The ESR of the Fast-rotating -CH_2 of the Radical Formed by the Photolysis of CH_2I_2 on Silica Gel

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The electron spin resonance spectra have been measured for the radical formed by the photolysis of methylene iodide adsorbed on silica gel. The spectra were anisotropic and were attributed to the radical of the ≡Si–O–CH_2 form by an analysis of the hyperfine splittings due to two protons, taking into consideration the photochemical processes on the silica gel surface. From a line-shape analysis of the observed spectrum, the following anisotropic hyperfine interaction parameters for the protons and g-value have been obtained:

$$\mathbf{A}_{/\!/} = 28.5 \pm 0.5\text{G}, \quad \mathbf{A}_{\perp} = 18.8 \pm 0.5\text{G}, \quad g = 2.0030 \pm 0.0005.$$

It has been concluded from the analysis of the spectra that the hyperfine structure observed with axially-symmetric tensors is a result of the fast internal rotation of the methylene group of the radical.

The effects of the internal motion of radicals on the ESR spectrum have been reported by many authors. The reorientation of terminal methylene has been found in the CH_2COO^- radical, formed by the irradiation of glycine,[1] triglycinesulphate,[2] zinc acetate, and sodium acetate.[3] Of these, CH_2COO^- in zinc acetate has been studied extensively by Hayes *et al.*[4] and by Ohigashi and Kurita,[5] who have studied the temperature dependence of the hyperfine pattern in the light of the internal rotation of the methylene group. Lefebvre and Maruani[6] have theoretically shown the effect of the fast-rotating methylene group on the spectrum of randomly-oriented radicals in solids, in particular the case of CH_2COOH, by means of computer simulation. More recently, McDowell, Raghunathan and Shimokoshi[7] have reported this effect in the interpretation of the anisotropic spectrum of an ethyl radical trapped in an argon matrix at 4.2 K, taking into consideration the free rotation of the methylene group in the radical.

On the other hand, the surface properties of silica gel have been the subject of much research. ESR investigations of the radicals formed on the surface have also provided detailed information about the surface properties, together with the mechanism of the radical formation. Recently, Melamund *et al.*[8] have observed the radical (≡Si–O–CH_2) formed by the photolysis of methylated Vycor glass and have discussed the mechanism of the formation of the radical. However, they did not give the anisotropic hyperfine coupling of the protons based on the internal rotation of the methylene group. This paper will report the results of our ESR studies of the fast-rotating methylene group of the radical formed by the photolysis of CH_2I_2 on silica gel.

Experimental

Silica gel (SILICAR TLC-7GF) was introduced into a 3 mm *i.d.* quartz tube and pretreated at various temperatures (200—900 °C) for 2—12 hr in a vacuum. Methylene iodide obtained from the Eastman Co., Ltd., was purified by vacuum distillation before use. After the pretreatment, the silica gel was brought into contact with various amounts of methylene iodide at room temperature. In order to obtain a high concentration on the surface, methylene iodide was condensed by cooling the samples to 77 K.

In addition to this procedure, the pretreated silica gel was exposed to a small amount of water vapor (0.1—2.0 Torr) before the contact of methylene iodide. Remarkable effects were thus observed in the case of the samples pretreated at temperatures higher than 600 °C.

After sealing off the tube, the samples were cooled in a liquid nitrogen Dewar, placed in an X-band cavity of a JES 3 BSX spectrometer, and irradiated by means of a low-pressure mercury lamp which emitted the 2537 and 1849 Å wavelengths. For purposes of comparison, samples which had never been exposed to methylene iodide were irradiated under the same conditions as those used for the methylene iodide samples.

Results and Discussion

After irradiation for several minutes, the samples turned brown and the ESR spectra were observed. The spectrum shown in Fig. 1 is typical; it was obtained at 77 K by the irradiation of samples pretreated at 400 °C or lower for 2—6 hr. When the samples pretreated at 700 °C or higher for 2—12 hr, the spectra obtained by the irradiation were complicated and very different from that shown in Fig. 1. However, the

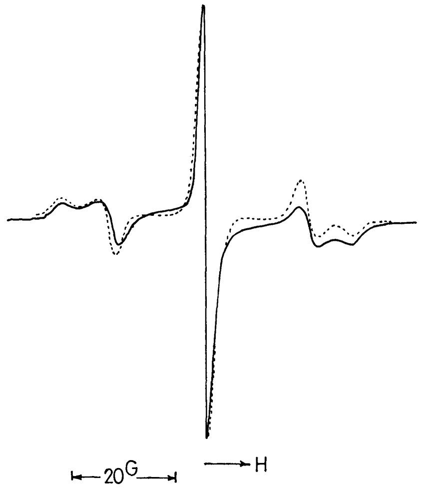

Fig. 1. The spectrum (full line) obtained by the photolysis of CH_2I_2 on silica gel at 77 K. The broken line shows calculated spectrum with the ESR parameters of $\mathbf{A}_{/\!/}$=28.5 G, $\mathbf{A}_{\perp}$=18.8 G and g=2.0030.

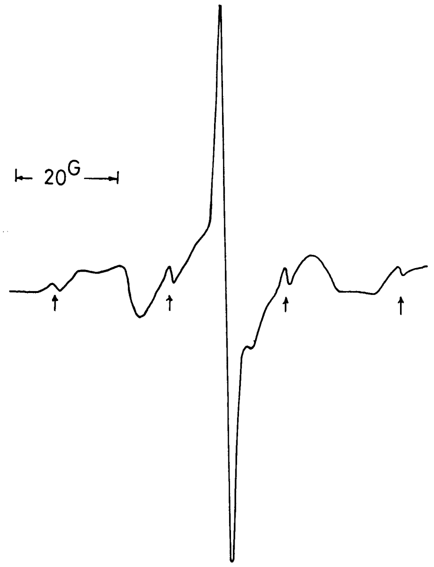

Fig. 2. The spectrum obtained by the photolysis of condensed CH_2I_2 on silica gel at 77 K. Arrows show the lines due to methyl radical.

same spectrum as that of Fig. 1 appeared again with much less intensity upon the irradiation of the samples treated at 700 °C when a small amount of water vapor was admitted onto the samples before they adsorbed the methylene iodide. The spectrum shown in Fig. 2 was obtained by the irradiation of concentrated methylene iodide on silica gel pretreated at 400 °C. Obviously, the spectrum is identical with that shown in Fig. 1 except that weak signals due to the methyl radical are present. This spectrum disappeared when the samples were warmed to 150 K. The irradiation of silica gel under the same conditions as in the case of methylene iodide samples showed very weak signals. The absorption lines due to the hydrogen atom and an asymmetric line near $g=2$, which is also seen in Figs. 1 and 2 with much less intensity than the other lines, were observed upon further irradiation.

Methylene iodide has absorption maxima at 2890, 2490, and 2120 Å.[9)] Gregory and Style[10)] have done the photolysis of this compound at 3100 Å mainly and have thus produced methylene, although they were not certain whether the primary process was

$$CH_2I_2 + h\nu \longrightarrow CH_2I + I \qquad (1)$$

followed by

$$CH_2I \longrightarrow CH_2 + I \qquad (2)$$

or a direct process;

$$CH_2I_2 + h\nu \longrightarrow CH_2 + I_2(2I) \qquad (3)$$

The primary process in the vacuum ultraviolet photolysis has been studied by Style and Ward,[11)] who suggested that the irradiation with 1250—2000 Å excites the fluorescence spectrum of iodine. They concluded that the process was as follows:

$$CH_2I_2 + h\nu \longrightarrow CH_2 + I_2^* \qquad (4)$$

Therefore, it is likely that methylene is formed primarily in the present system by photolysis.

It is also of interest to observe the ESR spectrum of the free methylene radical formed in the present system. The methylene radical is triplet in its ground state; its ESR spectrum has been observed by Bernheim *et al.*[12)] and by Wasserman *et al.*,[13)] who have reported the values of spin-spin interaction as $D=0.7$—$0.9\ \mathrm{cm}^{-1}$ and $E \cong 0.03\ \mathrm{cm}^{-1}$. However, no spectrum could be detected up to 10000 G in the present experiments except for that shown in Figs. 1 and 2. If the motion of the radical is random and rapid enough to average out such a large spin-spin interaction, it may be possible to observe the spectrum of the radical in the near $g=2$ region. In this case, however, the spectrum is expected to be rather isotropic in its hyperfine structure, unlike the spectrum shown in Fig. 1, even though the hyperfine splittings due to the protons of free methylene are comparable to that measured from the observed spectrum.[*1] Further, a preferential rotation of the radical around any axis may not cancel out the fine structure in the spectra of the randomly oriented powder specimens. Therefore, the spectrum shown in Fig. 1 could not be identified with that of the free methylene radical.

In the identification of the spectrum, a possibility of another radical, CH_2I, which may be formed by Process (1), may be excluded, because there seems to be no evidence for any further splitting or line-broadening due to a magnetic iodine nucleus ($\mathbf{I}=5/2,\ 7/2$).

The observed spectrum of Fig. 1 is very similar to that of ≡Si–O–CH_2 reported by Melamud *et al.*,[8)] who obtained the radical by the photolysis of methylated Vycor glass. Therefore, although the radicals on Vycor glass were more stable and although the line-shape of the outer components was slightly different from the present one, the radical species observed in the present experiments may also be ≡Si–O–CH_2 formed by processes on the silica gel surface subsequent to the photolysis, as will be discussed later.

It may readily be seen in Fig. 1 that the spectrum consists of three lines, *i.e.*, the intense, symmetrical, and sharp line in the center and two other asymmetric lines, suggesting the presence of two equivalent protons with axially-symmetric hyperfine tensors. The spectrum was then simulated with the aid of a HITAC 8700 computer, using a Fortran IV program that solved the spin Hamiltonian:

$$H = \beta \mathbf{H}\tilde{g}\mathbf{S} + \mathbf{I}\tilde{\mathbf{A}}\mathbf{S}$$

to the second order in hyperfine interaction with a good approximation for the present purposes.[6)] The best-fitting spectrum (shown in Fig. 1) was thus obtained, assuming an isotropic g value ($g=2.0030$) and

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[*1] Acording to a recent calculation by T. A. Claxton (*Trans. Faraday Soc.*, **66**, 1537, 1540 (1970)), the isotropic hyperfine splitting due to a proton in the NH radical, which has two unpaired electrons, is about twice that in the single unpaired electron radical, NH_2. However, the values of the spin-spin interaction $(D,\ E)$[12,13)] reported predict the bent structure for the free methylene radical. This may reduce the isotropic hyperfine coupling of the protons, because in the bent structure s-p hybridization is positive; it may therefore cancel out the negative contribution of the π-electron to the hyperfine couplings.[13)]

Table 1. ESR parameters of Si–O–CH_2

	Observed	Calculated by Eq. (7)[a]
g	2.0030	
$\mathbf{A}_{/\!/}$	28.5±0.5 G	−27.4 G
$\mathbf{A}_{\perp}$	18.8±0.5 G	−18.4 G
$\mathbf{A}_{\mathrm{iso}}$	22.0±0.5 G	−21.1 G

a) In the case of CH_2COOH produced in a single crystal of $CH_2(COOH)_2$ two α protons were not equivalent because of its different crystalline environment. Therefore, the averaged values were used.

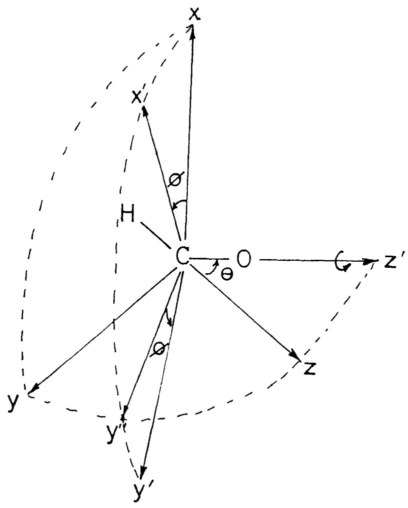


Fig. 3. Coordinate systems chosen for the transformation of hyperfine tensors from the principal system to the rotating system.

equal values of the hyperfine tensor ($\mathbf{A}_{\perp}=18.8$ G and $\mathbf{A}_{/\!/}=28.5$ G) for both protons, with a gaussian linewidth of 3 G. The parameters obtained in this way are listed in Table 1, where $\mathbf{A}_{\mathrm{iso}}$ was determined assuming that $\mathbf{A}_{\perp}$ and $\mathbf{A}_{/\!/}$ have the same sign.

The sharpness and the symmetricity of the central line show that when the two proton spins are antiparallel, the hyperfine anisotropy is cancelled out. This means that the two protons are magnetically equivalent and that the $-CH_2$ group reorients sufficiently rapidly for the hyperfine interaction by the protons to be averaged out over all the orientations of the $-CH_2$.

The averaged hyperfine coupling tensors can be obtained by first transforming from the principal-axis system to a coordinate system in which the rotation axis lies along the C–O bond, and then by rotating about this axis, as is shown in Fig. 3. The transformation is performed according to the following unitary relation;

$$\mathbf{A}_{\mathrm{r}} = \mathbf{U}\mathbf{A}^{0}\mathbf{U}^{-1} \tag{5}$$

where $\mathbf{A}_{\mathrm{r}}$ is the tensor for the rotating coordinate system and where U is the transformation matrix, which can be expressed by the angles, θ and ϕ, associated with the transformation between the two reference frames;

$$\mathbf{U} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \cos\theta\sin\phi & \cos\theta\cos\phi & -\sin\theta \\ \sin\theta\sin\phi & \sin\theta\cos\phi & \cos\theta \end{pmatrix} \tag{6}$$

One can obtain the following simple expressions for the tensor in the rotating system, as have been previously derived by the present author;[7)]

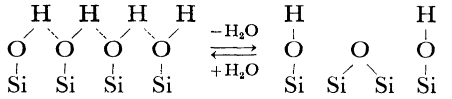
$$\begin{aligned} \langle \mathbf{A}^{\mathrm{r}}_{\mathrm{x'x'}} \rangle_{\mathrm{av}} &= \langle \mathbf{A}^{\mathrm{r}}_{\mathrm{y'y'}} \rangle_{\mathrm{av}} = 1/2(\mathbf{A}^{0}_{\mathrm{xx}} + \mathbf{A}^{0}_{\mathrm{yy}}\cos^2\theta + \mathbf{A}^{0}_{\mathrm{zz}}\sin^2\theta) \\ \langle \mathbf{A}^{\mathrm{r}}_{\mathrm{z'z'}} \rangle_{\mathrm{av}} &= \mathbf{A}^{0}_{\mathrm{yy}}\sin^2\theta + \mathbf{A}^{0}_{\mathrm{zz}}\cos^2\theta \\ \langle \mathbf{A}^{\mathrm{r}}_{\mathrm{x'y'}} \rangle_{\mathrm{av}} &= \langle \mathbf{A}^{\mathrm{r}}_{\mathrm{y'z'}} \rangle_{\mathrm{av}} = \langle \mathbf{A}^{\mathrm{r}}_{\mathrm{x'z'}} \rangle_{\mathrm{av}} = 0 \end{aligned} \tag{7}$$

where z′ is the rotation axis and where θ is the angle between the z axis in the principal system and the rotation axis. Apparently, these equations give the axially-symmetric tensor corresponding to the hyperfine coupling in the fast-rotating system, with

$$\langle \mathbf{A}^{\mathrm{r}}_{\mathrm{z'z'}} \rangle_{\mathrm{av}} = \mathbf{A}_{/\!/} \text{ and } \langle \mathbf{A}^{\mathrm{r}}_{\mathrm{x'x'}} \rangle_{\mathrm{av}} = \mathbf{A}_{\perp}.$$

It was not possible to obtain the principal values from the observed parameters and from those given by Eq. (7), for, in the present experiment, the spectrum of non-rotating $-CH_2$ could not be obtained. However, this type of radical may have a relatively narrow range of principal values whose principal axes are parallel to the C–H bond, perpendicular to the CH_2 plane, and parallel to the direction perpendicular to them. Therefore, using the values obtained for CH_2COOH trapped in irradiated single crystals of $CH_2(COOH)_2$[14)] and using Eq. (7), the rotationally-averaged values were obtained; they are listed in the second column of Table 1, where the HCH angle was assumed to be 120°.

According to the above discussion, the spectrum can be well explained in terms of the ≡Si–O–CH_2 radical formed on the silica gel. Therefore, it is of interest to consider the processes occurring on the surface. It has now been established by infrared studies[15)] that silica gel surfaces may possess both a "free" hydroxyl group and an "interacting" hydroxyl group, depending on their mutual distances. By dehydration at temperatures lower than 400 °C, the adsorbed water and part of the terminal hydroxyl group are eliminated to form both monomeric (free) and dimeric (interacting) surface hydroxyl groups, but most of the surface silanols remain. This process occurs reversibly; it can be shown as follows:



(8)

It has been established that evacuation at temperatures higher than 400 °C gives rise to an irreversible loss of surface hydroxyl groups, especially of interacting hydroxyl groups.[15)] This effect of the pretreatment upon the nature of the silica gel surface suggests the participation of the surface hydroxyl groups in the formation of the radical; this fact can be used in interpreting the observation of the spectrum shown in Fig. 1 upon the photolysis of the samples pretreated at lower temperatures and by admitting water vapor onto the silica gel pretreated at higher temperatures before the photolysis. Therefore, a possible mechanism for the formation of the radical is as follows:

A) methylene iodide photolized by 2537 or 1849 Å gives CH_2 and 2I and/or an excited iodine molecule, I_2^*; these iodine species then abstract hydrogen from the surface silanol to make it possible to form the $\equiv Si-O-CH_2$ radical through recombination, or

B) the recombination of CH_2 and the surface siloxy which was produced independently by the photolysis of the surface silanol.

Since the formation of atomic hydrogen from silica gel without methylene iodide was much less efficient than that of $-CH_2$ from methylene iodide, A) is more likely in this case.

The formation of CH_3 by the photolysis of condensed methylene iodide is possibly due to the abstraction of hydrogen from methylene iodide or to that of the surface silanol by the CH_2 formed primarily.

In conclusion, the photolysis of methylene iodide on the silica gel, which has surface hydroxyl groups, gives rise to the formation of the radical $-CH_2$ chemically bonded to the silica gel surface. The ESR spectrum of this radical observed at 77 K shows the anisotropic hyperfine structure to be expected from the axially-symmetric hyperfine interaction of two equivalent protons. The observed hyperfine splittings due to two protons can be reasonably explained by taking into consideration the free rotation of the methylene group.

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