U.v.–visible and E.s.r. Probing of the Reactions of the Photogenerated *p*-Nitrobenzyl Anion in Aqueous Media

Bruce B. Craig and M. Dale Pace

Code 6546 and Code 6120, Naval Research Laboratory, Washington, DC 20375, U.S.A.

U.v.–visible and e.s.r. probing of the photogenerated *p*-nitrobenzyl anion in aqueous media indicate that dimerisation may be a prominent decay mode; this is followed by electron transfer to the parent nitroaromatic.

There is considerable current interest in the unique photochemistry exhibited by nitroaromatic compounds in aqueous media.[1—5] Among this class of reactions is the photodecarboxylation of nitrophenylacetate anions (at $pH > 4$), which yields CO_2 and the corresponding nitrobenzyl anion as the primary dissociation products.[6] Employing short-pulse laser spectroscopy, we have recently postulated that, for *p*-nitrophenylacetate, decarboxylation occurs *via* a photoadiabatic mechanism to produce initially CO_2 and the triplet state of the *p*-nitrobenzyl anion.[7] The mechanism by which the *p*-nitrobenzyl anion generates the major isolable product, *p,p'*-dinitrobibenzyl (*p*-nitrotoluene is a minor product), has remained unclear. Here, we have used u.v.–visible and e.s.r. spectroscopy to monitor the decay kinetics of the *p*-nitrobenzyl anion. A mechanism is formulated which accounts for its transformation to the bibenzyl product.

The *p*-nitrobenzyl anion is characterised in aqueous solution by its intense u.v.–visible absorption ($\lambda_{max.}$ 356 nm).[6,7] Following excitation of aqueous *p*-nitrophenylacetate (10^{-5}—5×10^{-3} M, $pH > 6$) solutions with a 150 W xenon (*ca.* 10 ms pulse) or a 500 W mercury (1.4 s) flashlamp and a 7–54 Corning filter, we have followed the decay kinetics of the anion in a Cary 219 spectrophotometer. For N_2-saturated 10^{-5} M solutions with anion concentrations of < *ca.* 3×10^{-6} M

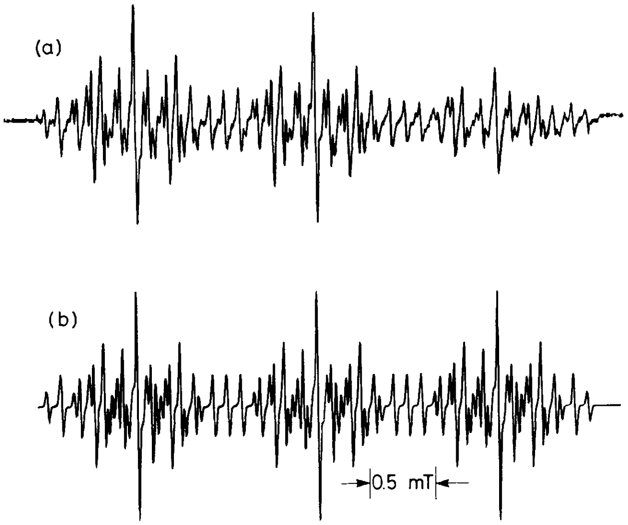

Figure 1. (a) The experimental e.s.r. spectrum of the *p*-nitrophenylacetate radical anion recorded immediately after a 1.4 s (500 W Hg lamp with 7–54 filter) irradiation of a 5×10^{-3} M aerated solution of *p*-nitrophenylacetic acid at pH 11 (pathlength 0.25 mm). The spectrum was recorded with a magnetic field sweep of 5 mT and sweep time of 10 s. Broadening of the high field $m_I = +1$ ^{14}N hyperfine coupling component is observed due to weak immobilisation of the radical anion in solution. (b) A computer simulation of the spectrum in (a) with a linewidth of 0.023 mT and hyperfine couplings: $a(^{14}N) = 1.42$ mT; $a(^{1}H$ *ortho*$) = 0.34$ mT; $a(^{1}H$ *meta*$) = 0.11$ mT; $a(^{1}H$ benzyl$) = 0.26$ mT.

[as determined by the initial optical density (o.d.) at 356 nm] the anion was remarkedly long-lived; it decayed with a first-order rate constant of 1.3×10^{-2} s^{-1}. In O_2-saturated solution the rate of decay was only slightly faster, 2.4×10^{-2} s^{-1}; a rate constant of 7.8 mol^{-1} dm^{3} s^{-1} for reaction of the anion with O_2 was determined. Below pH 5, protonation of the anion becomes significant and an enhanced decay rate was observed. When produced in larger concentrations, either through the use of higher *p*-nitrophenylacetate concentrations or higher flash intensities (while maintaining a relatively low overall % photodecomposition), the decay kinetics of the anion were distinctly nonexponential and exhibited a second order component. The decay curves are well fitted by a rate law of the form $dA/dt = -k_1A - k_2A^2/2$, where $k_1 = 1.3 \times 10^{-2}$ s^{-1}. The second order component dominated in the limit of high photolysis yields. Since no new transient species were observed under these conditions, we suggest that the second order decay represents dimerisation of the *p*-nitrobenzyl anion, which for high concentrations of the anion is competitive with the first order solvent protonation reaction.

There has also been considerable interest in the reactions of *p*-nitrobenzyl anions produced from *p*-nitrotoluene in highly basic nonaqueous media.[8—10] In these systems, *p,p'*-dinitrobibenzyl is again the major final product and the radical anion of *p*-nitrotoluene is detected (by e.s.r. spectroscopy) as a reduction product.[8] Following irradiation (1.4 s Hg flashlamp) of *p*-nitrophenylacetate ($>10^{-3}$ M) solutions in a Bruker TE_{102} e.s.r. cavity, we have observed an intense e.s.r. signal (Figure 1),[11] which is readily assigned to the radical anion of *p*-nitrophenylacetate.[12] In N_2-saturated solutions at pH 11.0, the radical anion had a lifetime of *ca.* 70 s and a delayed onset of formation. There is good qualitative agreement between the initial decay of the optically monitored *p*-nitrobenzyl anion and the rate of rise of the e.s.r. signal. It is concluded that the rate determining step in the production of the radical anion is the decay of the *p*-nitrobenzyl anion,† which has a significant second order component under these conditions. The importance of this component is substantiated by the fact that no e.s.r. signal was observed following irradiation of 10^{-5}—10^{-4} M solutions of *p*-nitrophenylacetate, *i.e.*, under conditions for which the optical data indicate that the *p*-nitrobenzyl decay is predominantly first order. The *p*-nitrophenylacetate radical anion, like many nitroaromatic radical anions,[13] has an absorption maximum at *ca.* 300 nm (and a much weaker one at 430 nm).[14] The large parent ground state absorption in this region, however, prevents us from optically monitoring the formation and decay of the radical anion.

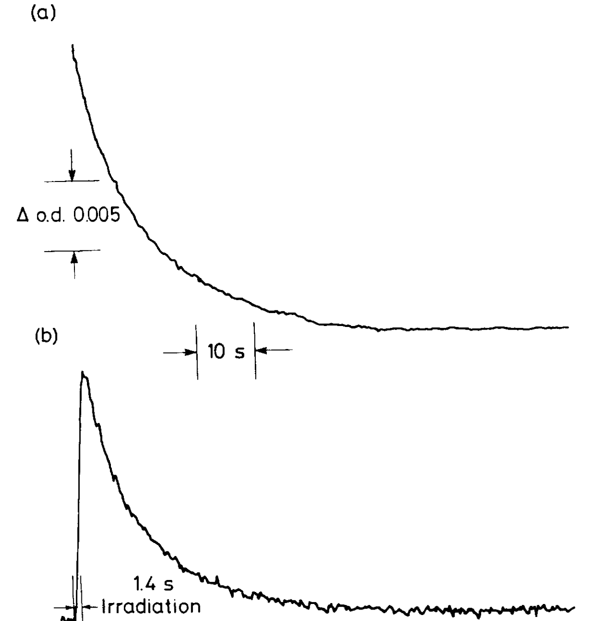

Figure 2. Time histories of (a) the *p*-nitrobenzyl anion absorption at 356 nm, *ca.* 5 s after irradiation of a 5×10^{-3} M aerated solution of *p*-nitrophenylacetic acid at pH 11.0, pathlength 0.2 mm; and (b) the e.s.r. signal of the *p*-nitrophenylacetate radical anion produced under the conditions in Figure 1.

To account for our observations we propose that the decay of the *p*-nitrobenzyl anion involves competition between protonation (first order) and dimerisation (second order) to yield the bibenzyl dianion, equations (1) and (2).‡ This species will then undergo electron transfer[13] to the most abundant electron acceptor in the system, *i.e.*, the parent *p*-nitrophenylacetate, equation (3) (probably *via* a two-step process). The

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† During the 1.4 s irradiation, the *p*-nitrobenzyl anion may itself be subject to excitation. Potentially, it may undergo photoionisation to yield the *p*-nitrobenzyl radical and the hydrated electron, scavenging of which by the parent compound would provide an alternative route to the *p*-nitrophenylacetate radical anion. Under our conditions this reaction would proceed with a pseudo first order rate of $>2 \times 10^{7}$ s^{-1}.[13,14] This route, however, does not account for the continued production of the radical anion several seconds after the irradiation period.

‡ Russell *et al.*[8] have also suggested that a dianion may be generated following formation of a charge transfer complex between the *p*-nitrobenzyl anion and the parent nitroaromatic, with subsequent loss of a proton. Our studies have demonstrated that this pseudo first order reaction is not a significant decay channel for the *p*-nitrobenzyl anion in our system.

electron transfer reactions of nitroaromatic radical anions in aqueous solutions have recently been investigated using the pulse radiolysis technique.[13] From these studies, we estimate that $k_3 = 10^6$ mol^{-1} dm^3 s^{-1}; at 5×10^{-3} M p-nitrophenylacetate, this corresponds to a first order rate of 5×10^3 s^{-1}. Consistent with our observations, then, equation (2) is the rate limiting step in production of the p-nitrophenylacetate radical anion. p,p'-Dinitrobibenzyl is the other product of the electron transfer reaction, observed in aqueous solutions as a pale yellow precipitate.

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^- + \text{H}_2\text{O} \rightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 + \text{OH}^- \tag{1}$$

$$2\,p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^- \rightarrow [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p]^{2-} \tag{2}$$

$$[p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p]^{2-} \xrightarrow{2\,p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CO}_2^-} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p + 2\,[p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CO}_2]^{\cdot-} \tag{3}$$

$$[p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CO}_2]^{\cdot-} + \text{O}_2 \rightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CO}_2^- + \text{O}_2^{\cdot-} \tag{4}$$

In aerated or O_2-saturated solutions, while the decay of the p-nitrobenzyl anion is essentially unchanged, the parent radical anion undergoes electron transfer to yield the superoxide ion[12b,13] with a rate constant of *ca.* 10^6 mol^{-1} dm^3 s^{-1},[13] equation (4). Under these conditions, the radical anion will have a lifetime in the millisecond range; *i.e.*, its rate of decay is faster than its rate of formation. Consequently, the decay of the e.s.r. signal is governed by the rate of formation of the p-nitrophenylacetate radical anion, *i.e.*, the rate of decay of the p-nitrobenzyl anion. This is demonstrated in Figure 2 and provides additional support for our mechanism.

In a concurrent communication,[15] Muralidharan and Wan have suggested that photogeneration of the p-nitrobenzyl anion and subsequent electron transfer reactions provide a convenient technique for generating nitroaromatic radical anions in aqueous media. In support of this, we have observed the e.s.r. spectrum of the p-nitrotoluene radical anion (minor product) following prolonged u.v. irradiation of p-nitrophenyl acetate solutions at neutral pH.[11]

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