

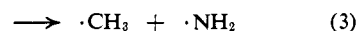
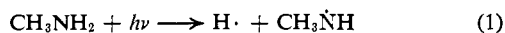
Photochemical Formation of Free Radicals from Aliphatic Amines as Studied by Electron Spin Resonance¹

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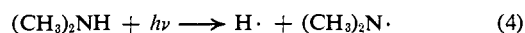
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Abstract: Electron spin resonance studies of ultraviolet-irradiated CH_3NH_2 , CD_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_2\text{ND}$, $(\text{CD}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$ have been made at 77°K. The primary processes established are $\text{CH}_3\text{NH}_2 + h\nu \rightarrow \text{H}\cdot + \text{CH}_3\dot{\text{N}}\text{H}_2$, $(\text{CH}_3)_2\text{NH} + h\nu \rightarrow \text{H}\cdot + (\text{CH}_3)_2\dot{\text{N}}\cdot$, and $(\text{CH}_3)_3\text{N} + h\nu \rightarrow \cdot\text{CH}_3 + (\text{CH}_3)_2\dot{\text{N}}\cdot$. Studies of solutions of H_2O_2 in CH_3NH_2 and in CD_3NH_2 irradiated at 77°K were also made and the secondary reaction established is $\cdot\text{OH} + \text{CH}_3\text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_3\dot{\text{N}}\text{H}_2$.

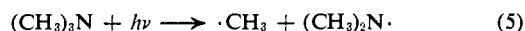
Studies of the photochemistry of aliphatic amines have indicated that there are several primary processes yielding free radicals. For methylamine, Michael and Noyes² have obtained evidence for three primary processes yielding free radicals.



For dimethylamine, Bamford³ proposed



For trimethylamine, the primary process proposed^{3,4} is



For methylamine it has not been established whether secondary radical reaction with the amine results in abstraction of hydrogen atom bonded to nitrogen or of hydrogen bonded to carbon.^{2,5,6} A principal objective of this work was to obtain electron spin resonance evidence for the primary processes in methylamines and for secondary processes in methylamine.

Experimental Section

Materials. Except where noted, compounds were commercial products used without purification. An especially pure sample of CH_3NH_2 was synthesized by the Gabriel method.⁷ CD_3NH_2 was prepared by generation of the gas from $\text{CD}_3\text{NH}_2\cdot\text{HCl}$ in concentrated KOH solution, the last traces of water being removed by using Linde 4A molecular sieves. $(\text{CH}_3)_2\text{ND}$ was prepared by exchanging $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$ with D_2O . After removing most of the water by distillation, the free amine was generated from CaO, the last traces of water being removed by molecular sieves.

Irradiations and Spectrometer. Samples for irradiation, spectrometer system, and observations were essentially as described previously.^{8,9} Quartz esr sample tubes 4 mm were used. Volatile compounds were collected by low-temperature condensation after

several bulb-to-bulb distillations. Less volatile compounds were introduced as liquids, degassed by several freeze-pump-thaw cycles, and sealed while frozen with liquid nitrogen. Irradiations and observations were carried out either at 77° by keeping the sample tube in a Varian liquid nitrogen quartz dewar insert, or at higher temperatures by keeping the tube in a Varian variable-temperature quartz dewar insert.

Three light sources were used: a low-pressure mercury resonance arc housed in Vycor from which the transmitted light was chiefly 2537 Å as Vycor is opaque to 1849 Å light; a similar arc except housed in quartz to allow 1849 Å light to be transmitted; and a high-pressure mercury arc housed in quartz.

The spectrometer was a Varian 4501 X-band esr spectrometer with 100-kc field modulation. Since our earlier work, the spectrometer has been modified by the addition of a Varian Fieldial for scanning the magnetic field. The scan was checked by using DPPH and, using published values for the hyperfine splitting constants, was found to be accurate within 2%. The constants reported are accurate within ± 1.5 gauss.

Results and Interpretation

The amines studied are essentially transparent above 2500 Å, and irradiations of the pure amines were, therefore, carried out with the resonance arc housed in quartz resulting in absorption of 1849 Å radiation. Mixtures with hydrogen peroxide were irradiated with the resonance arc housed in Vycor or with the high-pressure lamp and Pyrex filter so that absorption of light was limited to hydrogen peroxide.

Spectra obtained from the ultraviolet irradiation of CH_3NH_2 and CD_3NH_2 at 77°K are shown in Figure 1. For CH_3NH_2 , the spectrum consists of seven lines, approximately equally spaced with an average separation of 32 gauss. This spectrum may be attributed to $\text{CH}_3\dot{\text{N}}\text{H}_2$ radical resulting from primary process 1. Using equal coupling constants for a_{NH}^{H} , a_{CH}^{H} , and a^{N} of 32 gauss, the theoretical spectrum is seven lines with intensity ratios 1:5:11:14:11:5:1. The corresponding radical from CD_3NH_2 , $\text{CD}_3\dot{\text{N}}\text{H}_2$, should be a quartet (1:2:2:1) with a 32-gauss separation, resulting from coupling with N and H, split into septets (1:3:6:7:6:3:1) with a 4.9-gauss separation resulting from coupling with three D atoms. The theoretical spectrum should, therefore, contain 28 lines with a 4.9-gauss separation except that the end lines of each septet are separated by 2.6 gauss. Although the poor resolution of the spectrum obtained precludes a rigorous analysis of the spectrum, the general features conform to the theoretical prediction. The over-all spacing is 132 gauss, giving an average separation for 28 lines of 4.9 gauss, and, where sufficient resolution is avail-

(1) This investigation was supported by Public Health Service Research Grant No. CA-05528 from the National Cancer Institute.

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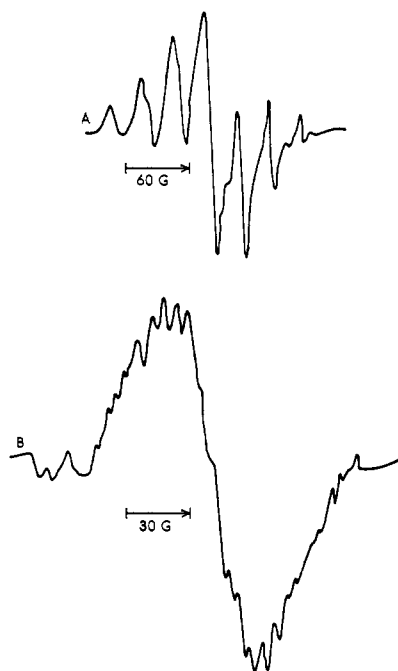


Figure 1. ESR spectra of methylamine irradiated at 1849 Å and 77°K (spectra recorded at 77°K): (A) CH_3NH_2 , (B) CD_3NH_2 .

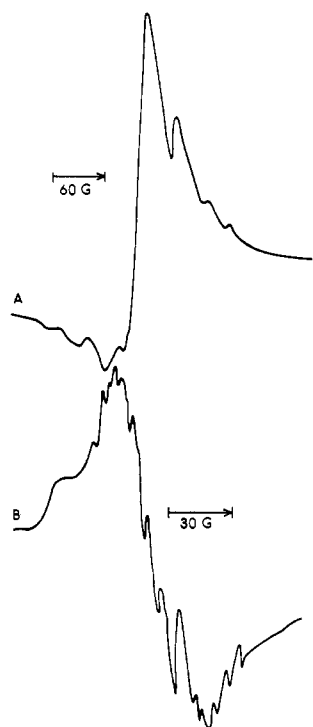


Figure 2. ESR spectra of a solution of hydrogen peroxide in methylamine irradiated at $\lambda > 2800$ Å and 77°K (spectra recorded at 77°K): (A) CH_3NH_2 , (B) CD_3NH_2 .

able, the peak-to-peak separations have about the same value of 4.9 gauss.

The reactions of hydroxyl radicals, derived from the photodecomposition of hydrogen peroxide, with CH_3NH_2 and CD_3NH_2 in the frozen state were studied by methods we have described previously.^{8,9} Aqueous solutions 1 M amine and 0.01 M H_2O_2 were irradiated at 2537 Å and 77°K at pH ~ 1 and ~ 12 . No evidence for reaction was obtained in the acid system. The

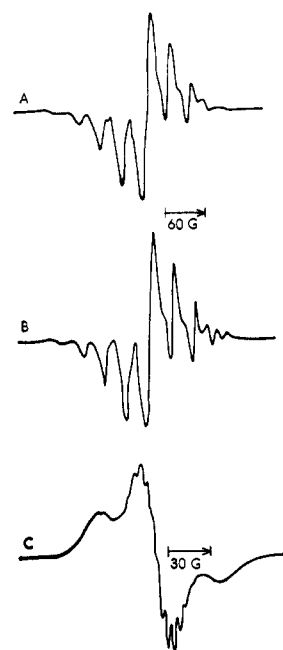


Figure 3. ESR spectra of dimethylamine irradiated at 1849 Å and 77°K (spectra recorded at 77°K.): (A) $(\text{CH}_3)_2\text{NH}$, (B) $(\text{CH}_3)_2\text{ND}$, (C) $(\text{CD}_3)_2\text{NH}$.

spectra obtained in the base systems are shown in Figure 2. Both spectra may be attributed to abstraction of a hydrogen atom linked to nitrogen to yield the same radicals as were obtained on direct irradiation of the amines. In Figure 2A, seven lines are clearly present although the outermost two lines are weak. The average spacing is, as before, 32 gauss. Together with the similarity between Figure 2B and Figure 1B, the evidence for the same radicals being formed is satisfactory. From these results it may be concluded that the reaction is



and that abstraction does not occur from the methylammonium ion, the acid system species.

Spectra obtained from the ultraviolet irradiation of $(\text{CH}_3)_2\text{NH}$, $(\text{CD}_3)_2\text{NH}$, and $(\text{CH}_3)_2\text{ND}$ are shown in Figure 3. The close correspondence between the spectra of irradiated $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_2\text{ND}$ indicates that the same radical is formed, which must be $(\text{CH}_3)_2\dot{\text{N}}$ corresponding to primary process 4. Using the same coupling constants as for methylamine, the theoretical spectrum should be nine lines separated by 32 gauss with intensity ratios 1:7:22:41:50:41:22:7:1. The agreement with this analysis is quite good although there is evidence of some other radical, unidentified, on the high-field side. The intensity ratios make it difficult to observe the outer lines, but under conditions of very high gain so that the center portion of the spectrum is off scale, these outer lines have been observed. The low-field half of the spectrum obtained under these conditions is shown in Figure 4, and the outer line is clearly evident. The spectrum of $(\text{CD}_3)_2\dot{\text{N}}$ should be a triplet (1:1:1) with a 32-gauss separation resulting from coupling with N, each member being split into 13 lines with a 4.9-gauss separation by coupling with six D nuclei to give a total of 39 lines with considerable overlap. The principal features discernible from the spectrum (Figure 3C), are the triplet with a 32-gauss

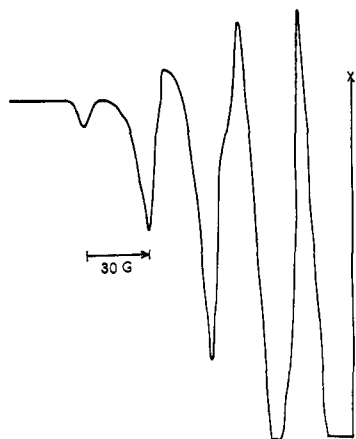


Figure 4. ESR spectrum of dimethylamine irradiated at 1849 Å and 77°K (spectrum recorded at 77°K); low-field half at high gain; X at center of spectrum.

separation between centers and, for the few resolvable lines, the D splitting of about 4.9 gauss.

The deviation of the $(\text{CD}_3)_2\text{N}\cdot$ triplet from a 1:1:1 intensity ratio may be explained by anisotropic broadening of the end lines. The increased line width of the $M_N = \pm 1$ members of the triplet compared with the central line for which $M_N = 0$ is due to the averaging of the anisotropic hyperfine interaction over the random orientations of the radical with respect to the external magnetic field. The end lines will reflect this anisotropy, whereas the central line will not. The width of the central line should, therefore, be about 59 gauss due to unresolved hyperfine interaction with six equivalent D nuclei. From the data of Weismann, Tuttle, and de Boer¹⁰ for peroxyamine disulfonate and from the data of Rowlands and Whiffen¹¹ for γ -irradiated sulfamic acid (which are in excellent agreement), anisotropic contributions due to nitrogen of 57 gauss for an isotropic coupling constant of 32 gauss may be calculated. The end lines will also be further broadened by 59 gauss due to hyperfine interaction with the six D nuclei, giving a total of 116 gauss for the width of the end lines. A spectrum constructed on the basis of a 32-gauss isotropic coupling, end lines of equal intensity and 116 gauss wide, a central line intensity equal to the end lines but 59 gauss wide, and Gaussian absorption line shape yields a pattern very similar to Figure 3C.

Spectra obtained from the irradiation of trimethylamine and from the irradiation of a 10% aqueous solution at a pH of 12 at 77°K are shown in Figure 5. When first obtained, the spectrum of irradiated $(\text{CH}_3)_3\text{N}$ shows the presence of $\cdot\text{CH}_3$ which decays leaving the spectrum shown. Irradiation in a water matrix gave a spectrum in which $\cdot\text{CH}_3$ is unmistakably present: a 1:3:3:1 quartet with a 24-gauss coupling constant. There is then good evidence for primary process 5 in which the radical formed is the same as that from dimethylamine. The close correspondence of these spectra (Figures 3B and 5A), particularly on the low-field side, is apparent. Irradiation of methylamine in

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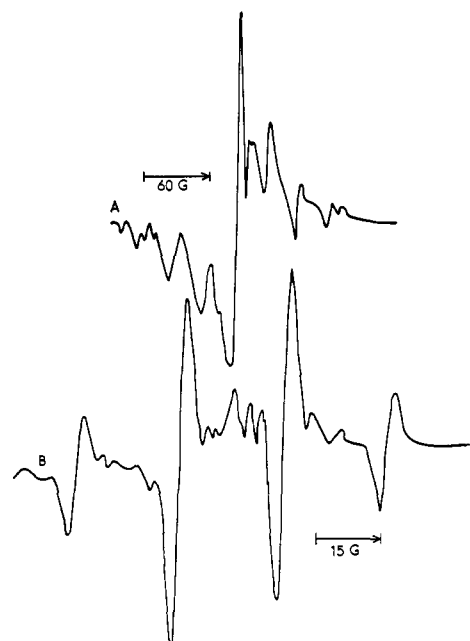


Figure 5. ESR spectra of trimethylamine irradiated at 1849 Å and 77°K (spectrum recorded at 77°K.): (A) pure $(\text{CH}_3)_3\text{N}$, (B) aqueous solution of $(\text{CH}_3)_3\text{N}$.

water matrices did not give evidence for methyl-radical formation.

Discussion

From the results, the conclusions that irradiation of methylamine and dimethylamine produces cleavage of an N-H bond and that irradiation of trimethylamine produces cleavage of an N-C bond are unambiguous. The coupling constants are in general accord with the theoretical relations of Barton and Fraenkel.¹² They give $Q_{\text{NH}^{\text{H}}} = 33.7$ gauss and $a_{\text{NH}^{\text{H}}} = \rho_{\text{N}} Q_{\text{NH}^{\text{H}}}$. Since ρ_{N} should be about unity in the CH_3NH radical, $a_{\text{NH}^{\text{H}}}$ should be about 33.7 gauss which is in good agreement with our experimental value of 32 gauss. Their further relationship, $a^{\text{N}} = 0.94 a_{\text{NH}^{\text{H}}}$, is in substantial agreement with our finding that a^{N} and $a_{\text{NH}^{\text{H}}}$ are about the same.

The conceivable alternative, formation of radicals with the unshared electron on C, cannot be reconciled with the experimental results. Additionally, the coupling constants for such a free radical would be quite different from those observed. In esr studies of γ -irradiated methylammonium alum crystals, Kohin and Nadeau¹³ report the formation of $\cdot\text{CH}_2\text{NH}_3^+$ radical with coupling constant $a^{\text{N}} = 4.1$, $a_{\text{NH}^{\text{H}}} = 19.2$, and $a_{\text{CH}^{\text{H}}} = 24.9$ gauss.

The observation that hydroxyl radicals abstract hydrogen atoms from CH_3NH_2 but not from CH_3NH_3^+ may be attributed to the electrophilic character of the hydroxyl radical,¹⁴ which would make abstraction from a positive center unfavorable.

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