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Transient free radicals are formed during photolysis of the 1-(2-nitrophenyl)ethyl ester of adenosine triphosphate (caged ATP)

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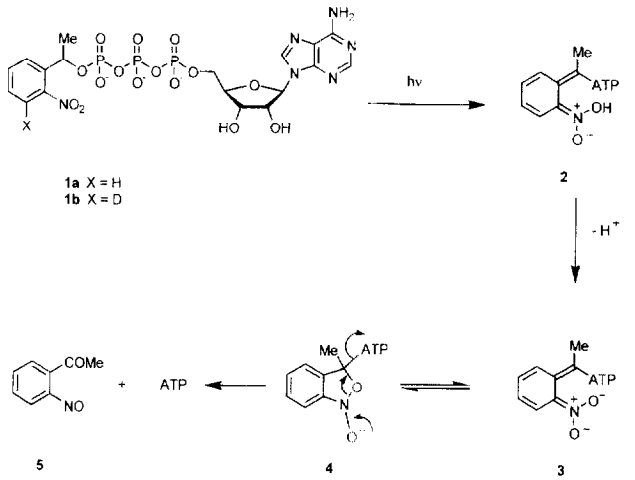
Abstract

Flash photolysis of the P^3-1-(2-nitrophenyl)ethyl ester of ATP (caged ATP) in the presence of dithiothreitol results in formation of a transient radical species in addition to the known paired-electron *aci*-nitro anion. The transient radical represents approx. 10% of the reaction flux and is proposed to be the radical anion of the nitroaryl group of caged ATP. The kinetics of its formation suggest that it arises by single electron transfer to the triplet excited state of the nitroarene. The electron donor has not been conclusively identified but tertiary amines present as buffer salts or as impurities are likely candidates.

Keywords: Transient free radicals; Photolysis; Adenosine triphosphate

1. Introduction

Biological effector species such as adenosine triphosphate (ATP), 1,4,5-inositol trisphosphate, calcium ions and many others can have their biological activity blocked by covalent binding or chelation to a suitably located photolabile protecting group. These derivatives, colloquially termed caged compounds, have been used in the study of rapid biological processes by flash photolysis, a technique which permits fast release of the effector species at or near its site of action [1–3]. The photocleavable moieties most commonly used are 2-nitrobenzyl groups and substituted variants thereof, which are sensitive to light of wavelength longer than 300 nm. The mechanism of photocleavage has been the subject of various studies. Yip et al. [4–6] have studied the photophysics of the excited state and concluded that the reaction proceeds via both singlet and triplet pathways. For the subsequent dark chemistry, there has been general agreement that the first ground state intermediate is a nitronic acid which in hydroxylic solvents rapidly dissociates to an *aci*-nitro anion [7–11]. Scheme 1 shows the steps leading to product release for a weakly ionised phosphate such as ATP. This mechanism, supported by several diverse but consistent strands of evidence, has as its rate-determining step the decomposition of the *aci*-nitro anion **3** via a rapid equilibrium with the bicyclic species **4**. None of the proposed intermediates or products involves a long-lived radical species and we were therefore surprised to observe that strong transient signals were generated in the course of experiments which involved flash photolysis of caged ATP **1** in the cavity of an EPR spectrometer.



Scheme 1. Mechanism of ATP release following photolysis of caged ATP, showing the accepted paired-electron intermediates. In the structures where ATP is depicted in abbreviated form, it is to be understood as attached via the γ-phosphate as shown for **1a** and **1b**. Where structures **2**–**5** are derived from the deuterated isotopomer **1b**, they would also be deuterated in the same position.

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We report here experiments which confirm that the radical species is derived from caged ATP and provide an estimate of the quantitative significance of the radical pathway. The observed species is assigned as the radical anion of the nitroaryl group of caged ATP and suggestions for its formation are presented.

2. Experimental details

2.1. Reagents

Caged ATP **1a** and its deuterated isotopomer **1b** (sodium salts) were prepared as previously described [7,12]. The spin-labelled ATP used as a calibration standard was the 2′,3′-spiro compound previously described [13]. Buffers were prepared from 200 mM aqueous solutions of 3-(*N*-morpholino)ethanesulphonic acid (MES; pH 6.0), $NaH_2PO_4 \cdot 2H_2O$ (pH 7.0), *N*-(2-hydroxyethyl)piperazine-*N*′-(3-propanesulphonic acid) (EPPS; pH 8.5) or 2-(*N*-cyclohexylamino)ethanesulphonic acid (CHES; pH 9.0), all adjusted to the required pH with NaOH.

2.2. EPR spectrometry and photolysis

Solutions for photolysis contained caged ATP and dithiothreitol (DTT) (each 10 mM) in 200 mM buffer (see above for buffer compositions). The solutions were filled into a 10×4×1 mm trough in a Kel-F cover plate and sandwiched onto a Suprasil flat cell, which was positioned in a TE102 cavity (ER4102TE; Bruker Instruments, Billerica, MA) of a Bruker ESP300 spectrometer. The cell was irradiated as required by a 10-ns pulse of 351-nm light from a XeF excimer laser (LPX200i, Lambda Physik, Acton, MA). The laser beam was focused through a port in the TE cavity to give uniform irradiation of the solution and the average energy of a single pulse reaching the sample cell was approximately 200 mJ. The spectrometer cavity was purged with cooled nitrogen gas to give a temperature of 1.5°C at the position of the sample cell. The nitrogen purge may have caused partial deoxygenation of the sample by gas exchange through the cell wall, but we have no quantitative measure of the extent of deoxygenation. In all cases, data were recorded only for the first flash irradiation of a sample.

2.3. Data acquisition and processing

Spectra were recorded with a centre field value of 3412.7 G and a sweep time of 3.84 s over 75 G with time resolution of 5 ms per data point (0.1 G). The laser was fired automatically 0.5 s after the start of a sweep. To correct the spectral intensity for the decay which took place during data acquisition, the signal intensity at 3394.65 G (the positive limb of the central line in the low-field triplet of the spectrum, marked in Fig. 1) was monitored continuously following irradiation of the sample. Data were acquired and digitised with ESP 1620 acquisition software (Bruker Instruments) and transferred to a personal computer. The decay curve was fitted to an arbitrary polynomial using Origin 3.5 (Microcal, Northampton, MA) and the spectral intensity was normalised using this expression. Integrated intensities of corrected spectra were computed and calibrated against a 41 μM solution of spin-labelled ATP in 100 mM EPPS buffer, pH 8.5. All measurements on solutions at pH 8.5 were the means of three determinations. The time resolved decay curves at other pH values (Fig. 4) were from single determinations.

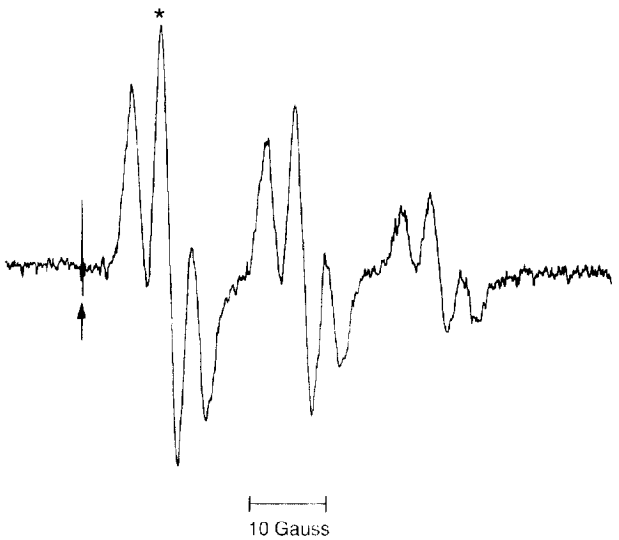


Fig. 1. EPR spectrum recorded as described in the text following flash photolysis of a solution containing caged ATP **1a** and dithiothreitol, pH 8.5, 1.5°C. The arrow marks the time point in the field sweep at which the laser was fired and the peak marked with an asterisk is that at which subsequent time-dependent measurement of the formation and decay was carried out (see Fig. 2 and related text). The spectrum is uncorrected for the decay which took place during the recording.

2.4. ATP analysis

Photolysed samples were recovered from the EPR cell and assayed for free ATP by hydrolysis with myosin subfragment 1 and subsequent assay of inorganic phosphate as previously described [14].

3. Results

The starting point in our investigations was the spectrum shown in Fig. 1, recorded immediately after flash photolysis of a pH 8.5 solution of caged ATP and dithiothreitol (DTT). This spectrum, which was centred at the same field position as a typical nitroxyl, decayed during the scan time (~5 s), as shown by the decreasing amplitude from low to high field across the spectrum, i.e., in the same direction as the field sweep. Experiments in different buffers (CHES, pH 9 and phosphate, pH 7) indicated that the form of the signal was not affected by the nature of the buffer, although the time course of its decay was influenced by the pH of the solutions

(see below). We note that the radical species identified here was also formed in the absence of DTT, but under these conditions, a further radical formed with a slower time course. It seems probable that the 2-nitrosoacetophenone formed by decay of the *aci*-nitro anion **3** (Scheme 1) is implicated in the appearance of the latter radical. However, the present investigation has been restricted to the single species observed in the presence of DTT, since either this exogenous thiol or an endogenous thiol such as glutathione will rapidly scavenge the nitrosoketone during most biological experiments involving caged ATP [1,7].

In order to obtain an estimate of the quantitative significance of the radical species observed in the presence of DTT, we required a spectrum corrected for the decay which occurred during recording. The spectral intensity at a single field strength was monitored continuously following flash irradiation of samples identical to those used to record the spectrum, and the result is shown in Fig. 2. The decay curve followed a complex time course and was fitted to an arbitrary polynomial expression. Normalisation of the recorded spectrum according to this expression gave the spectrum shown in Fig. 3a, which shows a triplet of triplets with hyperfine splittings of 16.7 and 3.6 G. The spike at the low-field end of the spectrum corresponds to the point in the sweep at which the laser was fired. Integration of the spectrum and comparison of the area under the peaks with that of a reference spectrum of spin-labelled ATP recorded under the same conditions gave an estimated radical concentration immediately after photolysis of 83 μM. In the same samples used to obtain these spectra, the measured mean concentration of photoreleased ATP was 0.94 mM and the maximum radical concentration was therefore 8.8% of the concentration of the released ATP.

To obtain additional information on the nature of the species responsible for the radical spectrum, we repeated the above experiments using the mono-deuterated isotopomer **1b** and obtained the corrected spectrum shown in Fig. 3b, with hyperfine splittings of 16.8 (triplet) and 3.9 G (doublet).

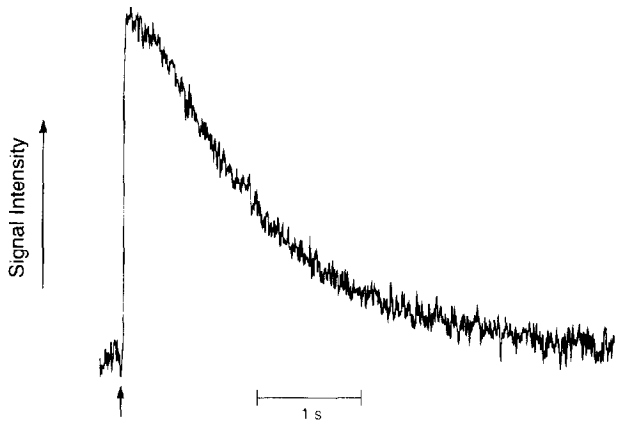


Fig. 2. Time-dependent monitoring of the signal intensity at 3394.65 G (marked * in Fig. 1) following flash photolysis of a solution of caged ATP under conditions identical to those of Fig. 1. The arrow marks the point at which the laser was fired.

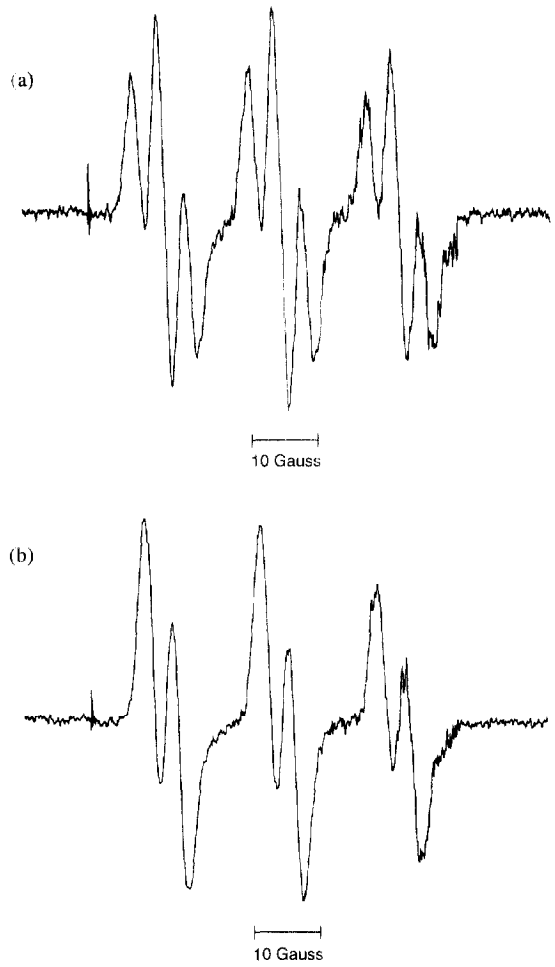


Fig. 3. (a) Spectrum of the radical formed from photolysis of caged ATP **1a** as in Fig. 1 but corrected for the intensity decay during the recording time (see text for details); (b) decay-corrected spectrum of the radical formed upon photolysis of the deuterated isotopomer **1b**. All conditions were identical to those of Fig. 1.

The integrated area under the peaks was 87% of that found for the non-deuterated compound **1a** and the relatively good agreement between these values is an indication of the degree of reproducibility of the data.

To estimate the pH dependence of the lifetime of the radical, transient measurements at a single field position as described above were made over a range of pH values. The times for the intensity to decay to half its maximum value were ~0.3 s (pH 6.0), ~0.4 s (pH 7.0) and ~1.2 s (pH 9.0). Note that the decay curves were not monoexponential. The effect of pH on the decay times is discussed below in the context of the pH stability of other radical species.

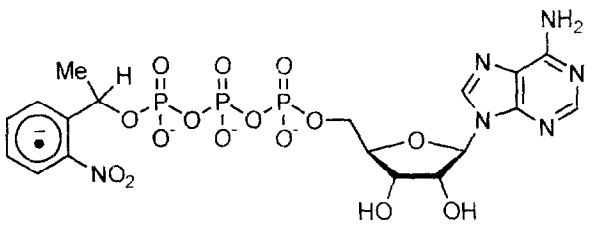
4. Discussion

4.1. Structure of the observed radical

Numerous studies have reported formation of long-lived or transient radicals upon irradiation of aromatic nitro compounds. These radicals can be divided into two groups, according to whether or not the nitrogen atom of the original nitro group carries a hydrogen atom in the radical. The pres-

ence of an N–H group is revealed by a hyperfine coupling constant in the range 8–9.5 G [15–18]. Since the spectra shown in Fig. 3 are not compatible with coupling constants of this magnitude or multiplicity, we exclude the presence of an N–H bond in the observed radical.

By contrast, the spectra of nitroarene radical anions show features much more consistent with the spectra observed here. Typical reported coupling constants are as follows: $a(N)$ 12.5–14.7 G; $a(H_o)$ 3–3.5 G; $a(H_m) \sim 1.1$ G; $a(H_p)$ 3–3.5 G, where the *o*-, *m*- and *p*-subscripts refer to positions relative to the nitro group [19–22]. The values above refer to the nitrobenzene radical anion and to radical anions for various *p*-nitroalkylbenzene derivatives. Some features of the present spectra require comment if they are to be interpreted as arising from the radical anion **6**. First and as described above, our spectra are averaged from a single scan of each of three samples. The use of a fresh sample for each scan ensures that the species observed does not arise from irradiation of photolysis products present in solution as the result of a previous flash illumination. The quality of the spectra is limited by the signal to noise ratio as well as by the speed of the field sweep, and only the larger couplings [$a(N)$ and $a(H_{o,p})$] are resolved. Nevertheless, the lines are much broader than for the spin-labelled ATP used for the intensity calibration (spectrum not shown). Simulations using the measured values for $a(N)$ and $a(H_{o,p})$ and with estimated values of ≤ 1.2 G for $a(H_m)$ and ≤ 1.5 G for $a(H_\alpha)$ reproduced the observed line shapes. With larger values of $a(H_\alpha)$, the simulated spectra began to show additional fine structure. The 1.5 G value $a(H_\alpha)$ is lower than the value of 2.75 G reported for the coupling to the benzylic protons in the radical anion of *p*-nitrophenylacetate [22], but may be associated with an unfavorable dihedral angle for the C–H bond in the *ortho*-substituted system that results in diminished orbital overlap [23].



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The second feature of the spectra concerns the observed hyperfine coupling patterns. Thus, the triplets with coupling of ~3.5 G in the spectrum of Fig. 3a are consistent with the presence of one *ortho* and one *para* hydrogen, each of which have similar coupling. Deuteration at the *ortho*-position (**1b**) greatly reduces one of these couplings and results in collapse to doublets. Finally, the ~16.6 G coupling to nitrogen is larger than in other reported *p*-nitroarene radical anions [19–22], but this parameter varies with solvent polarity [21] and for aromatic nitroarene radical anions is reported to be 3–4 G higher in water than in acetonitrile [24,25]. Furthermore, the radical anion of *o*-nitrotoluene in water has a 16.6 G coupling to the nitrogen, although in that case, the couplings to the *ortho*- and *para*-hydrogens were lower (~2–2.5 G) than those found for the species seen in the present study. The effect was attributed to the steric effect of the adjacent methyl group on the twist of the nitro group relative to the ring [26]. Evidently, there is a complex interplay between solvation, steric and electronic effects and we suggest that the spectroscopic data are consistent with **6** being the observed radical species. The weak dependence of the decay rate upon pH, with stability being higher as the pH increases, is consistent with other data on the behaviour of another nitroaryl radical anion, albeit over a range of higher pH values (reported half-lives of 240–790 s over the pH range 12.7–14.0, 23°C) [22].

4.2. Origin of the radical anion 6

As described in Section 3, the species now assigned as the radical anion **6** represents ~10% of the total reaction flux. It is therefore a significant component of the overall reaction and its origin and presence need to be considered as part of understanding the fundamental photochemistry of caged ATP and its application in biological experiments. With the aim of obtaining some mechanistic insight, we examined the kinetics of its formation and decay over the pH range 6.0–9.0. Fig. 2 illustrates the appearance and decay of the radical at pH 8.5, and comprises averaged data from three experiments. Fig. 4 shows related data obtained at pH 6, 7 and 9, which were from single runs at each pH value. Within the experimental error, the traces show three main features: (a) a gradual increase in lifetime as the pH increases; (b) rapid appearance (<20 ms) of the maximum concentration, and (c) a small lag phase in the early stage of decay, most evident in the data at pH 8.5. We note that the 20 ms limit for appearance of the radical is a deliberately conservative estimate, since the dead time following the laser pulse is 5–10 ms.

In the related *p*-nitrobenzyl case, generation of *p*-nitrobenzyl carbanion **7** by either thermal [19,20,27] or photochemical [22] methods in the absence of oxygen has been shown to lead to the formation of *p,p'*-dinitrobibenzyl **8** via the pathway shown in Scheme 2. In experiments at ambient temperature, only the EPR spectrum of the long-lived radical anion was observed, although the more highly substituted *p*-nitrocumyl radical as well as its companion radical anion has been observed in other reactions at low (150 K) temperature [21]. These experiments are potentially of relevance to the present study because the *p*-nitrobenzyl carbanion as shown in structure **7** is simply one canonical form (as the *para*-isomer) of the *ortho*-species represented as the *aci*-nitro anion **3** in Scheme 1. Furthermore, *o*-nitrotoluene is known to form *o,o'*-dinitrobibenzyl under strongly basic conditions [28], presumably by an analogous mechanism to that described above for the *p*-isomer.

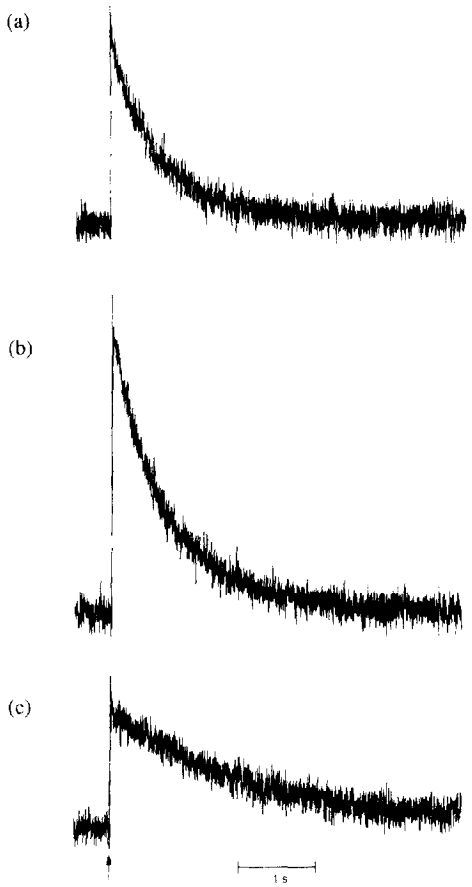
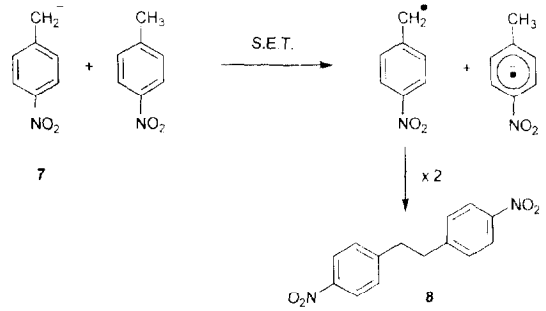


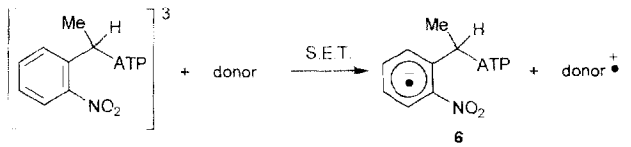
Fig. 4. Time-dependent monitoring of the signal intensity as in Fig. 2 for solutions of caged ATP **1a** at pH 6 (panel A), pH 7 (panel B) and pH 9 (panel C), all at 1.5°C. The arrow marks the point at which the laser was fired. Details of the buffer compositions are given in the text. The vertical scale is the same for each trace, so the records directly show the relative intensities at each pH value.



Scheme 2. Single electron transfer mechanism of the formation of *p,p'*-dinitrobibenzyl from *p*-nitrotoluene under basic conditions.

Given these data, it would appear reasonable to postulate that, in competition with the even-electron decay pathway shown in Scheme 1, the *aci*-nitro anion **3** could transfer an electron to unphotolysed caged ATP present in solution. However, this concept is not compatible with the kinetic data for appearance of the observed radical. From the *aci*-nitro decay rate of 92 s^{-1} determined at pH 7.0, 20°C (albeit in a buffer of higher ionic strength) and the measured Arrhenius energy of 62 kJ mol^{-1} [11], together with the known proportionality to proton concentration [7], the half-times for decay of the *aci*-nitro anion at 1.5°C and pH 6, 7, 8.5 and 9 are calculated to be 0.004, 0.04, 1.3 and 4.2 s, respectively. The formation of most or all of the maximum radical concentration within 20 ms cannot be reconciled with these lifetimes at pH values higher than 6.5, and kinetic simulations [29] that attempt to reproduce the observed time course of radical formation and decay do not readily accommodate formation of a significant proportion of the total radical concentration from the *aci*-nitro anion **3**. If in the kinetic simulations the reaction of the *aci*-nitro anion is taken to include a component of electron transfer and the rate of this process is assumed to be independent of pH, the proportion of the species decaying through this pathway would increase with increasing pH as the even-electron decay of the *aci*-nitro anion becomes slower. This is contrary to the observed results. Furthermore, kinetic studies suggest that electron transfer from the *p*-nitrobenzyl carbanion to *p*-nitroarenes occurs on a much slower time scale than is seen in the present case [27,30]. Evidently, the observed radical largely or wholly arises via an alternative, rapid pathway and a probable route involves direct electron transfer to a state upstream of the *aci*-nitro anion. The complex time course, most evident at higher pH values, may be related to the decay modes of the radical anion rather than to its formation by multiple pathways.

A feasible fast route for formation of the radical anion is revealed by picosecond laser flash photolysis studies [6,8], which have shown that singlet and triplet states contribute approximately 40% and 60%, respectively, to the reaction flux in photolysis of *o*-nitrobenzyl compounds and these data are consistent with the estimated 67% triplet yield from the $n \rightarrow \pi^*$ excited state of nitrobenzene itself [31]. Measured or estimated triplet lifetimes were in the range 300–500 ps and formation of a biradical from the triplet was also observed in one example [6]. The biradical lifetime was ~ 5 ns. Thus, two species with lifetimes in the range 0.5–5 ns are likely to be present after photolysis of caged ATP. Of these two species, the $n \rightarrow \pi^*$ triplet state of nitroaryl compounds is known to undergo photoreduction, initially to radical anions, under a variety of conditions [32,33] and we suggest that the data presently available are most readily explained by invoking such a reductive process (Scheme 3). The identity of a possible electron donor in the present case has not been established. Tertiary amines are present as buffer salts in some of these solutions and are known to act as donors to nitroarene triplets but a radical is also formed rapidly in solutions buffered by sodium phosphate, as shown in Fig. 4B. Alternative candidates include the adenine moiety of caged ATP or triv-



Scheme 3. Suggested route for the formation of the radical anion of caged ATP by a single electron transfer process to the triplet excited state. The structure of ATP is abbreviated as described in the legend to Scheme 1.

ially, the presence of amine contaminants in all the solutions. Of these, the latter is a likely contender but further work will be required to establish the level at which such contamination would be significant. However, since amines will invariably be present in biological preparations, the possibility of an amine being the electron donor is directly relevant to the use of caged compounds in biology.[1]

4.3. Implications of radical formation

Whether or not the preceding discussion is correct in every detail, our data indicate strongly that the radical anion of the nitroaryl group is present after photolysis of caged ATP in solutions of comparable composition to those typically used in biological experiments. Furthermore, unless electron donation is specifically from the adenine group as now appears unlikely (see [1]), it is probable that other caged compounds also give rise to radical anions. The fate of the radical anion has not been examined, except to the extent that anion-exchange HPLC analysis of the flash photolysed solutions (data not shown) showed no peaks other than those coincident with ATP and its caged precursor, together with the by-products known to arise from the further reaction of released 2-nitrosoacetophenone **5** with DTT [11]. It is possible that the radical anion undergoes $S_{RN}1$-like dissociation [35] to release ATP on a time scale (at pH 7) approximately two orders of magnitude slower than its release by decay of the *aci*-nitro anion **3** (Scheme 1). We have previously observed that sodium hydride treatment of the 2-*O*-(2-nitrobenzyl) ether of a glucose derivative under anaerobic conditions in DMF resulted in complete loss of the starting material and release of the alcohol [36]. The reaction course is presumably analogous to that described above for *p*-nitrotoluene, and demonstrates the potential for $S_{RN}1$-like dissociation. A low-amplitude release of ATP (or other effector) on a much slower time scale than the main release is probably unimportant for most biological experiments using caged compounds. However, the presence of a significant concentration of transient radical species immediately following photolysis may cause damage to biological tissues and could be particularly significant in experimental protocols involving repeated photolysis in the same tissue preparation. In this context, we note that photolysis in the EPR spectrometer as described above of 3′,5′-dimethoxybenzoin phosphate, an alternative type of caged phosphate [37], generated no observable radical spectrum (data not shown). Caged compounds based on this type of caging group may prove to be valuable in the study of EPR signals from spin-labelled probes following flash photolysis.

[1] Preliminary experiments to probe the identity of the electron donor were conducted after this work was complete (J.E.T Corrie, B.C. Gilbert, A.C. Whitwood, unpublished results), under conditions of continuous illumination from a 300-W xenon arc lamp [Model ILC302UV (ILC Technology, Sunnyside, CA) equipped with a 250–400-nm bandpass filter] and without deoxygenation of the solutions. In the absence of added buffer salts, no EPR spectrum was observed for either caged ATP **1a** or methyl 1-(2-nitrophenyl)ethyl phosphate [34] (caged methyl phosphate). In the presence of EPPS (200 mM, pH 8.5) and without DTT, an EPR spectrum identical to that described in the main part of this work initially appeared for both these compounds. Upon longer illumination, a further spectrum [characterised by $a(N)$ 11.2 G] appeared as photolysis proceeded and the concentration of nitrosoketone **5** increased, as was seen upon repeated flash photolysis but not discussed in detail (see first paragraph of Section 3). These data indicate that a tertiary amine can act as an electron donor for formation of the initial radical anion. Full details of these experiments will be described in a later publication.

5. Conclusion

The results and their discussion presented above leave a number of questions as subjects for future work. Our principal concern here has been to document the hitherto unrecognised formation of a long-lived radical species (τ 0.1–1 s) when caged ATP is photolysed and to set out a hypothesis to rationalise the kinetics of its formation. Future investigation would benefit from better time resolution to study the formation kinetics and will need to identify the electron donor which is postulated here. A preliminary follow up of the results reported here (see [1]) indicates that the same radical anion is formed under conditions of full oxygen saturation and that a tertiary amine can act as an electron donor in its generation. Further investigation will be required to establish the minimum concentration of amine that can function effectively in order to explain the observed formation of the radical anion in buffers that do not overtly contain tertiary amines. The results also raise the possibility that caged compounds which contain tertiary amines may undergo intramolecular electron transfer, with consequences for the nature and rate of product formation. Future investigations will explore this in detail.

Acknowledgements

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