1 (and **4**) is surprisingly rapid if it is a simple radical–molecule reaction, since the process

$$\mathbf{1} + H_2O_2 \longrightarrow \mathbf{1}\text{-H} + HOO\cdot$$

is endothermic by about 13 kcal/mol.[28] It therefore seemed possible that the oxidation of H_2O_2 involved ionic species present in equilibrium with the parent nitroxide. In view of the obvious possibility that the

$$\mathbf{1} + \mathbf{1} \rightleftharpoons \mathbf{1}^+\mathbf{1}^-$$

$$\mathbf{1}^+ + H_2O_2 \longrightarrow \mathbf{1}\text{-H} + H^+ + O_2$$

dimerization of **1** also involved ionic intermediates, this mechanism was tested in two ways. In the first place, direct measurement on the conductivity of **1** in acetonitrile (0.08 *M*) and benzene (0.07 *M*) did not reveal the presence of ions. Secondly, it is known that ionic oxidizing agents and hydrogen peroxide can give rise to singlet molecular oxygen.[15] However, attempts to trap singlet oxygen in the **1**–H_2O_2 reaction with 2-methyl-2-pentene were not successful.[30]

Reduction of **1** with 2-propanol-d_8 or with H_2O_2–D_2O mixtures led to insignificant deuterium uptake into the bridgehead positions of **1**-H (Table II). While these observations are consistent with either an ionic or a radical pathway for these reactions, it seems likely that neither proceeds through the intermediate **9** proposed to explain the irreversible dimerization. The kinetics of both reactions did not appear to be simple.

Although we isolated **1**-H from **1** in refluxing *tert*-butyl alcohol and cyclohexane, the yields were low and we suspect rather than solvent H-abstraction a process such as the following

$$2(\mathbf{1}) \longrightarrow \mathbf{7}$$

$$\mathbf{7} + \mathbf{1} \rightleftharpoons \mathbf{1}\text{-H} + \underset{\substack{\downarrow \\ \text{decomposition} \\ \text{products}}}{\text{nitroxide from } \mathbf{7}}$$

This reaction does not occur at lower temperatures because strong intramolecular H-bonding in **7** shifts the equilibrium to the left.

The mechanism of photoreduction of **1** in 2-propanol is also ambiguous. We cannot distinguish between an excited state of **1** and radicals, or excited states, derived from solvent (or from solvent oxidation products, *e.g.*, acetone) as the reactive intermediates.[31]

Conclusion

The behavior of two bicyclic nitroxides indicates that their reactivity is considerably greater than that of more hindered derivatives such as di-*tert*-butyl nitroxide. The differences between the azaoctane **1** and azanonane **4** toward dimerization are interesting, and we suggest that these are due to several factors, (a) the different OH bond strengths of **1**-H and **4**-H, (b) a lower concentration in **4** of the reversible dimer, which may be an intermediate in the irreversible dimerization, and (c) different degrees of overlap of the bridgehead C–H orbital with other orbitals in the radical.

Acknowledgment. We are grateful to Mr. L. Iton, Mr. N. Clements, and Mr. E. Yantha for assistance in the synthesis of **1** and **4**.

[28] Taking D[1-H] = 77 kcal/mol[21] and D[HOO–H] = 90 kcal/mol.[29]

[29] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[30] The significance of this experiment may be limited by potential quenching of any singlet oxygen produced by 1 or 1-H.

[31] The photoreduction of a hindered nitroxide has been reported: J. F. W. Keana, R. J. Dinerstein, and F. Baitis, *J. Org. Chem.*, **36**, 209 (1971).

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XI. Aminium Radicals[1]

V. Malatesta[2] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada. Received February 20, 1973

Abstract: The bimolecular self-reactions of two aminium radicals have been studied by kinetic epr spectroscopy. For dimethylaminium in 0.95 *M* H_2SO_4–CF_3COOH the rate constant for decay is given by $2k_t = 10^{9.5}\exp(-5000 \pm 1500\ \text{cal}/RT)\ M^{-1}\ \text{sec}^{-1}$ and for 2,2,6,6-tetramethylpiperidinium in CF_3COOH by $2k_t = 10^{9.8}\exp(-7600 \pm 1000\ \text{cal}/RT)\ M^{-1}\ \text{sec}^{-1}$. For both radicals $2k_t$ is independent of solvent viscosity (up to 20 cP) but decreases by about one order of magnitude on changing the acidity of the solvent from an H_0 value of -3 to a value of -8. This is attributed to a decrease in the activity coefficients of the radicals. Various mechanistic possibilities are considered including hydrogen atom transfer from alkyl to nitrogen, $2R_2NH\cdot^+ \rightarrow R_2NH_2^+ + R(R_{-H})NH^+$, and from nitrogen to nitrogen, $2R_2NH\cdot^+ \rightarrow R_2NH_2^+ + R_2N^+$.

The exceptionally high selectivity obtainable in the radical-chain chlorination of organic compounds with *N*-chloramines[3–5] has generated great interest in the reactions of these radicals. However, a rotating sector study[6] of the photochemically ini-

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[1] Issued as National Research Council of Canada No. 13422. Part X: J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3228 (1973).

[2] National Research Council of Canada Postdoctorate Fellow, 1972–1973.

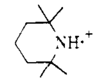
[3] F. Minisci, R. Galli, A. Galli, and R. Bernardi, *Tetrahedron Lett.*, 2207 (1967); F. Minisci, R. Galli, and R. Bernardi, *Chem. Commun.*, 903 (1967); *Chim. Ind.* (*Milan*), **49**, 594 (1967); *J. Chem. Soc.*, 324 (1968); F. Minisci, R. Galli, R. Bernardi, and M. Perchinumno, *Chim. Ind.* (*Milan*), **50**, 453 (1968); F. Minisci, G. P. Gardini, and F. Bertini, *Can. J. Chem.*, **48**, 544 (1970).

[4] J. Spanswick and K. U. Ingold, *Can. J. Chem.*, **48**, 546 (1970).

[5] N. C. Deno, W. E. Billups, R. Fishbein, C. Pierson, R. Whalen, and J. C. Wyckoff, *J. Amer. Chem. Soc.*, **93**, 438 (1971); N. C. Deno, R. Fishbein, and J. C. Wyckoff, *ibid.*, **93**, 2065 (1971); N. C. Deno, *Methods Free-Radical Chem.*, **3**, 135 (1972).

[6] J. Spanswick and K. U. Ingold, *Can. J. Chem.*, **48**, 554 (1970).

Table I. Epr Parameters for Aminium Radicals at Ambient Temperatures

Radical	Solvent	*g* factor	a^N, G	a^H_{NH}, G	$a^H_{CH_3}$, G	Ref
$Me_2NH\cdot^+$	90% H_2SO_4	2.0036	19.28	22.73	34.27	7
$Me_2NH\cdot^+$	$HClO_4$-H_2O	2.00354	19.23	(−)21.96	33.61	8
$Me_2NH\cdot^+$ [a]	CF_3COOH	2.00412	19.13	22.61	34.16	This work[b]
	CF_3COOH	2.00382	18.57	21.35	1.23[c]	This work[b]

[a] Chloramine added as the sulfate. [b] Parameters kindly determined by Dr. J. R. Morton on a Varian E-12 epr spectrometer. [c] a_γ^H values of 0.80 for $[(CH_3)_2CH]_2NH\cdot^+$ and 0.71 for $[(CH_3)_3CNHCH_3]\cdot^+$ have been reported previously.[7]

tiated chlorination of decanoic acid with *N*-chlorodimethylamine and *N*-chloropiperidine in acetic acid–sulfuric acid mixtures represents the only attempt to measure the rate constants for the bimolecular self-reactions of aminium radicals, and for a hydrogen atom

$$2R_2NH\cdot^+ \xrightarrow{2k_t} \text{inactive products}$$

abstraction by such radicals. Unfortunately, in this

$$R_2NH\cdot^+ + R'H \xrightarrow{k_p} R_2NH_2^+ + R'\cdot$$

study the rate of chain initiation in these reactions, R_i, could not be measured directly and had, perforce, to be estimated indirectly. As a consequence, only the approximate values of $2k_t$ and k_p could be obtained.

The recent observation of aminium radicals by photolysis of chloramines[7] and radiolysis of amines and chloramines[8] in acid solutions in the cavity of epr spectrometers prompted us to remeasure the termination rate constant, $2k_t$, directly by kinetic epr spectroscopy.

Two aminium radicals were chosen for study: dimethylaminium because most of the original kinetics were done with this radical,[6] and 2,2,6,6-tetramethylpiperidinium because the corresponding amino radical is relatively stable *and does not dimerize or disproportionate.*[9] Both radicals were generated by photolysis of the chloramines in the cavity of a Varian E-3 epr spectrometer.

Experimental Section

Materials. ***N*-Chlorodimethylamine** was prepared and stored as previously described.[4]

2,2,6,6-Tetramethyl-*N*-chloropiperidine was prepared by slow addition of 7.05 g of the amine to 100 ml of a stirred 0.5 *M* solution of sodium hypochlorite at 0–5°. A white solid separates during this time. Stirring was continued for a further 20 min at the same temperature after the addition was complete. The solution was extracted three times with 100 ml of ether; the ether was washed with cold 10% H_2SO_4, dried over Na_2SO_4, and evaporated under reduced pressure. The residual oil was distilled at 75° (17 Torr) (lit.[10] bp 65° (7 Torr)), yield 6.8 g, 77%.

Procedure. The general experimental technique has been described in previous papers in this series.[1]

The dimethylchloramine was used as the sulfuric acid salt.[4] In typical experiments, this was added to the acid solvent to make a 0.9–1.0 *M* solution. At room temperature under steady illumination the radical concentration was $\sim 3 \times 10^{-6}$ *M*. The tetramethyl-*N*-chloropiperidine was normally used at a concentration of 0.5 *M* and the radical concentration was generally $\sim 2 \times 10^{-6}$ *M*.

Acidity Function, H_0. This function provides a quantitative measure of acidity and was conceived originally by Hammett and Deyrup.[11,12] It is derived from the ionization equilibria of uncharged bases

$$B + H^+ \rightleftharpoons BH^+$$

and is defined by

$$H_0 = -\log K_{BH^+} - \log \frac{[B]}{[BH^+]} = -\log \frac{a_{H^+} f_B}{f_{BH^+}}$$

where K_{BH^+} is the thermodynamic ionization constant in molar concentration units (referred to ideal dilute solution in water). a_{H^+} is the hydrogen ion activity and the *f*'s denote molar concentration activity coefficients. In dilute aqueous solutions where each individual activity coefficient is taken, by convention, to approach unity the acidity function becomes equal to the pH.

The Hammett acidity function serves specifically as a measure of the tendency of the solution in question to transfer a proton to an uncharged base molecule, increasingly negative values corresponding to higher acidity. The H_0 values used in this work were taken from the literature.[13,14]

Results

Epr Spectra. The spectroscopic parameters for the two radicals studied in this work are listed in Table I together with the values reported previously for dimethylaminium.[7,8] For these radicals the hyperfine splittings due to the α and β hydrogens tend to decrease as the sizes of the alkyl groups increase.[7] The splittings due to these hydrogens also appear to be more solvent dependent than that due to the nitrogen.

Decay Kinetics. Both dimethylaminium and tetramethylpiperidinium decay with "clean" second-order kinetics under all experimental conditions. The bimolecular decay rate constants, $2k_t$, were measured at 25° in a variety of solvents having different acidities and viscosities. These data are summarized in Table II. It can be seen that $2k_t$ is independent of the solvent viscosity, *i.e.*, the reaction is not diffusion controlled even in the most viscous media studied. However, the rate constants decrease with increasing solvent acidity and plots of log $2k_t$ against H_0 yield surprisingly good straight lines (see Figure 1).

The decay rate constants in trifluoroacetic acid increase with increasing temperature (Table III and Figure 2). Some of this increase can probably be attributed to the change in solvent acidity since, at least in water, the protonating power of H_2SO_4 de-

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[7] W. C. Danen and R. C. Rickard, *J. Amer. Chem. Soc.*, **94**, 3254 (1972).

[8] R. W. Fessenden and P. Neta, *J. Phys. Chem.*, **76**, 2857 (1972).

[9] J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3228 (1973).

[10] T. Toda, E. Mori, H. Horiuchi, and K. Murayama, *Bull. Chem. Soc. Jap.*, **45**, 1802 (1972).

[11] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 54, 2721 (1932).

[12] For reviews on this function and its application, see L. P. Hammett, *Chem. Rev.*, **16**, 67 (1935); M. A. Paul and F. A. Long, *ibid.*, **57**, 1 (1957); R. J. Gillespie and T. E. Peel, *Advan. Phys. Org. Chem.*, **9**, 1 (1971).

[13] N. F. Hall and W. F. Spengeman, *J. Amer. Chem. Soc.*, **62**, 2487 (1940).

[14] H. H. Hyman and R. A. Garber, *ibid.*, **81**, 1847 (1959).

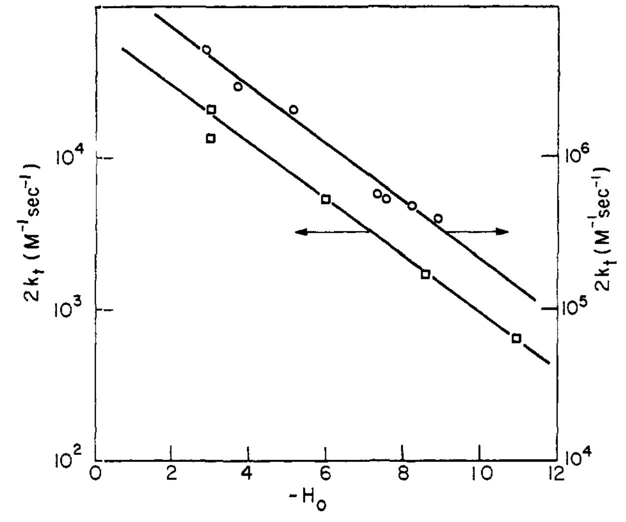

Figure 1. The rate constant for decay, $2k_t$, as a function of H_0 at 25°: (○) dimethylaminium radicals; (□) 2,2,6,6-tetramethylpiperidinium radicals.

Table II. Effect of Acidity and Viscosity on the Decay of Aminium Radicals at 25°

Reagent	$-H_0$	η, cP	$2k_t$, M^{-1} sec^{-1}
$Me_2NCl \cdot H_2SO_4$ in:			
1.24 M H_2SO_4–CH_3COOH	2.9[a]	3.3	5.3×10^6
2.3 M H_2SO_4–CH_3COOH	3.7[a]	7.5	3.0×10^6
5.5 M H_2SO_4–CH_3COOH	5.1[a]	>20	2.1×10^6
0.95 M H_2SO_4–CF_3COOH	7.3[a]	1.45	5.7×10^5
1.2 M H_2SO_4–CF_3COOH	7.5[a]	1.55	5.3×10^5
2.0 M H_2SO_4–CF_3COOH	8.2[a]	2.44	4.8×10^5
5.0 M H_2SO_4–CF_3COOH	8.9[a]	>4	4.0×10^5
2,2,6,6-Tetramethyl-N-chloropiperidine in:			
1.3 M H_2SO_4–CH_3COOH	3.02	3.3	2.1×10^4
CF_3COOH	3.03	0.8	1.35×10^4
0.19 M H_2SO_4–CF_3COOH	6.0	1.02	5.4×10^3
3.0 M H_2SO_4–CF_3COOH	8.6	3.35	1.7×10^3
H_2SO_4	11	22.5	6.6×10^2

[a] Corrected for the H_2SO_4 added as $Me_2NCl \cdot H_2SO_4$.

Table III. Effect of Temperature on Aminium Radical Decay Rate Constants in Trifluoroacetic Acid

$Me_2NCl \cdot H_2SO_4$		2,2,6,6-Tetramethyl-N-chloropiperidine	
Temp, °C	$2k_t \times 10^{-5}$, M^{-1} sec^{-1}	Temp, °C	$2k_t \times 10^{-3}$, M^{-1} sec^{-1}
−2	4.1	−2	4.4
12	4.7	13	8.7
25	5.7	25	13.5
41	10.7	41	34.5
60	16.6		

creases on raising the temperature.[15] However, this effect is likely to be rather small in view of the slight dependence of $2k_t$ on H_0 at 25°. The measured rate constants yield the following Arrhenius equations: for $Me_2NH\cdot^+$, $2k_t = 10^{9.5} \exp(-5000 \pm 1500 \text{ cal}/RT)$ M^{-1} sec^{-1}, and for 2,2,6,6-tetramethylpiperidinium, $2k_t = 10^{9.8} \exp(-7600 \pm 1000 \text{ cal}/RT)$ M^{-1} sec^{-1}.

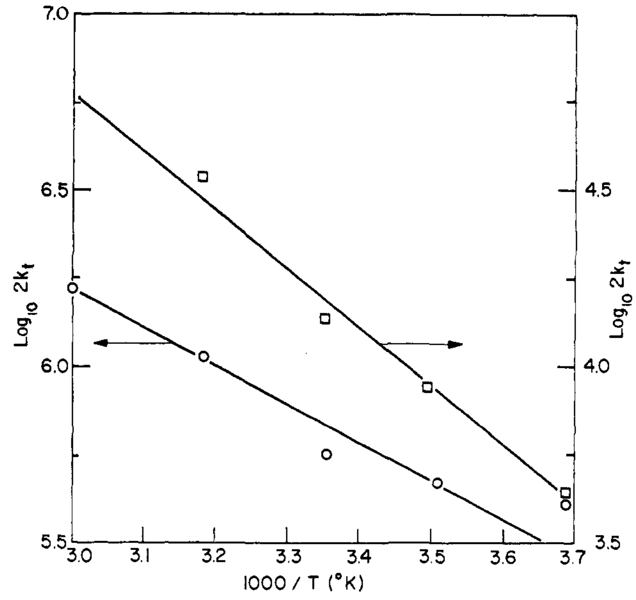

Figure 2. Log $2k_t$ in CF_3COOH as a function of $1/T$(°K): (○) dimethylaminium radicals; (□) 2,2,6,6-tetramethylpiperidinium radicals.

Comparison with Rotating Sector Results. The values of $2k_t$ for dimethylaminium estimated by Spanswick and Ingold[6] from their rotating sector experiments are in reasonable agreement with the present data. At 30° in 2 M H_2SO_4–CH_3COOH values of $2k_t = 1 \times 10^7$ and 5×10^7 M^{-1} sec^{-1} were estimated and in 4 M H_2SO_4–CH_3COOH $2k_t \simeq 7 \times 10^6$ and 5×10^7 M^{-1} sec^{-1}. In both cases, the lower value was calculated on the assumption that the efficiency of chain initiation upon photolysis of α,α'-azobiscyclohexylnitrile (ACHN) was inversely proportional to the square root of the solvent viscosity[16] while the upper value was calculated on the assumption of inverse proportionality to viscosity.[17] To judge from the present data (*e.g.*, $2k_t \sim 3 \times 10^6$ M^{-1} sec^{-1} at 25° in 2.3 M H_2SO_4–CH_3COOH) the former assumption would appear to be more nearly correct than the latter.

The present value of $2k_t$ can be combined with the rotating sector data to recalculate R_i and hence recalculate k_p, the overall rate constant for hydrogen abstraction from decanoic acid by dimethylaminium radicals at 30°. For 2 M H_2SO_4 the data yield $R_i = 5 \times 10^{-6}$ M sec^{-1} and $k_p = 240$ M^{-1} sec^{-1} and for 4 M H_2SO_4, $R_i = 1.8 \times 10^{-6}$ M sec^{-1} and $k_p = 320$ M^{-1} sec^{-1}. This unhindered aminium radical is therefore *about* as reactive as the methyl radical in hydrogen abstractions.[18] It is much more reactive

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(15) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, **91**, 6654 (1969).

(16) See, *e.g.*, T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968); T. Koenig, *ibid.*, **91**, 2558 (1969).

(17) See, *e.g.*, O. Dobis, J. M. Pearson, and M. Szware, *ibid.*, **90**, 278 (1968); K. Chakravorty, J. M. Pearson, and M. Szware, *ibid.*, **90**, 283 (1968); A. P. Stefani, G. F. Thrower, and C. V. Jordan, *J. Phys. Chem.*, **73**, 1257 (1969); F. E. Herkes, J. Friedman, and P. D. Bartlett, *Int. J. Chem. Kinet.*, **1**, 193 (1969).

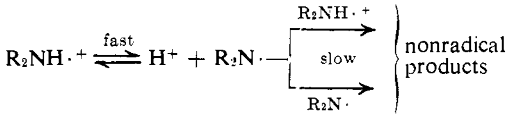
(18) A value for $k_p = 100$ M^{-1} sec^{-1} per secondary paraffinic hydrogen can be calculated for an abstraction by methyl at 30° in the gas phase.[19] In the reaction of dimethylchloramine with decanoic acid a 40% yield of $CH_3CHCl(CH_2)_7COOH$ was obtained.[6] The rate constant for dimethylaminium attack on one hydrogen of *this* methylene group is therefore $1/2(0.4 \times 280) = 56$ M^{-1}sec^{-1}.

(19) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. React. Kinet.*, **1**, 105 (1961).

than alkylperoxy[20] or 2,2,6,6-tetramethylpiperidyl[9] and much less reactive than *tert*-butoxy.[21]

Discussion

Although the present results do not allow the mechanism for the bimolecular self-reaction of aminium radicals to be unambiguously defined, they do seem to eliminate all of the simple and obvious possibilities. Thus, a prior deprotonation of one radical followed by some unspecified but rate controlling reaction with a second aminium (or amino) radical can be ruled out because the concentration of free amino radical present in these highly acidic media would be far too low to account for the observed decay rates.



$$\mathrm{R_2NH\cdot^+} \overset{\text{fast}}{\rightleftharpoons} \mathrm{H^+ + R_2N\cdot} - \left[\begin{array}{c}\xrightarrow{\mathrm{R_2NH\cdot^+}}\\ \text{slow}\\ \xrightarrow[\mathrm{R_2N\cdot}]{}\end{array}\right\}\text{nonradical products}$$

That is, the pK for the dissociation of dimethylaminium is 6.5–7.5.[8] Even if the *effective* pK were much lower in our solvents[22] than in water the values of $2k_t$ do not change sufficiently over the range of acidity studied for this mechanism to apply. That is, as the H_0 value of the solvent changes from -3 to -8 the proton donating power of the solvent increases 10^5-fold[23] but the decay rate constants for both radicals decrease by only a factor of 10. This suggests that the decrease in $2k_t$ with increasing acidity is merely due to a decrease in the activity coefficients of the aminium radicals.

Mechanistic possibilities for dimethylaminiums include, in principle, combination

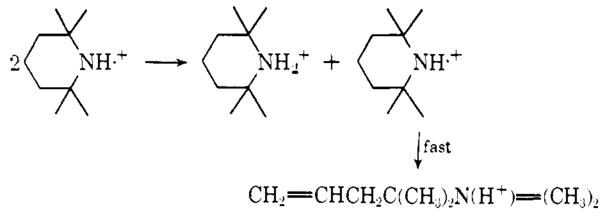
$$2\mathrm{Me_2NH\cdot^+} \longrightarrow [\mathrm{Me_2NNMe_2} + 2\mathrm{H}]^{2+}$$

and disproportionation with transfer of a β hydrogen.

$$2\mathrm{Me_2NH\cdot^+} \longrightarrow \mathrm{Me_2NH_2^+} + \mathrm{CH_2{=}NHMe^+}$$

The latter reaction is particularly attractive since it has, apparently, been identified by product studies on the *trans*-3-methyl-4-methylcarboxypiperidinium radical.[24] However, tetramethylpiperidinium could not undergo either reaction since even the *neutral* radical does not combine[9] and this radical has no β hydrogen. The possibility that these two aminium radicals react by different routes cannot, of course, be ruled out. However, even if dimethylaminiums react by one of the above routes this still leaves the problem of tetramethylpiperidinium. One solution to this problem is that the tetramethylpiperidinium radicals interact by a head-to-tail process,[25] so that a hydrogen atom is transferred with the positive charges separated as far as possible from one another. The biradical formed in this step would probably undergo β-scission much more rapidly than it would attack the chloramine and so two aminium radicals would be destroyed.

Yet another mechanism that would seem to fit our results involves the transfer of the aminium hydrogen atom



$$2\mathrm{R_2NH\cdot^+} \longrightarrow \mathrm{R_2NH_2^+} + \mathrm{R_2N^+}$$

This reaction is not written as a reversible process for two reasons. In the first place, raising the temperature rapidly during the course of a slow decay did not produce any increase in the radical concentraton.[26] Secondly, the addition of tetramethylpiperidine does not appear to reduce the $2k_t$ value for tetramethylpiperidinium in trifluoroacetic acid (see Table IV). The pre-exponential factors in the Arrhenius equations (*i.e.*, $10^{9.5}$ and $10^{9.8}$ M^{-1} sec^{-1}) are in the general range found for simple radical–radical reactions in solution provided the radicals and the solvent do not interact strongly, that is, provided solvent reorganization is not involved to any large extent in the transition state. In this hydrogen transfer reaction the degree of solvent reorganization in the transition state should be small because the reagents and the products are two monopositive ions. The alternative electron transfer process

Table IV. Effect of Tetramethylpiperidine on the $2k_t$ Values for Tetramethylpiperidinium in Trifluoroacetic Acid at 25°

Concn of chloramine, *M*	Concn of amine, *M*	$2k_t \times 10^{-4}$, M^{-1} sec^{-1}
0.5	0	1.35
0.5	0.5	1.0
0.5	1	2.6
0.5	1.5	1.9

$$2\mathrm{R_2NH\cdot^+} \longrightarrow \mathrm{R_2NH} + \mathrm{R_2NH^{2+}}$$

seems less probable since two monopositive ions are converted to a dipositive ion and the more localized charge will increase solvent orientation. The pre-exponential factor for this reaction would be expected to be $<10^9$ M^{-1} sec^{-1} (unless solvent relaxation around the electron acceptor fortuitously compensated for solvent striction around the donor).

The suggested formation of a nitrenium ion, $\mathrm{R_2\ddot{N}^+}$, from two aminium radicals may be surprising but we think it is not wholly unreasonable. Nitrenium ions are analogous to carbonium ions, $\mathrm{R_3C^+}$, except that they are more reactive and unstable because of the larger electronegativity of nitrogen and therefore

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(20) J. A. Howard, *Advan. Free-Radical Chem.*, 4, 49 (1971); S. Korcek, J. H. B. Chenier, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **50**, 2285 (1972).

(21) K. U. Ingold in "Free Radicals," J. K. Kochi, Ed., Wiley, New York, N. Y., 1973.

(22) In acetic acid 2,2,6,6-tetramethyl-*N*-chloropiperidine gave on irradiation a 12 line epr spectrum: $a_N = 19.00$ G; $a_H(3\ H) = 3.00$ G; $g = 2.0050$. This radical could not be identified. It decayed with second-order kinetics, $2k_t = 6.6 \times 10^6$ M^{-1} sec^{-1} at room temperature. In neutral solvents photolysis yielded the amino radical.[10] In neat chloramine this decayed with first-order kinetics, $k = 0.5$ sec^{-1} (*cf.* ref 9).

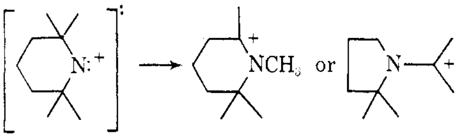
(23) Strictly speaking, this increase in proton donating power refers only to the bases used to determine the H_0 scale. However, there is no reason to suppose that amino radicals will have properties very different from these bases.

(24) M. Uskokovic, C. Reese, H. L. Lee, G. Grethe, and J. Gutzwiller, *J. Amer. Chem. Soc.*, **93**, 5904 (1971).

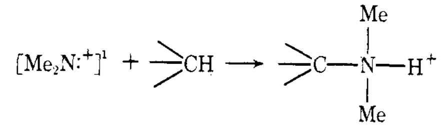
(25) Suggested to us by Professor F. Minisci.

(26) Compare with iminoxy radicals: J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7040 (1972).

its greater reluctance to accommodate a positive charge. Nitrenium ions are firmly established as intermediates in many chemical reactions.[27] The thermochemistry of the proposed reaction is uncertain as is the subsequent fate of the nitrenium ion. If aminiums react predominantly as singlet pairs the nitrenium ion will be formed in its singlet state. This is of higher energy than the ground state which is a triplet.[27,28] In principle, the singlet nitrenium ion may (i) rearrange, *e.g.*



(ii) insert into a convenient bond, *e.g.*



$$[\mathrm{Me_2N{:}^+}]^1 + {>}\mathrm{CH} \longrightarrow {>}\mathrm{C}{-}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{N}}}{-}\mathrm{H}^+$$

or (iii) interconvert to the triplet ground state. If the aminiums react as triplet pairs the nitrenium ion will be formed directly in this state and the reaction would probably not be chain terminating. That is, triplet nitrenes behave as biradicals[27,28] like triplet carbenes and so they would probably react with a suitable hydrogen donor to regenerate an aminium radical, *e.g.*

$$[\mathrm{Me_2N{:}^+}]^3 + \mathrm{R'H} \longrightarrow \mathrm{Me_2NH\cdot^+} + \mathrm{R'\cdot}$$

Gassman[27,29] and others[30] have undertaken extensive studies of the rearrrangement products formed from singlet bi- and tricyclic nitrenium ions and of the change in products that occurs when the singlet ion is converted to the triplet state before it can rearrange. Studies of the same kind on the products formed in the bimolecular self-reaction of structurally similar aminium radicals should reveal whether or not nitrenium ions are actually produced in this reaction.

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(27) For a detailed review of nitrenium ion chemistry, see P. G. Gassman, *Accounts Chem. Res.*, 3, 26 (1970).

(28) S. T. Lee and K. Morokuma, *J. Amer. Chem. Soc.*, **93**, 6863 (1971).

(29) P. G. Gassman and G. D. Hartman, *J. Chem. Soc., Chem. Commun.*, 853 (1972); *J. Amer. Chem. Soc.*, **95**, 449 (1973).

(30) V. Rautenstrauch, *Chem. Commun.*, 1122 (1969); D. C. Horwell and C. W. Rees, *ibid.*, 1428 (1969); P. Kovacic, J.-H. Liu, P. D. Roskos, and E. M. Levi, *ibid.*, 1034 (1970); *J. Amer. Chem. Soc.*, **93**, 5801 (1971); J.-M. Biehler and J.-P. Fleury, *Tetrahedron*, **27**, 3171 (1971).

Protonated Nitroxide Radicals[1]

V. Malatesta[2] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada.

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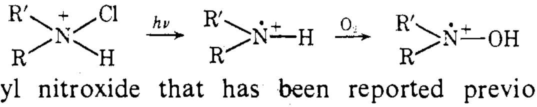
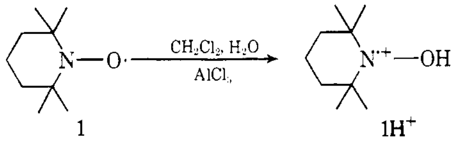
Abstract: In contrast to earlier reports, it is shown that dialkyl nitroxides are stable in strong acid solutions at room temperature. The nitroxides yield epr spectra indicating that they are protonated in solutions such as 100% H_2SO_4 which have Hammett acidity function values, H_0, more negative than *ca.* −7.5. In solutions having H_0 more positive than *ca.* −3.5 the unprotonated nitroxide epr spectrum is obtained. Between these two acidities no epr signal is observed because of line broadening resulting from rapid proton exchange. The pK_a for dialkyl nitroxides is −5.5 ± 1. It is concluded from the ^{14}N hyperfine coupling constants that the geometry of the nitrogen atom in a particular protonated nitroxide is very similar to that in the same unprotonated radical despite the fact that the absolute geometry for different dialkyl nitroxides varies substantially. The value of the proton hyperfine coupling constant decreases as the angle that the NO bond makes with the CNC plane increases.

While engaged in a kinetic study of aminium radicals by epr spectroscopy,[3] we observed that in the presence of oxygen spectra attributable to protonated nitroxide radicals were obtained as well as the desired aminium radicals. The only protonated dialkyl nitroxide that has been reported previously was that derived from 2,2,6,6-tetramethylpiperidine *N*-oxyl (**1**) by treating wet methylene chloride solutions of the radical with Lewis acids such as aluminum chloride.[4]



$$\mathrm{{}^{R'}_{R}{>}\overset{+}{N}{<}^{Cl}_{H}} \xrightarrow{h\nu} \mathrm{{}^{R'}_{R}{>}\dot{N}^{+}{-}H} \xrightarrow{O_2} \mathrm{{}^{R'}_{R}{>}\dot{N}^{+}{-}OH}$$



1 1H+

In contrast to the earlier report,[4] we find that the paramagnetic center of **1** is not completely destroyed by concentrated sulfuric acid at room temperature, nor is **1** destroyed by trifluoroacetic acid. In this paper we report some interesting observations on **1H**$^+$ and on two new radicals of this type, one derived from di-*tert*-butyl nitroxide (**2**)[5] and the other from 9-azabicyclo[3.3.1]nonane *N*-oxyl (**3**).

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(2) National Research Council of Canada Postdoctorate Fellow, 1972–1973.

(3) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6400 (1973).

(4) B. M. Hoffman and T. B. Eames, *ibid.*, **91**, 2169 (1969).

(5) This radical has also been reported to be unstable in acid: W. Brackman and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **85**, 221 (1966).