pulse radiolysis of 10^{-4}M-(5) in water containing 0.1M-t-butyl alcohol displayed along with the curve calculated (—●—) as in Figure 1 for pK_a ($4H_2^+$) 5.5, k_v 2.0 × 10^{10} l mol^{-1} s^{-1} (ΔΛ in Ω^{-1} cm^2)

Hydrazine radical cations and protonated hydrazine pK_a values

Radical cation	pK_a	Protonated hydrazine pK_a	pK_a (Hyd H$^+$) − pK_a (Hyd$^{+\cdot}$)
$(H_2NNH_2)^{+\cdot}$	7.1 ± 0.1 [a]	8.07	+1.0
$(Me_2NNH_2)^{+\cdot}$	7.9 ± 0.2 [a]	7.21	−0.7
($4H_2^{+\cdot}$)	5.3 ± 0.5 [b]	7.93 [c]	+2.6
($5H_2^{+\cdot}$)	5.5 ± 0.5 [b]		
($1H^{+\cdot}$)	7.0 ± 0.4 [c]	9.14 [c]	+2.1
($2H^{+\cdot}$)	8.3 ± 0.2 [c]	9.51 [c]	+1.2
($3H^{+\cdot}$)	10.4 ± 0.2 [c]	7.8 [c]	−2.6

[a] Ref. 7. [b] This work. [c] Ref. 8.

Discussion

The Table compares pK_a values for hydrazine radical cations and protonated hydrazines. The changes are not very regular, suggesting that opposing factors are involved where hydrogens are replaced by various alkyl groups. Replacing one NH of ($4H_2^{+\cdot}$) by a t-butyl group to give ($1H^{+\cdot}$) increases the pK_a by *ca.* 1.7 units. Given the rather large experimental errors, this may not be significantly different from the increase in pK_a of 1.2 of the corresponding protonated hydrazines. We previously discussed the large increase in hydrazine radical cation pK_a for ($3H^{+\cdot}$),[8] attributing it to increased NN bond twist in the hydrazyl relative to the hydrazine radical cation. Large twist differences in the other t-butylated hydrazyls ($1H^\cdot$) and ($2H^\cdot$) and their protonated forms are presumably precluded by the bicyclic alkyl groups in these systems. The saturated alkylhydrazine radical cations discussed here have pK_a values ranging over 4.9 pK units. It can be seen from the Table that knowing the pK_a for the protonated hydrazine (which is easy to measure) is not of much use in accurately predicting pK_a for the hydrazine radical cation, as differences of ±2.6 units have been observed.

The second deprotonation ($R_2N_2H^\cdot \rightleftharpoons R_2N_2^{-\cdot}$) has a p$K_a$ > 5.5 units greater than the first deprotonation ($R_2N_2H_2^{+\cdot} \rightleftharpoons R_2N_2H^\cdot$) of hydrazine radical cations; the azo-radical anions ($4^{-\cdot}$) and $5^{-\cdot}$) are too basic for measurement of these pK_a values by the method used here. This is probably not surprising, considering what is known about the two deprotonations of the semiquinone radical derived from 1,4-dihydroxybenzene. The second deprotonation [$HOC_6H_4O^\cdot \rightleftharpoons (OC_6H_4O)^{-\cdot}$, p$K_a$ 4.0 [11]] has a pK_a 4.8 units higher than the first deprotonation [$(HOC_6H_4OH)^{+\cdot} \rightleftharpoons HOC_6H_4O^\cdot$, p$K_a$ −0.8 [12]]. We would expect a larger ΔpK_a for the smaller hydrazine π system.

Experimental

The azo-compounds (4) and (5) were prepared by literature methods.[13]

The pulse radiolysis equipment (1.55 MeV Van de Graaff generator at the Hahn-Meitner-Institut, Berlin) with optical and 10 MHz a.c. conductivity detection has been described.[14] The dose per 1 μs pulse was typically 3 Gy (3 J kg^{-1} or 300 rad), corresponding to *ca.* 1 × 10^{-6}M of primary reducing radicals. Oxygen was removed by bubbling nitrogen through the solutions. Measurements were at room temperature (20—25 °C). The data obtained were digitized by a Biomation 8100 transient recorder and analysed on-line with a PDP 11 computer. The Runge–Kutta method [15] was used for calculations of concentrations of the various species.

Acknowledgements

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