reasonable assignment. A situation akin to this arose in the study of the RhC molecule where $g_{\parallel}$ was greater then g_e.[13] In that case it was conjectured that it was caused by a $^4\Pi$ state coupling with the ground $^2\Sigma$ state and/or by matrix effects. This very ionic molecule could interact more strongly with the matrix,[14] and if that is the case then $|\Delta g_{\perp}|$ may also represent an upper limit to the true value. It is difficult to make quantitative speculations about these possibilities.

$\Delta g_{\perp}$ measured here is in approximate accord with the small spin-rotation constant, γ, observed in the gas spectrum.[1] From the Curl equation[15]

$$\gamma = -2B\Delta g_{\perp}$$

where B is the rotational constant,[1] γ is derived to be $+0.0034(3)$ cm^{-1}. An accuracy of about 10% can usually be expected from this equation,[16,17] so that this value for γ is slightly larger but of the same magnitude as the gas-phase estimate, $|\gamma| < 10^{-3}$ cm^{-1}.[18]

The departure from complete s character for the odd electron on Yb^+ is probably mostly due to the distortion by the adjacent F^- ion, as in the alkaline earth fluorides.[4] The unpaired spin on Sr^+ and Ba^+ in those diatomic fluorides is about 60% s, and the larger s character in YbF can be attributed to the smallness of Yb^+ which resembles Ca^+ in size and polarizability.[5]

The smaller $\Delta g_{\perp}$ value of YbF compared to YbH (−0.062) is a consequence of the increased ionicity and increased s character in the ground-state wavefunction of the fluoride. As expected, the diatomic hydrides are all more covalent in that there is increased spin on the anion and increased pσ and dσ character in the wavefunctions.[8]

References and Notes

(1) R. F. Barrow and A. H. Chojnicki, *J. Chem. Soc., Faraday Trans. 2*, **71**, 728 (1975).
(2) H. V. Lee and R. N. Zare, *J. Mol. Spectrosc.*, **64**, 233 (1977).
(3) D. L. Hildenbrand, *Adv. High Temp. Chem.*, **1**, 205 (1967).
(4) L. B. Knight, Jr., W. C. Easley, W. Weltner, Jr., and M. Wilson, *J. Chem. Phys.*, **54**, 322 (1971).
(5) R. J. Van Zee, M. L. Seely, and W. Weltner, Jr., *J. Chem. Phys.*, **67**, 86 (1977).
(6) P. H. Kasai, E. B. Whipple, and W. Weltner, Jr., *J. Chem. Phys.*, **44**, 2581 (1966).
(7) W. C. Easley and W. Weltner, Jr., *J. Chem. Phys.*, **52**, 197 (1970).
(8) L. B. Knight, Jr., and W. Weltner, Jr., *J. Chem. Phys.*, **54**, 3875 (1971).
(9) W. Low, "Paramagnetic Resonance in Solids", Academic Press, New York, N.Y., 1960, p 60.
(10) A table of atomic A_{iso} and A_{dip} values may be found in P. B. Ayscough, "Electron Spin Resonance in Chemistry", Methuen, London, 1967, p 438.
(11) V. Kaufman and J. Sugar, *J. Opt. Soc. Am.*, **63**, 1168 (1973).
(12) H. H. Tippins, *Phys. Rev.*, **160**, 343 (1967).
(13) J. M. Brom, Jr., W. R. M. Graham, and W. Weltner, Jr., *J. Chem. Phys.*, **57**, 4116 (1972).
(14) See M. J. Linevsky, *J. Chem. Phys.*, **34**, 587 (1961); G. C. Pimentel and S. W. Charles, *Pure Appl. Chem.*, **7**, 111 (1963).
(15) R. F. Curl, *Mol. Phys.*, **9**, 585 (1965).
(16) L. B. Knight, Jr., and W. Weltner, Jr., *J. Chem. Phys.*, **53**, 4111 (1970).
(17) F. J. Adrian and V. A. Bowers, *Chem. Phys. Lett.*, **41**, 517 (1976).
(18) Professor Barrow has indicated, in a private communication, that the value of γ given in ref 1 should read $|\gamma| < 10^{-3}$ cm^{-1} rather than $<10^{-5}$ cm^{-1}.

Flash Photolysis Studies of 2,2,6,6-Tetramethyl-*N*-chloropiperidine. A Sterically Hindered Aminium Radical

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Flash photolysis of 2,2,6,6-tetramethyl-*N*-chloropiperidine in aqueous solution at pH 2–8 generated the 2,2,6,6-tetramethylpiperidinyl radical which was protonated very rapidly to give the 2,2,6,6-tetramethylpiperidinium radical; the latter decayed under second-order kinetics with rate constants ranging from 6.9×10^5 cm s^{-1} at pH 7 to 7.7×10^4 cm s^{-1} at pH 4. The aminium radical abstracted hydrogen from methanol and ethanol with the rate constants of 66 and 244 M^{-1} s^{-1}, respectively, and added to cyclohexene with a rate constant of 1.1×10^4 M^{-1} s^{-1}. These rate constants, in particular that for addition to cyclohexene, were much smaller than those of the corresponding piperidiniumyl radical reaction and attributed to steric crowding around the radical center. The pK_a of the aminium radical in water was determined to be 7.5–8.0 and its absorption curves in acetonitrile and in 10% acetonitrile–water were determined. In acetonitrile containing dilute sulfuric acid, the photolytically generated amino radical appeared to be protonated slowly having a lifetime in the order of 100 μs.

Introduction

Over the last several decades, aminium radicals, cation radicals of amines ($R_3N^{+}\cdot$, $R_2NH^{+}\cdot$, or $RNH_2^{+}\cdot$), have been implicated as the key reactive intermediate in the Hofmann–Löffler pyrrolidine synthesis which involves photolytic, thermal, or redox metal catalyzed decompositions of *N*-chloramines in strongly acidic media.[2–5] In view of their unusual reactivities, particularly in comparison to their uncharged aminyl radicals,[6,7] generation, reaction, and measurements of the physical properties of aminium radicals have attracted considerable attention in recent

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years; these investigations have established aminium radical as a synthetically important and physicochemically significant reactive transient in the radical ion field.

In addition to the well-known generation of aminium radicals by *N*-chloramine decomposition[1-5] mentioned above, a number of methods have been shown to generate aminium radical efficiently: for example, (i) photolysis of *N*-nitrosamines,[6] *N*-nitroamines,[7] and tetrazenes[8] in weakly acidic conditions and (ii) redox metal ion-catalyzed decomposition of hydroxylamines and amine *N*-oxides in acidic conditions.[9,10] These conventional methods are extensively utilized primarily as methods of generation in solution to study reactivities of aminium radicals. The occurrence of aminium radicals in solution or solid state during high energy radiolysis of amines or their derivatives[11,12] and in gas phase ionization of amines during high energy electron impact (in mass spectroscopic chamber)[13] are common knowledge. These methods, though less useful to study aminium radical reactivities, are routine methods utilized in investigations of magnetic and fragmentation properties of aminium radicals.

Anode oxidation of amines by one-electron transfer is probably the most unambiguous and direct method of generating aminium radicals and has been extensively utilized in studies of aromatic aminium radicals for considerable time.[14,15] Owing to the yet unknown physical properties of the electrode–solution interface where the aminium radicals are generated, it is unavoidable that the anodically generated aminium radicals exhibit unique chemical behavior somewhat different from that observed in solution. It is rather unsuspected, but not wholly unexpected, that chemical oxidation of amines with chlorine dioxide[16] and potassium ferricyanide[17] involve the one-electron transfer process to generate aminium radicals as the primary reaction step. These mechanistic facts, established only recently, suggest that oxidation of amines by other reagents might also follow the same aminium radical pathways.

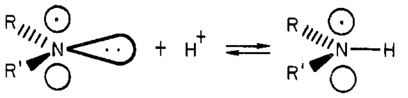
Quenching of electronically excited states of aromatic hydrocarbons, aromatic ketones, and some dyes (e.g., rose bengal) by amines are generally fast and have been shown to involve electron transfers to form aminium radicals (paired with the corresponding anion radical) as the transients.[18,19] In polar solvents, the aminium radical may dissociate from the pair and exhibit their reactions. These observations indicate that occurrence of aminium radicals in chemical reactions are more ubiquitous than has been suspected.

Reactivity studies on aminium radicals are generally carried out by conventional generation of these radicals starting with *N*-chloramines,[1-5] *N*-nitrosamines,[8] and hydroxylamines.[10] Nitroamine[6] and tetrazene[7] and amine *N*-oxide[9] methods are relatively recent entries in the field. Aminium radicals abstract unactivated alkyl hydrogen readily; when carried out intramolecularly it is very selective in attacking the δ hydrogen of the side chain (the Hofmann–Löffler reaction).[1] Intermolecularly unhindered aminium radicals abstract hydrogens with the usual preference order[20,21] of primary < secondary < tertiary. With hindered aminium radicals[20] such as 2,2,6,6-tetramethylpiperidinium radicals ($TMPH^{+}\cdot$) the order is tertiary < primary < secondary. For long chain hydrocarbon substrates, aminium radicals show propensity to abstract the penultimate ($\omega - 1$) methylene hydrogens over other positions and selectivity for monofunctionalization.[21] These all occurs in highly acidic conditions, e.g., sulfuric acid–acetic acid mixture.

In contrast to amino radicals, aminium radicals characteristically undergo electrophilic radical addition to unsaturated carbon–carbon bonds even when substrates carry readily accessible allylic hydrogens for abstraction.[6-8] Such selective reactivities are unique to aminium radicals and at variance with alkoxy radicals. However, in the absence of a suitable substrate, aminium radicals obviously undergo bimolecular decay in strong acidic media ($2M H_2SO_4$–AcOH or higher),[22,23] although the piperidinium radical in dilute acidic media undergoes first-order decay.[24] Whereas a good many synthetic studies using aminium radical intermediates are available, physical and kinetic studies of aminium radicals are less extensive owing to transient nature of the radicals.

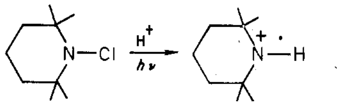
Using flash photolysis techniques, absolute rate constants of hydrogen abstraction, addition of olefins, and self-decay of the piperidinium radicals generated from the *N*-chloroamine and *N*-nitrosamine in dilute acidic conditions have been determined.[24] These studies indicate piperidinium radicals add to a π-bond system 5000–10000 times faster than they abstract methanol hydrogens.[24] These studies also demonstrate that aminium radicals do not react with oxygen, i.e., the rate of the reaction with oxygen is much slower than that of the self-decay of the aminium radical in dilute acidic conditions.[24,25]

ESR spectra of aminyl and aminium radicals can be recorded by photolysis of suitable substrates in the microwave spectrometer cavity.[26] This technique allows acid–base equilibria to be studied. A pK_a 6.5–7.5 has been reported for the dimethylaminium radical.[27] The pK_a of the anilinium radical $C_6H_5NH_2^{+}\cdot$ has been determined to be $\simeq 7$ by flash photolysis.[28] The comparable acidity of these alkyl or aryl aminium radicals in contrast to the vast difference of the acidity for the corresponding amines is structurally significant. Similarity in pK_a probably arises from the common π radical structure of the aminyl radicals[29] in which the lone pair electrons are accomodated in the Σ orbital.



R and R′ = alkyl, aryl, or H

In previous studies, the reactivity and decay kinetics of unhindered piperidinium and dimethylaminium radicals in dilute acidic aqueous solutions were determined.[24,25,30] Compared with the reported behavior of aminium radicals in strongly acidic solution,[22] piperidinium radicals were found to be relatively short lived with decay dominated by first-order kinetics. The reaction responsible for decay of piperidinium radical is not known but could involve deprotonation from the α positions. The substituted $TMPH^{+}\cdot$ severely crowded around the radical center and is structurally incapable of undergoing α deprotonation. The present flash photolysis studies of 2,2,6,6-tetramethyl-*N*-chloropiperidine (TMNCP) in dilute acid have been carried out with two objectives in mind: (i) to evaluate, quantitatively, steric effects on both the decay process and on the ability of aminium radicals to abstract hydrogens and to add to olefins and (ii) to establish the general pattern of reactivity of aminium radicals in weakly acidic solutions.



TMNCP TMPH+·

Experimental Section

TMNCP was prepared by chlorination of 2,2,6,6-

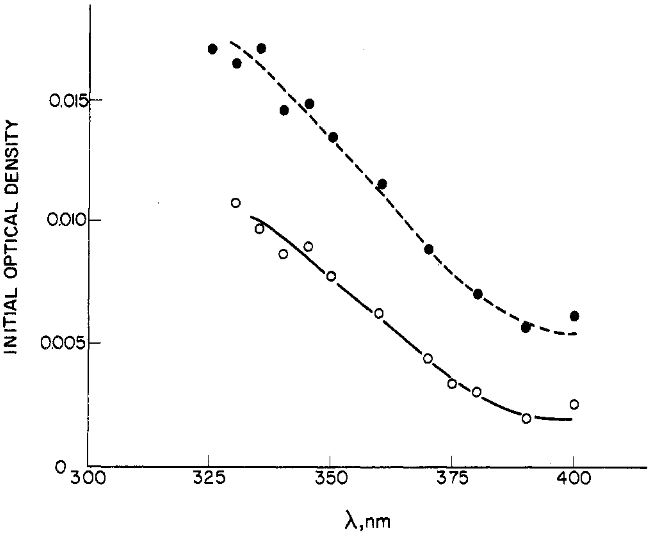


Figure 1. Absorption spectrum of the transient from the flash photolysis of TMNCP (1.0 × 10^{-3} M) in acetonitrile (●), and 10% acetonitrile–water (O), both acidified with H_2SO_4 (1.0 × 10^{-3} N). Solution undegassed. Excitation flash filtered through Vycor glass.

tetramethylpiperidine with sodium hypochlorite.[22] The second fraction boiling at 47.5 °C (1.3 mmHg) was collected and stored at liquid nitrogen temperature in the dark.

The double-beam 1 μs flash photolysis apparatus was as previously described[24,31,32] except a Biomation 610B transient recorder was used to collect the output from a Tektronix 1A7A differential amplifier–132 power supply combination.

Results

1. *Flash Photolysis Studies in Acetonitrile and Acetonitrile–Water Solution.* Preliminary experiments showed that flash photolysis of a TMNCP solution in various solvent systems rapidly depleted the *N*-chloramine and the calculated decay rate constants of the transient were systematically increased. Each flash photolysis was carried out with a freshly prepared solution. A very weak transient absorption was observed at 350 nm from flash excitation of an undegassed acetonitrile solution of TMNCP (1 × 10^{-3} M) containing no added acid or base. When 10^{-2} M NH_4OH was added, no transient was observed. When an acetonitrile solution of TMNCP containing 1.0 × 10^{-3} N H_2SO_4 was photolyzed, a relatively strong absorption was observed whether dissolved oxygen was present or not. The absorption spectra of the transient obtained from the flash photolysis of acidified (1.0 × 10^{-3} N H_2SO_4), undegassed solution of TMNCP in acetonitrile and in 10% acetonitrile–water are shown in Figure 1. Below ~330 nm, significant absorption by TMNCP itself interferes with the transient absorption; for this reason, the observed maximum at 325–330 nm should be considered as an approximate value only. However, the results do clearly indicate that the same transient is produced in the two solvents and the spectrum of the presumed $TMPH^{+}\cdot$ is red shifted with respect to the unsubstituted piperidinium radical.[24]

The results in acetonitrile with added base and acid suggest that acid is required to form the transient. To obtain further information, acetonitrile solutions containing TMNCP (1.0 × 10^{-3} M) and different concentrations of sulfuric acid (0, 1.0 × 10^{-5}, 2.2 × 10^{-5}, 6.8 × 10^{-5} N) were flash photolyzed. In all cases, the solutions were undegassed and the excitation flash was filtered through Vycor glass to prevent photolysis of solvent. The initial portion of the transients are shown in Figure 2. Note that the rise is compounded of two components: a fast component, whose risetime is beyond the time resolution of our apparatus, and a slow component. The rate of rise of the slow component clearly increases with acid concentration. The absorption ratio of the fast and slow components was constant in the 320–400-nm wavelength region and suggested that the transient was due to a single species. Thus far, the results strongly suggest that the transient is the $TMPH^{+}\cdot$ radical which is formed by protonation of the initially formed amino radical. A clue to what the fast component might be due to was obtained when the Vycor filter was replaced by a Corex filter (short wavelength cutoff ~260 nm) in the flash photolysis of TMNCP in acetonitrile containing 3.6 × 10^{-5} N H_2SO_4. As shown in Figure 3 it is striking to note that only the slow component is present when the photolytic flash was filtered through a Corex glass. Since only unprotonated TMNCP absorbs significantly >260 nm (vide infra),[33] in this photolysis only aminyl radical is expected to be generated; the slow rise must correspond to the formation of the $TMPH^{+}\cdot$ by protonation of the aminyl radical. The fast rise portion observed in Vycor filtered photoflash, therefore, could be ascribed to the direct formation of $TMPH^{+}\cdot$ from the electronically excited state of the protonated TMNCP. This result is consistent with the mechanism proposed previously in the flash photolysis studies of *N*-chloramines: namely, the aminium radical is formed directly from the photolysis of protonated *N*-chloramines and indirectly by protonation of amino radicals produced from photolysis of unprotonated *N*-chloramines.[24]

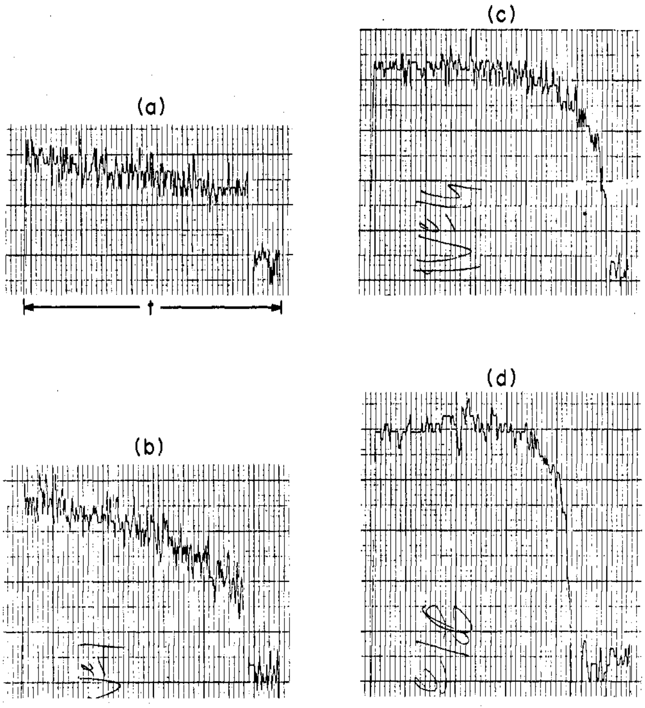


Figure 2. Traces showing the formation of the transients from the flash photolysis of TMNCP (1.0 × 10^{-3} M) in acetonitrile solution containing different concentrations of added H_2SO_4: (a) 0, (b) 1.0 × 10^{-5} N, (c) 2.2 × 10^{-5} N, (d) 6.8 × 10^{-5} N. The overall scan time, *t*, was 512 μs except for (d) which was 128 μs. A portion of the baseline before the flash is located on the right-hand side of each trace. Excitation flash filtered through Vycor glass. Solution degassed.

2. *Flash Photolysis Studies in Aqueous Solution.* Since most acids, including sulfuric acid, behave as weak acids in acetonitrile,[34] aqueous solutions of TMNCP were studied. TMNCP dissolves poorly in water, but aqueous solutions in concentrations of up to 1 × 10^{-3} M in TMNCP could be prepared.

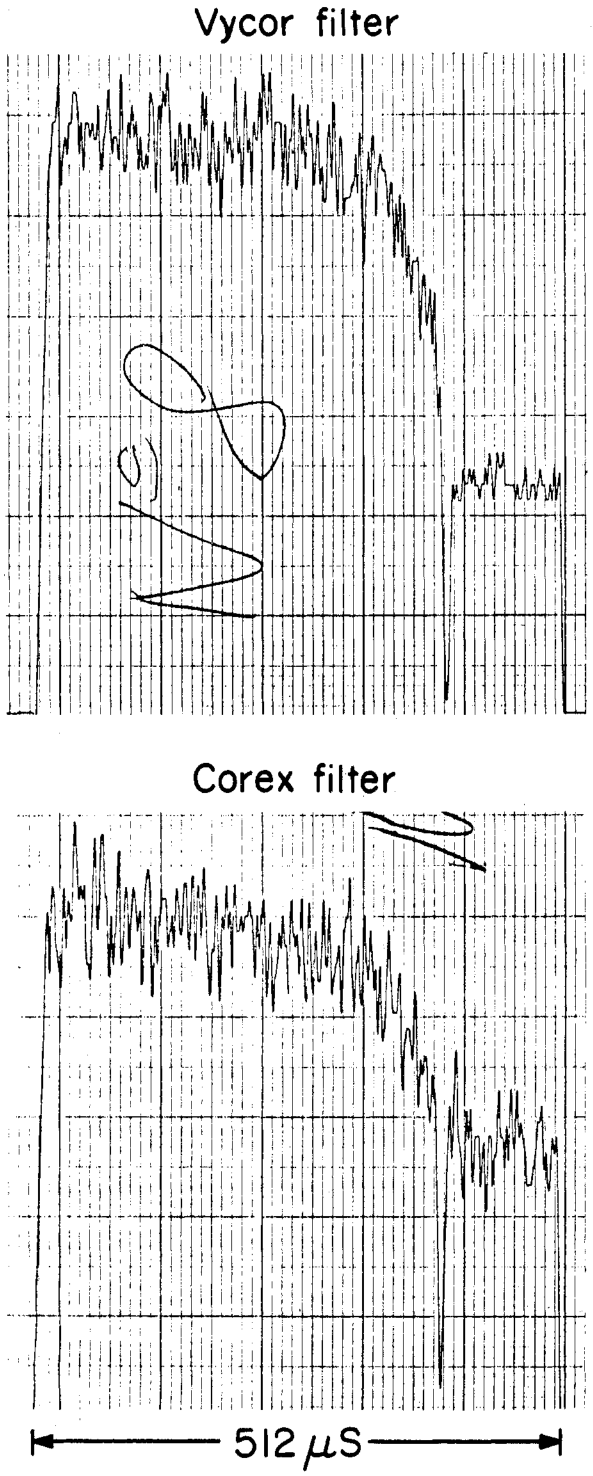


Figure 3. Traces of the transients from the flash photolysis of an acidic (3.6×10^{-5} N H_2SO_4), undegassed, solution of TMNCP (1.0×10^{-3} M) in acetonitrile using two different excitation filters.

Due to the solubility problem, UV absorption spectra were investigated in acetic acid and methanol solutions; in both solvents TMNCP exhibited absorption maximum at 280 nm. In the presence of increasing concentration of sulfuric acid from 10^{-5} to 10^{-3} M, this maximum decreased progressively with a concurrent buildup of absorption >250 nm. At a sulfuric acid concentration of $\sim 10^{-2}$ M, the 280-nm peak was replaced by the intense absorption below the 250-nm region. This suggested that a substantial fraction of TMNCP was protonated at 10^{-2} M sulfuric acid concentration to give TMNCPH$^+$.

TABLE I: Transient Absorption at Different pH in Aqueous Solution

Buffer, acid or base	pH	Initial OD at 350 nm
Borax/NaOH	10.2	0.0026
Bicarbonate/NaOH	10.2	0.0015
Bicarbonate/NaOH	9.6	0.0016
Borax/NaOH	9.5	0.0027
NaOH	8.6	0.0032
Phosphate/NaOH	8.0	0.0039
Phosphate/NaOH	7.5	0.0036
Phosphate/NaOH	6.0	0.0064
H_2SO_4	5.0	0.0060
H_2SO_4	4.0	0.0071
H_2SO_4	3.0	0.0075
H_2SO_4	2.0	0.0083

Flash photolysis of an undegassed solution and a solution degassed by bubbling with Ar for 1 min, both containing 0.83×10^{-3} M TMNCP and 1.0×10^{-5} N H_2SO_4, produced the identical transient absorption and decay curve. In these cases, only a fast buildup of the transient was observed; no slow rise component similar to that shown in acetonitrile was detected. In view of the known rates of oxygen removal from an aqueous solution by purging with inert gases,[35] the latter solution was believed to contain significantly less oxygen. For instance, Boag[35] has estimated the reduction in oxygen concentrations to be 5 times after 65 s and 25 times after 128 s, when a 100-mL aerated aqueous solution is purged with nitrogen at the rate of 1 mL/s. In a separate study we observed a large decrease in TMNCP concentrations, as indicated by the decreases in UV absorption, when aqueous TMNCP solutions were purged with either argon or oxygen for 5 min. The decrease in TMNCP concentration was not observed in acetonitrile solution. These observations suggest that in a solvent such as water, in which TMNCP is only sparingly soluble, significant amounts of TMNCP can be purged out of solution along with oxygen if deaerating time is not carefully controlled. However, since no change in either transient absorption or kinetics were detected for the degassed and undegassed solutions despite an expected large change in oxygen concentrations, it could be concluded that under the experimental conditions neither the transient nor its precursor was quenched by oxygen at a rate sufficiently rapid to compete with other processes. A similar result was observed previously in the flash photolysis of *N*-chloropiperidine in aqueous solution.[24,25]

The effect of pH on the initial optical density of the transient is shown in Table I. In each case the buffer solution itself was flash photolyzed but was shown to produce no measurable transient. However, at pH ~10, the transient generated in the borax buffer gave a larger absorption than that in the bicarbonate buffer. While the exact nature of the increase was obscure, it is conceivable that additional transient absorption could be produced by the presence of borate buffer when TMNCP was photolyzed even though photolysis of the buffer solution alone produced no transient. At pH $\lesssim 2$, contribution to the transient absorption arising from direct photolysis of protonated TMNCP could no longer be excluded since a large fraction of TMNCP would be protonated. Within the limit of these uncertainties, we could conclude that the transient absorption decreased by one half in the region of pH 7.5–8.0.

In the preliminary investigation, taking advantage of the known ESR spectrum of TMPH$^{+}\cdot$ in strongly acidic conditions,[22] effects of acidity on the lifetime of the TMPH$^{+}\cdot$ signal were investigated. Degassed acetic acid solution of TMNCP (1 M) containing 1 M sulfuric acid or higher gave a strong signal of the reported TMPH$^{+}\cdot$ ESR signal when irradiated in the cavity. The ESR signal,

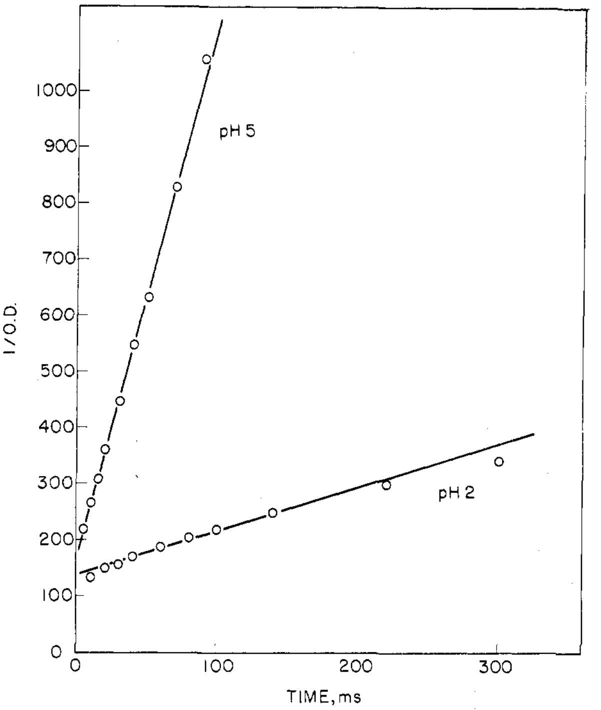


Figure 4. Second-order plots of the transient decay from the flash photolysis of TMNCP (1.0 × 10^{-3} M) in undegassed aqueous solution at pH 2 and at pH 5. Vycor filter.

TABLE II: Dependence of the Slope of the Second-Order Decay of the Transient on pH in Aqueous Solution[a]

pH	Slope × pathlength, cm s^{-1}
7	6.9×10^5
6	3.4×10^5
5	1.8×10^5
4	7.7×10^4

[a] λ_{mon} 350 nm.

however, became progressively weaker below 1 M sulfuric acid and at 0.1 M H_2SO_4 concentration, the signal was no longer observable. The intensity of $TMPH^+\cdot$ ESR signal in 1 M sulfuric acid solution was reduced by one half in the presence of 0.146 M cyclohexene and was totally absent in the presence of either 0.44 M cyclohexene or 1 M methanol. The observations indicate that the $TMPH^+\cdot$ reacts with these substrates. Attempts to use sulfuric acid (7 × 10^{-3} M) in acetic acid as the solvent system for TMNCP flash photolysis studies were hampered by complex decay curves and nonreproducibility. However from these studies, it became clear that the transient has long lifetimes in the order of seconds, and the presence of oxygen smooths the decay curves of the transient by scavenging other neutral radicals as have been observed in flash photolysis of *N*-chloropiperidine.[24,25] In view of difficulties encountered, the investigation in this solvent system was not pursued further.

The decay of the transient produced from the flash photolysis of undegassed aqueous solutions of TMNCP (0.83 × 10^{-3} M) were studied in the pH range 2–8. Above pH 8, kinetics measurements were not reliable owing to the weakness of the transient (OD < 0.002). In the pH range 4–7, the transient decay followed fairly good second-order kinetics. At pH 3, a definite deviation from the second-order plot could be observed; the deviation was sufficiently marked at pH 2 that the decay no longer obeyed second-order kinetics. The second-order plots for pH 2 as shown in Figure 4 exhibited a significant downward deviation from linearity at pH 2 as compared to that for pH 5 (Figure 4). The deviation observed at high acidity might indicate that the decay is compounded of two processes. Initially, decay is accelerated due to the high concentration of the aminium radical reacting with Cl· or radicals derived from Cl·. As these neutral radicals are spent, the aminium radicals decay by slower reactions with itself and with a (low) equilibrium concentration of the aminyl radical. The slopes obtained from second-order plots of 1/OD vs. time of the transient decay in the pH range 4–7 are summarized in Table II. The rate constants double approximately with each increment of one pH unit and show continuous decreases at higher hydrogen ion concentrations.

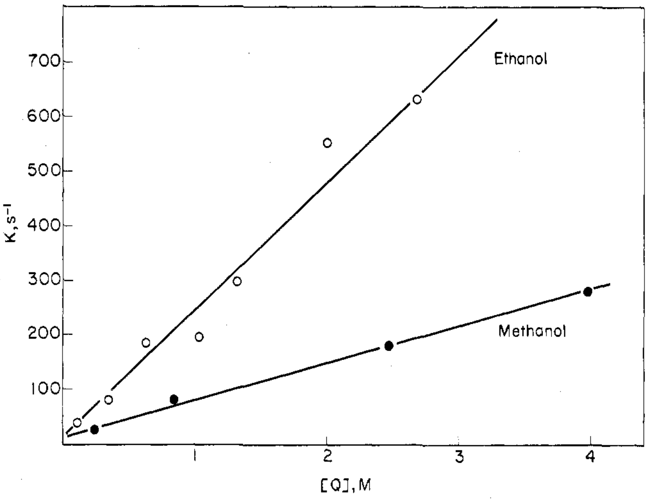


Figure 5. Plots of the first-order decay constants of the transient against quencher concentrations. Photolysis conditions are recorded in Table III.

TABLE III: Rate Constants for Quenching of the Transient from TMNCP in Solution[a]

Quencher	Solvent	k_q M^{-1} s^{-1}
Methanol	Water	66
Ethanol	Water	244
Cyclohexene	10% AN[b]-water	1.1×10^4

[a] In undegassed solutions containing 1.0 × 10^{-3} M TMNCP and 1.0 × 10^{-3} N H_2SO_4. λ_{mon} 350 nm. Photoflash filtered through a Vycor filter. [b] AN = acetonitrile.

3. *Quenching Studies in Aqueous Solution.* The decay rates of the transient from the flash photolysis of TMNCP in aqueous acidic solution were increased enormously in the presence of quenchers such as alcohols and cyclohexene. For the last quencher, flash photolysis was carried out in 10% acetonitrile–water in which up to ~2 × 10^{-3} M cyclohexene could be dissolved. No residual or unquenched transient was observed. In the concentration of quenchers (Q) used, decay of the transient followed good first-order kinetics; that is for large concentrations of quenchers with respect to extremely low concentrations of transient [T], $k_{obsd} = k_s[T] + k_q[Q] \approx k_q[Q]$, where k_{obsd} is the observed first-order decay constant of the transient obtained from the plot of log OD vs. time, and k_s and k_q are the bimolecular rate constants of the transient ($TMPH^+\cdot$) self-reaction and the reaction with quenchers. Obviously the rates of the quenching were so much faster that the $k_s[T]$ term became insignificant, and the reaction assumed a pseudo-first-order profile. Quenching plots for methanol and ethanol are shown in Figure 5 and the rate constants are summarized in Table III. Flash photolysis of TMNCP in neat ethanol containing 1.0 × 10^{-3} N H_2SO_4 gave rise to complete quenching, whereas in 2-propanol, the ketyl radical[36] was observed. Therefore, quenching results for 2-propanol could not be obtained due to in-

terference from the ketyl radical.

Discussion

Previously we have ascertained that the principal transient generated in the flash photolysis of *N*-chloro- and *N*-nitrosopiperidine in dilute aqueous acidic solution is the piperidinium radical and have described the kinetic profile of the radical.[24] In contrast to the estimated pK ~0.4 for unhindered *N*-chloramines,[33] TMNCP is nearly completely protonated in 10^{-2} M H_2SO_4 in acetic acid solution; this means below this acidity, primarily unprotonated TMNCP is photolyzed to give the amino radical which could be protonated to $TMPH^{+}\cdot$ at the acidity. The transient observed from the flash photolysis of TMNCP in various acidic solvent systems behaves similarly to the piperidinium radical and can be assigned to $TMPH^{+}\cdot$ on the basis of the following. Both the rates as well as concentrations of the transient increase with acid concentration since the primary amino radical generated is protonated faster and larger amounts in higher acidity. Secondly, the reactivity pattern of the transient toward cyclohexene and alcohols parallels that of piperidium radical[24] (vide infra).

Similar to flash photolysis of *N*-chloropiperidine in aqueous solution at pH 2, that of TMNCP in weakly acidic aqueous solution is also not affected in the presence of oxygen in spite of the reported oxidation to the corresponding nitroxide radical in highly acidic media.[37,38] Protonation of aminyl radical in aqueous solution is, as shown by the rapid rise of the transient, very fast, probably within <10 μs range. On the other hand, the rate of the aminyl radical reaction with oxygen has been reported to be comparable to its hydrogen abstraction in benzene, i.e., both reactions are very slow in view of generally low reactivity of aminyl radicals toward hydrogen abstraction.[39] The reaction of aminium radicals with oxygen is, as shown before,[24] a very slow process.

The acid dependent risetime of $TMPH^{+}\cdot$ in acetonitrile (Figure 2) arises from the fact that sulfuric acid behaves as a weak acid in acetonitrile[34] but ordinary acid–base equilibria cannot be applied due to an unknown quantity of water. Thus while the risetime is faster and the transient signal stronger at higher sulfuric acid concentrations, a quantitative treatment is not possible. Under such slow protonation conditions with a lifetime of ~100 μs duration, oxygenation of the aminyl radical could become a faint possibility. However since the observed absorption curve of $TMPH^{+}\cdot$ falls in the region where the corresponding nitroxide radical ($\lambda_{max}^{CH_3CN}$ 460 nm, ϵ 11242 nm, ϵ 2075) is transparent, it is concluded that the nitroxide radical, if it is formed, is likely to be a very small amount and does not interfere with our observations.

The pK_a of $TMPH^{+}\cdot$ in aqueous solution can be deduced from the change in aminium radical absorptions with pH utilizing the acid–base equilibrium relation

$$\log\left([R_2NH^{+}\cdot]/[R_2N\cdot]\right) = pK_a - pH$$

Hence, the pH where $[R_2NH^{+}\cdot] = [R_2N\cdot]$ corresponds to the pK_a of the aminium radical. The absence of significant transient absorption at high pH suggests that the aminyl radical absorbs only weakly or insignificantly at 350 nm, the wavelength at which the transient was monitored. Assuming that $[R_2N\cdot]_0 = [R_2N\cdot] + [R_2NH^{+}\cdot] = [R_2NH^{+}\cdot]_{max}$, the relation at the 50% protonation point is $[R_2N\cdot] = [R_2NH^{+}\cdot] = [R_2NH^{+}\cdot]_{max}/2$, where $[R_2N\cdot]_0$ is the initial amino radical concentration from photolysis, and $[R_2NH^{+}\cdot]_{max}$ is the limiting concentration of aminium radicals at a low pH, e.g., 3. Absolute values of both concentrations could not be obtained in the flash photolysis but could be represented by the absorbancy of the transient. The dependence of the transient absorption at different pH (Table I) shows that the pK_a of $TMPH^{+}\cdot$ is 7.5–8, slightly less acidic than that of the piperidinium radical (6.5–7.5) determined by the ESR method. Owing to the fact that at the pH 3~2 region, substantial amounts of protonated TMNCP are present and photolyzed to afford additional $TMPH^{+}\cdot$ concentration (and, therefore, the higher absorbancy) the true pK_a of $TMPH^{+}\cdot$ might be suspected to be higher than 7.5–8.0. The absence of a slow protonation in the aminium radical buildup in water at high pH was somewhat surprising. In view of the pK_a of the aminium radical, it may be due to proton transfer from water which is acting both as a solvent and as a general acid, that is

$$R_2N\cdot + H_2O \rightleftharpoons R_2NH^{+}\cdot + OH^{-}$$

The decay kinetics of aminium radicals have been studied in air-saturated acidic aqueous solutions containing low concentration of *N*-chloramines (typically 1×10^{-3} M TMNCP). Under these conditions, chain processes such as that involved in the chlorination of substrates with *N*-chloramines in strong acid are unimportant for several reasons: (i) carbon centered radical (R·) are inefficiently formed because of the combination of the low concentration of substrates (TMNCP) and low rate constants for hydrogen abstraction; (ii) R· are rapidly scavenged by O_2; (iii) low concentrations of R· and TMNCP reduce the importance of the propagation step, the chlorine abstraction by R· from TMNCP, compared with the radical termination reaction; and (iv) lower acidity in the present studies (compared to decay in high acidity) results in the increased rate of termination due to the nonnegligible equilibrium concentration of the aminyl radicals compared with the rate of termination involving aminium radicals alone. In basic solution, the absorption of $TMPH^{+}\cdot$ is weak and could be easily complicated by transient absorption arising from the presence of a buffer agent such as borate. At pH ≪ pK_a of the aminium radical, decay of the aminium radical is expected to be dominated by two processes:

$$R_2NH^{+}\cdot + R_2N\cdot \xrightarrow{k_1} \text{products} \qquad (1)$$

$$R_2NH^{+}\cdot + R_2NH^{+}\cdot \xrightarrow{k_2} \text{products} \qquad (2)$$

The decay of the aminium radical then is given by

$$\frac{d[R_2NH^{+}\cdot]}{dt} = -\left(2k_2 + \frac{k_1K_a}{[H^+]}\right)\left[R_2NH^{+}\cdot\right]^2$$

It is therefore expected that second-order decay kinetics with the observed decay constant, k_{obsd}, equal to $2k_2 + k_1K_a/[H^+]$, that is, k_{obsd} should vary inversely as the proton concentration. The slopes of the second-order decay kinetics of the aminium radical obtained from plots of 1/OD vs. time (Table II) are related to k_{obsd} by slope $\times\ l = k_{obsd}/\epsilon_{350\ nm}$ since $c = OD/\epsilon l$. The results show that k_{obsd} varies approximately as $1/[H^+]$ in the pH range 4–7. At higher acidity range of 0.1–1.3 M H_2SO_4 in acetic acid, the ESR results show a trend of progressively longer lifetimes (therefore smaller k_{obsd}) for $TMPH^{+}\cdot$ with increasing acidity. At very high acidity, i.e., >1 M H_2SO_4 in acetic acid, decay of $TMPH^{+}\cdot$ is due mainly to reaction 2 and is expected to be very slow because of the replusion of two positively charged species.[22] However at this very high acidity range, the above relation of k_{obsd} vs. $1/[H^+]$ may not be applicable because the $k_1K_a/[H^+]$ term becomes too small in comparison to k_2. It has been observed that the

k_{obsd} of the self-reaction decreases by an order of magnitude on changing acidity of the solvent from an H_0 value of −3 to −8 in the highly acidic region; the decreases have been attributed to the decrease in the activity coefficient of the radical.[22]

While the nature of the bimolecular self-reaction of aminium radicals is not clear, it appears to occur more in the higher acidity region presumably owing to higher concentrations of aminium radicals arising from increased stability of aminium radicals in acidic environment. The first-order decay kinetics of the unhindered piperidinium radical in dilute acid solution start to show a small component of second-order kinetics at 0.1 M H_2SO_4 and increases considerably at 0.5 M H_2SO_4;[25] excellent first-order decay plots below this acidity region[24] and second-order decay plots above[22] have been demonstrated previously.

In view of rather scarce absolute rate constants for bimolecular radical reaction with substrates, the flash excitation technique is a valuable one to elicite more rigorous data in this respect. Owing to the presence of severe steric hindrance the reactivities of $TMPH^{+}\cdot$ in both addition to olefins and hydrogen abstraction are severely reduced in comparison to those of piperidinium radical; the addition reactivity more drastically than abstraction. This must mean that approach to a carbon–carbon π bond is more susceptible to steric hindrance because closer approach is required for the bond formation. The quenching rate constants by methanol and ethanol places the hydrogen abstraction reactivity of $TMPH^{+}\cdot$ comparable to the methyl radical.[40]

References and Notes

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(2) E. Wolff, *Chem. Rev.*, **63**, 55 (1962).
(3) F. Minisci, *Synthesis*, 1 (1973); R. S. Neale, *ibid.*, 1 (1971).
(4) G. Sosnovsky and D. J. Rawlinson, *Adv. Free Radical Chem.*, **4**, 203 (1972).
(5) P. Kovacic, M. K. Lowery, and K. W. Field, *Chem. Rev.*, **70**, 639 (1970).
(6) Y. L. Chow, *Acc. Chem. Res.*, **6**, 354 (1973).
(7) R. W. Lockhart, R. W. Snyder, and Y. L. Chow, *J. Chem. Soc., Chem. Commun.*, 52 (1976).
(8) L. T. Magdzinski and Y. L. Chow, *J. Am. Chem. Soc.*, in press.
(9) J. R. L. Smith, R. O. C. Norman, and A. G. Rawley, *J. Chem. Soc., Perkin Trans. 1*, 566 (1973).
(10) C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. J. Jenner, and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).
(11) M. Simic and E. Hayon, *J. Am. Chem. Soc.*, **93**, 5982 (1971).
(12) T. Henriksen, T. B. Melo, and G. Saxebol in "Free Radicals in Biology", Vol. 2, W. A. Pryor, Ed., Academic Press, New York, N.Y., 1976, p 213.
(13) H. Budzikiwicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967, p 297.
(14) G. Cauquis and V. D. Parker in "Organic Electrochemistry", M. M. Bazier, Ed., Marcel Dekker, New York, N.Y., 1973, p 115.
(15) A. J. Fry, "Synthetic Organic Electrochemistry", Harper and Row, New York, N.Y., 1973.
(16) G. T. Davis, M. M. Demek, and D. H. Rosenblatt *J. Am. Chem. Soc.*, **94**, 3321 (1972), and the referenece cited therein.
(17) J. R. Lindsay Smith and L. A. Mead, *J. Chem. Soc., Perkin Trans. 2*, 206 (1973), and the reference cited therein.
(18) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 144 (1973).
(19) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).
(20) N. C. Deno, D. G. Pohl, and H. J. Spinneli, *Bioorg. Chem.*, **3**, 66 (1974); N. C. Deno, R. Fishbein, and J. C. Wyckoff, *J. Am. Chem. Soc.*, **93**, 2065 (1971).
(21) N. C. Deno, W. E. Billups, R. Fishbein, C. Pierson, R. Whalen, and J. C. Wyckoff, *J. Am. Chem. Soc.*, **93**, 638 (1971); N. C. Deno, *Meth. Free Radical Chem.*, **3**, 135 (1972).
(22) V. Malatesta and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 6400 (1973).
(23) J. Spanswick and K. U. Ingold, *Can. J. Chem.*, **48**, 546–554 (1970).
(24) A. J. Cessna, S. E. Sugamori, R. W. Yip, M. P. Lau, R. W. Snyder, and Y. L. Chow, *J. Am. Chem. Soc.*, **99**, 4044 (1977); M. P. Lau, A. J. Cessna, Y. L. Chow, and R. W. Yip, *ibid.*, **93**, 3808 (1971).
(25) R. W. Snyder, R. W. Yip, and Y. L. Chow, unpublished results.
(26) W. C. Danen and R. C. Rickard, *J. Am. Chem. Soc.*, **94**, 3256 (1972).
(27) R. W. Fessenden and P. Neta, *J. Phys. Chem.*, **76**, 2857 (1972).
(28) E. J. Land and E. J. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).
(29) W. C. Danen and T. T. Kensler, *J. Am. Chem. Soc.*, **92**, 5235 (1970).
(30) M. P. Lau, Ph.D. Thesis, Simon Fraser University, Burnaby, British Columbia, 1970.
(31) R. W. Yip, *Rev. Sci. Instrum.*, **40**, 1035 (1969).
(32) R. W. Yip, W. D. Riddell, and A. G. Szabo, *Can. J. Chem.*, **48**, 987 (1970).
(33) R. S. Neale and M. R. Walsh, *J. Am. Chem. Soc.*, **87**, 1285 (1965).
(34) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).
(35) J. W. Boag, *Curr. Top. Radiat. Res.*, **5**, 180 (1969).
(36) G. Porter, S. K. Dogra, R. O. Loutfy, S. E. Sugamori, and R. W. Yip, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1462 (1973).
(37) J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 3228 (1973); V. Malatesta and K. U. Ingold, *ibid.*, **95**, 6404 (1973).
(38) T. Toda, E. Mori, H. Horiuchi, and K. Murayama, *Bull. Chem. Soc., Jpn.*, **45**, 1802 (1972).
(39) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc. B*, 1114 (1966); D. Mackay and W. A. Waters, *J. Chem. Soc. C*, 813 (1966); C. J. Michejda and W. P. Hoss, *J. Am. Chem. Soc.*, **92**, 6298 (1970).
(40) J. K. Thomas, *J. Phys. Chem.*, **71**, 1919 (1967).