BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1144—1148 (1973)

# ESR Study of $\gamma$-Irradiated Ammonia-Silica Gel System

Siro Nagai

*Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, Mii, Neyagawa-shi, Osaka 572*

(Received September 22, 1972)

Ammonia-silica gel system was $\gamma$-irradiated at $-196$ °C. ESR spectrum observed from samples with low ammonia content showed a marked linewidth anomaly in the hf lines at $-196$ °C and changed with temperature reversibly. The free radical responsible for the spectrum was assigned to $NH_2$ radical which undergoes a preferential rotation about an axis perpendicular to the radical plane at low temperatures and a substantially free rotation above $-90$ °C.

In the previous papers[1-4] of our ESR studies on the $\gamma$-irradiated adsorbed systems, we reported the structures of free radicals produced at $-196$ °C and also the effects of temperature on the ESR spectra. The investigation of the temperature effects on the spectra gave us some informations concerning not only to the structural change but also to the thermal motion of adsorbed radicals. The change of the structure was observed in adsorbed methylbenzenes where monomer cations formed by $\gamma$-irradiation at $-196$ °C change to the corresponding dimer cations by raising the temperature.[2] Restricted motion of adsorbed radicals was suggested from the asymmetry and/or linewidth variations appeared in the spectra.[2-4] More detailed analysis as for the motion on silica gel, however, can be made when we can observe ESR spectra of adsorbed radicals containing some nucleus with a larger anisotropy in the hf interaction. In this viewpoint, $NH_2$ radical is suitable for such study because of the large anisotropy in the nitrogen splitting.[5]

## Experimental

$NH_3$ was obtained commercially from Takachiho Trading Co. Ltd. Deuterated ammonia $ND_3$ was synthesized from $Mg_3N_2$ and $D_2O$ in an evacuated system. $^{15}NH_3$ was synthesized from $(^{15}NH_4)_2SO_4$ ($^{15}N$ atom 90%) and NaOH. Silica gel was the same as that reported.[2] For deuteration of silica gel, the heat-treated gel was immersed in $D_2O$ at 100 °C for 2—3 hr and then degassed at 500 °C *in vacuo*. The other procedures employed in the present study were the same as those described in the previous paper.[2]

---

[1] S. Nagai, S. Ohnishi, and I. Nitta, *J. Phys. Chem.*, **73**, 2438 (1969).

[2] S. Nagai, S. Ohnishi, and I. Nitta, This Bulletin, **44**, 1230 (1971).

[3] S. Nagai, S. Ohnishi, and I. Nitta, *Chem. Phys. Lett.*, **13**, 379 (1972).

[4] S. Nagai, S. Ohnishi, and I. Nitta, This Bulletin, **45**, 1934 (1972).

[5] J. R. Morton and D. R. Smith, *Can. J. Chem.*, **44**, 1951 (1966).

## Results and Discussion

*ESR Spectra at Low Temperature.* ESR spectra of adsorbed ammonia after γ-irradiation at −196°C were dependent on the ammonia content. In the samples with the content larger than the monolayer value $2\times10^{-3}$ mol/g, the observed spectrum consists of poorly resolved nine lines and is similar to that of $NH_2$ radical in solid ammonia matrix.[6–8] When the ammonia content was below the monolayer coverage, the complex spectrum shown in Fig. 1a was observed predominantly. It consists of a dominant quintet with a central triplet splitted by 25 gauss and outermost broad signals, and several weak lines. The spectrum arises from single species in view of the thermal behavior to be discussed later. When the ammonia content became still lower, the spectrum showed additional weak signals other than the predominant one described above(see Fig. 1b). No change was observed in the overall feature of the spectrum when the adsorption amount was further reduced.

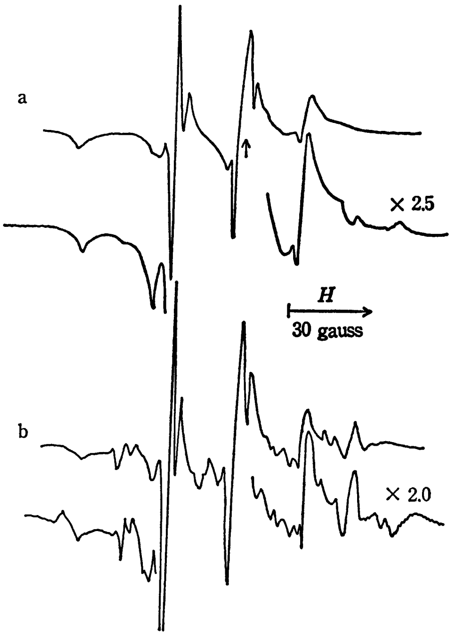

Fig. 1. ESR spectra of γ-irradiated ammonia-silica gel at $^{14}NH_3$ content, a; $1.1\times10^{-3}$ mol/g, and b; $1.2\times10^{-4}$ mol/g. The arrow in a denotes the position of DPPH signal.

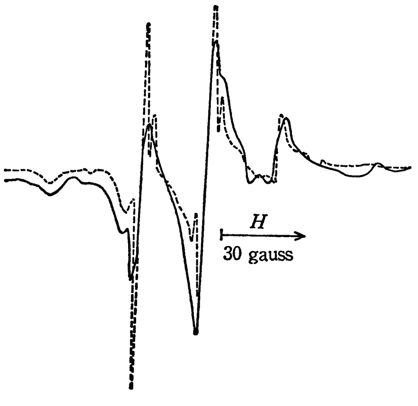

Fig. 2. A comparison of the predominant spectrum on silica gel (broken line) with that of γ-irradiated aqueous ammonia (solid line).

It should be noted that the central triplet in the dominant quintet shows a marked linewidth anomaly, linewidths being 1.9 gauss, 4.8 gauss, and 3.0 gauss from the low field side. A similar triplet spectrum has been previously observed from photolyzed hydrazoic acid in inert gas matrices.[9]

For comparison, frozen aqueous solutions of ammonia were γ-irradiated and examined at −196 °C. When the concentration of ammonia was 30%, the spectrum showed a quintet structure quite similar to that in Fig. 1a (see Fig. 2). ESR spectra of γ-irradiated aqueous ammonia have been previously observed and assigned to $NH_2$ radical by other workers.[10,11] Al-Naimy *et al.*[10] observed a triplet spectrum similar to the central triplet in our spectrum and assigned it to $NH_2$ radical with the assumption that the nitrogen splitting is quenched due to the hindered rotation of the radical. Tupikov *et al.*, [11] on the other hand, observed a poorly resolved five-line spectrum and obtained hf splitting values of 24.5 gauss for proton

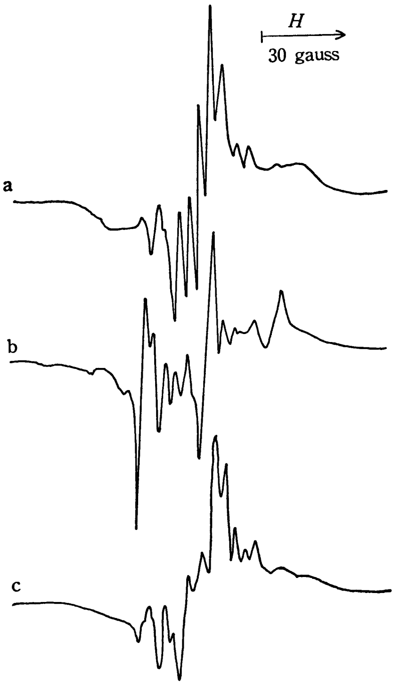

Fig. 3. ESR spectra of γ-irradiated ammonia-silica gel at −196 °C, a; $ND_3$-deuterated silica gel, b; $NH_3$-deuterated silica gel, and c; $ND_3$-silica gel.

---

[6] R. Marx and J. Maruani, *J. Chim. Phys.*, **61**, 1604 (1964).

[7] D. R. Smith and W. A. Seddon, *Can. J. Chem.*, **48**, 1938 (1970).

[8] V. I. Tupikov, V. I. Tsivenko, S. Ya. Pshezhetskii, A. G. Kotov, and V. K. Milinchuk, *Zh. Fiz. Khim.*, **37**, 138 (1963), V. I. Tupikov and S. Ya. Pshezhetskii, *ibid.*, **37**, 1900 (1963).

[9] P. H. H. Fischer, S. W. Charles, and C. A. McDowell, *J. Chem. Phys.*, **46**, 2162 (1967).

[10] B. S. Al-Naimy, P. N. Moorthy, and J. J. Weiss, *J. Phys. Chem.*, **70**, 3654 (1966).

[11] V. I. Tupikov and S. Ya. Pshezhetskii, *Zh. Fiz. Khim.*, **38**, 2511 (1964).

and 31 gauss for nitrogen. Their value for nitrogen, however, seems to be too large compared with that of the same radical in ammonia matrix.⁷⁾ The assignment of the splitting value should be made by taking into account an anisotropic motion of $NH_2$ radical as shown in the present investigation.

The deuterated samples showed ESR spectra as given in Fig. 3a, b, and c. Fig. 3a is the spectrum of $ND_3$ adsorbed on deuterated silica gel. The central part of the spectrum consists of five intense lines with a hf splitting value of 4 gauss which is about one-sixth of the value of the central triplet in Fig. 1. The triplet splitting in Fig. 1, therefore, is ascribed to two equivalent protons. Both the spectrum Fig. 3b for $NH_3$ on deuterated silica gel and the spectrum Fig. 3c for $ND_3$ on silica gel are well explained by appropriate superpositions of the non-deuterated spectra Fig. 1 and the deuterated spectrum Fig. 3a. The hydrogen-deuterium exchange reaction occurs to some extent.

*Temperature Dependence of Spectra.* On raising the temperature, the nine-line spectrum of high content samples diminished in intensity without any change of the feature. The spectrum observed from samples with low content, on the other hand, showed a remarkable temperature dependence as represented in Fig. 4. The linewidth anomaly in the central triplet as well as some weak lines observed at low temperature gradually disappeared at higher temperatures. The separation of the outermost broad signals became smaller with temperature while the splitting of the central triplet remained constant in the whole temperature range. Above −90 °C was observed only the narrowing of the widths of the hf lines. On recooling the sample, the lower temperature spectra were reproduced satisfactorily.

The sample with the lower content of adsorbed ammonia showed essentially the same reversible change of the spectrum (see Fig. 5). In addition, the four weak lines indicated by arrows in Fig. 5b increased in intensity at an early stage of the rise of temperature and then diminished above −150 °C. The four-line spectrum might be attributed to $NH_3^+$ [13] possibly formed by charge transfer reaction from silica gel to adsorbed ammonia. A similar reaction was found to play an important role in the formation of cation radicals of benzene on silica gel.[14]

*Assignment of Spectra.* The spectra observed above −90 °C consist of nine lines and may be assigned to $NH_2$ radical with hf splitting values of 25 gauss for proton and 19 gauss for nitrogen. The assignment is supported by studying the spectrum of adsorbed $^{15}NH_3$ after $\gamma$-irradiation. An apparent four-line spectrum shown in Fig. 6c is the same as that of $^{15}NH_2$ radical in solid $^{15}NH_3$ matrix.⁷⁾ Because the nine-line spectrum for $^{14}NH_2$ and the four-line one for $^{15}NH_2$ are explained by the isotropic values of hf splittings, the adsorbed $NH_2$ radicals are consi-

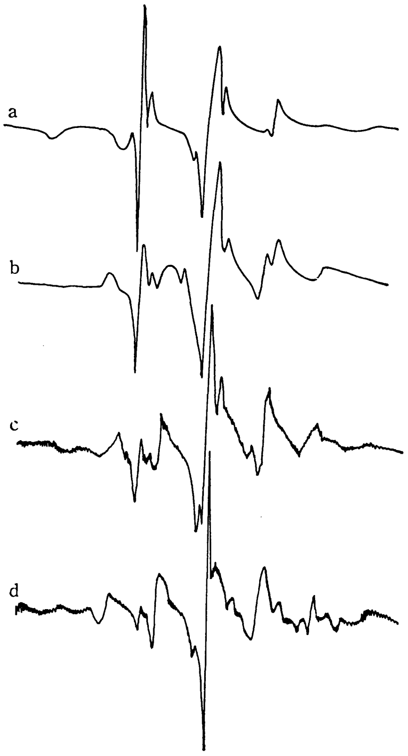

Fig. 4. Change of ESR spectrum of $\gamma$-irradiated $^{14}NH_3$-silica gel with $^{14}NH_3$ content; $1.1\times10^{-3}$ mol/g. a; −196 °C, b; −125 °C, c; −90 °C, and d; −30 °C.

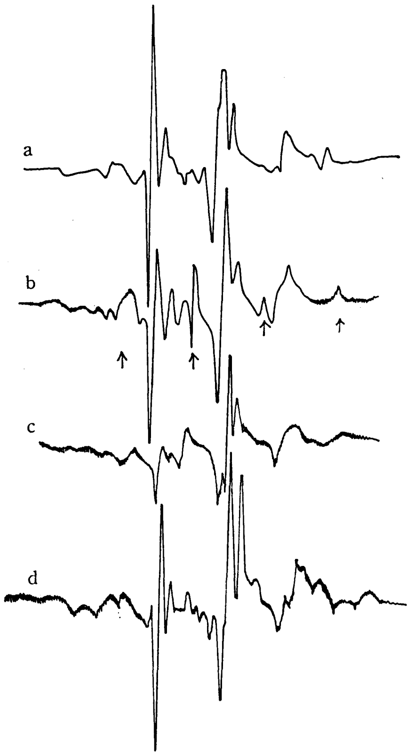

Fig. 5. Change of ESR spectrum of $\gamma$-irradiated $^{14}NH_3$-silica gel with $^{14}NH_3$ content; $1.2\times10^{-4}$ mol/g. a; −196 °C, b; −135 °C, c; −90 °C, and d; −196 °C (recooled). Hf lines indicated by arrows in b are most likely due to $NH_3^+$, see text.

---

12) O. Kikuchi, This Bulletin, **42**, 1187 (1969).

13) J. S. Hyde and E. S. Freeman, *J. Phys. Chem.*, **65**, 1636 (1961).

14) S. Nagai, S. Ohnishi, and I. Nitta, *Shokubai*, **13**, 48 (1971).

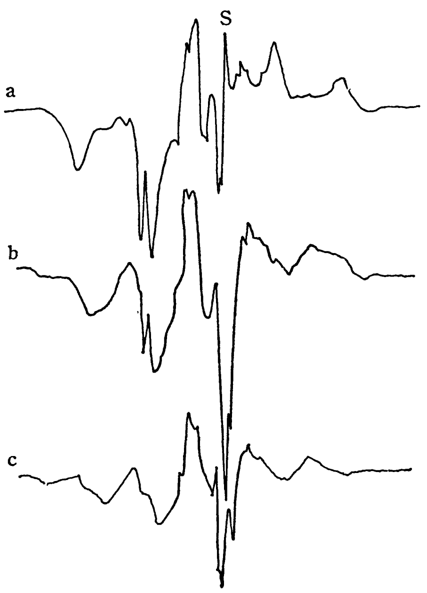

Fig. 6. Change of ESR spectrum of $\gamma$-irradiated $^{15}NH_3$-silica gel a; $-196$ °C, b; $-150$ °C, and c; $-90$ °C. A line designated by S in a is due to the silica gel defect.

dered to carry out a substantially free rotation at the relatively high temperatures. The reversible temperature dependence, therefore, arises from motional change of adsorbed $NH_2$ radicals from fixed or some restricted state at low temperatures to free rotation above $-90$ °C.

The low temperature spectrum in Fig. 1a can now be explained on the basis of the anisotropic data of $NH_2$ radical. The ESR data in the coordinate axis system in Fig. 7 are summarized in Table 1. Anisotropies in the proton hf splitting and in the $g$ value are fairly small compared with the anisotropy in the nitrogen splitting. Since the central triplet is due to two protons and the splitting value is constant in the whole temperature range, the other part of the spectrum may be ascribed to the hf splitting of nitrogen. If the separation of the outermost broad signals$\sim$114 gauss is assumed to be a sum of hf splittings of proton and nitrogen, $a_H$ and $a_N$, we obtain 32 gauss for $a_N$ by taking 25 gauss for $a_H$ from the splitting value of the central triplet. As can be seen from Table 1, such a large value of $a_N$ is expected when the adsorbed $NH_2$ radical remains immobile or carries out a preferential rotation about $z$-axis. The rotation hypothesis seems to be more probable in view of the linewidth anomaly in the central triplet as well as the narrow linewidths.

Table 1. ESR data of $NH_2$ radical

| | Isotropic | $x$ | $y$ | $z$ | Ref. |
|---|---|---|---|---|---|
| $a_N{}^{a,b)}$ | $+13.3$ | $-13.1$ | $-12.9$ | $+25.0$ | 5 |
| $a_H{}^{b)}$ | $-27.3$ | $-4.1$ | $+1.8$ | $+2.3$ | 5 |
| $g$ | 2.0037 | 2.0029 | 2.0058 | 2.0023 | 12 |

a) Calculated values from $^{15}NH_2$ data in Ref. 5.
b) Splitting values are given in gauss.

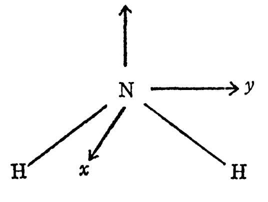

Fig. 7. A coordinate axis system of $NH_2$ radical.

*Linewidth Anomaly.* The linewidth anomaly similar to that in the central triplet has been often observed in the spectra of adsorbed radicals[2–4] and may arise from the modulation of the anisotropic hf and $g$ tensor interactions coupled with molecular rotation. To shed some light on the nature of the tumbling of $NH_2$ radical, a qualitative analysis of the triplet was made according to the theory of ESR linewidth in solution.[15,16] The linewitdh of each line of the triplet can be written;

$$T_2^{-1}(M_H) = A + BM_H + CM_H^2 \tag{1}$$

where $M_H$ is the total field-direction component of spin angular momentum for two protons, and $A$, $B$ and $C$ are parameters. The term $B$ arises from the anisotropic $g$ tensor in conjunction with the anisotropic hf interaction between the unpaired electron and the protons. The theoretical expression for $B$ is given by

$$B = \frac{16}{3} j_H{}^{(DG_2)}(0) B_0, \tag{2}$$

where $B_0$ is the external magnetic field and $j_H{}^{(DG_2)}(0)$ is the spectral density due to the cross term between anisotropic hf and $g$ tensor interactions. Equation (2) is valid for the case that a condition $\omega^2\tau_R{}^2 \gg 1$ holds, where $\omega$ is the angular resonance frequency of the electron, and $\tau_R$ the correlation time for molecular tumbling. This condition seems to be satisfied for the central triplet because of the narrow widths, 2—5 gauss.

Relative linewidth of $M_H = -1$ and $M_H = +1$ depends on the sign of $B$, that is, $T_2{}^{-1}(-1) < T_2{}^{-1}(+1)$ for $B > 0$, and $T_2{}^{-1}(-1) > T_2{}^{-1}(+1)$ for $B < 0$.

For the isotropic rotation, the spectral density $j_H{}^{(DG_2)}(0)$ is given by

$$j_H{}^{(DG_2)}(0)/\tau_R = \frac{1}{5} \sum_m F_{D,H}{}^{(m)} F_G{}^{(-m)}, \tag{3}$$

where $F_{D,H}{}^{(m)}$ and $F_G{}^{(-m)}$ are the irreducible tensor components corresponding to the anisotropic hf interaction and $g$ tensor interaction, respectively.

Evaluation of the $F_{D,H}{}^{(m)}$ and $F_G{}^{(m)}$ using the values in Table 1 gives

$$\left.\begin{aligned} F_{D,H}{}^{(0)} &= 24.8 \times 10^6\,\text{sec}^{-1}, \\ F_{D,H}{}^{(\pm 2)} &= -26.0 \times 10^6\,\text{sec}^{-1}, \\ F_G{}^{(0)} &= 0.0074 \times 10^6\,\text{sec}^{-1}\,\text{gauss}^{-1}, \\ F_G{}^{(\pm 2)} &= 0.0065 \times 10^6\,\text{sec}^{-1}\,\text{gauss}^{-1}. \end{aligned}\right\} \tag{4}$$

The spectral density in Eq. (3) becomes using the results in Eq. (4) and $B_0 = 3260$ gauss as

$$j_H{}^{(DG_2)} B_0/\tau_R = -1.00 \times 10^{14}\,\text{sec}^{-2}. \tag{5}$$

---

15) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

16) J. H. Freed, *ibid.*, **41**, 2077 (1964).

17) B. L. Barton and G. K. Fraenkel, *ibid.*, **41**, 695 (1964).

Since $a_H<0$ and $j_H^{(DG_2)}(0)$ and $B$ should have the same sign,[17] $B$ should be negative for the isotropic rotation, which is inconsistent with our spectrum.

When anisotropic rotation is taken into account, the appropriate spectral density can be written in place of Eq. (3),[16]

$$j_H^{(DG_2)}(0)=\frac{1}{5}\sum_{m,m'}F_{D,H}^{(m)}F_G^{(m')}\lambda_{mm'}. \tag{6}$$

where $\lambda_{mm'}$ are functions of the principal values of the molecular diffusion tensor, $R_1$, $R_2$, and $R_3$. In our calculation, the principal axes of the diffusion tensor are chosen as molecule-fixed axes in Fig. 7, that is, $R_1$, $R_2$, and $R_3$ denote the principal values along $x$, $y$, and $z$ axis, respectively.

We obtain using Eq. (4);

$$j_H^{(DG_2)}(0)B_0=[1.20\lambda_{00}-0.41\lambda_{02}-2.20\lambda_{22}-2.20\lambda_{2-2}] \times 10^{14}\,\mathrm{sec}^{-2}. \tag{7}$$

Results of our calculation of Eq. (7) using values $\lambda_{mm'}$ for various ratios of $R_1:R_2:R_3$ show that the sign of $j_H^{(DG_2)}(0)$ can be positive only when $R_3>R_1$, $R_2$. For the special case of the axial rotation, *e.g.* $R_1=R_2$, the third principal value $R_3$ should be larger than twice of $R_1$. A preferential rotation about $z$ axis, therefore, may explain the observed linewidth anomaly, $T_2^{-1}(-1)<T_2^{-1}(+1)$.

## Summary

The dominant species produced in γ-irradiated ammonia–silica gel system is assigned to $NH_2$ radical. The observed dependence of the ESR spectrum on both the ammonia content in the sample and temperature is due to the motional change of the radical on silica gel surfaces. The $NH_2$ radical in the high content samples is considered to carry out a substantially free rotation even at −196 °C. The radical produced in the low content samples, on the other hand, carries out a preferential rotation about the axis perpendicular to the radical plane at low temperatures and becomes free above −90 °C.

Finally, the observed dependence of the $NH_2$ radical spectrum on three matrices, silica gel, frozen aqueous ammonia and solid ammonia, is ascribed to the result of the different environments of the radical.

The author wishes to express his hearty thanks to Professor Isamu Nitta and Professor Shun-ichi Ohnishi for their helpful discussions.