An ESR Study of Methylamino Radicals Photoproduced on the Porous Vycor Glass Surface

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The photochemical decomposition of methylamines adsorbed on the surface of the porous Vycor glass was studied at 77 K by the ESR method, and the ESR spectra of the methylamino radicals, CH_3NH, CH_3ND, CD_3NH, CD_3ND, CH_2DNH, and CH_2DND, were observed as primary radicals from variously-deuterated methylamines upon irradiation with the light of a low-pressure mercury lamp. This result shows that the primary process is preferentially a rupture of the N–H or N–D bond of methylamine. These spectra were characterized by an apparent quenching of the *N*-hyperfine splitting resulting from large hyperfine anisotropy, and by nearly isotropic proton hyperfine splittings in both methyl and amino groups. The hyperfine splitting constants of the N, H, and D nuclei of each radical were determined, and consequently a D-substitution effect on the β-proton hf splitting in the methyl group was found. The characteristics of the ESR spectra were discussed in relation to the adsorbed state of the methylamino radical on the porous Vycor glass surface.

It has generally been accepted that the CH_3, NH_2, CH_3NH, CH_2NH_2, and H radicals are produced in the primary processes of the photochemical decomposition of methylamine in the gas and liquid phases.[1] Among these radicals, the CH_3, NH_2, and H radicals have been studied extensively, and their ESR spectra have been unambiguously defined in various matrices and adsorbed states.[2] However, those of the CH_3NH[3] and CH_2NH_2[4] radicals have only been obtained as poorly-resolved spectra in randomly-oriented states; especially, the anisotropic hyperfine interaction of the ^{14}N-nucleus in the methylamino radical has not yet been studied extensively.[5]

As has been reported previously, simple molecules adsorbed on the surface of the porous Vycor glass (PVG) are photolyzed efficiently with the light of a low-pressure mercury lamp at room temperature and 77 K into simple radicals, which exhibit well-resolved hf splittings.[6] For example, the NH_2 radical, which is the simplest *N*-centered radical, has been photoproduced from NH_3 molecules adsorbed on the PVG surface and stabilized on the surface at 77 K.[7] Under appropriate conditions, well-resolved anisotropic hf splittings of ^{14}N have been clearly observed; from them one can deduce the adsorbed state of the radicals on the surface. A similar effect is expected to be observed in the case of the CH_3NH radical, which may be formed by the photolysis of the methylamine adsorbed on the PVG surface. The primary object of this work was to identify radical species generated by the primary photolysis of methylamine. For this purpose, variously deuterated methylamines were utilized as adsorbates. As a result, the dominant radical species produced by the photolysis of methylamines was identified conclusively as of the CH_3NH type, and at the same time valuable information on the interaction between the radical and the surface of the PVG was obtained.

In this report, the ESR findings on the photochemical decomposition of methylamines in the adsorbed state and on the analysis of the ESR spectra of the radical species will be presented.

Experimental

Materials. Two commercial reagents, CH_3NH_2 in an aqueous solution (Wako Junyaku, GR) and $CD_3NH_2\cdot HCl$ (Merck, GR), were used without further purification. $CH_2DNH_2\cdot HCl$, a special product of Merck, was kindly offered by Professor Masamichi Tsuboi and Dr. Keietsu Tamagake in this faculty.

Gaseous methylamine was prepared by adding an aqueous solution of methylamine or methylamine hydrochloride to a concentrated potassium hydroxide solution, and dried by passing it through a column packed with potassium hydroxide tablets.

The deuteration of the NH_2 group in methylamine was carried out in the usual manner, D_2O and KOD being used in place of H_2O and KOH.

Procedures. PVG rods (Corning code No. 7930; 4 mm in diameter; 2 cm in length; surface area 75 m^2/sample) were used in all the experiments. The PVG rod was dipped in conc. HNO_3 for a day and then in distilled water for several days. After several repetitions of this procedure, the PVG rod was dried in air at 100 °C and then preheated in air at 500 °C. After the retreatment of the PVG rod with oxygen and evacuation for several hours at 550—600 °C in a quartz sample tube attached to a conventional high-vacuum system, a specified amount of methylamine was introduced into the sample tube at room temperature. The sample tube was then gradually cooled from room temperature to that of liquid nitrogen in order to secure the homogeneous adsorption of methylamine on the PVG surface; it was subsequently submitted to the irradiation and the ESR measurement.

The sample tube was irradiated at 77 K with the light of a low-pressure mercury lamp (UL2-2HQ, 200 W, Ushio Electric Inc.) without any filter, after which the sample tube was immediately transferred into a Dewar vessel inserted in the cavity.

The ESR spectra were recorded at 77 K with a JEOL P-10 spectrometer (X-band, 100 kHz field modulation) equipped with a Dewar insert and a temperature-controlling apparatus.

Results and Discussion

Photoproduced Radical Species. The ESR spectra

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of the photoproduced radicals did not practically alter with the change in the amount adsorbed in the range from the monolayer to less than 1/10 of the monolayer. Figures 1, 2, 3, 4, 5, and 6 show some typical ESR spectra of radicals trapped on the surface of PVG at 77 K by the photolysis of CH_3NH_2, CH_3ND_2, CD_3NH_2, CD_3ND_2, CH_2DNH_2, and CH_2DND_2 respectively. Since the free radicals produced from the variously-deuterated methylamines seem to have a common structure, it is appropriate to analyze the ESR spectrum of the simplest one.

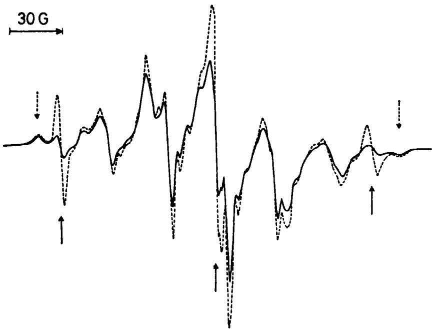

Fig. 1. ESR spectrum of CH_3NH radical on PVG.
Solid line: irradiated for 3 min.
Dotted line: irradiated for 10 min.
Arrows: ←——, CH_2=N radical; ←----, hump

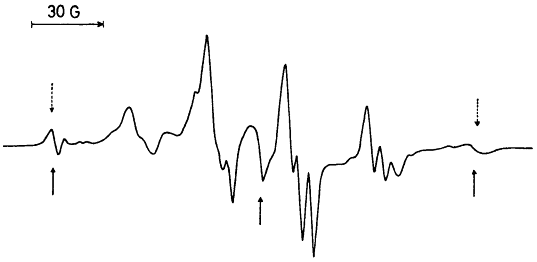

Fig. 2. ESR spectrum of CH_3ND radical on PVG.
Arrows: ←——, CH_2=N radical; ←----, hump

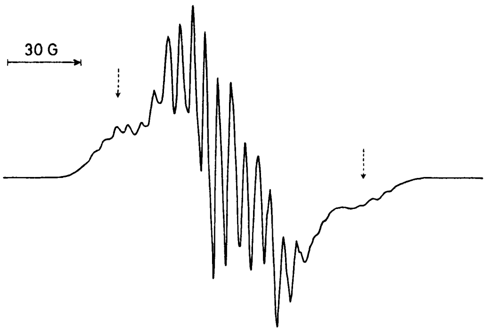

Fig. 3. ESR spectrum of CD_3NH radical on PVG.
Arrows: hump

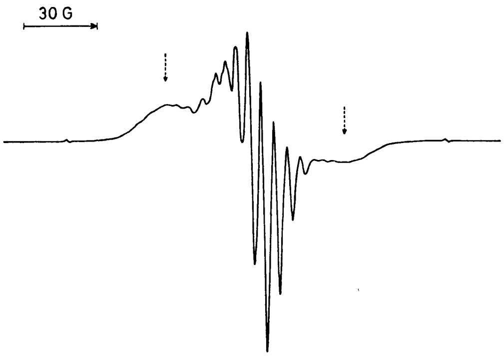

Fig. 4. ESR spectrum of CD_3ND radical on PVG.
Arrows: hump

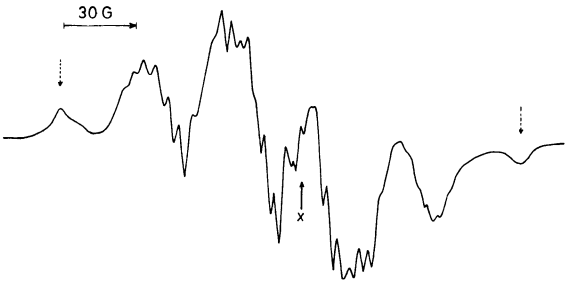

Fig. 5. ESR spectrum of CH_2DNH radical on PVG.
Arrows: ←——x, defect signal; ←----, hump

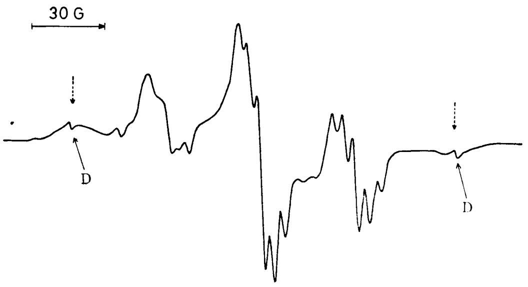

Fig. 6. ESR spectrum of CH_2DND radical on PVG.
Arrows: ←——D, D atom; ←----, hump

In Fig. 2, the spectrum consists of a quartet, whose component splits into a triplet in the higher magnetic field, and of two humps which are on the outer sides of the quartet. Furthermore, besides these lines, there is observed a triplet which is denoted with arrows in the figure. Since this triplet becomes more distinct than the other lines upon prolonged irradiation, it can be attributed to a different radical species from that of the main quartet and humps. A similar distinctive effect of prolonged irradiation on the spectral pattern was also observed in the case of CH_3NH_2, as is shown in Fig. 1.

As to the spectrum of the quartet with a triplet, it can easily be interpreted that the quartet with the splitting of 34 G and the approximate intensity ratio of 1 : 3 : 3 : 1 arises from the hf interaction with three equivalent proton nuclei and its triplet component with one deuteron nucleus, taking account of its approximate intensity ratio of 1 : 1 : 1 and its splitting of 4 G. Moreover, considering that this radical is generated by the photolysis of CH_3ND_2, it can unambiguously be assigned to the CH_3ND radical. The absence of the hf splitting due to the ^{14}N nucleus can reasonably be explained by the fact that the ^{14}N-hf splitting in the NH_2 radical is obscured by a large anisotropy, as has been reported recently by many workers.[8] This interpretation is supported by the existence of outer humps in the spectrum. The present assignment of the radical species is confirmed by mutual and comparative analyses of the spectra in Figs. 1—6, making use of the theoretical ratio of $a^H/a^D=6.5$. For example, the spectrum in Fig. 1 can be understood to consist of 5 main lines, which arise from the three protons in the methyl group and from one proton in the amino group of the CH_3NH radical; the latter is approximately equivalent with the former. The observed a^H/a^D ratio between the CH_3NH and CH_3ND radicals, 5.5, is close to the theoretical one.

Thus, all the spectra in Figs. 3, 4, 5, and 6 can be identified as those of CD_3NH, CD_3ND, CH_2DNH, and CH_2DND radicals respectively.

TABLE 1. HYPERFINE COUPLING PARAMETERS OF METHYLAMINO RADICALS (G)

Species	a^H_{CH}	a^D_{CD}	a^H_{NH}	a^D_{ND}	$a^N_\perp$	$a^N_\parallel$
CH_3NH	34		22		$\sim$0	$\sim$40
CH_3ND	34			4	$\sim$0	$\sim$40
CD_3NH		5	22		$\sim$0	$\sim$40
CD_3ND		5		5	$\sim$0	$\sim$40
CH_2DNH	37	4	22		$\sim$0	$\sim$40
CH_2DND	37	4		4	$\sim$0	$\sim$40

Observed $a^H/a^D=5\sim8$ (theor.; 6.5)
a^N; estimated from the position of the humps.

The ESR parameters of these radicals are listed in Table 1. The values of the anisotropic hf splitting constants of the ^{14}N nucleus are estimated approximately from the positions of the humps, assuming an axial symmetry in the ^{14}N hf tensors.

The extra triplet lines, growing on prolonged irradiation, may be assigned to the methyleneimino radical, $H_2C=N$,[9] judging from the extraordinary large hf splitting constant of $\sim$87 G. Together with these two radicals, the spectrum of the H or D atom was observed to be small in intensity, in accordance with the poor trapping efficiency for hydrogen atoms on the PVG surface.[11] The ESR spectra of other radicals, such as CH_3 and NH_2, were hardly observed under irradiation for several minutes by means of the light of a low-pressure mercury lamp.

From the above results, the primary process of the photochemical decomposition of methylamine on the surface of PVG can be described as:

$$CH_3NH_2 \xrightarrow{h\nu} CH_3NH + H.$$

The methyleneimino radical may secondarily be produced from the methylamino radical by means of the light of a low-pressure mercury lamp;

$$CH_3NH \xrightarrow{h\nu'} H_2C{=}N + H_2.$$

However, this process does not seem to be a very efficient one, since the signal intensity of this radical is much smaller than that of the methylamino radical, regardless of the prolonged irradiation.

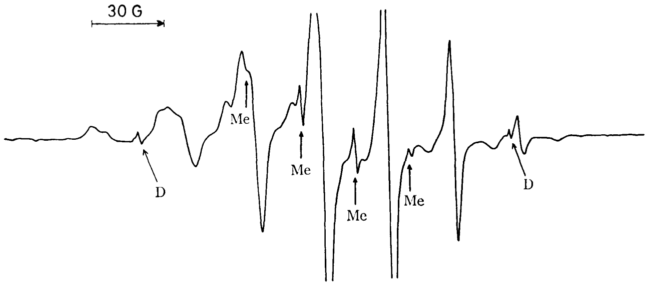

Fig. 7. ESR spectrum of $(CH_3)_2N$ radical on PVG.
Arrows: Me, CH_3 radical; D, D atom

For comparison, the photolysis of the dimethylamine-d_1 ($(CH_3)_2ND$) adsorbed on the surface of the PVG was carried out under the same conditions. The result is shown in Fig. 7. Although the methyl radical is slightly perceptible in the spectrum, as is indicated by the arrows in the figure, its signal intensity is very small compared with that of the $(CH_3)_2N$ radical. Therefore, the primary photochemical process is considered to be the rupture of the N–D bond, as in the case of monomethylamine, and the possibility of the C–N bond scission seems to be negligibly small. This was further supported by the finding that the $H_2C{=}N$ radical, which might secondarily be produced from the CH_3NH radical, was not observed, not even on prolonged irradiation.

It may be worthwhile to refer here to the important role of the PVG in the photodecomposition of methylamine. Since gaseous methylamine is essentially transparent above 240 nm, and since the PVG is opaque below 220 nm, it seems that the quantity of light quanta limited in a narrow range of wavelengths between 220 and 240 nm are not sufficient for the photodecomposition of methylamine as far as the direct absorption of photons by the methylamine molecule is concerned. Really, the efficiency of the photodecomposition of methylamine, as deduced from the signal intensities of the photoproduced radicals, is considerable. Therefore, the methylamino radicals are considered to be produced from methylamines not by the photochemical direct process, but by a photosensitized process resulting from some metal impurities in the PVG, analogously to our previous findings on the photosensitized decompositions of hydrocarbons and hydrogen molecules on the surface of the PVG coated with transition-metal oxides.[10,11]

Anisotropic ^{14}N-hf Splitting of the Methylamino Radical. As was described in the previous section, the hf interaction of ^{14}N is expected to have a large anisotropy. The angular-dependent hf values of $a_\perp{}^N\sim0$ and $a_\parallel{}^N\sim40$ G were estimated on due basis of the anisotropic spectral patterns of the radicals and the findings on the NH_2 radical.[8] Because of this anisotropy, the linewidth of the lines due to $m_I{}^N=\pm1$ is expected to be spread over about 40 G, so that the $m_I{}^N=\pm1$ lines are obscured. As a result, only the isotropic proton lines are observed as sharp lines, while the $m_I{}^N=\pm1$ lines are recognized as humps on both sides of the proton lines. This is the reason why the hf splitting due to ^{14}N is apparently quenched in all the spectra of the methylamino radicals observed in this study.

On the other hand, the linewidth of each line is too broad compared with the difference in the g tensors, $\Delta g=g_\perp-g_\parallel$, for the precise value of Δg to be decided, However, a linewidth alternation with a change in the proton quantum numbers is clearly observable in most spectra. For example, in the case of the CD_3ND radical (Fig. 4), the hf splittings due to the D nucleus are much more distinct in the higher magnetic field. This phenomenon in the linewidth shows the simultaneous existence of small anisotropies in both g and hf tensors.[12] Therefore, the magnitude of the anisotropies in g and hf tensors is considered to be as small as the order of the linewidth of the spectra.

Isotope Effect of D-Substitution in the Methyl Group on the β-Proton Hf Splitting. As is shown in Table 1, the substitution of a D atom in the methyl group of the methylamino radical causes an abnormal increase in the β-proton hfs constant over than the value expected from that of the undeuterated radical; that is, it increases from the value of $a^{H}_{CH_3}=34$ G in the CH_3NH (or CH_3ND) to that of $a^{H}_{CH_2D}=37$ G in the CH_2DNH (or CH_2DND) radical. This rather large isotope effect can not be explained by that observed in deuterated methyl radicals, which has been extensively investigated by many workers from both experimental and theoretical aspects.[13] The latter isotope effect has now been established to be attributable to the change in the s-character of the carbon 2pπ-orbital occupied by an unpaired electron due to the change in the out-of-plane vibration, and the magnitude of this effect has been shown to be quite small; moreover, the effect due to the D-substitution is in the negative direction. Therefore, it seems that the isotope effect in the β-position is different from that in the α-position. This may be quite natural considering that the origin of the hf splitting of the β-proton can be explained by the hypercojugation mechanism, while that of the α-proton can be explained by the spin-polarization mechanism.

As is well known, the hf splitting of the β-proton is given by a relation such as:

$$a_{\beta}^{H} = B + A\cos^2\theta$$

where B and A are constants, and θ, the dihedral angle between the 2pπ-orbital and the C–H bond in the methyl group. For a rapidly-rotating methyl group in the methylamino radical, neglecting B compared with the second term, the $\cos^2\theta$ in the second term is averaged to 1/2, thus leading to this equation: $a_{\beta}^{H}=1/2A$. As long as the isotropic free rotation of the methyl group is assumed, the ratio between the hfs constants of H and D in the methyl group of the CH_2DNH (or CH_2DND) radical should also coincide with the theoretical one. However, this is not the case. This rather large deviation may be explained by the following postulation;[14] the internal rotation of the methyl group resulting from asymmetric substitution with a deuterium atom is no longer isotropic, and an anisotropic averaging may occur over internal rotation, with a preferential orientation of the 2pπ-orbital coplanar with the C–H bond in the methyl group of the β-substituted methylamino radical.

The same isotope effect has recently been observed more distinctively in a complete set of deuterated ethyl radicals, which have been produced by the trapping of hydrogen atoms with ethylene molecules preadsorbed on the surface of the PVG coated with vanadium oxide, which acts as a photosensitizer for the dissociation of hydrogen molecules with the light of a wavelength longer than 350 nm.[11]

According to the above explanation, it is necessary also that $a^{D}_{CH_2D}$ be smaller than $a^{D}_{CD_3}$. Unfortunately, however, the experimental accuracy is not sufficient to ascertain this point because of the rather large linewidth of the adsorbed radicals.

Rotational State of the Methylamino Radical on the PVG Surface. As has been described above, the methylamino radicals trapped on the surface of the PVG have the following characteristics:

(1) Little anisotropy is observed in the methyl-proton hf splitting.

(2) The anisotropy in the nitrogen-proton hf is relatively larger than that of the methyl-proton, judging from the linewidth difference between the CH_3ND and CH_2DNH radicals.

(3) The anisotropy in the ^{14}N hf splitting is quite large, and the values of $a_{\parallel}^{N}\sim 40$ and $a_{\perp}^{N}\sim 0$ G were estimated.

From (1), the rotation of the methyl group around the axis of the C–N bond is inferred to be rapid enough, and the methyl group is judged to be free from interaction with the surface of the PVG. The (2) and (3) show that the NH group interacts strongly with the surface, and that it rotates approximately around the axis of the 2pπ-orbital of nitrogen. The rotation around the 2pπ-axis may be explained by the fact that the value of $a_{\parallel}^{N}\sim 40$ G for the methylamino radical is very close to that of $a_{\parallel}^{N}=\sim 38$ G for the NH_2 radical, which is the principal value for the direction of the 2pπ-orbital of the nitrogen of the NH_2 radical.[7,8]

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