Review Commentary
Singlet and triplet states in the reactions of nitrenium ions

Daniel E. Falvey*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742-2021, USA

ABSTRACT: Nitrenium ions (R—N—R$^+$) are reactive intermediates which are isoelectronic with carbenes. Like the more familiar carbenes, nitrenium ions have low-energy singlet and triplet states. Recent experiments have been directed at understanding how singlet and triplet nitrenium ions differ in their chemical reactivity. Singlet nitrenium ions typically react rapidly with nucleophiles whereas the triplet nitrenium ions tend to abstract H atoms. Several specific cases are discussed including the parent system, NH_2^+, and several arylnitrenium ions. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: nitrenium ions; singlet state; triplet state; carbenes; photochemistry

INTRODUCTION

Nitrenium ions[1–3] have the general formula RR′N$^+$, making them nitrogen analogs of carbenes (RR′C). The nitrenium ions differ from the more familiar nitrenes (R—N) in that they are divalent and cationic rather than univalent and neutral. Like the nitrenes and carbenes, nitrenium ions are extremely reactive species and this presents some interesting challenges to the experimentalist.

One long-standing motivation for studying nitrenium ions comes from the field of chemical toxicology. It has been proposed that DNA damage caused by enzymatically activated aromatic amines proceeds via arylnitrenium ion intermediates. This type of DNA damage can, under certain circumstances, convert a healthy cell into a cancer cell. This proposal has been discussed at length in a number of recent articles and reviews[3–10] and it will not be considered further here other than to note that the relevant reactions appear to be characteristic of the singlet state (see below).

This review will focus instead on a much more neglected aspect of nitrenium ions: their singlet and triplet states and how these different electronic configurations influence their chemical reaction mechanisms. It will be of special interest to evaluate recent progress from both computational chemistry and experimental chemistry. Time and space considerations prohibit a comprehensive survey of all calculations and experiments. Instead, several selected examples will be presented where both theory and experiments have been applied to the same systems with special emphasis on work from the author's own laboratory. The reader should realize that a number of interesting recent computations and experiments on nitrenium ions will escape mention herein.

It will become apparent from the following discussion that much work remains to be done in uniting theory and experiment. A general problem that arises in comparing electronic structure calculations with mechanistic experiments in solution is that the two methods emphasize different types of information. The sort of data that are readily accessible from experiments (shapes and positions of UV–visible absorption bands, rate constants for reactions and distributions of stable products) are notoriously difficult to calculate to the requisite accuracy. Likewise, the sort of parameters that can be calculated to high accuracy (bond lengths, bond angles, singlet–triplet energy gaps, heats of formation) are extremely difficult to measure experimentally, especially when the species in question is a highly reactive intermediate.

GENERAL CONSIDERATIONS

Nitrenium ions, like carbenes and nitrenes, have two low-energy electronic states, a singlet state and a triplet state.[11–14] This follows because nitrenium ions possess two non-bonding electrons and two non-bonding orbitals. This is illustrated in Fig. 1(A). In the triplet state the electrons have parallel spins and are distributed between the two non-bonding orbitals, σ and p. In the singlet state the electrons have antiparallel spins and occupy the σ

Correspondence to: D. E. Falvey, Department of Chemistry and Biochemistry, University of Maryland, Maryland 20742-2021, USA.
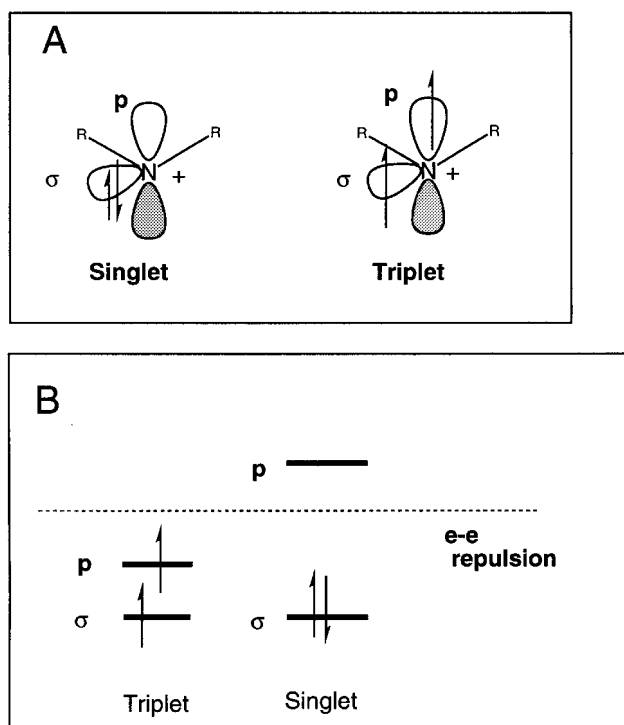E-mail: df37@umail.umd.edu

Figure 1. A simplified picture of (A) the non-bonding orbitals and (B) their relative energies for the singlet and triplet states of a typical nitrenium ion

orbital (i.e. σ^2), leaving the p orbital vacant. (Singlet states having σp and p^2 configurations are also possible but they are generally much higher in energy.)

The difference in the energy between the singlet and triplet states (singlet–triplet gap or ΔE_{st}) is determined by the energy difference between the two non-bonding orbitals. Given the bent geometry shown in Fig. 1(A), the p and σ orbitals will have different energies as indicated in Fig. 1(B). In the absence of any special considerations, the σ orbital, having s character, will be lower in energy than the p orbital. It might seem from casual inspection of the orbital energy diagram in Fig. 1(B) that the σ^2 singlet state would inevitably be the lowest energy configuration. However, this simple diagram fails to account for two additional effects. First, electrons repel each other and these electrostatic forces will tend to favor the σp configuration. Also, parallel electron spins gain a favorable electron exchange interaction (as seen in Hund's rule). This too will tend to favor the triplet state. If the orbital energy spacing is smaller than the exchange and coulombic forces, then the triplet will be the lower energy state. If the orbital energy spacing is larger than these forces, then a singlet ground state will result. Thus, any structural changes that destabilize the p orbital or stabilize the σ orbital will favor the singlet state. Likewise, changes that destabilize the σ or stabilize the p orbital will favor the triplet state.

It is difficult to measure directly singlet–triplet energy gaps in carbenes, nitrenes or nitrenium ions. In certain cases this has been accomplished using gas-phase photoionization spectroscopy. Interpretation of these spectra can be complicated by hot bands or in cases where a large number of vibrational modes obscure resolution of the electronic states. For this reason, these experiments are most successfully applied to very small and/or highly symmetric molecules. Application of this technique to larger species (e.g. phenylnitrene[15]) is still far from routine.

Triplet states, being paramagnetic, give characteristic EPR signals.[16,17] Detection of a triplet EPR spectrum is a good indication either that the triplet state is the ground state or that ΔE_{st} is very small. This experiment has been used to assign triplet ground states to various carbenes and nitrenes. Unfortunately, this method generally does not provide a numerical value for the singlet–triplet gap. Moreover, if the singlet state is the ground state, no signal of any sort is observable. Of course, the same negative result could also mean that the species in question is too short-lived to be detectable or that spin relaxation processes broaden the signal to the point where it cannot be detected. An EPR spectrum of a triplet nitrenium ion has not yet been reported.

The third way in which experimental evidence for either singlet or triplet states can be obtained is through chemical trapping experiments. Generally, singlet states, having both a non-bonding pair of electrons and an empty orbital, behave as Lewis acids or Lewis bases. They therefore tend to participate in chemical reactions involving shifts of electron pairs. For example, both nitrenes[18] and carbenes[19] can act as bases, abstracting protons via their non-bonding pair. In contrast, triplet states, having two semi-occupied orbitals, tend to behave as radicals. For example, triplet carbenes[20] and nitrenes[21] both abstract H atoms, a reaction that is very typical for free radicals.

THE PARENT NITRENIUM ION, NH$_2$$^+$

The parent system is unique among nitrenium ions in that its singlet–triplet energy gap has been characterized both by theory and by experiment, with both approaches converging on the same numerical value. As early as 1979, Peyerimhoff and Buenker[22] calculated (MRD-CI) a ΔE_{st} of $+29.9$ kcal mol^{-1} (a positive sign means that the triplet is lower in energy) (1 kcal = 4.184 KJ). This early prediction has withstood the test of time. It was verified experimentally by the mass-selective photoionization spectroscopy study of Gibson, *et al*,[23] who measured a value of 30.1 ± 0.2 kcal mol^{-1}. Additional *ab initio* calculations by Pople and Schleyer[24] and van Huis *et al*.[25] and also density functional theory calculations by Cramer *et al*.[14] are essentially in agreement with these values. Analysis of the IR spectrum[26] of NH$_2$$^+$ reveals that it is quasi-linear. That is, the molecule is bent with an equilibrium bond angle of 153°. However, the energy
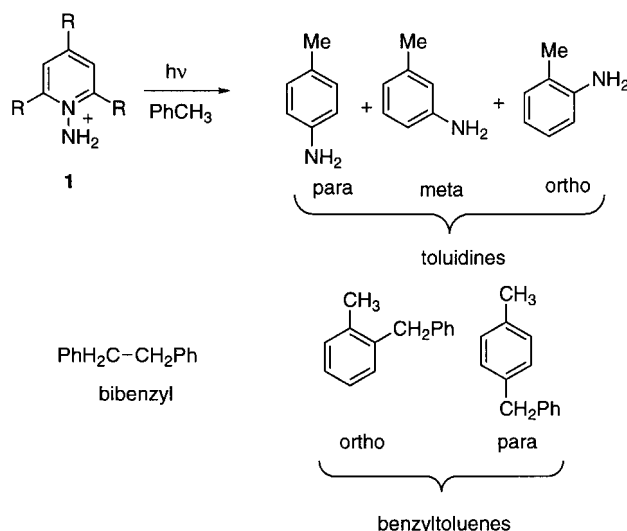
Scheme 1. Photochemistry of 1-aminopyridinium ions

required to bend it to the linear geometry is less than the zero-point vibrational energy. Hence it can be concluded with reasonable certainty that NH_2^+ is a quasi-linear ground-state triplet with an energy gap of $+30\ kcal\ mol^{-1}$.

The carbene analog to NH_2^+, methylene or CH_2, is also a ground-state triplet,[27] but its ΔE_{st} is only $+9\ kcal\ mol^{-1}$. Cramer *et al.*[14] attributed this to contraction of the MOs around the more electronegative nitrogen, which leads to increased coulombic repulsion in the singlet state of NH_2^+ and forces the electrons into separate orbitals. In contrast, CH_2 has more diffuse MOs and the electrons feel less coulombic repulsion in the singlet state.

While the most precise structural and energetic data come from gas-phase studies of NH_2^+, the only information available concerning its reaction pathways comes from photochemical studies in solution. Takeuchi and co-workers[28–30] first examined the behavior of NH_2^+ generated from the photolysis of 1-amino-2,4,6-triphenylpyridinium tetrafluoroborate (**1**) ions. It was found that photolysis of the latter in toluene ($PhCH_3$) containing 10–50% trifluoroacetic acid (TFA) gives *o*-, *p*- and *m*-toluidines (i.e. aminotoulenes that result from the

addition of an NH_2^+ to toluene), 2,4,6-triphenylpyridine, bibenzyl ($PhCH_2CH_2Ph$) and *o*- and *p*-benzyltoulenes (Scheme 1).

These earlier workers attributed the toluidine isomers to reactions of the initially formed singlet NH_2^+ with toluene.[28] Bibenzyl and the benzyltoluenes were attributed to reactions of triplet NH_2^+ (presumably from H atom transfer from toluene to the triplet and subsequent coupling of the benzyl radicals). Their work focused on the presumed singlet products. It was found that the relative yields of the *o*-, *p*- and *m*-toluidines depends on the gegenion of the pyridinium salt in addition to substitutions on the pyridine leaving group. On this basis, it was concluded that the singlet state was not formed freely in solution, but rather it reacted via some loose complex with the pyridine leaving group and/or the gegenion.

Experiments carried out in our laboratories[31,32] are in general agreement with the basic results of Takeuchi and co-workers. Further studies were carried out in order to ascertain the origins of bibenzyl and the benzyltoluene isomers. We noted that whereas bibenzyl is often seen as the coupling product from two benzyl radicals, the formation of the benzyltoluenes from radical coupling is apparently unprecedented.[33–35] This lead us to propose a modification to Takeuchi and co-workers' mechanism, shown in Scheme 2. The singlet ($^1NH_2^+$) abstracts a hydride from toluene to give NH_3 along with the benzyl cation ($PhCH_2^+$). The latter attacks an unreacted toluene to give either *o*- or *p*-benzyltoluene. In competition with hydride transfer, $^1NH_2^+$ also can relax to the lower energy triplet $^3NH_2^+$. The triplet in turn abstracts an H atom from toluene, as previously suggested. This process gives $PhCH_2^\bullet$, which finally dimerizes to give bibenzyl.

This mechanism is supported by two experiments:

1. Addition of a non-reactive diluent favors the formation of the triplet product (bibenzyl) at the expense of the singlet products (toluidines and benzyltoluenes). This experiment is easily understood by reference to Scheme 2. The hydride transfer step has a rate that is proportional to the concentration of the trap (toluene), whereas the intersystem crossing rate is independent of the trap. Thus, diluting the toluene causes a greater fraction of the initial $^1NH_2^+$ ions to relax to the lower
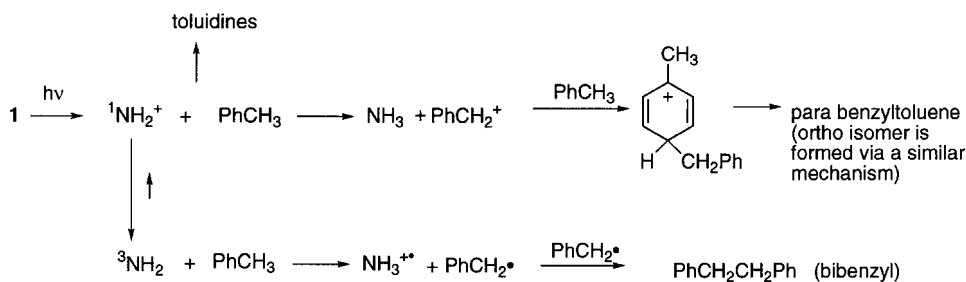
Scheme 2. Mechanism of the reaction of the parent nitrenium ion with toluene

Table 1. Stable product distributions from generation of NH_2^+ in the presence of $PhCH_3$ with 10% trifluoroacetic acid

Conditions[a]	Bibenzyl (%)	Benzyltoluenes (%)
$PhCH_3$	23	24
1:1 (v/v) $PhCH_3$–C_6F_6	85	5
1:1 (v/v) $PhCH_3$–CCl_4	80	6
$PhCH_3$–triplet sensitizer[b]	52	14

[a] 10% trifluoroacetic acid added. Irradiations were carried out using the >295 nm output of a medium-pressure Hg lamp.
[b] 9-Fluorenone was used as a triplet sensitizer and wavelengths >320 nm were employed.

energy $^3NH_2^+$. Table 1 shows that the behavior is in fact consistent with these predictions. Addition of 50% (v/v) CCl_4 or 50% (v/v) hexafluorobenzene (C_6F_6) causes both a decrease in the yields of the benzyl-toluenes and an increase in the yield of bibenzyl. Although not indicated in Table 1, the yields of toluidines are affected in a similar way to the benzyltoluenes.

2. Photolysis via triplet energy transfer favors formation of the triplet product, bibenzyl. When **1** is photolyzed via a triplet sensitizer (9-fluorenone), light is first absorbed by the sensitizer, which rapidly suffers intersystem crossing to its excited triplet state and then relays the energy to compound **1**, creating its triplet excited state. Spin conservation dictates that decomposition of triplet excited **1** will give the triplet nitrenium ion $^3NH_2^+$. Hence triplet sensitization provides a method by which $^3NH_2^+$ can be produced bypassing the singlet manifold. This predicts that the yield of bibenzyl would be increased at the expense of benzyltoluenes. Table 1 shows that this is indeed the case. The yield of bibenzyl increases from 23 to 53% and the yield of benzyltoluenes decreases from 24 to 14%.

While this result also supports the mechanism in Scheme 2, there remains a question as to how benzyltoluenes are formed at all under triplet sensitization. There are two possibilities. First, the triplet-sensitized irradiations employed wavelengths >320 nm. At these wavelengths, the sensitizer absorbs the majority of light. However, it is impossible to prevent some direct absorption by the precursor **1**. Hence the singlet products could be the consequence of undesired direct irradiation. The second possibility is that the benzyltoluenes come from reactions of the triplet. Following Scheme 2, $^3NH_2^+$ abstracts an H atom from toluene to give $PhCH_2^\cdot$ and $NH_3^{+\cdot}$. The benzyl cation would then result from a secondary electron transfer between these two intermediates (i.e. $PhCH_2^\cdot + NH_3^{+\cdot} \rightarrow PhCH_2^+ + NH_3$). We favor the former explanation. The dilution experiment establishes a limit on the amount of benzyltoluenes that could come from the triplet pathway.

In any case, these two experiments make it clear that
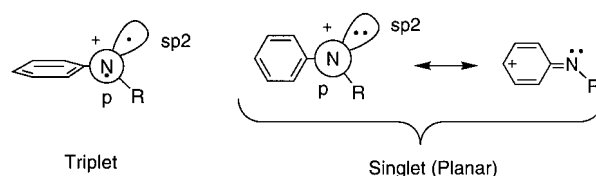
**Figure 2.** Geometries of the singlet and triplet states of phenylnitrenium ion

bibenzyl and the benzyltoluenes arise from different pathways. Benzyltoluenes form from the initially generated state and bibenzyl forms from a subsequent intermediate. If they were both formed from benzyl radical dimerization, then constant ratios of the two types of products would form regardless of the reaction conditions.

ARYLNITRENIUM IONS

In contrast to the parent system, it is generally agreed that arylnitrenium ions (e.g. $PhNH^+$) are ground-state singlets. In the case of $PhNH^+$, *ab initio* calculations at both the post-Hartree–Fock[11,36] and the DFT[14] levels converged on a ΔE_{st} of *ca* -20 kcal mol^{-1}. Qualitatively this is explained by donation of electron density from the filled π-orbitals of the aromatic ring into the vacant p orbital at the nitrenium center. This effect delocalizes the charge to the *ortho* and *para* positions of the phenyl ring as depicted by the resonance hybrids in Eqn. (2). In terms of the MOs in Fig. 1(B), this interaction raises the energy of the p non-bonding orbital and thus favors the singlet state.

From this argument it further follows that substituting the aromatic ring with π-donating groups will further stabilize the singlet and destabilize the triplet. Likewise, addition of π-withdrawing groups will tend to decrease the orbital splitting and thus favor the triplet state. This latter prediction will become important when we consider nitrenium ion **2g** (see below).

The computational results above also reveal an unexpected feature of triplet arylnitrenium ions. The triplet state of phenylnitrenium ion is not a planar structure. Instead, the N—H bond is perpendicular to the aromatic ring (Fig. 2). In contrast, the singlet possesses a planar structure and a shortened C—N bond (1.311 Å) consistent with its cyclohexadienyl imine cation character. This finding holds true at all levels of theory starting with AM1 semiempirical calculations[11,37–39] all the way up to DFT calculations (BVWN5/cc-pVTZ//BVWN5/cc-pVDZ).[40] Apparently the triplet behaves as a protonated triplet nitrene. The C—N bond is longer and shows only a very low barrier to rotation. The non-planar minimum can be explained by a slight steric bias caused by the *ortho* H atoms. In sum, calculations on arylnitrenium ions
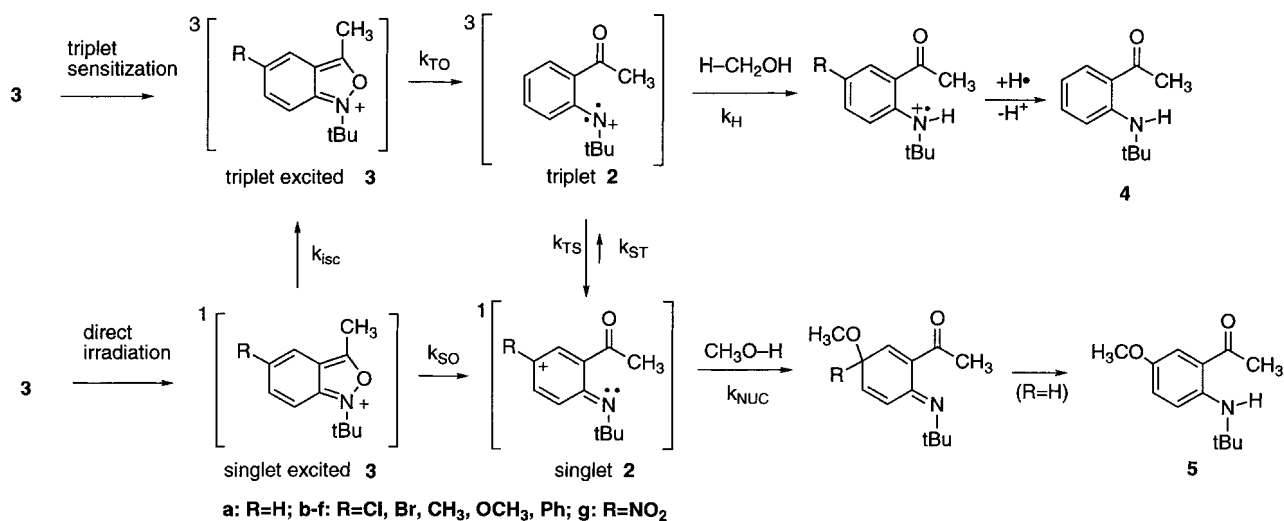
Scheme 3. Mechanism of the methanol trapping of the *N-tert*-butyl-*N*-(2-acetylphenyl)nitrenium ion **2**

show that there is a low-energy singlet state that is planar and possesses the ring bond alternation along with a short C—N bond distance that would be expected for a cyclohexadiene imine cation. This is accompanied by a non-planar triplet where the charge is localized and the C—N bond is more or less single. In the simplest case (PhNH$^+$) the triplet is higher in energy than the singlet by *ca* 20 kcal mol^{-1}.

Arylnitrenium ions have been studied extensively in connection with their involvement in carcinogenesis. Relatively few studies, however, had addressed the issue of their spin states until investigations of *N-tert*-butyl-*N*-(2-acetylphenyl)nitrenium (**2a**) were carried out several years ago.[41] This particular arylnitrenium ion was chosen for study mainly because there was a previously characterized method for its generation.[42] The mechanism of its photochemical formation is complex and a detailed discussion is available elsewhere.[41] Here we will focus on the key results that first revealed the dichotomy between the singlet and triplet state chemistry and compare this behavior to the nitro derivative **2g**.

Direct photolysis of the precursor **3a** in CH$_2$Cl$_2$ solvent containing 2.7 M CH$_3$OH gives the adduct *N-tert*-butyl-*N*-(2-acetyl-4-methoxyphenyl)amine (**5a**) in nearly quantitative yield (Scheme 3). The origin of this product can be readily understood by reference to Fig. 2. The singlet state, having significant positive charge in the position *para* to the nitrenium center,[43] reacts with nucleophiles (i.e. lewis bases) at that position. The stable product is formed from nucleophilic attack at the *para* position followed by a net proton shift from the *para* position to the nitrogen atom.

These results can be compared with the stable products obtained via triplet sensitization. In the presence of 0.12 M CH$_3$OH, a 73% yield of the same methoxy adduct is detected along with 24% of the parent amine [*N-tert*-butyl-*N*-(2-acetylphenyl)amine (**4a**), Table 2]. However,

as the concentration of CH$_3$OH is increased the yield of the methoxy adduct actually decreases! In neat (24.7 M) CH$_3$OH, the yield decreases to 32%. Simultaneously the yield of the parent amine increases with increasing CH$_3$OH concentration. This apparent contradiction is explained as follows: (1) CH$_3$OH can act as an H atom donor through its methyl hydrogens and also as a nucleophile through its O—H group; (2) the triplet state nitrenium ion prefers to abstract H atoms (a one-electron process) rather than suffer nucleophilic attack (a two electron process); and (3) the singlet state of the nitrenium ion is lower in energy than the triplet state or else close enough in energy to be thermally accessible.

Following the mechanism in Scheme 3, we see that at high concentrations of CH$_3$OH, the triplet will be kinetically trapped by H atom transfer, a process that ultimately yields the parent amine **4a**. As the concentration of CH$_3$OH is reduced, a larger fraction of the initially formed nitrenium ions survive the H atom transfer process and relax to the lower energy singlet state. The singlet is then trapped via nucleophilic addition of CH$_3$OH.

The results of the experiments with **2a** established that singlet- and triplet-state nitrenium ions react via different mechanisms and yield different stable products. The singlet is attacked by nucleophiles and the triplet tends to react via H atom transfer. Furthermore, the fact that there

Table 2. Yields of methoxy adduct **5a** and parent amine **4a** from triplet sensitized photolysis of **3a**

[CH$_3$OH] (M)	Methoxy adduct **5a** (%)	Parent amine **4a** (%)
0.12	73	24
1.18	57	42
2.69	44	51
24.7	32	66
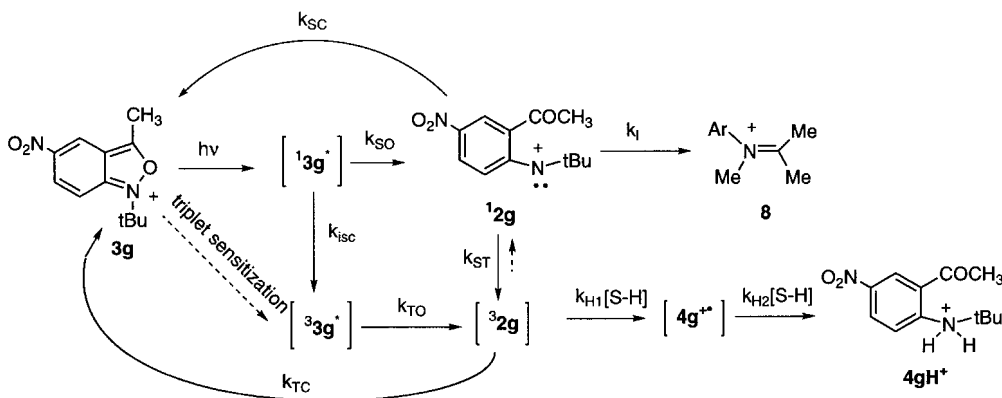
Scheme 4. Photochemical generation and trapping of nitrenium ion **3**

is a kinetically viable pathway from the triplet to the singlet implies that the singlet is lower in energy than the triplet. This is consistent with theoretical studies which predict these species to be ground-state singlets.[11]

Derivatives of **2** with various ring substituents (Br, Cl, CH$_3$, CN, Ph) have also been examined.[44–47] They all show similar trapping behavior. The predominant stable products result from nucleophilic trapping on the carbons of the aromatic ring (e.g. **5**) Again this is consistent with the singlet being the lowest energy state. More recent attention has turned to the diphenylnitrenium ion (Ph$_2$N$^+$).[48,49] Although an extensive analysis of its singlet–triplet state dynamics is not complete, it is clear that the major decay pathways occur from the singlet state. For example, Ph$_2$N$^+$ reacts rapidly with nucleophiles such as halides, alcohols, water and amines giving adducts analogous to **5**. Again, this behavior is consistent with DFT calculations which hold that this species is a ground-state singlet with a ΔE_{st} of -11.6 kcal mol^{-1}.

Finally, we turn our attention to the 4-nitro-substituted arylnitrenium ion **2g**, which we shall argue is a ground-state triplet.[50] Scheme 4 presents our mechanism for the photolysis of its precursor **3g**. The stable products from this nitrenium ion are qualitatively different to that seen from the unsubstituted arylnitrenium ion **2a**. Only two types of products are observed, the parent amine **4g** and an iminium ion **8**. The latter product arises from a 1,2-migration of a methyl group from the *tert*-butyl residue to the electron-deficient nitrenium ion center. This was shown to be a characteristic product of the singlet state through a comparison of direct and triplet-sensitized irradiations. Interestingly, no nucleophilic adducts analogous to **5** could be detected even when neat methanol or 27 M H$_2$O were added as traps. Apparently the 1,2 shift leading to **8** is faster than addition of any external nucleophile.

Laser flash photolysis of nitrenium ion **2g**'s precursor (**3g**) gives a transient absorption spectrum that is assigned to its excited triplet state. This species appears within the 10 ns window of the laser pulse and its decay rate is not affected by H atom donors (traps for the triplet nitrenium

ion) or nucleophiles (traps for the singlet nitrenium ion). However, addition of O$_2$, a quencher of excited triplet states, does reduce its lifetime. In the absence of O$_2$ the excited triplet state of **3g** decays with a lifetime of 300 ns. The formation of the excited triplet state of **3g** indicates that intersystem crossing in the precursor (i.e. process k_{isc}) effectively competes with excited state ring opening (k_{so}).

We were unable to detect a transient absorption that could be attributed to either the singlet or triplet state of nitrenium ion **2g**. However, its lifetime and reaction rates could be monitored through the use of a probe substrate. Addition of triphenylmethane (Ph$_3$CH) caused formation of the trityl radical (triphenylmethyl, Ph$_3$C$\cdot$) only when **3g** was also present in the reaction medium. The appearance of the trityl radical absorption band[51] at 340 nm could be monitored using laser flash photolysis. One important consequence of this experiment is that it confirmed a previous assumption that the parent amine arises from sequential hydrogen abstractions.

A kinetic waveform from this experiment is shown in Fig. 3.[50] This particular trace was taken at 370 nm. At this wavelength, both the trityl radical and the excited triplet state of **3g** absorb. Following the laser pulse, there is a rapid decay in absorption of the excited triplet state of **3g** (due mainly to process k_{to}). This is followed at later times by the growth of the trityl radical (through process k_{H2}). Careful kinetic analysis of the growth of trityl radical at various Ph$_3$CH concentrations reveals a delay between disappearance of the excited triplet state of **3g** and the appearance of the trityl radical. This delay corresponds to the lifetime of the unseen nitrenium ion **2g**. In the absence of the trap, the lower limit of the nitrenium ion lifetime is calculated to be >2 μs.

This very long lifetime should be sufficient to allow for spin equilibration. Carbenes, for example, reach spin equilibrium in times usually of the order of 1 ns or less.[21,52–54] The implication of this result, coupled with the assumption that the radical products derive from triplet state reactions, is either that **2g** must be a ground-state triplet or that the singlet and triplet states must be
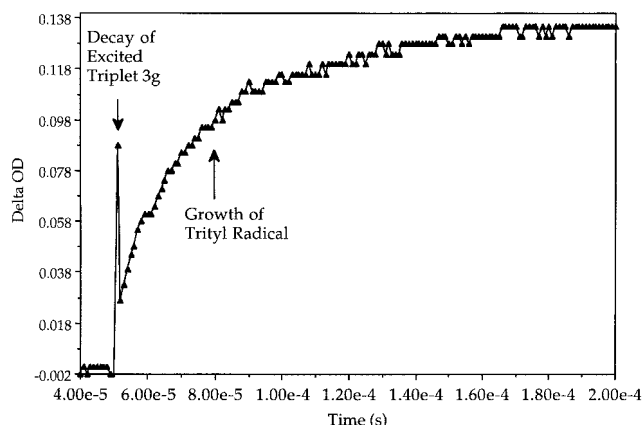
Figure 3. Kinetic waveform from laser flash photolysis of nitrenium ion precursor **3g**

close enough in energy that the singlet state can react via an equilibrium with the higher energy triplet. If the latter case were operative, we would have expected to observe some singlet products (i.e. iminium ion **8**) when the triplet is selectively generated.

To test for rapid spin equilibration, triplet energy transfer experiments were carried out in CH_2Cl_2 solvent using 9-fluorenone as the sensitizer. These experiments produced no detectable yields of **8**. This result leads to the conclusion that **2g** is a ground-state triplet. The only alternative that would be consistent with our observations would be that the singlet is the ground state, but for some reason there is an unexpectedly large kinetic barrier to spin inversion.

N-tert-Butyl-*N*-(2-acetyl-4-nitrophenyl)nitrenium ion **2g** is an interesting case because it appears to be an example of a arylnitrenium ion with a triplet ground state. This is readily understood from qualitative considerations. Removal of π-electron density from the aromatic ring tends to favor the triplet state over the singlet. Although **2g** itself has not been the subject of a computational investigation, a recent paper by Sullivan *et al.*[55] on *para*-substituted phenylnitenium ions is relevant. High-level DFT calculations verify the qualitative prediction that π-acceptors such as nitro and acetyl substituents stabilize the triplet state by 2.0 and 5.3 kcal mol^{-1}, respectively, compared with PhNH$^+$. The mono substituted phenylnitrenium ions were all calculated to have singlet ground states. However, possible synergistic effects of disubstitution and the steric effect of the bulky *tert*-butyl group might be responsible for making the triplet the ground state in the case of **2g**. Further computational studies of these effects are clearly warranted.

CONCLUSIONS

Recent work has shown the singlet and triplet states of

nitrenium ions can be distinguished via characteristic chemical reactions. The singlets react via hydride transfer and addition to nucleophiles. Triplets react via H atom abstraction. Generally, quantum mechanical calculations at various levels have proved to be a good qualitative guide to predicting singlet–triplet energy gaps. Thus the parent system, NH$_2^+$, is almost certainly a ground-state triplet. Experimental data in the gas phase and in solution are generally in agreement with that. Aromatic nitrenium ions are predicted by *ab initio* methods and also DFT to be ground-state singlets. This prediction is generally consistent with most experimental data. However, no experiment to date has directly addressed the magnitude of the singlet–triplet gap in arylnitrenium ions.

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