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ESR Studies of Methyl Radicals Stabilized on Silica-gel Surfaces

Shozo Kubota, Masamoto Iwaizumi, and Taro Isobe
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira-nichome, Sendai

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The methyl radicals produced on silica-gel surfaces by the photolysis of methyl iodide or methane have been investigated by ESR. When the silica gel is preheated at high temperatures (above *ca.* 300°C), two methyl radicals which have abnormally small hfs constants are trapped on the surfaces. In the case of the photolysis of methyl iodide, these two radicals disappear by continuing uv-irradiation, and instead an ordinary type of methyl radical is produced. The former two radicals have nearly isotropic g-values, and these values are approximately equal to that of a free electron and are considered to have a non-planar structure. The adsorption sites for these radicals were estimated to be siloxane groups. On the other hand, when the silica gel is preheated at low temperatures (below *ca.* 300°C) the methyl radicals produced have hfs constants of the same magnitude as that of the ordinary type of methyl radical, but each proton line of the radicals is accompanied by four satellite lines. The outer satellite lines have been confirmed by measurements of the X- and K-band spectra to be a concurrent spin-flip transition of an odd electron and a nearby proton of the silica-gel surface. The models of the adsorption state of the radicals are considered.

Since Kazanskii's work,[1] several interesting investigations[2-7] have been reported on the ESR of methyl radicals stabilized on solid surfaces. As the methyl radical shows a well-resolved hyperfine structure, even in the adsorbed state, it is possible to detect a small perturbation of the methyl radical caused by the interaction with solid surfaces. The studies of the methyl radical, therefore, seem of interest and seem to be useful from the point of view of studies of the nature of radical-solid surface interaction and also studies of the surface structure.

In this work, methyl radicals trapped on silica-gel surfaces were studied by ESR. The methyl radicals on the silica-gel surfaces show characteristics similar in several points to those trapped on porous Vycor glass.[6,7] In this paper, the characteristics of the ESR of the radicals and of radical-surface interactions observed in silica-gel systems pretreated at different temperatures, the effect of the irradiation time on radical formation by the photolysis of methyl iodide, and the satellite lines in the ESR will be presented. Some of our results may be useful in understanding problems of the methyl radicals in the porous Vycor glass system already reported.

Experimental

Methyl radicals were produced by the photolysis of methyl iodide or methane adsorbed on silica-gel surfaces at the temperature of liquid nitrogen. The methyl iodide was ob-

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[1] V. B. Kazanskii, G. B. Pariiskii, I. V. Aleksandrov, and G. M. Zhidomirov, *Solid State Physics* (*USSR*), **5**, 649 (1963).

[2] J. Turkevich and Y. Fujita, *Science*, **152**, 1619 (1966).

[3] M. Fujimoto, H. D. Gesser, B. Garbutt, and A. Cohen, *Science*, **154**, 381 (1966).

[4] M. Fujimoto, H. D. Gesser, B. Garbutt, and M. Shimizu, *Science*, **156**, 1105 (1967).

[5] G. B. Garbutt, H. D. Gesser, and M. Fujimoto, *J. Chem. Phys.*, **48**, 4605 (1968).

[6] N. Shimamoto, Y. Fujita, and T. Kwan, This Bulletin, **43**, 580 (1970).

[7] G. B. Garbutt and H. D. Gesser, *Can. J. Chem.*, **48**, 2685 (1970).

tained from the Koso Chemical Co., Ltd., and purified according to the procedure used by Cowley and Partington.[8] The purified methyl iodide was degassed in a vacuum line and stored over P_2O_5. The methane was obtained from the Takachiho Co. and was used after drying over P_2O_5. The silica gel obtained from the Kanto Chemical Co., Ltd., (60—80 mesh for chromatography) was heated in oxygen at 300°C to remove organic impurities and then stored in a glass bottle. Prior to the adsorption of methyl iodide or methane, this silica gel was heated *in vacuo* to dehydrate the surface. To see the effect of the dehydration on the methyl-radical formation, the silica gel was heated at various temperatures from room temperature to 700°C. After the methyl iodide or methane had adsorbed on the silica gels, the resulting samples were irradiated with the light of a mercury lamp. An Ushio 6-w low-pressure mercury lamp and a Hitachi ultra-high pressure mercury lamp were used as the light sources. The measurements of ESR spectra were carried out with a Hitachi 771 X-band spectrometer. For the measurements of the satellite lines, a Hitachi MES 4001 K-band spectrometer was used as well as the X-band spectrometer. The magnetic field was calibrated with an aqueous solution of potassium nitrosodisulfonate and DPPH powder for the determination of the *g*-values.

Results and Discussion

The Methyl Radicals Stabilized on Silica Gel Preheated at High Temperatures. The ESR spectra for the methyl radicals trapped on the silica-gel surfaces depend on the dehydration temperature of the silica gel. Figure 1 shows the ESR spectra obtained from the methyl radicals produced by the photolysis of methyl iodide when the silica gel was preheated at 600°C *in vacuo* for 5 hr. The spectra obviously show marked changes with the uv-irradiation time. In an early stage of the irradiation, two sets of quartet splittings due to two methyl radicals, Me(a_1) and Me(a_2), are observed. The intensities of these two methyl radicals increase with the progress of the irradiation until about 90 sec.[9] However, upon further irradiation the intensities of the radicals begin to decrease and another quartet (Me(n_1)) appears. The intensity of this latter quartet increases as the first two decrease with the continuation of the photolysis, until only the latter radical, Me(n_1), remains. For heating the samples, the former two methyl radicals, Me(a_1) and Me(a_2), are very unstable, but the latter one, Me(n_1), is stable and can be observed even at room temperature. The radical existing at the final stage of irradiation, Me(n_1), has about the same hfs constant and amplitude distribution for the quartet as those already reported by Kazanskii *et al.*[1] On the other hand, Me(a_1) and Me(a_2) radicals have abnormally small hfs constants compared to that of the ordinary methyl radical and have *g*-values close to that of a free electron (see Table 1). The line broadening for the quartets of these methyl radicals, Me(a_1) and Me(a_2), are approximately symmetric to the center of the spectrum, showing a marked contrast to the line-broadening effect in the Me(n_1) radical or the previously-reported normal methyl radicals, which reveal unsymmetric line broadening to the center of the spectrum (see Fig. 2).

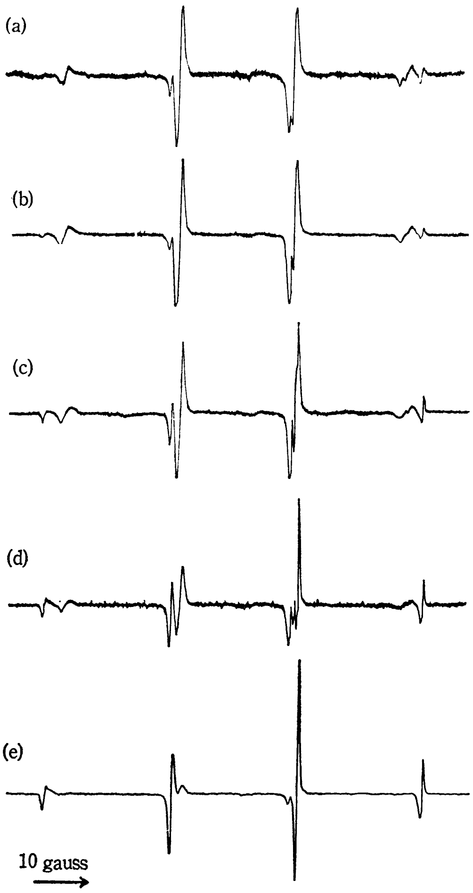

Fig. 1. Change of ESR spectra with uv-photoirradiation time observed for the photolysis of methyl iodide on the silica gel preheated at 600°C *in vacuo*. Irradiation time: (a) 20 sec. (b) 90 sec. (c) 3 min. (d) 6 min. (e) 12 min.; Temp=77°K.

TABLE 1. HFS CONSTANTS AND *g*-VALUES FOR THE METHYL RADICALS, Me(a_1), Me(a_2) AND Me(n_1), ON THE SILICA-GEL SURFACE AT 77°K

	Hfs constants (in gauss)	*g*-values
Me(a_1)	20.7	2.0024
Me(a_2)	21.2	2.0023
Me(n_1)	23.0	2.0027

Recently Fujimoto,[3] and also Shimamoto,[6] found in the porous Vycor glass system a methyl radical with an abnormally small hfs constant. Shimamoto *et al.* pointed out that this new type of methyl radical shows an inverse line-broadening effect compared to that of the normal methyl radical; that is, in the normal methyl radical the low-field lines are broader than the high-field lines, but in the new methyl radical the higher-field lines are broader than the low-field lines. In the present case, if a large amplitude of

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[8] E. G. Cowley and J. R. Partington, *J. Chem. Soc.*, **1938**, 977; "Organic Solvents" ed. by A. Weissberger, Interscience Publishers, New York (1955), p. 427.

[9] The time is not strict because it changes somewhat with sample.

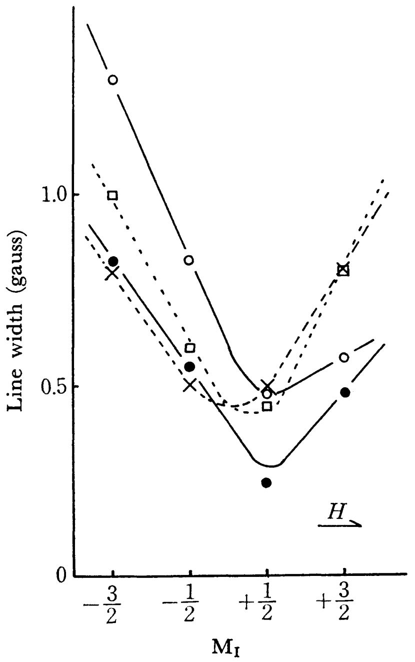

Fig. 2. Line width as a function of M_I at 77°K. X: Me(a_1), □: Me(a_2), ●: Me(n_1), ○: Main proton lines for Me(n_2). The line widths for Me(a_1) and Me(a_2) are evaluated by computer simulation.

field modulation is used for the measurements of ESR, the absorptions for Me(a_1) and Me(a_2) can not be distinguished as two species any more, but shows a hyperfine pattern quite similar to that observed in the porous Vycor glass system. This fact implies that the quartet splitting for the new type of methyl radical observed in the porous Vycor glass system may consist of two overlapped quartets which are due to two species of methyl radicals.

According to the electron-spin-relaxation theory,[10–12] the fact that the line-width-broadening effect is symmetric to the center of the spectra in the Me(a_1) and Me(a_2) radicals implies that the g-values of the radicals are nearly isotropic. In the present case, as is indicated in Table 1, the g-values for the Me(a_1) and Me(a_2) radicals are also almost equal to the value for a free electron. The g-value of the Me(n_1) radical is larger than the value of a free electron and is estimated to be anisotropic from the line-width-broadening effect in the spectrum. From the changes in the g-values of the free radicals, it may be estimated that the structures of the new types of methyl radicals, Me(a_1) and Me(a_2), are different from that of the normal type, Me(n_1); *i.e.*, the new one probably has a non-planar structure. The deformation from a planar structure corresponds to the increase in the s-character in an odd electron orbital; this in turn leads to a g-value close to that of a free electron. The facts that the proton hfs constants of the Me(a_1) and Me(a_2) radicals are smaller than that of the normal methyl radical is also a good indication of the non-planar structure. Although there may be some effect due to charge transfer to the surface sites, the contribution of the charge transfer to the decrease in hfs constants is probably small. If there is any appreciable effect of charge transfer to the surface sites, such as the boroxane groups suggested by Garbutt *et al*,[7] the g-value would probably deviate more from the value of a free electron because of the larger effect of spin-orbit coupling at the adsorption sites.

The formation of the nonplanar methyl radicals can be attributed to the strong interaction with the silica-gel surface. The formation of such radicals could not be observed when the silica gel was preheated at low temperatures. This fact suggests that the adsorption sites for the non-planar methyl radicals are siloxane groups formed by the dehydration of surface silanol groups. In the study of methyl radicals in the porous Vycor glass system, Garbutt *et al*, proposed that boroxane groups are adsorption sites for the methyl radical, which has an abnormally small hfs constant. Their conclusion was based on Zammit's experiment, which reported that this new type of methyl radical could not be observed on the pure (boron-free) silica gel. The present result using silica gel implies that siloxane groups are adsorption sites for this new type of methyl radical in the porous Vycor glass system, too. It seems interesting that there are two different adsorption states for the non-planar methyl radicals. From the intensity ratio of the two radicals, Me(a_1) and Me(a_2), it can be estimated that the populations of the two strong adsorption sites on the silica-gel surface are approximately the same.

As has been mentioned above, in the photolysis of the methyl iodide the new methyl radicals, Me(a_1) and Me(a_2), appear at the early stage of irradiation, but as the photolysis continues the intensities of the radicals decrease, and instead an ordinal methyl radical, Me(n_1), appears. In the photolysis of methane, the observed spectra (Fig.3) did not show such a change, indicating that the iodine produced in the photolysis of methyl iodide disturbs the stabilization of the non-planar form of the methyl radical by covering the active sites for adsorption.

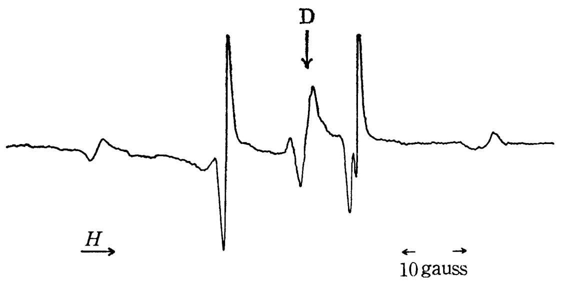

Fig. 3. ESR spectrum of the methyl radicals produced from methane at 77°K. The silica gel was preheated at 600°C *in vacuo* for 5 hr. D: Defect signal.

The Methyl Radical Formed on the Silica Gel Preheated at Low Temperatures, and the Satellite Lines about the Four Proton Lines. When the silica gel is preheated at temperatures below about 300°C, the methyl radicals with abnormally small hfs constants are not ob-

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[10] H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).
[11] D. Kivelson, *ibid.*, **33**, 1094 (1960).
[12] J. Freed and K. Fraenkel, *ibid.*, **39**, 326 (1963).

served. The observed quartet for the methyl radical has about the same splitting and amplitude distributions as those of the ordinary methyl radical (Fig.4). In this case, however, each proton hyperfine line is accompanied by four satellite lines, as is shown in Fig. 5. Such satellite lines were not observed when the silica gel was preheated at high temperatures, implying that they are related to the interaction with the proton of the silanol groups on the silica-gel surface. By measurements of both the X- and K-band spectra, it has been found that the outer satellite lines are affected by the magnetic field, although the inner satellite lines are not affected (see Figs. 5 and 6). The separations between the two outer satellite lines were 11.5 and 26.2 gauss at the X- and K-band spectra respectively; the spectra were approximately equal to $2g_N\cdot\beta_N I\cdot H$. That is, the values calculated by the use of $2g_N\beta_N I\cdot H$ are 10.9 and 25.8 gauss respectively and are in good agreement with the observed values.

Fig. 4. ESR spectrum of the methyl radical on the silica gel surface at 77°K. The silica gel was pretreated by evacuating for 15 hr without heating.

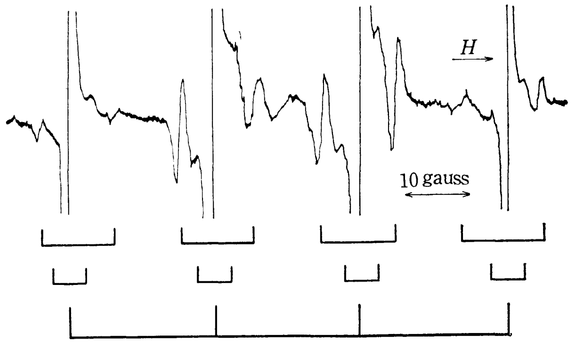

Fig. 5. ESR spectrum showing the satellite lines at X-band. Temp: 77°K.

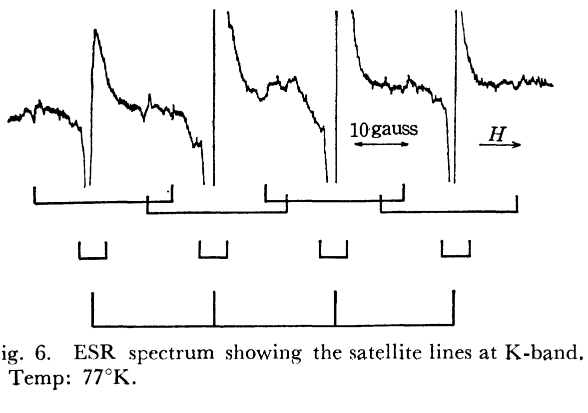

Fig. 6. ESR spectrum showing the satellite lines at K-band. Temp: 77°K.

Previously Rogers *et al.*[13] explained the two satellite lines observed for the methyl radicals in irradiated single crystals of sodium acetate trihydrate as arising from the concurrent spin flip of the electron of the methyl radical and the proton of the water of crystallization. They showed in their study that the separation of the satellite lines is close to $2g_N\beta_N I\cdot H$, which is to be expected from the theory that there is some second-order effect in the hyperfine interaction.[14,15] In such concurrent spin flip-type transitions of the unpaired electron and a nearby proton, if it is assumed that the central line is associated with satellite lines, as in the above example, the ratio of the intensity of either satellite line, T_1, to that of the central line, $2T_2$, is given by:

$$T_1/2T_2 = (3g^2\beta^2/20H^2)\langle r^{-6}\rangle \tag{1}$$

This equation indicates that the $T_1/2T_2$ ratio is inversely proportional to the square of the external field. The $T_1/2T_2$ ratio in the K-band spectrum can, therefore, be expected to be about 1/6 for the case of the X-band spectrum. In the present case, the ratio of the intensity of the outer satellite lines to that of the central line, $T_1/2T_2$, in the K-band spectrum was about 1/3—1/6 of the value in the X-band spectrum, in good agreement with the expectation from Eq. (1).

It may be concluded, therefore, that the outer satellite lines are due to the spin flip-type transition of the unpaired electron and a nearby silanol proton coupled by dipole-dipole interaction. As has been mentioned above, the central line can probably be associated with the outer satellite lines (the Me(n_2) radical), and so the inner satellite lines may be attributed to the other species of methyl radical, which has Fermi-type interaction with protons on the silica-gel surface (the Me(n_3) radical). It seems interesting that in this case, too, there are two different adsorption states for the methyl radicals. Figure 7 is one possible model for Me(n_2) and Me(n_3). By using the $T_1/2T_2$ intensity ratio for the outer satellite lines, the mean distance, $\langle r\rangle$, for the Me(n_2) methyl radical is calculated to be 2 Å from Eq. (1).

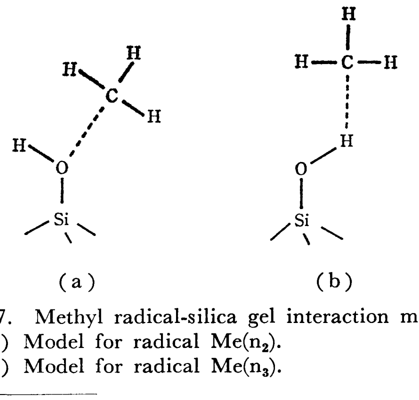

Fig. 7. Methyl radical-silica gel interaction models.
(a) Model for radical Me(n_2).
(b) Model for radical Me(n_3).

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[13] M. T. Rogers and L. D. Kispert, *ibid.*, **46**, 221 (1967).

[14] G. T. Trammell, H. Zeldes, and R. Livingston, *Phys. Rev.*, **110**, 630 (1958).

[15] I. Miyagawa and W. Gordy, *J. Chem. Phys.*, **32**, 255 (1960).

As has been shown, the methyl radicals show well-resolved ESR spectra even in the adsorbed state, although the hyperifine interaction between the $2p_z$ unpaired electron and a α proton has a large anisotropy. This can be well explained by the rapid rotation of the molecules around the three-fold axis. However, the tumbling of the molecules should be greatly restricted by the interaction with solid surfaces, as may be seen from the line-width broadening, showing the deviation of the amplitude distribution from the binomial law. The observation of the satellite lines due to the magnetic dipole-dipole interaction between the electron spin and a neighboring surface proton gives useful information about the lifetime of adsorbed states or the tumbling of the molecules. That is, the tumbling frequency of the $Me(n_2)$ radical was estimated to be lower than 2×10^8 Hz from the relation:

$$\tau_c \gg 1/2\pi\Delta\nu \qquad (2)$$

where τ_c is the correlation time for fluctuation in the interaction between the electron and the proton or a reciprocal of the tumbling frequency, and where $\Delta\nu$ is the separation of the doublet.