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N-METHYL-*N*-PHENYLNITRENIUM ION FROM PHOTOLYSIS OF *N*-(METHYLPHENYLAMINO)-2,4,6-TRIMETHYLPYRIDINIUM TETRAFLUOROBORATE

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The photochemical reactions of *N*-(methylphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate were studied to find evidence of photodecomposition to a nitrenium ion reactive intermediate. Stable products were formed that were consistent with a singlet-state methylphenylnitrenium ion precursor. The methoxy and chloro adducts. *N*-methyl-p-anisidine and 4- (and 2-)chloro-*N*-methylaniline, were identified and quantified by high-performance liquid chromatographic analysis. A hydride shift from the *N*-methyl group of the nitrenium ion is also proposed based on the detection of aniline which would result from hydrolysis of the iminium ion rearrangement product. The rate constant for this rearrangement is estimated to be 10^8 s^{-1}. The reduction product, *N*-methylaniline, is produced, and is believed to form, at least in part, from the hydrogen atom abstractions of the triplet nitrenium ion. This is supported by the results of triplet sensitized irradiations. Laser flash photolysis studies yielded the transient spectrum of a long-lived intermediate absorbing at 470 nm. This transient species is believed to be the cation radical of *N*-methylaniline. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Nitrenium ions are short-lived reactive intermediates that contain a cationic divalent nitrogen atom.[1] There has been an interest in these species owing to the possible role of aryl-substituted nitrenium ions in chemical carcinogenesis.[2–5] The chemistry of carbenes and nitrenes, which are closely related isoelectronic species, is fairly well characterized.[6–8] Although much less is known about the chemical reactivity of nitrenium ions, the last decade of research has greatly illuminated some of the trends in reactivity unique to arylnitrenium ion chemistry.[9–12] Theoretical investigations have examined the electronic structure of nitrenium ions. Like their isoelectronic species, carbenes and nitrenes, nitrenium ions can exist in either a singlet state, with two non-bonding electrons occupying the same orbital, or a triplet state, with two non-bonding electrons of parallel spin in different orbitals. The simplest possible nitrenium ion, NH_2^+, has been shown to be a ground-state triplet.[13–15] However, aryl substitution is predicted to make the singlet nitrenium ion the ground state.[16–19] Recent experimental research has demonstrated that these two possible spin states have very different chemical reactivities: the singlet behaves as an electrophilic species and the triplet behaves more like a radical.[12, 20–22]

Photochemical generation of nitrenium ions has proven advantageous in that the triplet state, which is typically the excited state of arylnitrenium ions, is more easily accessible. Use of triplet sensitizers can lead to triplet nitrenium ion directly, whereas intersystem crossing from the singlet manifold would have to be somewhat efficient to study the triplet nitrenium ion under any other reaction conditions. Photochemical generation also allows for the use of laser flash photolysis methods to obtain evidence for nitrenium ion intermediacy and to measure rate constants for their various reactions. The photochemical ring opening reaction of 3-methyl-*N*-alkylanthranilium ions, which leads to arylakylnitrenium ion intermediates, has been valuable in that it allows for the direct observation of these intermediates by laser flash photolysis methods.[12, 20–22] However, this chemistry only allows for the characterization of 2-acetyl-substituted arylnitrenium ions.

Abramovitch and co-workers[23, 24] have shown that arylacyl- and diacylnitrenium ions can be generated photochemically from appropriate *N*-aminopyridinium salts due to the photoinduced heterolysis of the N—N bond in the pyridinium cation. Recent work in our laboratories involved pyridinium salt substrates used to generate diarylnitrenium

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ions photochemically.[20] However, few results have been reported for the photochemical generation of unsubstituted arylalkylnitrenium ions. The present work involves the photochemical reactions of a pyridinium salt substrate, *N*-(methylphenyl)amino-2,4,6-trimethylpyridinium tetrafluoroborate (MPAP). Product distributions obtained from the photolysis of MPAP under various conditions have been examined. These results are consistent with the formation of a methylphenylnitrenium ion intermediate ($PhMeN^+$). A comparison of direct and triplet sensitized irradiation shows that the singlet decays via nucleophilic attack on the phenyl ring or by rearrangement involving the *N*-methyl group while the triplet decays by radical pathways to form the reduction product, *N*-methylaniline. The photo-decomposition of MPAP was also studied by laser flash photolysis methods, but the transient absorbance detected was not attributed to a nitrenium ion intermediate. More likely, the transient species detected was an intermediate product of nitrenium ion reactions.

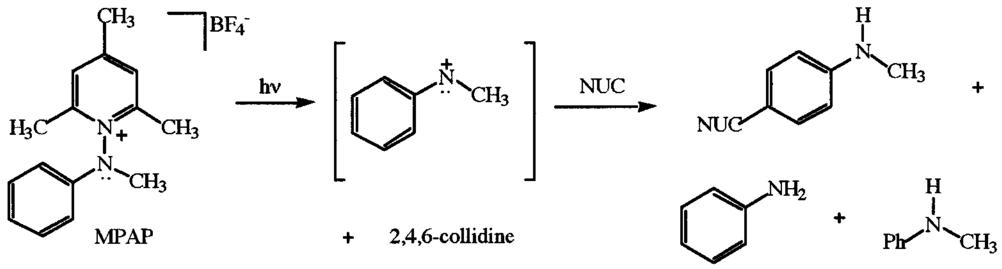
EXPERIMENTAL

Laser flash photolysis studies with N-(methylphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate (MPAP). Laser flash photolysis experiments were carried out with an excimer laser using Xe–HCl reagent gas in an He buffer. This supplies 308 nm pulses of 10 ns duration. The gas mixture and pressure were adjusted in order to create pulses of 30–70 mJ. However, during a given experiment the pulse energy varied by *ca* 5%. The transient behavior was monitored using a probe beam from a CW 300 W Xe arc lamp passed through the sample cuvette perpendicular to the excitation beam. Transient waveforms were recorded with a LeCroy 9420 digital oscilloscope, which digitizes at a rate of one point per 10 ns with a bandwidth of 350 MHz. Sample concentrations were adjusted to an optical density of 0·5–1·5 cm^{-1} at 308 nm. Using 100 mg of MPAP in 50 ml of freshly distilled acetonitrile in a standard flow cell set-up with N_2 purging, waveforms were collected for wavelengths ranging from 300 to 800 nm in increments of 5 or 10 nm. The system was then purged with O_2 and waveforms were collected at 460 nm for comparison.

Photolysis of MPAP. Photolyses of MPAP for product studies were carried out using a 150 W Hg–Xe lamp with a 295 nm cut-off filter. Standard conditions involved using 3 ml of N_2-purged samples of stock solution in a quartz cuvette. To investigate the reactivity of MPAP with methanol, stock solutions were prepared that were typically 2 mg ml^{-1} of MPAP in 10% (v/v) MeOH–MeCN solvent. Reactivity with chloride ion was investigated using stock solutions of 2 mg ml^{-1} of MPAP in MeCN with added Bu^n_4NCl as the source of Cl^-. Photolysis times for various experiments ranged from 2 to 10 min to minimize secondary photoprocesses unless the primary intent was to observe the results of these secondary processes. Triplet sensitized photolyses with 9-fluorenone were carried out with a 420 nm cut-off filter to prevent the occurrence of any direct photolysis. The sensitizer was used in a *ca* 4:1 molar excess with the pyridinium salt. Longer photolysis times (20–30 min) were necessary for this slow reaction.

Analytical results for all photolyses were obtained using a Rainin Instruments high-performance liquid chromatographic (HPLC) system with a C_{18} reversed-phase column and a UV detector. All injections were 20 μl and the solvent system used was water–acetonitrile (1:1). Absorbance was measured at 254 nm. HPLC peaks were identified by co-injecting photolysis mixtures with authentic products, which were purchased from Aldrich Chemical or synthesized as necessary (e.g. 2-chloro-*N*-methylaniline[25]). Concentrations of photoproducts were measured based on concentration curves generated from authentic products. Yields of various photoproducts (e.g. in Figure 2) were measured by calculating the concentration of the product as a percentage of the initial concentration of starting material. In addition to identification of products by HPLC, ^1H NMR spectroscopy was used to confirm the presence of various photoproducts in crude photolyzed solutions.

Synthesis of MPAP. 2,4,6-Trimethylpyrylium tetrafluoroborate was prepared as outlined by Balaban and Boulton.[26] HBF_4 (7·0 ml of 48 wt% solution) was added slowly to 50 ml of acetic anhydride containing 4 ml of *tert*-butyl alcohol. The rate of addition of HBF_4 solution was controlled such that the temperature remained below 80°C for this very exothermic process. The reaction mixture was cooled on an ice-bath and the product, 2,4,6-trimethylpyr-



Scheme 1

ylium tetrafluoroborate, was precipitated by the addition of diethyl ether. Filtration yielded 3·9 g (44% yield). A 2·31 g amount of this pyrylium salt was stirred in 30 ml of ethanol and combined with an additional 30 ml of a solution of ethanol containing 2·0 g of 1-methyl-1-phenylhydrazine (1·5 molar equivalents). This mixture was stirred at room temperature for 2 h, then concentrated by rotary evaporation at 40 °C. Addition of 40 ml of diethyl-ether precipitated 1·8 g of MPAP product (m.p. 141–142 °C, 52% yield): IR (CH_2Cl_2), 3680 (vw), 3040 (m), 2950 (w), 2370 (w), 1635 (s), 1600 (m), 1550 (w), 1500 (s), 1380 (w), 1300 (m), 1060 (vs), 860 cm^{-1} (w); ^1H NMR (CD_3CN), δ 7·72 (s, 2 H), 7·34 (t, $J=8$ Hz, 2 H), 7·00 (t, J=8 Hz, 1 H), 6·42 (d, J=8 Hz, 2 H), 3·51 (s, 3 H), 2·59 (s, 3 H), 2·51 (s, 6 H); ^{13}C NMR (CD_3CN), δ162·2, 159·6, 144·9, 131·3, 130·6, 122·3, 111·8, 39·3, 22·2, 19·5; HRMS, *m/z* 227·1537 ($M^+ - BF_4$; calculated for $C_{15}H_{19}N_2$, *m/z* 227·1548).

RESULTS AND DISCUSSION

Photolysis of MPAP in acetonitrile solutions with nucleophiles present resulted in the formation of the three major products shown in Scheme 1. These products were detected and quantified by HPLC based on comparison with the authentic compounds. Identification of products was further confirmed by ^1H NMR spectroscopy of crude photolysis mixtures. The results depicted in Scheme 1 are not unexpected for reactions proceeding via a nitrenium ion intermediate. The ring-substituted *N*-methylaniline derivatives, such as *N*-methyl-*p*-anisidine (NMPA), are consistent with other reported results involving nucleophilic attack on an arylnitrenium ion.[12, 20, 21] Arylnitrenium ions exist as delocalized cations and react with nucleophiles at the *para* and *ortho* ring positions [e.g. *para* addition illustrated in equation (1)]. Also, 1,2-sigmatropic shifts have been observed previously, and serve to explain the formation of aniline as one of the photoproducts.

The *N*-*tert*-butyl substituent in other reported nitrenium ion chemistry undergoes a 1,2-methyl shift on to the nitrogen center, leading to an iminium ion intermediate which upon work-up is hydrolyzed to the *N*-methylaniline derivative.[12, 21, 22] In the present system, we believe a 1, 2 hydride shift from the *N*-methyl group followed by hydrolysis of the iminium ion is the mechanism for the formation of aniline [equation (2)]. Finally, the detection of *N*-methylaniline, the reduction product, is consistent with previous work,[22] and can be attributed to hydrogen atom abstraction reactions of the radicaloid triplet nitrenium ion [equation (3)].

Various conditions were employed to measure the effect on the relative yields of these three product types and to test the proposed mechanisms for their formation.

Nucleophilic addition to methylphenylnitrenium ion

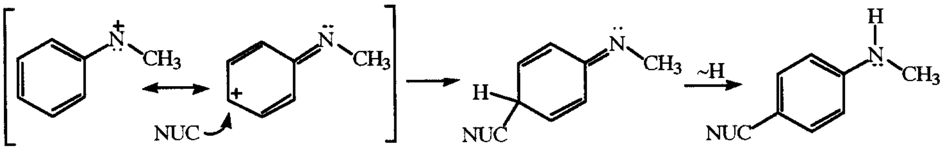
Nucleophilic addition to the proposed nitrenium ion intermediate was studied using methanol and Cl^- as nucleophiles. The *para* addition of methanol resulting in NMPA was observed and quantified by HPLC analysis. In solutions of MPAP and acetonitrile with tetrabutylammonium chloride added, Cl^- addition occured at both *ortho* and *para* positions on the ring of the proposed $PhMeN^+$ intermediate [equation (4)]. The *para* position was consistently favored by approximately 2 : 1 at various concentrations of Cl^-. Again, detection and yield measurements were carried out by HPLC analysis.

We considered the possibility that these addition products did not form via a nitrenium ion intermediate and were, in fact, the result of an S_N2' reaction involving the excited state MPAP and the nucleophile. If an S_N2' mechanism were operative, then the photodecomposition of MPAP to form these adduct products would be sensitive to the concentration of nucleophile present. To test for this alternative mechanism, experiments were performed in which the decay of the UV–visible spectrum of MPAP was monitored as a function of photolysis time and methanol concentration. Generally, UV measurement proved to be the most convenient method for monitoring the extent of MPAP photodecomposition owing to its characteristic band at 365 nm. It was found that the absorbance by MPAP decays with photolysis time, showing little or no difference in the extreme cases of 100% methanol as solvent and 100% acetonitrile. We therefore concluded that photodissociation of MPAP to $PhMeN^+$ was the operative mechanism, and addition occurred via a bimolecular reaction of $PhMeN^+$ and nucleophile [equation (5)].

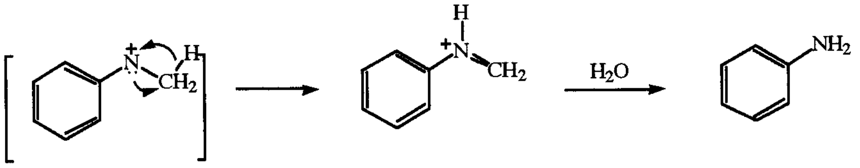
Rearrangement products

Another reaction pathway available to the singlet methylphenylnitrenium ion is its rearrangement leading ultimately to the formation of aniline. This observed product is attributed to a hydride shift from the *N*-methyl group on to the nitrogen atom followed by subsequent hydrolysis of the resulting iminium ion either during work-up or by the water–acetonitrile solvent system used in HPLC analysis.

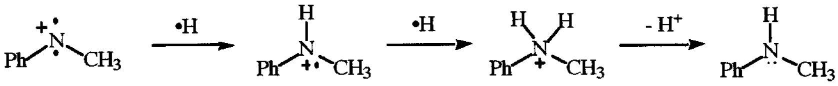
We considered that an imine intermediate may form as the result of an *E*2 mechanism involving the concerted deprotonation of the *N*-methyl group and elimination of 2,4,6-collidine from excited-state MPAP. An *E*1 mechanism involving deprotonation of the *N*-methyl group of a nitrenium ion intermediate was also possible as an alternative to the hydride shift mechanism. Both the *E1* and *E2* mechanisms would be sensitive to the concentration of base, and an enhancement of the yield of aniline at the expense of other photoproducts should be observed as the concentration of base is increased. The photolysis of MPAP was repeated in the presence of 0·5 molar equivalents of 2,4,6-collidine, which is present in these solutions anyway as a byproduct of these photolyses. With methanol present at nucleophile, the added collidine caused no enhancement of the aniline yield relative to NMPA yield (Table 1). The insensitivity to added base lends support to the hydride shift mechanism.



(1)



(2)



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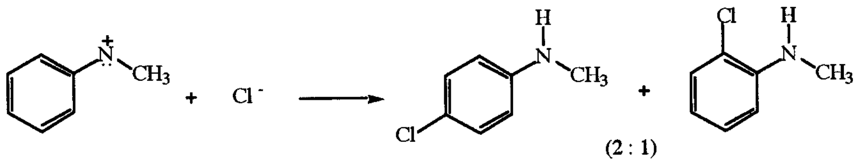

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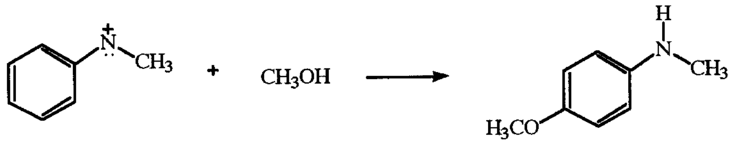


(5)

Since only two major photoproducts are identified from the proposed singlet nitrenium ion intermediate, the following equality can be derived:

$$[\mathrm{NMPA}]/[\mathrm{PhNH_2}] = k_{\mathrm{MeOH}}[\mathrm{MeOH}]/k_{\mathrm{hyd}} \qquad (6)$$

The $[\mathrm{NMPA}]/[\mathrm{PhNH_2}]$ ratio from photolysis of MPAP was measured as a function of [MeOH]. This experiment gave the linear function with slope $k_{\mathrm{MeOH}}/k_{\mathrm{hyd}}$ of approximately $0{\cdot}6 \pm 0{\cdot}1$ (Figure 1). The rate constant k_{MeOH} for nucleophilic attack of methanol on arylnitrenium ions can be estimated as $1 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ on the basis of previous work.[12] The rate constant for rearrangement to the iminiumion intermediate is therefore estimated to be on the same order of magnitude, $10^8\ \mathrm{s}^{-1}$.

Formation of reduction product

N-Methylaniline (NMA), the reduction product, is detected in relatively large amounts in these photolyses. Its formation is believed to be at least in part the result of the triplet nitrenium ion undergoing two consecutive hydrogen atom abstractions followed by deprotonation. This has been the typical source of reduction product in previous work in which a triplet nitrenium ion was indicated as an intermediate species.[22] The presence of the reduction product is taken as confirmation that the triplet nitrenium ion is produced to some extent along with the singlet nitrenium ion, despite the fact that it is the higher energy species. Our general model is based on the assumption that intersystem

Table 1. Relative yields of photoproducts

Conditions	$PhNH_2$	NMPA	NMA
Standard[a]	1	2·3	0·4
Collidine[b]	1	3·0	<0·1
NMPA[c]	0·2	n.d.	10
Triplet[d]	<0·1	<0·1	10
CHD[e]	1	2·0	1·1
Extended[f]	1	0·6	3·3

[a] Standard conditions unless specified otherwise were 2 min photolysis with a 295 nm cut-off filter, initial concentration of 6·4 mM MPAP and 2·5 M (10%) MeOH in acetonitrile solutions.
[b] 5·0 mM collidine present prior to photolysis.
[c] 4·4 mM NMPA present prior to photolysis.
[d] Triplet sensitized iradiation with a 420 nm cut-off filter; 9-fluorenone present at its solubility limit (*ca* 4 molar equivalents).
[e] 0·11 M cyclohexadiene present prior to photolysis.
[f] Standard conditions, but photolyzed for 20 min.

crossing of the singlet nitrenium ion to the triplet would be unlikely since the singlet is predicted to be the ground-state species for this arylnitrenium ion. Therefore, intersystem crossing of the singlet excited state of MPAP to the triplet state prior to dissociation is believed to be the source of triplet nitrenium ion.

We wanted to confirm our assumption that *N*-methylaniline was formed via the triplet manifold, and conducted triplet sensitized irradiation experiments toward this goal. Triplet sensitized irradiations, which produce the triplet excited state of MPAP directly through energy transfer, should produce only triplet nitrenium ion as the result of dissociation. We would therefore expect products of the singlet nitrenium ion only if intersystem crossing of triplet to singlet can compete with other reactions which consume the triplet nitrenium ion. Since triplet to singlet intersystem crossing would be energetically favorable based on the theoretical calculations of the singlet triplet energy gap, our model would predict an enhanced yield of the presumed triplet product but also some products derived from the singlet nitrenium ion intermediate following triplet to singlet intersystem crossing.

We conducted triplet sensitized photolyses of MPAP using 9-fluorenone as our triplet sensitizer. Direct photolysis of MPAP is presumably eliminated by use of a 420 nm cut-off filter in this experiment. These triplet sensitized photolyses did result in NMA as the major photoproduct, with only trace amounts of singlet products detected (Table 1), and we take this result as confirmation that NMA is a photoproduct derived from the triplet nitrenium ion intermediate. The trace yield of singlet products seems to suggest that there is little intersystem crossing of triplet to singlet. However, it may be that singlet products aniline and NMPA react with the triplet excited state of MPAP to be consumed by secondary photoprocesses, and are in fact under-represented in the results shown in Table 1. The nature of these secondary photoprocesses is discussed in more detail below.

It is worthwhile to consider the results of direct photolysis experiments that were conducted with added 1,4-cyclohexadiene (CHD). This efficient hydrogen atom donor present at a concentration of 0·11 M is apparently able to trap triplet nitrenium ion to increase the yield of NMA slightly relative to singlet products. This result implies that intersystem crossing of triplet nitrenium ion to singlet nitrenium ion will occur when the concentration of

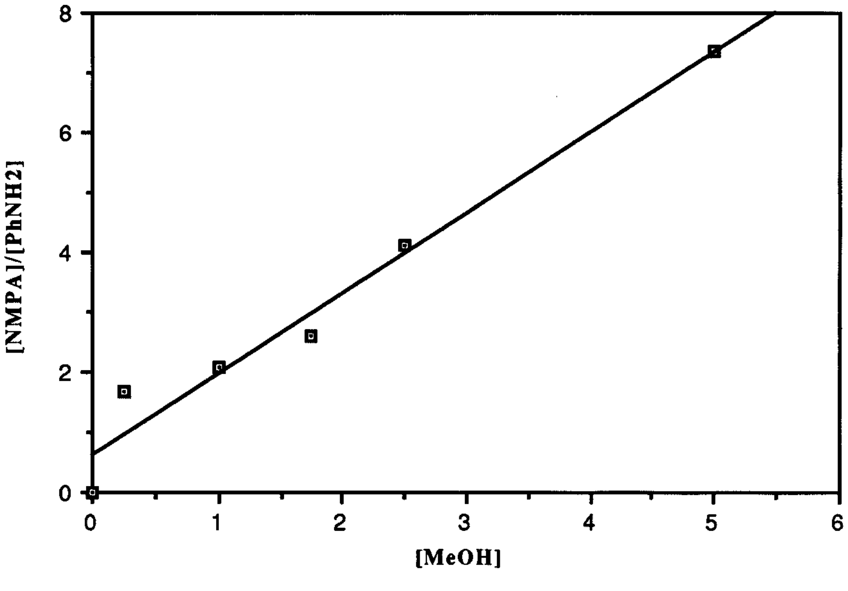


Figure 1. [NMPA]/[PhNH2] derived from product yields in photolyses of MPAP solutions of various [MeOH]

hydrogen atom donors is sufficiently low. Taken together, the results of the CHD experiment and the triplet sensitized photolysis lead us to conclude that the singlet nitrenium ion can be accessed from the triplet nitrenium ion but this process does not compete well with the fast hydrogen atom abstractions.

Secondary photoprocesses

We had reason to believe that significant secondary photoprocesses were occurring. What is inferred regarding the chemical reactivity of the nitrenium ion intermediate is necessarily based on short photolysis times and very low percentage conversion of MPAP in our attempt to minimize these secondary processes. However, we were curious about the nature of the secondary photochemistry and concerned about any impact it might have on our interpretation of the data. The evidence of and nature of these secondary processes are now discussed in more detail. It was observed that with 2·5 M MeOH solutions and short photolysis times, NMPA is produced in higher yield relative to other photoproducts. However, experiments conducted using longer photolysis times show that NMPA is actually consumed in the photolysis until it is no longer detected. The yield of aniline also decayed over time, although its decay was not as pronounced as that for NMPA. Chloro-substituted *N*-methylaniline products also showed slow decay but seemed more impervious to secondary photochemical processes.

The greater complication in proposing an accurate mechanistic model is the relative yield of NMA. This product, which has been attributed to a triplet nitrenium ion intermediate, shows an increasing rate of formation coinciding with the decay of other species. Data illustrating this are presented in Figure 2, which shows the yields of the three major products as a function of photolysis time when methanol is present. At very short photolysis times and low MPAP conversion, only trace amounts of NMA are detected. Longer photolysis times result in proportionately greater amounts of NMA formation and NMPA disappearance. Thus, the growth curve of NMA as a function of time is sigmoidal in shape [Figure 2(B)]. The results of the triplet sensitized irradiation experiments make us reasonably certain that at least some NMA forms via the triplet nitrenium ion. However, the greater portion is probably due to secondary photoprocesses that may not involve a nitrenium ion species. An explanation that is consistent with our observations is that photoinduced single electron transfer occurs from the relatively electron-rich aniline derivatives which are formed from the reactions of singlet nitrenium ion. *N*,*N*-Dimethylaniline is a well known photochemical electron donor.[27] It is likely that NMPA, another electron-rich aniline derivative, will behave similarly although perhaps not as efficiently. If excited-state MPAP accepts an electron from NMPA, the result of this electron transfer process would be *p*-methoxy-*N*-methylanilino radical cation and neutral radical MPAP. The neutral radical MPAP species can then undergo homolytic N—N bond cleavage to yield neutral collidine and *N*-methylanilino radical. The latter would abstract a hydrogen atom to form NMA. Thus a process which does not involve a nitrenium ion intermediate can produce NMA and would explain the eventual disappearance of the NMPA being produced from the nitrenium ion pathway.

This possibly was investigated by conducting the photolysis of MPAP with added NMPA (0·5 molar equivalents) under identical conditions. We expected an enhanced yield of NMA at the expense of the photoproducts of the nitrenium ion pathway since these photoinduced SETs consume MPAP by a different pathway, reducing the quantum yield of the nitrenium ion intermediate. The results did indeed show a greatly enhanced yield of NMA and a diminished yield of aniline (Table 1). (The change in the yield of NMPA could not be quantified because of the relatively large amount added prior to photolysis). These results are consistent with our proposed electron transfer mechanism.

In contrast to this dramatic increase in the yield of NMA, we consider again the results of the experiment with 0·11 M CHD in which the enhanced yield of NMA is much less pronounced. This compound is a very efficient hydrogen atom donor but is not likely to behave as a photochemical electron donor. The difference in the degree to which CHD and NMPA enhance the yield of NMA is attributed to their

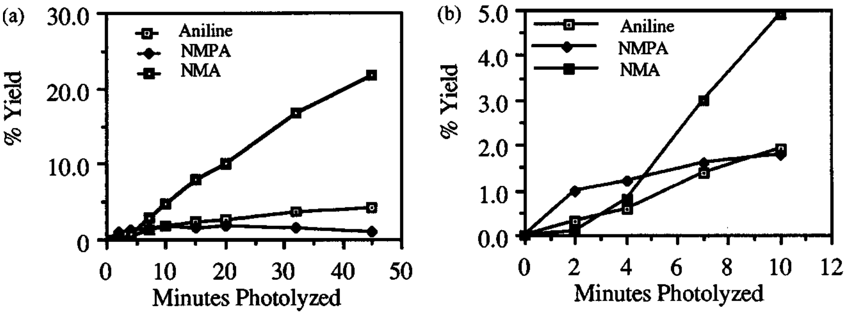
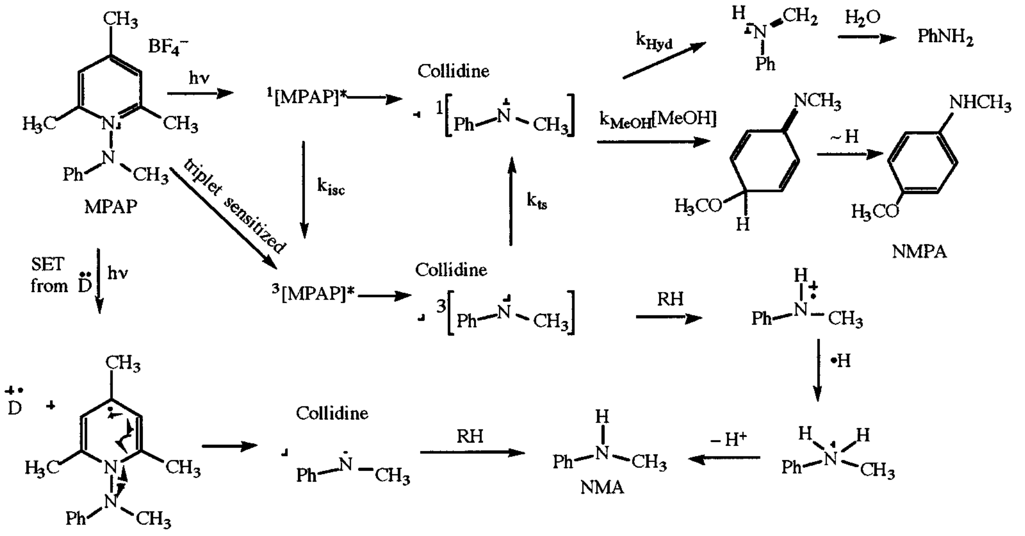


Figure 2. (a) Time-resolved product yields. (b) Expansion of early times



Scheme 2

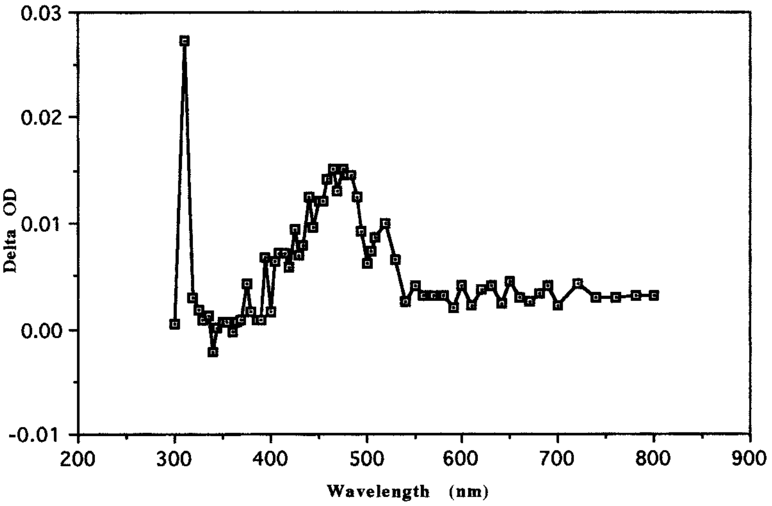


Figure 3. Transient absorbance spectrum 1.6 microseconds after laser pulse.

respective mode of reactivity in two distinctly different chemical pathways. CHD traps triplet nitrenium ion, while NMPA participates in secondary electron transfer processes ultimately to produce NMA. It has been shown that one-electron oxidations of various aniline derivatives result in the polymerization of these substrates, particularly for those with methoxy substituents.[28] It is likely that a polyaniline derivative is the ultimate photoproduct, which would be consistent with our proposed electron transfer process and with the observed decline of NMPA for extended photolyses. A detailed mechanism that incorporates the SET processes we propose is shown in Scheme 2.

Laser flash photolysis

Laser studies were carried out to detect the nitrenium ion intermediate. The transient absorbance was fairly long-lived and, therefore, not attributed to the nitrenium ion intermediate which would presumably have a much shorter lifetime.[12] The transient absorbance was very weak with a maximum at about 470 nm (Figure 3). This λ_{max} is typical of anilino radical cations,[29] and it is assumed that this transient absorbance is due to the radical cation of NMA which would form as the product of a hydrogen atom abstraction by triplet PhMeN$^+$. The fact that the absorbance is very weak despite the high extinction coefficients of these radical cations is in agreement with our belief that the triplet nitrenium ion forms to a minimal extent in these reactions. Purging the system with oxygen weakened the absorbance at this wavelength. Since molecular oxygen can act as a quencher of the triplet excited state of MPAP, it would diminish the yield of triplet nitrenium ion and thus diminish the yield of *N*-methylanilino radical cation.

CONCLUSIONS

Experimental results indicate that methylphenylnitrenium ion is produced in the photolysis of *N*-(methylphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate. The reactions of singlet and triplet nitrenium ions lead to different products depending on the spin state that is formed. Similarly to the previously reported reactivity of arylalkylnitrenium ions, nucleophilic addition to the aryl substituent is observed, as is rearrangement via 1,2-shifts from the alkyl substituent of the nitrenium center. Both of these product types are attributed to a singlet-state nitrenium ion intermediate. Parent amines form, and are attributed to two different pathways that both involve the formation and reaction of radical species. One of these pathways is proposed to be a secondary photoprocess. This process involves photoinduced electron transfer in which the primary photoproducts, various aniline derivatives, act as electron donors to the pyridinium ion, causing its decomposition. The other pathway resulting in *N*-methylaniline is the hydrogen atom abstractions of the triplet nitrenium ion.

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