Kinetic and Spectral Properties of the Photogenerated *p*-Nitrobenzyl Carbanion in Aqueous Media

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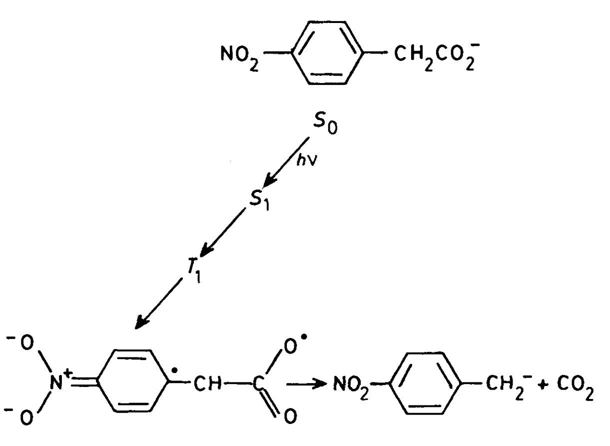
The *p*-nitrobenzyl carbanion is a photoelimination product from various *p*-nitrobenzyl (p-$NO_2C_6H_4CH_2R$, R = CO_2^-, PO_3^{2-}, CH_2OH, *etc.*) compounds in aqueous media. Following millisecond flash photolysis of N_2-saturated *p*-nitrophenylacetate (pH > 6) solutions, we have shown that the carbanion decays *via* mixed first-(solvent protonation) and second-(dimerisation) order processes. Rate constants $k_1 = 1.3 \pm 0.1 \times 10^{-2}\ s^{-1}$ and $2k_2 = 1.7 \pm 0.3 \times 10^{3}\ dm^3\ mol^{-1}\ s^{-1}$, respectively, are determined. Reactions of the anion with O_2, H^+, and an efficient one-electron oxidant, $IrCl_6^{2-}$, are also examined. Studies in dimethyl sulphoxide–water mixtures indicate that the anion exists as a hydrated form (λ_{max} 356 nm) in water and an 'unspecifically' solvated species in dimethyl sulphoxide (λ_{max} *ca.* 440 nm). A reaction mechanism is developed which accounts for transformation of the carbanion to *p,p′*-dinitrobibenzyl and *p*-nitrotoluene, the major isolable nitro products from these systems.

The high pK_a values of most 'hydrocarbon acids' have meant that the ground-state properties and reactions of many carbanions have been investigated in polar, aprotic, highly basic solvents.[1] The *p*-nitrobenzyl carbanion is no exception and its absorption spectrum,[2,3] protonation rate,[2] and reactions[4] have been studied generally in basic alcoholic dimethyl sulphoxide solutions. Recently, it has been demonstrated that the *p*-nitrobenzyl anion is an elimination product from certain photoreactions in aqueous media: (i) the photodecarboxylation of *p*-nitrophenylacetate,[5,6] (ii) the photodephosphorylation of *p*-nitrobenzylphosphonate,[7] and (iii) photoretro-aldol-type reactions for several *p*-nitrobenzyl derivatives.[8,9] These photoelimination reactions, then, provide us with the unique opportunity to examine the properties of the *p*-nitrobenzyl carbanion in aqueous media and to compare them with those reported in polar, aprotic solvents.

Laser transient absorption studies have demonstrated[6,7,9] that, for N_2-saturated solutions, the *p*-nitrobenzyl anion is produced in (i), (ii), and for several compounds in reaction (iii) with a formation rate constant of *ca.* $1.1 \times 10^7\ s^{-1}$. This led us[6] to speculate that the anion is formed *via* a common, or very similar, precursor species. Two possibilities were offered: the triplet state of the *p*-nitrobenzyl anion (*i.e.*, a photoelimination process on the lowest excited triplet surface), or a charge-transfer intermediate in which there is intramolecular electron-transfer from the methyl carbon substituent to the nitrophenyl group [*e.g.*, equation (1)]. The latter mechanism was also postulated by Okamoto *et al.*[7] for (ii).



(1)

CT intermediate
(τ 90 ns)

The mechanism by which the *p*-nitrobenzyl anion generates the major isolable nitro products from (i)—(iii), *p,p′*-dinitrobibenzyl and *p*-nitrotoluene, has remained unclear. Here, we have carefully studied the decay kinetics of the *p*-nitrobenzyl anion produced from aqueous solutions of *p*-nitrophenylacetate and have formulated a mechanism which accounts for production of the bibenzyl product. In addition, the pronounced solvent effect upon the absorption spectrum of the *p*-nitrobenzyl anion ($\lambda_{max.}$ 356 nm in water[5–7] *vs.* $\lambda_{max.}$ 430—450 nm in aprotic media[2,3]), which has been considered previously,[6] is examined in more detail.

Results

Decay Kinetics of the p-*Nitrobenzyl Carbanion.*—(*a*) *Effect of concentration.* The large quantum yield of photodecarboxylation (*ca.* 0.6)[5] makes the *p*-nitrophenylacetate system particularly convenient for investigation of the reaction kinetics of the *p*-nitrobenzyl carbanion. Following laser flash photolysis of *p*-nitrophenylacetate solutions (pH > 4) we observed no decay of the anion over 0.4 s, the instrumental limit of our detection system. Its decay kinetics, however, were readily followed in a u.v.–visible spectrophotometer. Figure 1 illustrates the absorption changes measured for an N_2-saturated 3×10^{-5} mol dm^{-3} solution of *p*-nitrophenylacetate at pH 11 after irradiation with a 10 ms xenon flashlamp pulse. For this parent concentration, the earliest spectrum shows an intense *p*-nitrobenzyl anion absorption ($\lambda_{max.}$ 356 nm) and a loss of intensity at 285 nm, which can be attributed to removal of the parent *p*-nitrophenylacetate. Decay of the *p*-nitrobenzyl anion

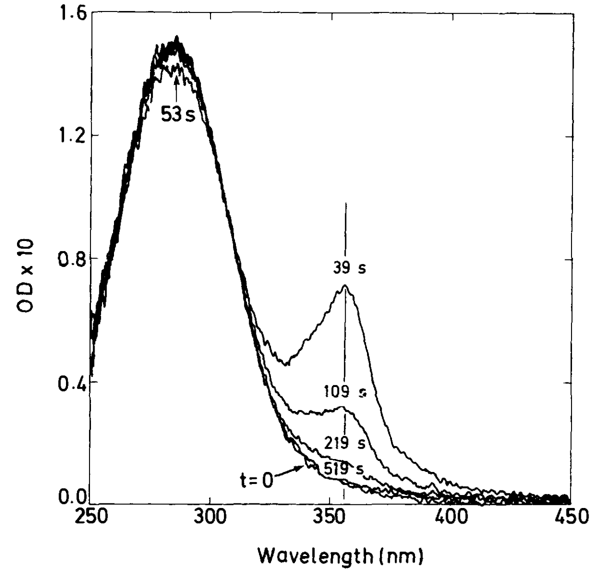


Figure 1. Absorption spectra recorded before and after irradiation of an N_2-saturated 3×10^{-5} mol dm^{-3} aqueous solution of *p*-nitrophenylacetate at pH 11 with a 10 ms xenon lamp pulse, pathlength 0.5 cm. Scan rate 10 nm s^{-1}; times after irradiation are given at 355 and 285 nm

band is accompanied by a slight growth of absorption at 285 nm, such that the final spectrum is essentially indistinguishable from that of the starting material. Under these conditions, the anion exhibited a simple first-order decay [Figure 2(a)] with a rate constant of $1.3 \pm 0.1 \times 10^{-2}$ s^{-1} ($\tau = 77$ s, which is in reasonable agreement with the previously determined value[5b] of 53 s from an aerated $< 4 \times 10^{-5}$ mol dm^{-3} *p*-nitrophenylacetate solution at pH 13). Further, no pale yellow precipitate, characteristic of the *p,p'*-dinitrobibenzyl product,[7b,10] was observed. The final product of the photolysis is *p*-nitrotoluene, which is formed *via* a first-order solvent protonation reaction. Since the absorption spectrum of *p*-nitrotoluene is very similar to that of *p*-nitrophenylacetate, the initial and final spectra in Figure 1 show no evident change.

As the *p*-nitrophenylacetate concentration was increased in the range $10^{-4} - 5 \times 10^{-3}$ mol dm^{-3} (pH > 6), the decay of the anion became increasingly non-exponential, which could be correlated with the appearance of the *p,p'*-dinitrobibenzyl product (pale yellow precipitate). In addition, the kinetics exhibited a marked dependence upon the excitation intensity, which is indicative of a second-order component of decay; this is demonstrated in Figure 2. When a 5×10^{-3} mol dm^{-3} *p*-nitrophenylacetate solution was photolysed with a reduced lamp intensity (attenuated such that the initial yield of the *p*-nitrobenzyl anion (OD_{356}) was similar to that produced from a 10^{-5} mol dm^{-3} solution with the full intensity), the anion decay was first-order [Figure 2(b)]. The best-fit exponential yields a decay constant of $1.7 \pm 0.1 \times 10^{-2}$ s^{-1}, not substantially larger than the value obtained from the 10^{-5} mol dm^{-3} solution. For the full lamp intensity, Figure 2(c) shows that the decay of the anion is distinctly faster and non-exponential. The curve was fitted with the mixed first- and second-order decay function given in equation (2), where OD_t and OD_0 are the 356 nm

$$OD_t = OD_0 k_1 \exp(-k_1 t)/ \{k_1 + OD_0 4k_2 \varepsilon^{-1}[1 - \exp(-k_1 t)]\} \quad (2)$$

optical densities for a pathlength of 0.5 cm at time, t, and $t = 0$, k_1 and k_2 are the first- and second-order decay constants, and ε is the molar extinction coefficient of the *p*-nitrobenzyl anion at 356 nm. With k_1 as 1.3×10^{-2} s^{-1}, the best-fit curve gives $2k_2/\varepsilon = 3.6 \pm 0.3 \times 10^{-2}$ cm s^{-1}. Similar k_1 and $2k_2/\varepsilon$ values were obtained with an analysis which allowed a free parameter fit and for 10^{-3} mol dm^{-3} *p*-nitrophenylacetate solutions. From a series of experiments, in which a 10^{-5} mol dm^{-3} *p*-nitrophenylacetate solution was repeatedly flash photolysed, we estimated $\varepsilon = 4.6 \pm 0.5 \times 10^4$ dm^3 mol^{-1} cm^{-1} assuming a quantum yield of 0.6;[5] thus $2k_2 = 1.7 \pm 0.3 \times 10^3$ dm^3 mol^{-1} s^{-1}. Our observations are in accord with the findings of Okamoto *et al.*,[7b] which indicated that removal of the anion obeyed a second-order decay law.

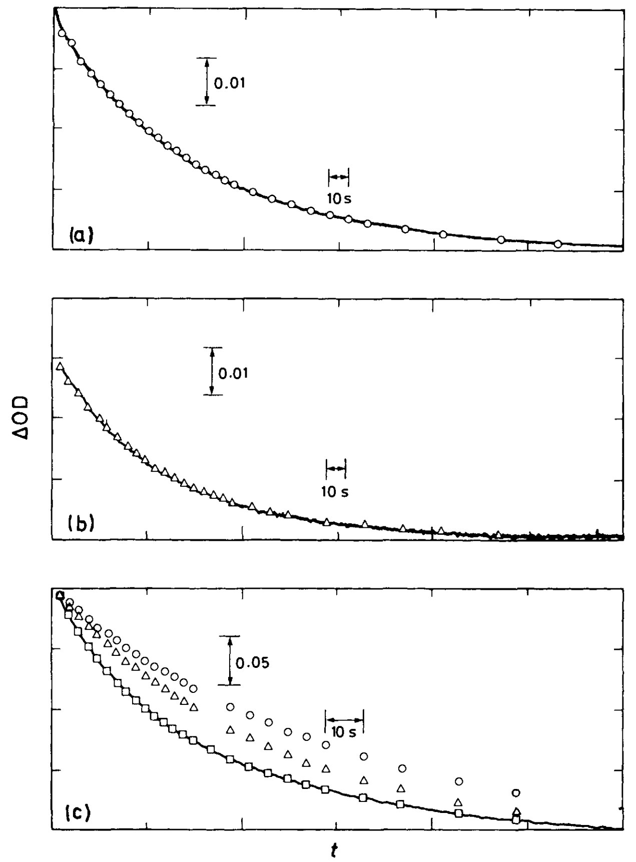


Figure 2. Decay curves at 356 nm of the *p*-nitrobenzyl anion in N_2-saturated aqueous solutions, *ca.* 20 s after photolysis of different concentrations of *p*-nitrophenylacetate with different flash intensities: (a) 1×10^{-5} mol dm^{-3}, full intensity; the circles represent the best-fit exponential curve with $k_1 = 1.3 \times 10^{-2}$ s^{-1}; (b) 5×10^{-3} mol dm^{-3}, attenuated intensity; the triangles are the best-fit exponential with $k_1 = 1.7 \times 10^{-2}$ s^{-1}; (c) As (b) but full intensity; the squares are the best-fit curve according to equation (2) with $k_1 = 1.3 \times 10^{-2}$ s^{-1} and $2k_2/\varepsilon = 3.6 \times 10^{-2}$ cm s^{-1}. Also included are the exponential fits from (a) and (b)

In order to demonstrate further that there is no significant reaction of the anion with nitroaromatic substrates, we carried out kinetic studies of 10^{-4} mol dm^{-3} *p*-nitrophenylacetate solutions containing 10^{-3} mol dm^{-3} *p*-nitrotoluene. For this *p*-nitrophenylacetate concentration with the full flashlamp intensity, the *p*-nitrobenzyl anion decay would normally exhibit a non-exponential component. However, *p*-nitrotoluene, being essentially photochemically inert and having a very similar absorption spectrum to *p*-nitrophenyl acetate, serves as an internal filter and effectively reduces the yield of the carbanion. Under these conditions, we obtained $k_1 = 1.4 \pm 0.2 \times 10^{-2}$ s^{-1}.

(b) *Effect of* O_2. Employing a 10^{-5} mol dm^{-3} O_2-saturated *p*-nitrophenylacetate solution, we observed a slightly faster decay rate for the anion; $k_1 = 2.4 \pm 0.2 \times 10^{-2}$ s^{-1}. From this value and those in aerated and N_2-saturated solutions, a bimolecular

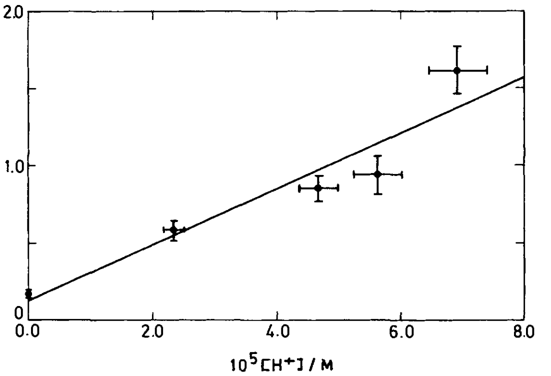


Figure 3. Dependence of the pseudo-first-order decay constant k_1 of the p-nitrobenzyl anion upon H^+ concentration. From the slope, a rate constant of 1.8×10^3 dm^3 mol^{-1} s^{-1} is determined

rate constant of 7.8 dm^3 mol^{-1} s^{-1} is determined. The lack of a pronounced O_2 effect is consistent with the observations of previous workers,[5,7b] who reported essentially no change in the product quantum yields of (i) and (ii) for O_2-saturated solutions (parent concentrations $> 10^{-3}$ mol dm^{-3}). In addition to the usual nitro products, Okamoto *et al.*[7b] noted a small yield of p-nitrobenzaldehyde.

(c) *Effect of* H^+. For solutions < pH 6, protonation of the anion becomes significant and an enhanced rate of decay was observed. In order to investigate this reaction, we monitored the decay of the anion, under pseudo-first-order conditions, for aerated solutions in the pH range 4.1—4.7. From the slope of the Stern–Volmer-type plot of Figure 3, a bimolecular rate constant of $1.8 \pm 0.4 \times 10^3$ dm^3 mol^{-1} s^{-1} is determined. Assuming a pK_a value[2b] of 22, we estimate that deprotonation of p-nitrotoluene in water occurs with a pseudo-first-order rate of 1.8×10^{-25} s^{-1}.

(d) *Effect of solvent.* The decay kinetics of the carbanion were briefly examined in aqueous solutions containing high mole fractions of methanol or dimethyl sulphoxide (see below). For basic 40% (v/v) methanol and 40% (v/v) dimethyl sulphoxide solutions (2×10^{-5} mol dm^{-3} p-nitrophenylacetate), the decay rates were substantially faster;* half-lives of < 5 s and *ca.* 14 s, respectively, were estimated. Studies on the laser flash photolysis system indicated that in dimethyl sulphoxide mixtures the anion also exhibited an initial fast component of decay (k *ca.* 6×10^3 s^{-1}).†

(e) *Effect of sodium hexachloroiridate*(IV). $IrCl_6^{2-}$ is an efficient one-electron oxidant; its rate of reaction can be conveniently measured by monitoring the removal of the $IrCl_6^{2-}$ absorption at 490 nm.[11] Employing laser flash photolysis, we have observed a rapid decay of the p-nitrobenzyl anion in the presence of $IrCl_6^{2-}$ [Figures 4(a) and (b)]. Figure 4(c) demonstrates a bleaching of $IrCl_6^{2-}$ concomitant with the removal of the carbanion. This may be explained by the conversion of $Ir^{IV}Cl_6^{2-}$ into Ir^{III} species, which do not absorb at 490 nm[12] [equation (3)]. From a series of

$$Ir^{IV}Cl_6^{2-} + p\text{-}NO_2C_6H_4CH_2^- \longrightarrow Ir^{III} + \text{products} \quad (3)$$

measurements, a rate constant of $2.6 \pm 0.2 \times 10^8$ dm^3 mol^{-1} s^{-1} was determined for this reaction, which is in good agreement with the value of $2.3 \pm 0.2 \times 10^8$ dm^3 mol^{-1} s^{-1} measured for the o-nitrobenzyl anion, produced from laser photolysis of o-nitrotoluene.[13] The one-electron oxidation product of the carbanion is the p-nitrobenzyl radical, which has a $\lambda_{max.}$ of 350 nm[6,14] but was not observed in our work. This is perhaps understandable since the radical would be susceptible to further oxidation: alkyl radicals react with $Ir^{IV}Cl_6^{2-}$ *via* chlorine transfer with near diffusion-controlled rate constants (*e.g.*, 3.1×10^9 dm^3 mol^{-1} s^{-1} for the ethyl radical).[11c]

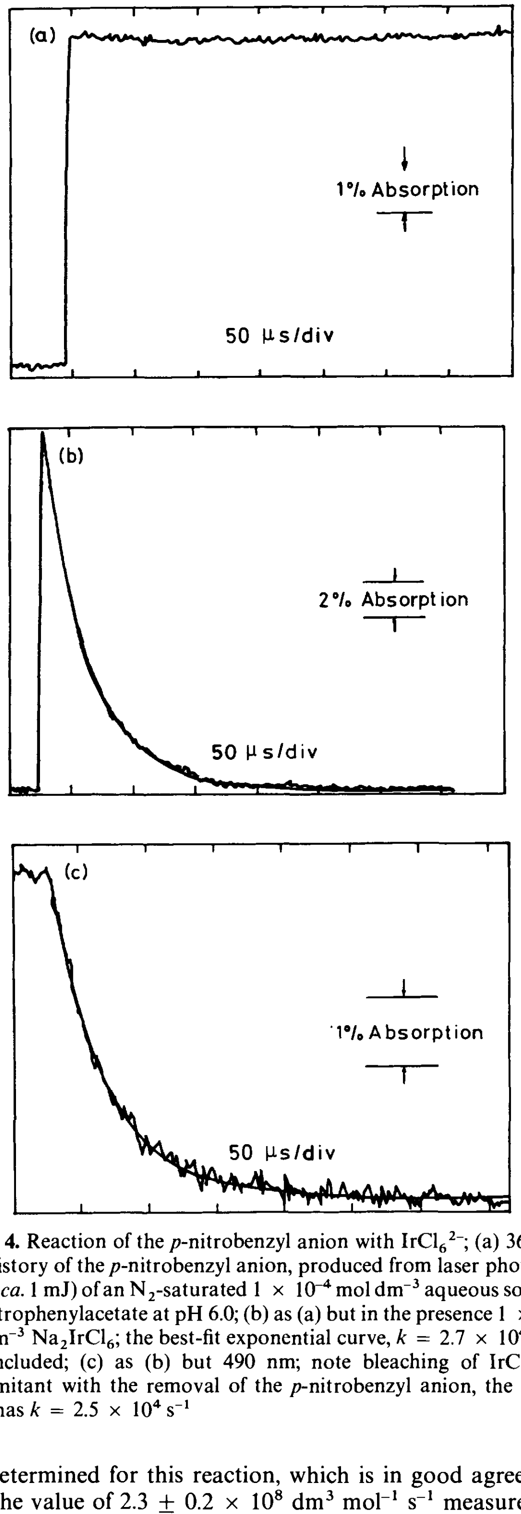


Figure 4. Reaction of the p-nitrobenzyl anion with $IrCl_6^{2-}$; (a) 360 nm; time history of the p-nitrobenzyl anion, produced from laser photolysis (11 ns, *ca.* 1 mJ) of an N_2-saturated 1×10^{-4} mol dm^{-3} aqueous solution of p-nitrophenylacetate at pH 6.0; (b) as (a) but in the presence 1×10^{-4} mol dm^{-3} Na_2IrCl_6; the best-fit exponential curve, $k = 2.7 \times 10^4$ s^{-1} is also included; (c) as (b) but 490 nm; note bleaching of $IrCl_6^{2-}$ is concomitant with the removal of the p-nitrobenzyl anion, the model curve has $k = 2.5 \times 10^4$ s^{-1}

Effect of Solvent upon the Absorption Spectrum and Formation Kinetics of the p-*Nitrobenzyl Carbanion.*—Previous workers

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* It is possible that the enhanced decay rates represent reaction of the carbanion with solvent impurities.

† Higher laser excitation energies were employed for the dimethyl sulphoxide–water mixtures, because of the apparent lower yield (ΔOD) of the carbanion. The initial fast decay component appeared to exhibit a dependence upon laser energy and may result from a non-linear excitation process.

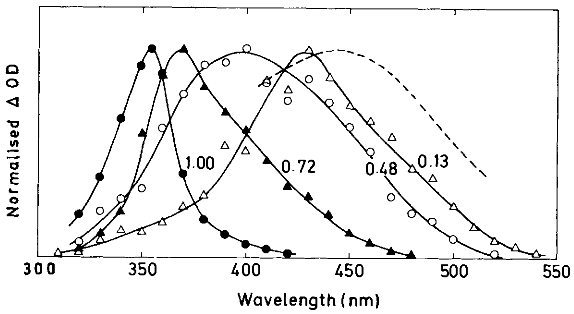


Figure 5. Normalised uncorrected spectra of the *p*-nitrobenzyl anion recorded 5 μs after laser photolysis of an N_2-saturated 1×10^{-4} mol dm^{-3} aqueous dimethyl sulphoxide solution of *p*-nitrophenylacetate; (●) aqueous solution, (▲) aqueous mole fraction 0.72, (○) 0.48, (△) 0.13. The spectrum of the anion in pure dimethyl sulphoxide (broken line) is also included, taken from ref. 3*b*

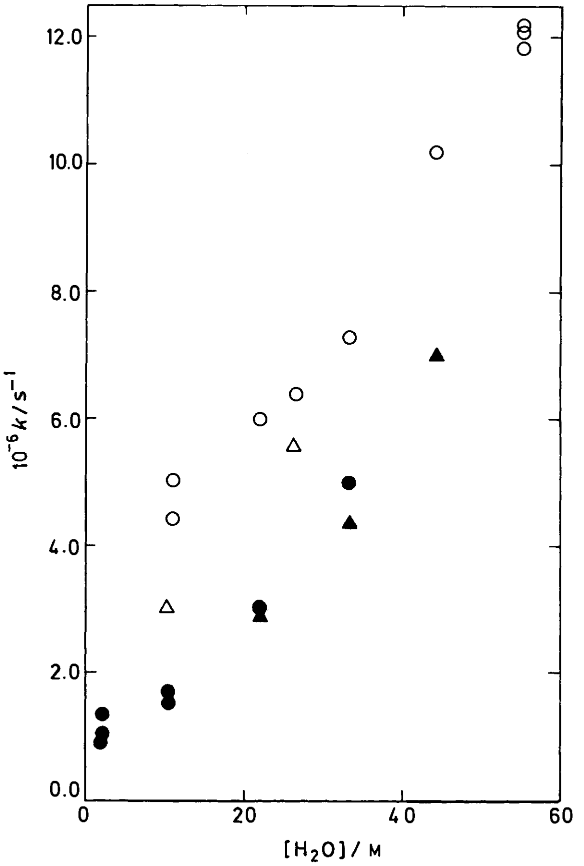


Figure 6. Dependence of the formation rate constant for the *p*-nitrobenzyl anion upon the concentration of water in aqueous–solvent mixtures; (○) methanol, (△) acetonitrile, (●) dimethyl sulphoxide, (▲) tetrahydrofuran. The points at 55.6M are for aqueous solutions

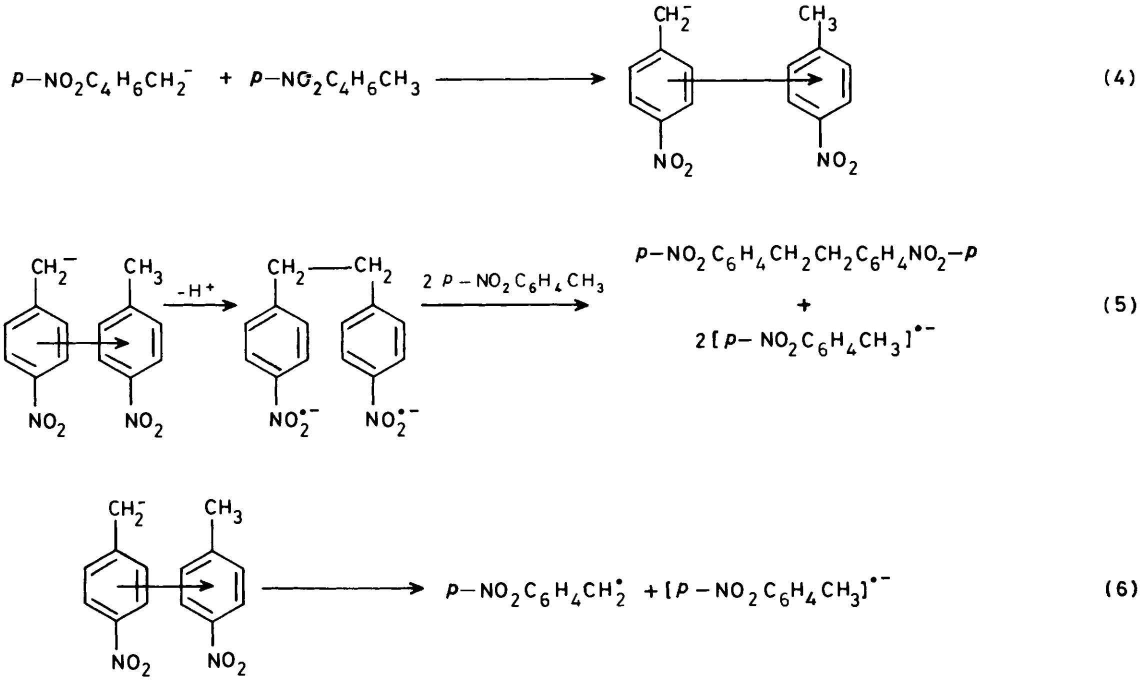
have reported that the *p*-nitrobenzyl anion in aprotic media has a $\lambda_{max.}$ in the 430—450 nm region,[2,3] indicating a pronounced solvent effect upon the absorption spectrum. This was considered in our initial assignment of the anion.[6] Figure 5 illustrates that for dimethyl sulphoxide–water mixtures the absorption spectrum of the anion appears to undergo a progressive shift to the red with increasing mole fraction of dimethyl sulphoxide, such that at 96% v/v (0.87 mole fraction) dimethyl sulphoxide $\lambda_{max.} = 430$ nm. This is accompanied by a decrease in the rate of formation of the anion (Figure 6). The continuous variation in both the absorption spectrum and the rate data provide further support to our assignment of the 356 nm absorption in aqueous media to the *p*-nitrobenzyl carbanion.

Previously, we demonstrated that the formation rate constant of the anion produced from (i) exhibited a roughly linear dependence upon the concentration of water in methanol–water mixtures.[6] Consistent with our findings, Okamoto *et al.*[7b] determined a formation rate constant of 0.5×10^7 s^{-1} for the anion from *p*-nitrobenzylphosphonate [process (ii)] in aqueous 80% ethanol solutions. Figure 6 shows that the approximately linear relationship also holds for aqueous–aprotic solvent mixtures, even for the relatively non-polar tetrahydrofuran. However, for a particular aqueous mole fraction, the formation rate consant is appreciably larger for methanol mixtures than for the aprotic solvent mixtures. In our interpretation, this decrease in the formation rate reflects an increase, in non-aqueous solvents, in the lifetime of the precursor to the anion (either a charge-transfer intermediate or the triplet state of the *p*-nitrobenzyl carbanion). Further, the $\lambda_{max.}$ of this species undergoes a red shift analogous to that observed for the ground-state anion.

Since there is such a large solvent effect upon the absorption spectrum of the carbanion, it is difficult to assess whether the decrease in the formation rate with increasing mole fraction of dimethyl sulphoxide is accompanied by a decrease in the yield of the anion. However, for high mole fractions of dimethyl sulphoxide the yield appears to increase slightly. At 0.87 mole fraction of dimethyl sulphoxide, the time-dependent waveforms, obtained from nanosecond flash photolysis studies, exhibited an instantaneous component of anion formation in addition to the normal delayed channel. Whereas the latter process is associated with a triplet pathway, we suggest that this new channel of formation arises through a singlet mechanism. Since the S_1 states ($\tau \leqslant 5$ ps) of nitrobenzyl derivatives undergo rapid internal conversion, competitive with intersystem crossing,[6,15] we believe that the progenitor to the anion in this pathway is a vibrationally hot ground-state of *p*-nitrophenyl acetate. This would be consistent with the observations of Buncel *et al.*,[3b] who reported production of the *p*-nitrobenzyl carbanion in aprotic media from the thermal decarboxylation of *p*-nitrophenylacetate.

Discussion

There has been considerable interest[3,4,16] in the reactions of the *p*-nitrobenzyl carbanion produced from *p*-nitrotoluene in highly basic t-butyl alcohol or aprotic media. In these systems, the major product is again *p,p'*-dinitrobibenzyl, and the radical anion of *p*-nitrotoluene is observed (by e.s.r. spectroscopy) as a reduction product.[4] Russell *et al.*[4b] suggested that following deprotonation of *p*-nitrotoluene, the *p*-nitrobenzyl anion initially undergoes reaction with either (a) *p*-nitrotoluene [Scheme 1, (4)], (b) the *aci* form of *p*-nitrotoluene, or (c) a second *p*-nitrobenzyl anion to yield a charge-transfer complex. Two distinct reaction routes were then proposed: formation of a dianion of *p,p'*-dinitrobibenzyl [subsequent to loss of a proton for (a) and (b)] with transfer of two electrons to two *p*-nitrotoluene molecules, equation (5); and complete electron-transfer to yield a *p*-nitrobenzyl radical (coupling of which produces the bibenzyl compound) and a *p*-nitrotoluene radical anion, equation (6). Since *p,p'*-dinitrobibenzyl was also produced in the presence of O_2, which is an efficient scavenger of the *p*-nitrobenzyl radical, it was suggested[4b] that process (5) is the more likely channel. In a spectrophotometric study of *p*-nitrotoluene in a variety of highly basic systems, Buncel *et al.*[3a] considered similar reaction schemes suggesting that reaction of the anion with *p*-nitrotoluene was the initial step after deprotonation.



Scheme 1.

$$p\text{-}NO_2C_6H_4CH_2^- + H_2O \longrightarrow p\text{-}NO_2C_6H_4CH_3 + OH^- \qquad (7)$$
$$k_1 = 1.3 \times 10^{-2}\ s^{-1}$$

$$p\text{-}NO_2C_6H_4CH_2^- + p\text{-}NO_2C_6H_4CH_2^- \longrightarrow [p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p]^{2-} \qquad (8)$$
$$2k_2 = 1.7 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$$

$$p\text{-}NO_2C_6H_4CH_2^- + O_2 \longrightarrow \qquad (9)$$
$$k = 7.8\ dm^3\ mol^{-1}\ s^{-1}$$

$$p\text{-}NO_2C_6H_4CH_2^- + H^+ \longrightarrow p\text{-}NO_2C_6H_4CH_3 \qquad (10)$$
$$k = 1.8 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$$

$$p\text{-}NO_2C_6H_4CH_2^- + p\text{-}NO_2C_6H_4CH_2CO_2^- \text{ or } p\text{-}NO_2C_6H_4CH_3 \longrightarrow \qquad (11)$$
$$k < 1.0\ dm^3\ mol^{-1}\ s^{-1}$$

$$[p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p]^{2-} + p\text{-}NO_2C_6H_4CH_2CO_2^- \longrightarrow [p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p]^- + [p\text{-}NO_2C_6H_4CH_2CO_2^-]^{\bullet-} \qquad (12a)$$

$$[p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p]^- + p\text{-}NO_2C_6H_4CH_2CO_2^- \longrightarrow p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p + [p\text{-}NO_2C_6H_4CH_2CO_2^-]^{\bullet-} \qquad (12b)$$
$$k \simeq 10^6\ dm^3\ mol^{-1}\ s^{-1}$$

Scheme 2.

In Scheme 2, we have summarised our rate data for the *p*-nitrobenzyl anion in aqueous media. Our observations are consistent with a decay of the anion in N_2-saturated solutions involving competition between a first-order solvent protonation reaction (7) and a second-order coupling process (8), which could yield the bibenzyl dianion as proposed by Russell *et al.*[4b] The dianion will then undergo electron-transfer to the most abundant electron acceptor in the system (the parent *p*-nitrophenylacetate), probably *via* a two-step process [(12a) and (12b)], to yield the bibenzyl product. In fact, we have observed an intense e.s.r. signal, assignable to the radical anion of *p*-nitrophenylacetate, when *p*-nitrophenylacetate ($> 10^{-3}$ mol dm^{-3}) solutions were irradiated in a Bruker TE_{102} e.s.r. cavity.[10] When the photolysis was carried out in the presence of a high concentration of *p*-nitrotoluene, the radical anion of *p*-nitrotoluene was detected, which provides additional support for our mechanism. Employing the technique of pulse radiolysis, Meot-Ner and Neta[17] have recently investigated intermolecular electron-transfer reactions of nitroaromatic radical anions in aqueous solution. From their work, we estimate that reactions (12a) and (12b) proceed with a rate constant of *ca.* 10^6 dm^3 mol^{-1} s^{-1}. Consistent with our e.s.r. studies,[10] then, decay of the *p*-nitrobenzyl anion is the rate-limiting step in production of the radical anion.

Although the coupling of carbanions *via* the carbon atoms formally bearing the negative charge has no precedent in the literature, we suggest that resonance and solvent effects may contribute to the importance of this reaction in aqueous media (we note that the reaction is over 10^6 times slower than that for *p*-nitrobenzyl radicals[6]). The carbanion will exhibit a high degree of conjugative and inductive stabilisation, which will tend to reduce the effective charge on the methyl carbon. Further, specific solvation of the anion through hydrogen bonding in aqueous media will play a significant role in overcoming the coulombic repulsive forces (this may also be important for the reaction of the anion with $IrCl_6^{2-}$, which likely proceeds *via* an electron-transfer mechanism). Dimerisation of the anion may well proceed *via* a charge-transfer complex (similar to that proposed by Russell *et al.*[4]), which could rearrange to the bibenzyl form either before or after electron-transfer to the parent nitroaromatic.

Our data clearly demonstrate that reaction of the anion with the nitroaromatic substrate [equations (4) and (11)], which was the decay mode favoured by previous workers, does not contribute significantly to its disappearance in aqueous media. However, this may not be the case in aprotic media. In dimethyl sulphoxide, the *p*-nitrobenzyl anion will exist as a 'free' anion and the rate constant for dimerisation may be substantially smaller than in water. Consequently, reaction (11) could be of greater relative importance. It is unclear whether this reaction or a pseudo-first-order solvent impurity reaction is reflected in the enhanced rate of decay in dimethyl sulphoxide–water solutions.

The final product studies[5,7,8] of reactions (i)—(iii) have generally been conducted at high pH for substrate concentrations $> 10^{-3}$ mol dm^{-3}. Under these conditions, we have demonstrated that the decay of the *p*-nitrobenzyl anion is predominantly second-order, which is consonant with the appearance of *p,p'*-dinitrobibenzyl as the major product. Further, we emphasize the remarks of Margerum and Petrusis (footnote to Table 3 in ref. 5*b*) in their work on the decarboxylation of *p*-nitrophenylacetate: 'the *p*-nitrotoluene product is favoured by lower concentration, lower pH, and lower u.v. intensity'. These points are all consistent with our proposed decay mechanism of the anion, involving a competition between protonation and dimerisation. From the work of Margerum and Petrusis,[5b] we estimate that a steady-state *p*-nitrobenzyl anion concentration of *ca.* 1×10^{-4} mol dm^{-3} would be necessary to account for the observed bibenzyl/*p*-nitrotoluene final product ratios. Based upon their concentration of the nitroaromatic substrate (5×10^{-2} mol dm^{-3}) and their conditions of irradiation, such a concentration is not unreasonable.

For the dephosphorylation of *p*-nitrobenzylphosphonate in ethanol–water mixtures, Okamoto *et al.*[7b] showed that, as the aqueous portion of the solvent was decreased, a decrease in the yield of *p,p'*-dinitrobibenzyl was accompanied by an increase in the yield of *p*-nitrotoluene. This is in agreement with our observation that the *p*-nitrobenzyl anion, produced under conditions for which process (8) is not a significant decay mode, exhibits a distinctly faster rate of decay in methanol–water mixtures. We suggest that this represents a more efficient solvent protonation reaction in alcoholic media. In addition, Okamoto *et al.*[7b] reported a small yield of *p*-nitrobenzaldehyde in O_2-saturated solutions. It is proposed that this may be formed *via* reaction (9) or through reactions involving the superoxide anion or the peroxide dianion. These species will be present following electron-transfer from the radical anion of the *p*-nitrobenzyl substrate[10] or from the bibenzyl dianion,[4b,c] respectively, to O_2.

The relatively long lifetime and large extinction coefficient of the *p*-nitrobenzyl anion in aqueous media facilitate its excitation in steady-state photolysis studies of reactions (i)—(iii). This may afford an additional mechanism for formation of the *p,p'*-dinitrobibenzyl in these systems. Photoionisation of the carbanion would yield the hydrated electron and the *p*-nitrobenzyl radical. Further, scavenging of the hydrated electron by the nitroaromatic substrate provides an additional route to the radical anion. In our e.s.r. studies,[10] we have shown that such a channel does not account for the continued production of the radical anion for several seconds after an irradiation period.

Finally, we address the pronounced solvent effect on the absorption spectrum of the carbanion. A blue shift, observed with increasing mole fraction of water in dimethyl sulphoxide–water mixtures (Figure 5), is indicative of the anion participating in a solvent hydrogen-bond framework and functioning as a proton acceptor.[18] Anomalously large spectral shifts have previously been reported for the cyano(*p*-nitrophenyl)methyl[19,20] and 2,4-dinitrobenzyl[21,22] anions. It was suggested that there are two forms of the anion: an unspecifically solvated form and one in which a water molecule(s) is strongly hydrogen bonded to the nitro group. It is this interaction which is thought to generate an increase in the energy of the $\pi \longrightarrow \pi^*$ transition of the nitro carbanion. The spectra of the anion in dimethyl sulphoxide–water mixtures (Figure 5), thus, are probably not assignable to a unique species but rather represent equilibrium concentrations of the 356 nm hydrated form and the 440 nm unspecifically solvated species. The establishment of this equilibrium is beyond the instrumental response (< 10 ns) of the nanosecond flash photolysis system.

In summary, we have demonstrated that the important decay modes of the *p*-nitrobenzyl carbanion in aqueous media are solvent protonation and self-association. The latter process (predominant for anion concentrations $> 10^{-4}$ mol dm^{-3}, pH > 6) leads to production of *p,p'*-dinitrobibenzyl, *not* reaction of the carbanion with the nitroaromatic substrate as previously proposed.[8] We emphasise that the anion is highly solvated in an aqueous environment; this undoubtedly plays an important role in facilitating the dimerisation reaction. In aprotic polar media, where the anion exists as a non-specifically solvated form, this reaction may not be as significant. Our observations are consistent with final product studies for several photoreactions in which the *p*-nitrobenzyl anion is a primary elimination product.

Experimental

Materials.—*p*-Nitrophenylacetic acid (Aldrich), *p*-nitrotoluene (Eastman), and *p,p'*-dinitrobibenzyl were recrystallised twice from ethanol–water solutions. Sodium hexachloroiridate(IV) hexahydrate (Aldrich) was used as supplied. Water was triply distilled and other solvents were spectrophotometric or h.p.l.c. grade. Solutions for kinetic study were all freshly prepared and adjusted to the appropriate pH with either 1 mol dm^{-3} NaOH or 0.5 mol dm^{-3} HCl.

Kinetic Measurements.—The laser flash photolysis system has been described previously.[6,21] Excitation was provided by the fourth harmonic (266 nm, 11 ns) of a Nd:YAG laser (Quantel YG 581). Pulse energies up to *ca.* 12 mJ were available with a pulse to pulse reproducibility of *ca.* 5%. Absorption changes in the sample were measured perpendicular to the excitation beam with a pulsed-xenon analysing light. For studies beyond 400 ms, a 10 ms xenon light pulse (PRA M 302 supply and PRA M 305 pulser) with a Corning 7-54 filter was employed as an excitation source. Solutions were shaken thoroughly and absorption changes followed in a Cary 219 spectrophotometer. Measurements of the unattenuated flash intensity with a Scientech 362 energy meter indicated *ca.* 10^{17} photons per pulse were delivered to the sample. Solutions were saturated with N_2 or O_2 directly in the photolysis cell, of pathlength 0.5 or 1.0 cm.

Measurement of ε.—An estimate of the extinction coefficient of the *p*-nitrobenzyl anion at 356 nm was obtained by repeatedly (three times) flash photolysing the same N_2-saturated 10^{-5} mol dm^{-3} *p*-nitrophenylacetate solution. At time *t* (*ca.* 20 s) after each irradiation an OD_t at 356 nm was determined, from which OD_0 was calculated. By assuming: (*a*) a quantum yield of 0.6 for production of the anion, (b) that the absorption spectra of *p*-nitrophenylacetate and the *p*-nitrotoluene product are identical, and (c) a reproducible flash-lamp intensity, we estimate ε through solution of simultaneous equations of the form given in equation (13); where *y* is the fraction of ground-states which are excited, *d* is the pathlength, and OD_0' and OD_0'' are the OD_0 values after the first and second irradiation periods. An average ε was calculated from a series of such experiments.

$$0.6y\varepsilon d \times 10^{-5} = OD_0'; \quad 0.6y(1 - 0.6y)\varepsilon d \times 10^{-5} = OD_0'' \qquad (13)$$

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