8-ring cation sites in dehydrated $Rb_{11}Na_1$-A and Tl_{12}-A. Although the cationic radii are the same,[7] 1.47 Å, Tl(2) lies off (0,½,½) while Rb(2) does not, resulting in Rb-O 8-ring distances that are considerably longer than the corresponding shortest Tl-O distance. This demonstrates the greater tendency of Tl^+ to maintain some relatively short approach distances to framework oxide ions, and agrees with the observed reluctance of a twelfth Tl^+ ion to move to a position of unambiguous zero-coordination.

The crystal studied was dehydrated. Tl(4) cannot be attributed to residual water molecules. The dehydration conditions employed were more than sufficient to remove all water from Na^+, K^+, Rb^+, Co(II), and Mn(II) exchanged zeolite A.[23] If Tl(4) were occupied by water molecules instead of a Tl^+ ion, the hydration distance to Tl(1) would be 1.35 Å, far from the values near 2.86 Å found in hydrated Tl_{13}-A.

It appears that the assumption made in previous work,[8] that full Tl^+-exchange had been achieved, and that the composition of the zeolite A framework was therefore $Al_{11}Si_{13}O_{48}{}^{11-}$, was incorrect. The correct unit cell composition was probably $Tl_{11}NaAl_{12}Si_{12}O_{48}$.

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Supplementary Material Available: Listings of the observed and calculated structure factors for both structures (Supplementary Tables 1 and 2) (4 pages). Ordering information is given on any current masthead page.

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Flash Photolysis Studies of *N*-Chloro- and *N*-Nitrosopiperidine in Aqueous Solution. Assignment and Reactivity of the Piperidinium Radical[1a]

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Abstract: Flash photolyses of *N*-chloro- and *N*-nitrosopiperidine in acidified aqueous solution (pH ~2) gave a common transient with an average lifetime of $\tau = 124 \pm 10\ \mu s$, which was assigned as the piperidinium radical. The piperidinium radical exhibited monotonic increases of UV absorption from ~400 nm toward 280 nm and its lifetime was not affected by acidity changes in the 0.01–0.50 N range nor quenched by oxygen. The absolute reaction rate constants of hydrogen abstraction and addition of the piperidinium radical on various substrates were determined by monitoring the decay kinetics of the transient. Flash photolysis studies of *N*-chloropiperidine are complicated by instability of the starting material under the conditions and by various transients generated in the chain processes. The latter complication was eliminated by low concentrations of *N*-chloropiperidine and the presence of oxygen. The implication of these effects to photodecomposition of *N*-chloro amines was discussed.

The aminium radical[3] (R_2NH^+) is an important reactive intermediate in the cyclization of N-halogenated amines (the Hofmann-Löffler reaction),[4-6] in the addition of chloro amines to olefins,[7,8] and in the chlorination of hydrocarbons and other organic compounds by chloro amines.[9-11] The mechanism of nitrosoamine photoreaction, which has been interpreted in terms of the chemistry of the aminium radical in the presence of nitric oxide,[12] has received further support from flash photolysis results on *N*-nitrosopiperidine (in the presence of dilute acid) in which direct evidence was obtained for the primary generation[13] of $R_2\dot{N}H^+$.

The chloro amine reactions are generally carried out in strongly acidic solutions such as sulfuric acid or sulfuric acid-acetic acid mixtures, and proceed by free-radical chain processes in which the aminium radical is the principal chain propagating species.[10,14] The primary step in the photolytically

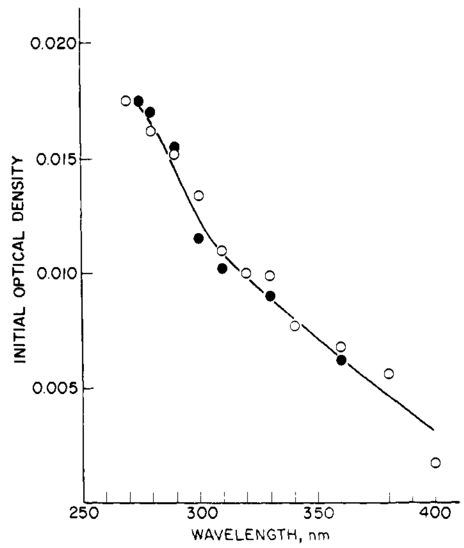

Figure 1. Absorption spectrum of the transient from flash photolysis of a deoxygenated aqueous solution containing *N*-nitrosopiperidine (5.5 × 10^{-5} M) and sulfuric acid (0.01 N). Flash energy 78 J filtered through 2-mm Vycor glass. Legend: ○, 13 nm bandwidth; ●, 33 nm bandwidth.

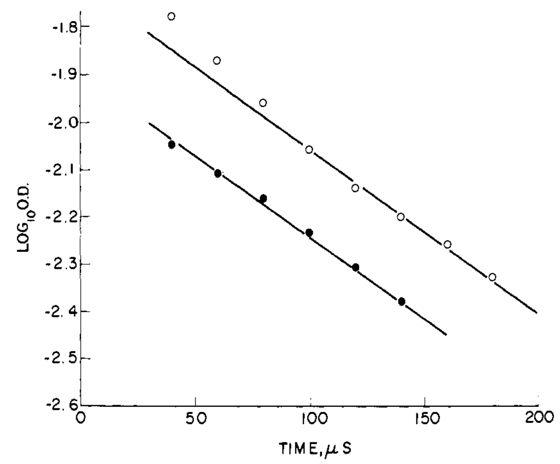

Figure 2. First-order decay kinetics of the transient from flash photolysis of a deoxygenated aqueous solution of *N*-nitrosopiperidine (5.5 × 10^{-4} M) and sulfuric acid (0.01 N). Legend: ○, flash energy 78 J; ●, 53 J.

induced chlorination by chloro amines has not been established unequivocally. Under usual experimental conditions for photochemical chlorination, aminium radicals are undoubtedly formed indirectly[15]—possibly from the photolysis of dichloroamine[6a] or chlorine[11a] (both have been detected in the reaction solution), or even from the photolysis of solvent.

ESR spectra have been recorded for di- and trimethylaminium radical produced by γ-radiolysis of the amines,[16] and for dialkylaminium radicals[17] and the 2,2,6,6-tetramethylpiperidinium radical[18] produced by photolysis of sulfuric acid solutions of the chloro amines. The hindered 2,2,6,6-tetramethylpiperidinium radical shows a very strong signal in acetic acid solution containing 1.3 M sulfuric acid. However, when the sulfuric acid concentration was decreased to 0.1 M, the ESR signal could no longer be detected.[19] The less hindered piperidinium radical could not be detected, even at −15 °C, when an acetic acid solution of *N*-chloropiperidine (1.0 M) containing 1.0 or 1.3 M sulfuric acid was photolyzed under the same experimental conditions used to detect the tetramethylpiperidinium radical.[19] The ESR observations suggest that in dilute acid solutions, aminium radicals are relatively short lived.

In the present study, the flash photolysis of both *N*-nitroso- and *N*-chloropiperidine (NNP and NCP, respectively) has been studied in mildly acidic solutions to determine if an identical intermediate could be produced from the two different compounds. The observation of such a common intermediate would provide strong confirmatory evidence that the transient is indeed the piperidinium radical as previously suggested. In addition, we report the spectra, decay kinetics, and reactivities of the transients produced from the flash photolysis of NCP and NNP. Until now, information on the aminium radical has almost exclusively been derived from results obtained by indirect means and in extremely strong acid solvents such as acetic acid–sulfuric acid mixtures, or trifluoroacetic acid.

Experimental Section

Chemicals. NCP was prepared by chlorination of piperidine with sodium hypochlorite. All liquids were kept near 0 °C throughout the synthesis. Piperidine was added dropwise, with stirring, over a period of 1 h to a sodium hypochlorite solution, 12% in available chlorine. The amount of sodium hypochlorite used was ~25% in excess of the amine. The product was extracted from the reaction mixture with cooled ether and the ether extract washed successively with water, 0.1 N sulfuric acid, and sodium carbonate, and dried over magnesium sulfate. The ether was flash evaporated at 10 °C. The resulting oil was distilled at 43 °C (20 mm) to yield the almost colorless, oily NCP. The chloro amine was stored at liquid nitrogen temperature in the dark. NNP (Eastman Organic Chemicals) was distilled at 88.5 °C (10 mm).

Isopropyl alcohol was refluxed over CaH_2 and distilled. Ethanol was doubly distilled. Methanol (Fisher spectroscopic grade), *tert*-butyl alcohol (Harleco fluorometric grade), and *p*-dioxane (MCB spectroquality grade) were used without further purification. The ultraviolet spectra of the purified alcohols showed end absorption only.

Flash Photolysis. The apparatus was a modified version of the double beam apparatus using a pulsed monitoring source reported previously.[13,20,21] Using two independent, synchronously triggered, capacitor-spark gap circuits (0.1 μF, 35 kV capacitors in each circuit), a flash duration of 0.85 μs with a typical input energy of 78 J at 28 kV was obtained. The optical path length of the sample was 20 cm.

NNP solutions were generally flashed four times before being discarded. The resulting decomposition, as indicated by the decrease in UV absorption, was less than 5%.

NCP tended to decompose in acidic solutions. To minimize decomposition and obtain reproducible results, solutions of NCP were freshly prepared before each photolysis run. Immediately before flash photolysis, the solution was acidified. In general, each sample solution was flashed twice and discarded.

Results

Flash Photolysis of NNP. Flash photolysis of a degassed aqueous solution of NNP containing either 0.01 N HCl or 0.01 N H_2SO_4 produced a transient with an absorption maximum below 280 nm (Figure 1). No transient was observed in the absence of either acid or NNP.

At low concentrations in degassed aqueous solution (NNP concentration 5.5 × 10^{-5} M), the transient decayed exponentially with a lifetime of 124 ± 10 μs.[22] At high transient concentrations, the initial portion of the decay deviated from first-order kinetics—due possibly to radical-radical reactions. Plots of decay kinetics at two different initial transient concentrations are shown in Figure 2.

In the concentration range studied, acidity and the presence of oxygen and NNP had no significant effect on the lifetime of the transient except possibly for a slight decrease at high sulfuric acid concentrations. The results are summarized in Table I.

The transient lifetime (τ) was reduced by the presence of added organic quenchers according to $\kappa = \kappa_0 + \kappa_q[Q]$, where $\kappa = 1/\tau$ is the transient decay constant and κ_0 is the decay constant in the absence of added quencher, Q. The rate constants obtained for quenching by cyclohexene, 1,3-pentadiene, benzene, methanol, ethanol, 2-propanol, tetrahydrofuran, and

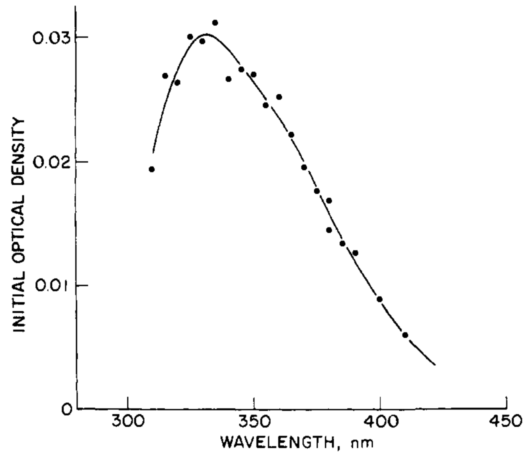

Figure 3. Absorption spectrum of the transient from flash photolysis of a deoxygenated aqueous solution containing *N*-chloropiperidine (0.9 × 10^{-3} M) and hydrochloric acid (0.01 N). Flash energy 68 J.

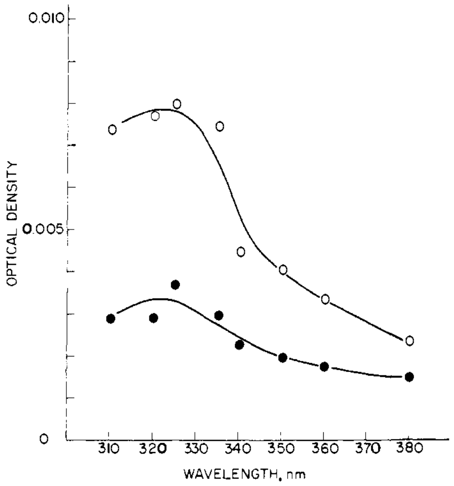

Figure 4. Absorption spectrum of the transient from flash photolysis of an aqueous solution containing *N*-chloropiperidine (5.1 × 10^{-3} M) and sulfuric acid (0.01 N). Solution undeoxygenated. Legend: ○, 0 μs; ●, 160 μs after the photoflash. Flash energy 62 J.

dioxane are recorded in Table II. Above ~6 M methanol, an upward deviation from linearity in the plot between κ and [Q] was observed. The deviation was most marked at concentrations approaching pure methanol. In the present study, κ_q for methanol was based on data obtained at low methanol concentration, which corresponded to the linear portion of the plot.

Flash Photolysis of NCP. Flash photolysis of an undegassed aqueous solution of NCP (1 × 10^{-3} M) in the absence of added acid gave a weakly absorbing transient which decayed by second-order kinetics ($\kappa/\epsilon_{330\text{ nm}} = 5.1 \times 10^6$ cm s^{-1}).

Next, experiments on the flash photolysis of NCP in acid solutions were carried out in attempts to produce the piperidinium radical from the corresponding *N*-chloro amine. When an aqueous solution containing NCP (1 × 10^{-3} M) and HCl (0.01 N) was flash photolyzed, a strongly absorbing transient (λ_{max} ~335 nm, Figure 3) decaying by first-order kinetics (τ = 60 ± 10 μs) was observed. The absorption spectrum of the transient was identical with that of the well-known $Cl_2^-\cdot$ radical anion produced by means of flash photolysis[23] and pulse radiolysis.[24]

To prevent the formation of $Cl_2^-\cdot$ from Cl· and Cl^-, NCP was flash photolyzed in aqueous solutions acidified with H_2SO_4. The transient absorption spectra obtained from a 5.1 × 10^{-3} M NCP solution (0.1 N H_2SO_4) is shown in Figure 4.

Table I. The Influence of *N*-Nitrosopiperidine Concentration, Acidity, and Oxygen on the Lifetime of the Transient Formed from the Flash Photolysis of *N*-Nitrosopiperidine in Aqueous Solution

[NNP], M	[H_2SO_4], N	Presence of O_2	Lifetime, μs
5.5 × 10^{-5}	0.01	Absent	124 ± 10
5.5 × 10^{-5}	0.01	Saturated with O_2	121 ± 14
5.5 × 10^{-4}	0.01	Absent	126 ± 12
5.5 × 10^{-5}	0.10	Absent	108 ± 8
1.1 × 10^{-4}	0.50	Absent	98 ± 10

Table II. Rate Constants or Quenching of the *N*-Nitrosopiperidine Transient in Aqueous Solution[a]

Quencher	k_q, M^{-1} s^{-1}
Methanol	(2.4 ± 0.3) × 10^3
Ethanol	(1.4 ± 0.2) × 10^4
2-Propanol	(4.4 ± 0.2) × 10^4
tert-Butyl alcohol	(3.6 ± 0.5) × 10^3
Cyclohexene	(2.4 ± 0.1) × 10^7 [b]
1,3-Pentadiene	5.3 × 10^7 [b]
Benzene	≤3 × 10^2 [b]
Dioxane	9.3 × 10^3 [c]

[a] Deoxygenated solution containing 0.01 N H_2SO_4. [b] In 2/1 (by volume) methanol/water solution. [c] Result of Y. Iida, unpublished data.

The absorption spectra obtained from data recorded at 0 and 160 μs after the photoflash suggest that the absorption is compounded of a short and longer lived transients, the latter peaking at ~325 nm. Consistent with, and further indicating, the presence of two transients, the absorption decayed by complex kinetics. Apparent lifetimes ranging from 163 to 300 μs were obtained, depending on the wavelength.

Investigations carried out with samples containing different concentrations of NCP revealed that the fraction of the total absorption due to the longer lived transient decreased with decreasing concentrations of NCP. The lowest NCP concentration that could be used was found to be ~0.7 × 10^{-3} M. At lower NCP concentrations, the amount of background transient absorption resulting from the photolysis of acidified solvent became, despite the use of an acetic acid short-wavelength cutoff filter, significant in comparison with the transient under study. The absorption spectrum of the transient obtained from flash photolysis of a 1 × 10^{-3} M NCP (0.01 N H_2SO_4) appears in Figure 5. The absorption spectrum is similar to that found for the *N*-nitroso compound. Because of absorption by the NCP, it was not possible to carry out reliable measurements below 310 nm.

The decay of the transient from the photolysis of undegassed acidic aqueous solutions containing low NCP concentrations of 7-10 × 10^{-4} M followed good first-order kinetics ($\tau \sim$ 130 μs). The decay was not significantly affected by the acid used, H_2SO_4 or $HClO_4$, nor by the acidity in the concentration range 0.01-0.25 N. The concentration of NCP was increased at the higher acidities to compensate for the reduced UV absorption due to protonation of the NCP. When oxygen was excluded, the decay of the transient did not obey good first-order kinetics. The measured lifetimes are summarized in Table III.

The lifetime of the transient produced from flash excitation of NCP in water containing 0.01 N H_2SO_4 was quenched by methanol, isopropyl alcohol, and cyclohexene. Measurements of the decay constants at the different isopropyl alcohol concentrations were complicated by the appearance of an additional transient. At an isopropyl alcohol concentration of 0.5

Table III. Lifetime of the Transient Produced from the Flash Photolysis of *N*-Chloropiperidine in Aqueous Solution[a]

[NCP], M	Acid	τ, μs	r^b
8×10^{-4}	0.01 N $HClO_4$	131 ± 22	0.996
$\sim 7 \times 10^{-4}$	0.01 N H_2SO_4	131 ± 16	0.996
5×10^{-3}	0.01 N H_2SO_4	168 ± 14[c]	0.960
8×10^{-4}	0.10 N H_2SO_4	115 ± 6	0.994
1.2×10^{-3}	0.25 N H_2SO_4	114 ± 10	0.988
6×10^{-4}	0.01 N H_2SO_4	163 ± 23[c,d]	0.981

[a] Monitored at 335 nm. Photoflash filtered through 1 cm glacial acetic acid. Flash energy 0.2 μF, 32 kV. Solutions undegassed. [b] Coefficient of correlation for first-order decay kinetics ($0 \geq r \leq 1$). [c] Poor first-order kinetics. [d] Deoxygenated.

M, the absorption data of the transient no longer corresponded to that observed from a solution containing NCP alone in the presence of acid. In addition, the nonlinearity at high methanol concentration previously noted in the quenching study of the transient generated from NNP was also observed for the transient generated from NCP. Based on limited decay constants measured at low alcohol concentrations, the approximate rate constants obtained for quenching by methanol and isopropyl alcohol were 2.6×10^3 and 3.1×10^4 M^{-1} s^{-1}, respectively. The rate constant for quenching by cyclohexene in a 2:1 (by volume) methanol-water solvent system was found to be 2.0×10^7 M^{-1} s^{-1}.

Discussion

Radical chain reactions, which have been shown to occur in the decomposition of *N*-chloro amines in strong acid,[14] suggest (and the present results confirm) that flash photolysis of NCP in deoxygenated solutions containing dilute acid can produce complex kinetics. It was observed, however, that if a solution containing a low concentration of NCP (consistent with adequate transient signal to noise ratio) were flash photolyzed in the presence of oxygen, a single transient (λ_{max} <310 nm, Figure 5) decaying by first-order kinetics ($\tau \sim 130$ μs) could be time resolved. The common identity of this transient and the one produced from NNP under similar experimental conditions can be deduced from the following observations: (1) Both the lifetimes and spectra of the transients produced from NCP and NNP are, within experimental errors, identical. (2) The set of rate constants obtained for quenching of the NCP transient by methanol, isopropyl alcohol, and cyclohexene are in good agreement with that observed for quenching of the NNP transient under identical conditions. Since aminium radicals have been firmly established as the reactive intermediate in the photochemical reactions of *N*-chloro amines,[3-7] the above-mentioned observations substantiate the identity of the transient as the piperidinium radical. The correctness of the assignment is also supported by the reactivity pattern exhibited by the transient. The selective manner in which the transient reacted with the alcohols containing primary, secondary, and tertiary hydrogens (Table II), and the significantly higher quenching constants for cyclohexene and 1,3-pentadiene compared with the alcohols, show that the transient is an electrophilic radical. Such chemical behavior had previously been observed for the piperidinium radical on the basis of reaction rate studies.[9]

The selective reactivity of the piperidinium radical toward the alcohols illustrates a striking difference between the behavior of the aminium radical in dilute and concentrated acid solutions. The data recorded in Table II clearly show that the important structural factor in determining the reactivity of the piperidinium radical toward alcohols in dilute acidic solutions is the presence of hydrogens α to the OH groups (relative reactivity tertiary > secondary > primary). In contrast, previous work on the selectivity for chlorination of C_6 and C_8 alcohols involving the aminium radical showed that the closer the CH bond was to the OH group the less reactive it became.[11a] The dichotomous results can be readily understood in terms of acidity differences. In the chlorination study, the acid concentrations used were sufficiently high (~72% H_2SO_4) to cause protonation of the alcohols.[11a] As a result, electrostatic repulsion between the positive charges on the substrate and the aminium radical retards the reactivity of those CH bonds located close to the site of protonation at the OH group. The effect of such electrostatic repulsion is absent under the conditions used in the present study.

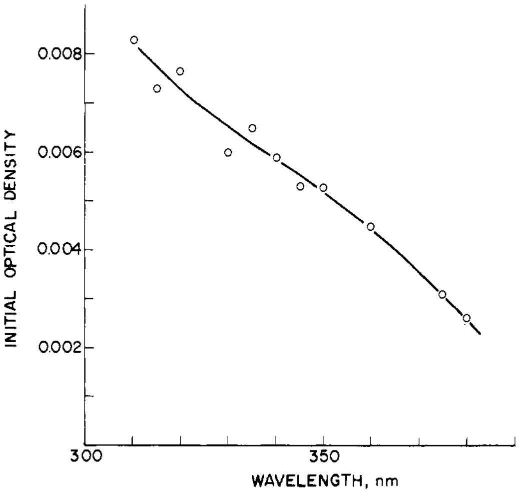

Figure 5. Absorption spectrum of the transient from flash photolysis of an aqueous solution containing *N*-chloropiperidine (1.0×10^{-3} M) and sulfuric acid. Solution undeoxygenated. The photoflash was filtered through 2-mm Vycor. Flash energy, 78 J.

The primary steps in the formation of piperidinium radicals from NCP are the photochemical excitation of the unprotonated NCP followed by fragmentation to produce amino radicals and chlorine atoms. In contrast with most previous studies in concentrated acid solutions where the initiation steps are obscure,[4,6a,11a] the absorbing species in the present study can unambiguously be identified as the unprotonated NCP which possesses an absorption maximum at ~260 nm in aqueous solution. Our results suggest that the piperidino radicals produced in the initial photolysis are rapidly and completely converted to the piperidinium radicals by protonation. Firstly, the tentatively identified piperidino radical observed in the photolysis of NCP neutral solution could not be detected in the acidic solutions used. Secondly, in solutions containing 0.01-0.25 N H_2SO_4, the transient piperidinium radical was formed faster than the time resolution of the apparatus (~2 μs) and showed no change in its decay kinetics with changes in acidity. Although the pK_a of the piperidinium radical is not known, the pK_a of the closely related $(CH_3)_2NH^{+\cdot}$ radical has been estimated to be 6.5-7.5.[16] Unless the pK_a of the piperidinium radical were radically different from that of the dimethylaminium radical, complete protonation of the piperidino radical is again indicated.

The suppression of chain processes by oxygen in the photolysis of NCP can be understood in terms of conversion of carbon-centered radicals to the less reactive peroxy radicals at rates approaching diffusion-controlled values.[26] Preparative studies have shown that the photodecomposition of chloro amine follows a chain process which can be interrupted in the presence of oxygen.[4,6,27] Oxygen thus effectively acts as a chain terminator and minimizes the formation of aminium radicals by radical chain reactions[14] which would result in more complex kinetics. In the time domain, the transformation of carbon-centered radicals to the less reactive (longer lived) peroxy radicals tends to minimize, if not altogether eliminate, overlapping decay times between the carbon-centered radicals and the transient piperidinium radical. It is noteworthy that oxygen, an efficient triplet quencher, does not quench the photophysical process in the photolysis of NNP or NCP[28] but does lead to the formation of oxidation products such as nitrates,[29] alcohols, or ketones.[30]

The mechanism for the photodecomposition of NCP in dilute acidic solution is summarized below.

$$C_5H_{10}NCl \xrightarrow{h\nu} C_5H_{10}N\cdot + Cl\cdot$$

$$C_5H_{10}N\cdot + H^+ \overset{\text{fast}}{\rightleftharpoons} C_5H_{10}NH^+$$

$$C_5H_{10}NH^{+}\cdot \text{ (or Cl}\cdot\text{)} + RH \rightarrow R\cdot + C_5H_{10}NH_2^+ \text{ (or HCl)}$$

$$R\cdot + C_5H_{10}NCl \rightarrow C_5H_{10}N\cdot + RCl$$

$$R\cdot + C_5H_{10}N^+HCl \rightarrow C_5H_{10}NH^+ + RCl$$

$$R\cdot + O_2 \rightarrow R\text{-}O\text{-}O\cdot$$

Although the mechanism responsible for the first-order decay of the piperidinium radical in aqueous solution (in the absence of substrate) is not clear, some possibilities can be eliminated. First of all, the piperidinium radical is unreactive toward oxygen, which has been shown to react with alkyl and amino radicals with close to the diffusion controlled rates.[27,31] For the latter reactions nitroxides have been identified as products.[31] Secondly, the reaction with the starting material, NNP (or NCP), does not appear to be important in the concentration range utilized. This is readily understood since alkyl hydrogen abstraction of an aminium radical has a low rate constant[18] of 200-300 $M^{-1}\ s^{-1}$. Assuming that our apparatus is capable of detecting a 20% change in the decay constant, the upper limit of the reaction rate constant with NNP is estimated to be $<3 \times 10^6\ M^{-1}\ s^{-1}$. Thirdly, in agreement with the conclusion arrived at a high acidity region[18] ($-H_0$ 3-9), the bimolecular decay of the piperidinium radical in the dilute acid solution is not significantly fast. Finally, the lack of influence of acidity on the decay constant eliminates, as a significant decay pathway, the reaction of the piperidino radical in equilibrium with the piperidinium radical.

In conclusion, piperidinium radicals are produced in the photolysis of NCP or NNP in aqueous solution at pH 2. In the presence of oxygen, and at low NCP concentrations, the formation of piperidinium radicals by chain processes is unimportant in comparison with the formation of piperidinium radicals by photolysis of unprotonated NCP. Absolute rate constants for the reaction of the piperidinium radical with alcohols and alkenes have been measured. The variation in rate constants suggests that the amminium radical abstracts hydrogen atoms from the alcohols (with the hydrogens α to the OH group being the most important) and adds to the alkenes. In the absence of added substrate, the piperidinium radical decays principally by first-order kinetics ($\tau \sim 130\ \mu s$) by an as yet unspecified mechanism.

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