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NH_2 Radicals Trapped on the Surface of Porous Vycor Glass at 77 K*

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The results of ESR studies of the amino radicals produced by the photolysis of ammonia adsorbed on the surface of porous Vycor glass at 77 K are described. The observed ESR signal patterns of the amino radicals were remarkably affected by the amount of ammonia on the surface. The isotropic and anisotropic spectra were analyzed by the use of isotopically-substituted amino radicals.

Although several ESR studies have been devoted to the formation of NH_2 radicals by the irradiation of ionizing radiation on ammonia in various matrices[1-3] and on solid surfaces,[4-6] there are few studies of the photolysis of ammonia on solid surfaces. In this report, the results of ESR studies of the amino radicals produced by the photolysis of ammonia adsorbed on the surface of porous Vycor glass (PVG) at 77 K will be presented, in connection with a previous study of methylamino radicals.[7]

Experimental

PVG rods (Corning code No. 7930; 4 mm in diameter; 2 cm in length; surface area of 75 m^2/sample) were used. After the pretreatment of the PVG rod with oxygen at 550—600 °C and evacuation for a few hours in a quartz sample tube attached to a conventional high-vacuum system, a specified amount of ammonia was introduced into the sample tube at room temperature. The sample tube was then gradually cooled to the temperature of liquid nitrogen and then submitted to irradiation and ESR measurements. Gaseous ammonia from a concentrated aqueous solution was dried by passing it through a column packed with potassium hydroxide tablets; it was subsequently purified by vacuum distillation. Gaseous $^{15}NH_3$ was prepared from a $(^{15}NH_4)_2SO_4$ (99.8 ^{15}N atomic %) solution by alkalifying with KOH. The ESR spectra were recorded at 77 K with a JEOL P-10 spectrometer. The irradiation of the sample was carried out with a low-pressure mercury lamp (UL2-2HQ, 200W, Ushio Electric Inc.) at 77 K without any filters.

Results and Discussion

The observed ESR signal patterns of the amino radicals were greatly affected by the preadsorbed amount of ammonia on the surface of PVG.

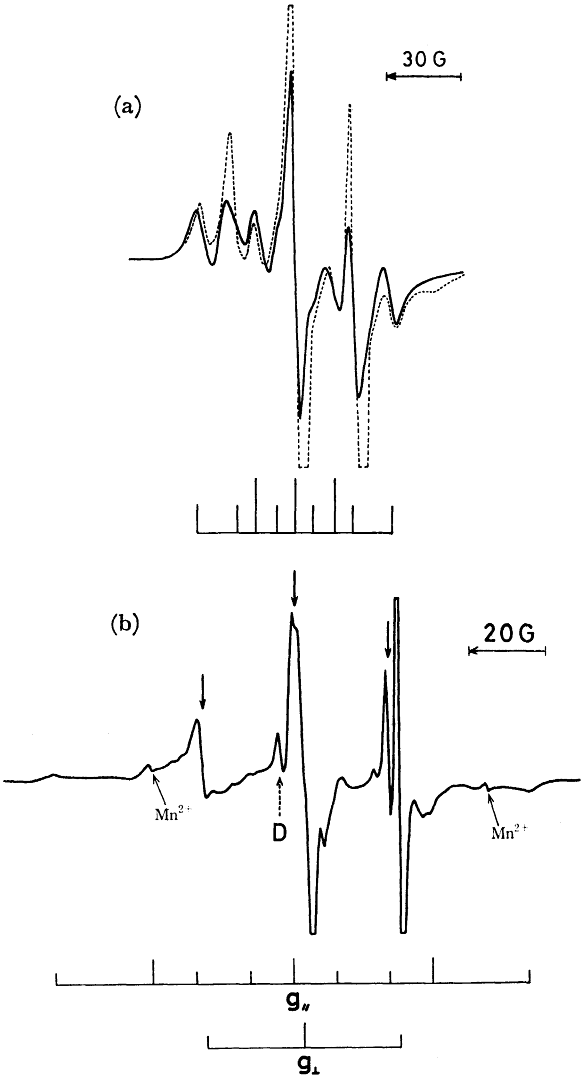

Fig. 1. ESR spectra of $^{14}NH_2$ radicals trapped on PVG surface at 77 K. (a): isotropic spectrum. solid line spectrum: irradiated for 5 min, dotted line spectrum: irradiated for 20 min. (b): anisotropic spectrum. Mn^{2+}: Mn^{2+} signal, D: defect signal, arrows: signal of R_3 radical.

Larger than the Monolayer Amount. An isotropic spectrum of apparent seven lines such as is shown in Fig. 1a was observed after irradiation with the full light of a low-pressure mercury lamp for 5 min at 77 K. A similar spectrum of the NH_2 radical produced by γ-irradiation on anhydrous ammonia at 77 K has been reported by Al-Naimy *et al.*[2] The spectrum can be assigned to the freely tumbling NH_2 radicals, free from any interaction with the surface. Further irradiation caused a selective growth of a particular triplet with an anisotropic nature, as can be seen from the dotted line spectrum in Fig. 1a. On slight warming, the isotropic spectrum decayed faster than the remaining triplet. Hereafter, the radicals with the isotropic and anisotropic natures will be denoted as A-type and B-type radicals respectively. The A-type

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spectrum of the ND_2 radical is shown in Fig. 2a. The ratio of the hf constants of the H and D nuclei in the NH_2 and ND_2 radicals, $A^H/A^D=6.5$, is exactly in agreement with the theoretical ratio, supporting the above assignment. The A-type spectrum of $^{15}NH_2$ is shown in Fig. 3a; in this case the linewidth is too broad for the hf constants of H and ^{15}N to be determined separately. However, the total spreading of the spectrum, 72 G, coincides well with the expected value of $(A^{15N}+2A^H)=(A^{14N}\times g^{15N}/g^{14N}+2A^H)=71$ G, where $A^H=25$ G, $A^{14N}=15$ G of $^{14}NH_2$, and $g^{15N}/g^{14N}=1.4$ were used. Thus, the hf constants of the A-type of $^{15}NH_2$ radical can reasonably be evaluated as is shown in Table 1.

Less than 1/10 of the Monolayer Amount. When the adsorbed amount was in the range $1>\theta>1/10$, a similar ESR spectrum of the triplet, such as is shown in Fig. 1a, was observed even after short irradiation.

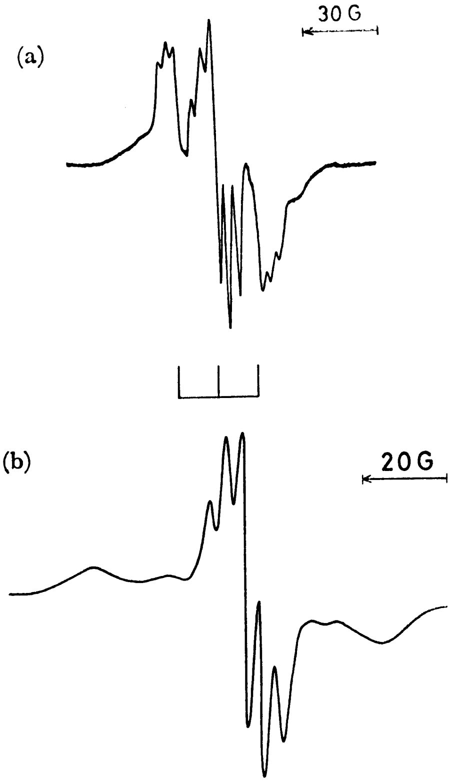

Fig. 2. ESR spectra of $^{14}ND_2$ radicals trapped on PVG surface at 77 K. (a): isotropic spectrum. (b): anisotropic spectrum.

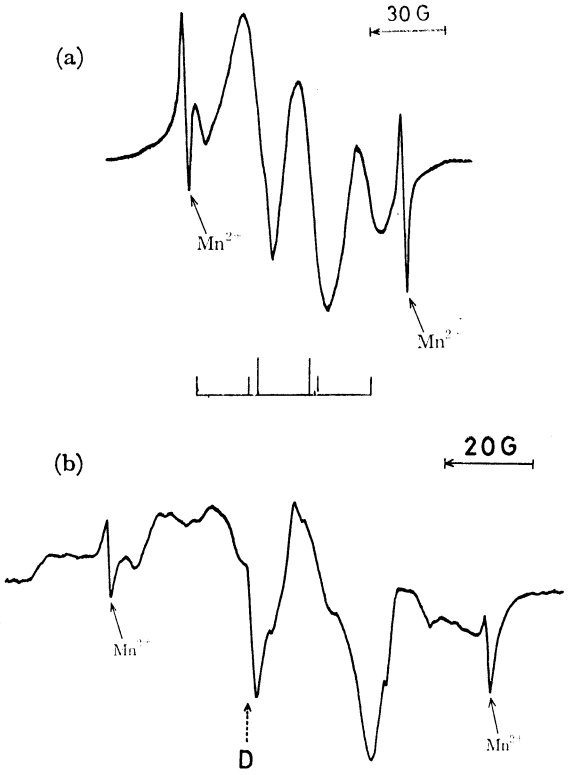

Fig. 3. ESR spectra of $^{15}NH_2$ radicals trapped on PVG surface at 77 K. (a): isotropic spectrum. (b): anisotropic spectrum. Mn^{2+}: Mn^{2+} signal, D: defect signal.

Table 1. ESR data for amino radicals in various matrices

Matrix	Radical	T/K	$A_{//}^{14N}$/G	$A_{\perp}^{14N}$/G	A_{iso}^{14N}/G	A^H/G	Ref.
Argon	NH_2	4.2			10.4	23.8	11
NH_3	NH_2	77			15.0	24.5	1
NH_3	NH_2	77			16.5	23.4	9
NH_3	NH_2	118			15.2	25.4	3
NH_3 on PVG	NH_2 (A-type)	77			15	25	This work
ND_3	ND_2	118			15.2	3.9 (D)	3
ND_3 on PVG	ND_2 (A-type)	77			15	~4 (D)	This work
NH_3	$^{15}NH_2$	77			21.3 (^{15}N)	25.4	3
NH_3 on PVG	$^{15}NH_2$ (A-type)	77			21 (^{15}N)$^{a)}$	25$^{a)}$	This work
NH_3 on PVG	NH_2 (B-type)	77	36	~0		25	This work
NH_3 on SiO_2	NH_2	77	37.5	3		24	4
NH_3 on MS	NH_2	77	35	3		26	5
NH_3 on SiO_2	NH_2	77	32	—		25	6
NH_3–H_2O	NH_2	77	41	0		24	9
NaN_3–H_2O	NH_2	77	39	3		24	12
ND_3 on PVG	ND_2 (B-type)	77	36	~0		~4 (D)	This work
NH_3 on PVG	$^{15}NH_2$ (B-type)	77	50 (^{15}N)$^{a)}$	5$^{a)}$		25$^{a)}$	This work

a) The values are evaluated from the total spreading of the spectra.

A further decrease in the adsorbed amount, $\theta<1/10$, resulted in the appearance of a well-resolved complicated spectrum, as is shown in Fig. 1b. The photolysis of ND_3 $(1>\theta>1/10)$ was also carried out to ascertain whether the extra triplet in Fig. 1a or 1b is caused by two protons or a single ^{14}N nucleus in the radical. Since the triplet was replaced by a quintet in the case of ND_3 photolysis, as is shown in Fig. 2b, and since the ratio of the hf constants between both radical species coincided with the expected value, the triplet is attributable to the proton hf splitting of the NH_2 radical.

In general, the ^{14}N hf splitting has an anisotropic nature in adsorbed states; this is the reason why the deuteron hf splitting on $m_I=\pm1$ lines of nitrogen is only partially resolved. Morton *et al.*[8] have reported a large anisotropy in the ^{15}N hf splitting of the $^{15}NH_2$ radical trapped in γ-irradiated $K^{15}NH_2SO_3$ single crystals: the principal values of the ^{14}N hf splitting calculated from their data by using the nuclear g-factor ratio are $A_{xx}^{14N}=38.3$, $A_{yy}^{14N}=1.4$, and $A_{zz}^{14N}=0.2$ G, where the x-axis is taken along the 2pπ orbital of the nitrogen atom. Assuming an axial symmetry of ^{14}N hf splitting and a nearly isotropic splitting for the proton in the NH_2 radical rotating about the unpaired spin orbital,[9] the hf constants of ^{14}N and H were determined to be as is shown in Table 1.

Although almost all the ESR lines in Fig. 1b can thus be assigned to the NH_2 radical of the B-type, there exist some other lines which are not due to this radical species, indicating the existence of other radical species. Recently, Brotikovskii *et al.*[4] have observed spectra due to the overlap of three different radical species in γ-irradiated NH_3–SiO_2 systems at 77 K; namely, the R_1, R_2, and R_3 radicals in their notation. Among these radicals, the R_1 radical obviously corresponds to the B-type radical in our case: the hf constants of the R_1 radical are $A_{/\!/}^{14N}=37.5$, $A_{\perp}^{14N}=3$, and $A^H=24$ G, values which almost coincide with those of our B-type radical. The three lines marked with arrows in Fig. 1b correspond to those of the R_3 radical, which can probably be assigned to another NH_2 radical species interacting more strongly with a different site from that of the R_1 or B-type radical species, resulting in an apparent quenching of the ^{14}N hf splitting as a result of a strong interaction with the surface. The spectrum corresponding to the R_2 radical, which has been tentatively assigned by Brotikovskii *et al.* to the S–NH radical (S denotes a surface site), was perceptible only at an initial stage of irradiation on a sample evacuated at higher temperatures; this is in accordance with their results, where the R_2 radical was the predominant species on the surface of SiO_2 preheated at 800 °C *in vacuo*.

When $^{15}NH_3$ was photolyzed under the same conditions as are shown in Fig. 1b, the ESR spectrum shown in Fig. 3b was observed. The total spreading of the $^{15}NH_2$ spectrum should be equal to $(A_{/\!/}^{15N}+2A^H)=(A_{/\!/}^{14N}\times g^{15N}/g^{14N}+2A^H)=100.5$ G, which is exactly in agreement with the observed total spreading of 100 G.

From the above results, it may be concluded that the primary radical of the photodecomposition of ammonia adsorbed on the surface of PVG with the light of a low-pressure mercury lamp is the NH_2 radical, and that the spectral pattern of the NH_2 radical depends remarkably on the amount of ammonia preadsorbed on the surface.

For comparison, the ESR data for NH_2 radicals trapped in various matrices are listed in Table 1, along with those for the photoproduced NH_2 radicals on the surface of PVG.

The isotropic ^{14}N and H hf constants of NH_2 trapped in anhydrous NH_3 and on PVG are nearly in accordance with each other, while the A_{iso}^{14N} of NH_2 trapped in an argon matrix is significantly smaller than the others. The latter change in the hf constants is a common phenomenon arising from the different radical environment. Rao and Symons[9] have discussed their observation of various values of A_{iso}^{14N} with changes in the medium. The change in A_{iso}^{14N} observed with the change of medium from argon to anhydrous NH_3 or NH_3 adsorbed on PVG may be due to a weak hydrogen-bonding interaction between the radical and host NH_3 molecules. However, this hydrogen bond is considered to be not strong enough to prevent the free tumbling of the radical, since the observed ESR signal pattern shows an isotropic nature even at 77 K. Nearly constant values of A_{iso}^{14N} both in anhydrous ammonia and on PVG indicate that the A-type NH_2 radical is trapped in a condensed phase of ammonia free from any interaction with the PVG surface. Accordingly, the A-type radical may be said to decay rapidly by means of the radical recombination due to the softening of the matrix on slight warming.

The values of $A_{/\!/}^{14N}$ scatter slightly depending on the radical environments, as is shown in Table 1. This may be partly due to an ambiguous estimation of the value from the positions of the outermost humps of the powder-pattern spectra, and partly to different interaction forces with the surfaces, as in the case of methyl radicals trapped on the PVG surfaces.[10] The radicals of the B-type with an axially symmetric hf tensor of ^{14}N, interacting strongly with the surface silanol group through the 2pπ orbital of the radical rather than the hydrogen bond, are immobilized on the surface and, consequently, are allowed to rotate only around the 2pπ orbital. Thus, the translational motion of the radical is so restricted to prevent the radical recombination that the B-type NH_2 radical was observed even at −20 °C in a thermal-decay experiment.

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