The Photochemical Decomposition of Ethylamine as Studied by Means of the Electron Spin Resonance

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The photochemical decomposition of ethylamine at low temperatures was studied using ultra-violet light of various wavelengths (120—400 nm), and the photochemical reactions were examined. The initial stage of the decomposition is the release of the hydrogen atom by far ultra-violet light. As the decomposition proceeds, the effective wavelengths for the succeeding reactions become longer. The final products of the decomposition are the methyl radical and other diamagnetic species. The effects of the matrix and the counter ion on the reaction are also discussed.

In the field of radiation chemistry, alkylamines have been investigated intensively as hole-trap reagents.[1] Because most alkylamines have their optical absorption peaks in the far ultra-violet (FUV) region, the peaks being assigned as n-σ^* excitations, photochemical study by direct photolysis with FUV light is difficult. Wood *et al.* reported that, upon X-ray irradiation, many alkylamines decompose into π-radicals with the structure of $R\dot{C}HNH_2$.[2-4] This π-radical converts into the $RCH{=}\dot{N}$ radical after a short UV-irradiation.

Richerzhagen and Volman[5] irradiated ethylamine in an adamantane matrix with mercury resonance lines (184, 253 nm). Both X-ray and UV studies indicate complex reactions, however, and the mechanism of its decompositions is not clear. Also, the effective wavelength of the radiation has not been specified.

By selecting the light source well, the primary and succeeding processes of the decomposition can be observed selectively. The control of the matrix is also informative for the study of the reaction mechanism.

In this study, the photochemical decomposition of ethylamine was investigated by means of selective illumination. The primary process of the photochemical decomposition of ethylamine was the elimination of an α proton, much as in the case of X-ray irradiation. The primary process was affected strongly by its counter ion and the state of the matrix.

Experimental

Materials. The ethylamine used was obtained by the dehydration of 70% aqueous solution by potassium hydroxide. An especially purified sample was obtained by the neutralization and dehydration by KOH of an aqueous solution of ethylamine hydrochloride of a guaranteed grade.

Aqueous solutions of different concentrations were prepared by the volumetric dilution of pure ethylamine. The amino group was deuterated by the exchange reaction of heavy water with the ethylamine in the solution.

Irradiation. FUV light from a hydrogen (~120 nm) or a mercury (~180 nm) discharge lamp which was excited by microwave discharge was irradiated in the sample through a LiF window *in vacuo*. The apparatus for the irradiation has been reported elsewhere.[6] The sample was deposited on the outside of the quartz coldfinger cooled with liquid nitrogen and was thought to be amorphous.

UV light and near UV light from a 1-kW high-pressure mercury arc were irradiated using Toshiba UVD-1B and UVD-25 filters respectively. Samples were placed in quartz or spectrosil tubes, evacuated several times, and then irradiated at the temperature of liquid nitrogen. These samples, when cooled to 77°K, became polycrystalline.

Temperatures higher than −150°C were obtained by mixing isopentane and liquid nitrogen and by putting the irradiated samples into the mush.

Results and Discussion

FUV Irradiation. Amorphous pure ethylamine, which consists of FUV (120—180 nm) irradiated for 1 hr, gives the ESR spectrum shown in Fig. 1A.

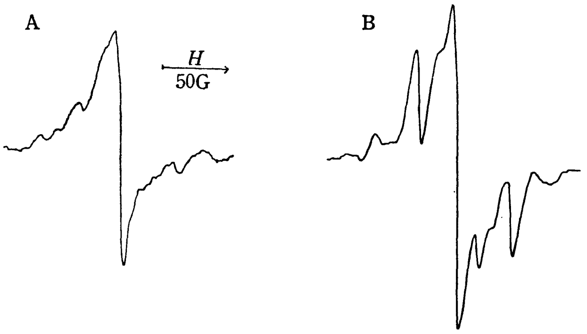

Fig. 1. A: ESR spectrum of FUV irradiated ethylamine at 77°K. B: UV (240 nm) re-irradiated to A.

This unresolved spectrum, which spreads over 70 gauss, is assigned to the $CH_3\dot{C}HNH_2$ radical. Wood and Lloyd[4] identified the $CH_3\dot{C}HNH_2$ radical by the X-ray irradiation of ethylamine in an adamantane matrix and obtained $a_{H\alpha}=15.3$, $a_{H\beta}=20.2$, $a_{HN}=4.9$, and $a_N=4.9$ gauss. The envelope of the spectrum is consistent with these assignments. The poor resolution of the spectrum may be attributed to the fact that the sample is amorphous and that other radicals may also exist. The poor resolution also prevented the detection of the deuterium substitution effect of amino hydrogen.

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UV Irradiation. By the subsequent irradiation of UV light (~240 nm) for 2 or 3 min, the FUV-irradiated sample gave another radical, the spectrum of which is shown in Fig. 1B. This spectrum shows, in addition to the spectrum of the CH_3CHNH_2 radical, a comparatively sharp doublet with a separation of 79 gauss. By further irradiation by UV light the methyl radical was also produced.

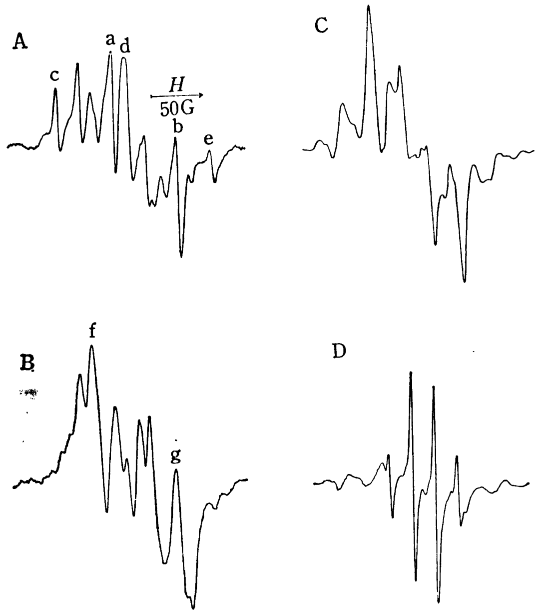

Fig. 2. ESR spectra of UV (240 nm) irradiated ethylamine at 77°K. A: 100% B: added trace of water C: 75 vol % aqueous solution D: 30 vol% aqueous solution.

Aqueous Solution of Ethylamine. The ESR spectra of several kinds of aqueous solutions of ethylamine observed after a 1 hr irradiation of UV light (240—400 nm) are shown in Fig. 2. In concentrated ethylamine solutions, the spectra show complex features (Fig. 2A), indicating the conversion of the primarily-produced radicals. However, the most striking feature of this spectrum is the sharp 64G doublet, marked a, b, and the 87G triplet of the methylene imino radical,[7,8] marked c, d, and e. Also another unidentified radical exists in this spectrum. By irradiating UV light, ethylamine containing a trace of water gives the spectrum shown in Fig. 2B. Instead of the 64G sharp doublet peak, the 79G sharp doublet peaks are revealed (f, g). By increasing the amount of water, a methyl radical was observed with the 79G doublet (Fig. 2C, 2D).

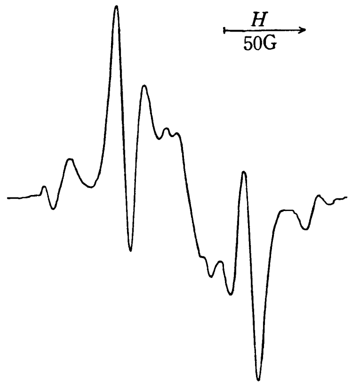

Fig. 3. ESR spectrum of UV (240 nm) irradiated ethylamine 75 vol % aqueous solution at 77°K which is observed at $-150°C$ ($CH_3CH{=}\dot{N}$ radical).

The spectra shown in Fig. 2C changed to Fig. 3 when the sample was warmed to $-150°C$. At this temperature, the methyl radical disappeared, and only the radical which shows the 79G doublet survived. This radical may be assigned to the ethylidenimino (CH_3-$CH{=}\dot{N}$) radical. Many investigators[2–5,9,10] have observed this radical in the solid and liquid phases, and it has an isotropic hydrogen splitting of 79—80 gauss. In this study, the radical shown in Fig. 3 shows no deuterium-substitution effect of amino hydrogen. This 79-gauss doublet agrees with the radical produced by the UV irradiation following the FUV irradiation of ethylamine.

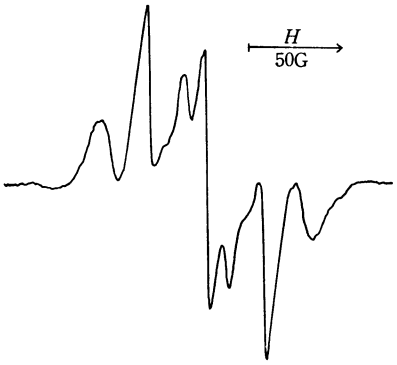

Fig. 4. ESR spectrum of UV (240 nm) irradiated ethylamine hydrochloride at 77°K ($\dot{C}H_2CH_2NH_3^+Cl^-$ radical).

Ethylamine Hydrochloride. Ethylamine hydrochloride gives the spectrum shown in Fig. 4 upon irradiation with UV light longer than 240 nm at 77°K. In the spectra of Fig. 4, the splitting of both side lines is 64G; this coincides with the a and b lines of Fig. 2A. This spectrum is very similar to the spectrum obtained for FUV- and UV-irradiated *n*-propanol.[6] In the case of *n*-propanol, this was assigned to the CH_2–CH_2–CH_2–OH radical, while the radical from irradiated ethylamine hydrochloride can be assigned to the CH_2–CH_2–NH_3^+–Cl^- radical. Taniguchi *et al.*[11] observed this radical in the flow system of an aqueous solution of ethylamine with hydrogen peroxide and $TiCl_3$, and they reported $a_{H\alpha}=26.6$, $a_{H\beta}=22.7$, and $a_N=5.1$ gauss. These coupling constants satisfactorily explain the spectrum of Fig. 4.

Mechanism of Decomposition. The radical species generated by the photolysis show absorption maxima of progressively longer wavelengths as the decomposition proceeds. Ethylamine has its optical absorption peak in the far ultraviolet region; CH_3CHNH_2, at 240—400 nm, and $CH_3CH{=}\dot{N}$, at wavelengths longer than

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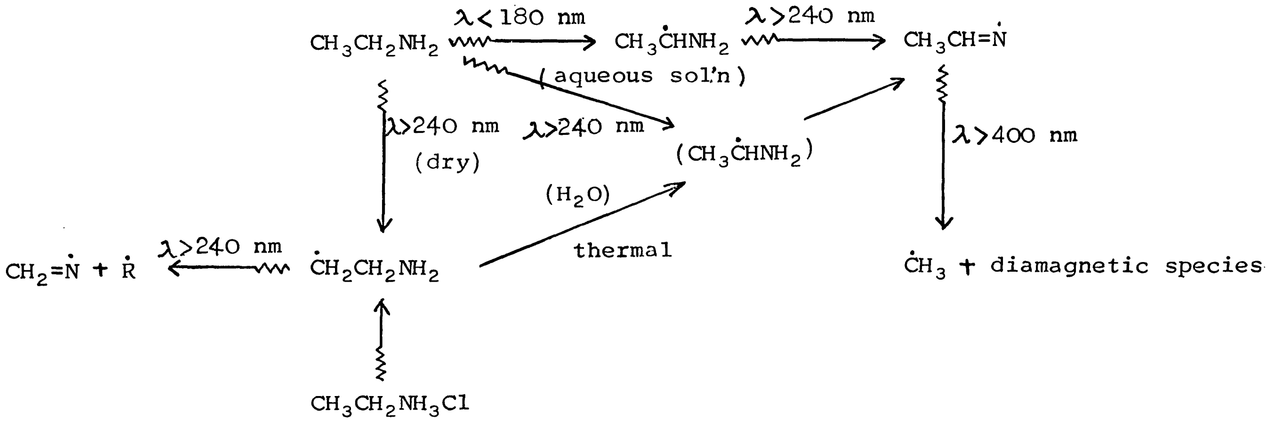

Fig. 5. Photochemical reaction scheme of ethylamine.

400 nm. The ethylidenimino radical decomposes into the methyl radical and other diamagnetic species upon irradiation with light longer than 400 nm. This fact indicates that the precursor of the methyl radical formed in the aqueous solution of less than a 75 vol % of ethylamine is the ethylidenimino radical.

Wood *et al.*[2] reported that several alkylamines gave no ESR signal upon UV irradiation unless the sample had previously been X-ray irradiated. Though alkylamines have their optical absorption peaks in the FUV region, they usually gave tailing absorptions in the UV region, and prolonged irradiation gives products with poor quantum yields. All the features of the photochemical reaction sequence are shown in Fig. 5.

The slightly different primary product for each sample may be attributed to the difference in the trapping states of the radicals. In addition, in the case of ethylamine hydrochloride the strong counter ion of chlorine may interfere with the secondary photochemical decompositions. The role of the water molecule seems to be mainly to affect the rigidity of the matrix. Also, it isolates the amine molecule and promotes the unimolecular decomposition. The dependence of the matrix state on the amount of water is exemplified by the result that the methyl radical in an ethylamine aqueous solution of less than 30% disappeared at about −100°C, while in a 75% solution it disappeared at −150°C.