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Electron Spin Resonance Study of the Radiolysis of Monocarboxylic Acids Adsorbed on Silica Gel

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Electron spin resonance measurements were carried out on γ-irradiated monocarboxylic acids (formic, acetic, and propionic acids) adsorbed on silica gel. In the case of formic acid, the spectrum assigned to the CO_2^- radical was mainly observed, but also observed was the signal caused by the defects of γ-irradiated silica gel, whereas for the acetic acid a quartet due to the methyl radical was obtained. These spectra, however, were not found in the frozen acids alone. As regards propionic acid, ethyl radicals were produced in both the adsorbed and frozen states. It was concluded from these results that the characteristic radiolysis of monocarboxylic acids on the adsorbed state is to be attributed to interaction between the acids adsorbed on silica gel as monomers and the surface. On the basis of these spectra, the adsorbed state of the acids and the stability of the radicals have been discussed.

The investigation of radicals adsorbed on solid surfaces seems to be of interest not only in the field of catalysis, but also in connection with the behavior of radicals on the surfaces.$^{1-4)}$ Recent studies of the radiolysis of substances adsorbed on insulators with high surface areas have indicated that the radiolysis yield is higher on the adsorbed state than on the homogeneous state as a result of the energy migration from the solid surface to the adsorbate.$^{5-7)}$ The behavior of hydrogen atoms and of methyl and ethyl radicals on silica gel has been studied by the ESR technique by Kazanskii *et al.*$^{8)}$ They have determined the state of the adsorbed radicals by an analysis of the hyperfine structure and the coupling constant; they have found that these radicals are much stabilized on silica gel in comparison with those in a solid matrix.

In connection with their reports, we have attempted a study of the radicals formed by the radiolysis of monocarboxylic acids adsorbed on silica gel. For the adsorbate which interacts with the surface by means of the hydrogen bond, the characteristic radiolysis due to the change in the electronic state can be expected, among other things, when the coverage is less than unity. For this purpose, the ESR technique was used to obtain information on the radicals of the adsorbed state and on the nature of their thermal motion.

Experimental

The silica gel was prepared from water glass and sulfuric acid. It was purified by washing and electrodialysis, and was then calcinated in the air for 10 hr at about 450°C. Its surface area was measured by the BET method (S=790 m^2/g). The formic, acetic, and propionic acids used as adsorbates were dehydrated and distilled by the ordinary method.

The silica gel was outgassed in a vacuum of 10^{-5} mmHg for 5 hr at 450°C. The adsorption isotherms of these three acids on the silica gel were then measured by using a thermo-balance. The amounts of these acids adsorbed in a complete monolayer film were determined from these isotherms. The gel in a sample tube was exposed to the vapor of acid in a vacuum. When the desired coverage was attained, the tube was sealed off. In such a way samples with various coverages were obtained. The γ-irradiation was carried out by exposure to a ^{60}Co source at −196°C. The sample tubes used here were of quartz glass for acid on silica gel and of spectrosil for acid alone. The ESR spectra were obtained by using a Japan Electron Optics Laboratory JES-3BS-X type ESR spectrometer. The magnetic field was modulated at 100 kc/sec, and the g-value was determined by comparison with the value for DPPH.

Results and Discussion

γ-Irradiated Silica Gel. The spectra of the silica gel irradiated at −196°C and at room temperature are illustrated in Figs. 1a and 1b respectively. The spectrum shown in Fig. 1a

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1) V. B. Kazanskii, G. B. Pariiskii and V. V. Voevodskii, *Discussions Faraday Soc.*, **31**, 203 (1961).
2) R. J. Kokes, *J. Phys. Chem.*, **66**, 99 (1962).
3) J. H. Lunsford and J. P. Jayne, *ibid.*, **69**, 2182 (1965).
4) C. L. Gardner, *J. Chem. Phys.*, **46**, 2991 (1967).
5) R. R. Hentz, *J. Phys. Chem.*, **68**, 2889 (1964).
6) J. G. Rabe, Birget Rabe and A. O. Allen, *ibid.*, **70**, 1098 (1966).
7) Yu. A. Sorokin, A. G. Kotov and S. Ya Pshezhetskii, *Zhur. Fiz. Khim.*, **40**, 2277 (1966).
8) V. B. Kazanskii, G. B. Pariiskii, I. V. Aleksandrov and G. M. Zhidomirov, *Fiz. Tverdogo Tela (USSR)*, **5**, 649 (1963).

consists of a doublet with the coupling constant of 506.5 gauss and broad lines. This is in good agreement with the spectrum reported by Kazanskii *et al.*[1] The doublet is due to hydrogen atoms formed by the cleavage of hydroxyl groups on the surface, while the broad lines are caused by residual oxygen radicals and by radiation defects in the irradiated silica gel.[9] The hydrogen atoms and residual oxygen radicals gradually decreased with a rise in the temperature and disappeared at a high temperature, while the defects were still present at room temperature. When the silica gel was irradiated at room temperature, only one singlet spectrum coincident with that of the defects appeared at $g=2.0009$, as is seen in Fig. 1b.

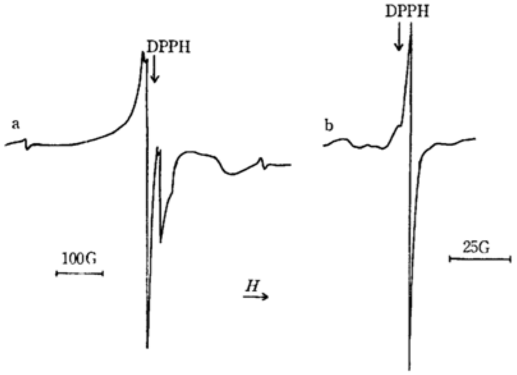
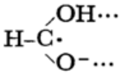
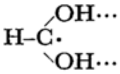
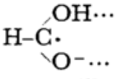
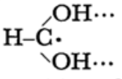


Fig. 1. ESR spectra of γ-irradiated silica gel (a) at liquid nitrogen temperature and (b) at room temperature.

γ-Irradiated Formic Acid Adsorbed on Silica Gel. The spectrum of the radicals which are produced by the radiolysis of the formic acid adsorbed on silica gel is different from that of formic acid alone (Fig. 2a, 2b). It has been reported regarding the X-irradiated formic acid that the radical,  $\mathrm{H{-}C}\cdot\begin{array}{l}\diagup\mathrm{OH}\cdots\\ \diagdown\mathrm{O^-}\cdots\end{array}$ or  $\mathrm{H{-}C}\cdot\begin{array}{l}\diagup\mathrm{OH}\cdots\\ \diagdown\mathrm{OH}\cdots\end{array}$, is formed by the radiation-induced reaction of the formic acid dimer.[10] The dotted lines indicate the hydrogen bond with the other molecule. From the close similarity of the spectrum obtained here to that previously reported, the spectrum shown in Fig. 2a can be assigned to the radical described above.

In the case of the adsorbed state, besides the defects of the γ-irradiated silica gel, another radical was formed, as is seen in Fig. 2b. In addition to these signal, a weak signal due to the radical,  $\mathrm{H{-}C}\cdot\begin{array}{l}\diagup\mathrm{OH}\cdots\\ \diagdown\mathrm{O^-}\cdots\end{array}$ or  $\mathrm{H{-}C}\cdot\begin{array}{l}\diagup\mathrm{OH}\cdots\\ \diagdown\mathrm{OH}\cdots\end{array}$, also appeared; this became still weaker with a decrease in the coverage.

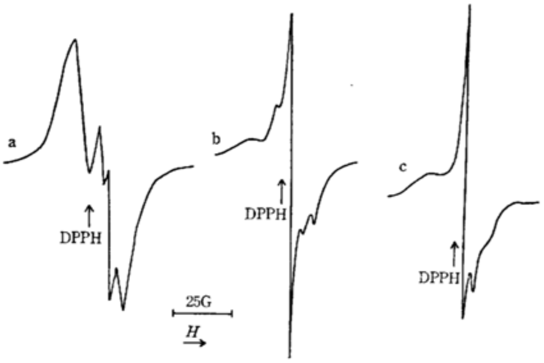


Fig. 2. (a) Spectrum of γ-irradiated formic acid, (b) spectra of γ-irradiated formic acid on silica gel at −196°C and (c) at −140°C.

The new signal became distinct at elevated temperatures as is seen in Fig. 2c. This radical may be assigned to the CO_2^- by a comparison of its g-value with the literature values.[3,11] The formation of carbon dioxide from the decomposition of formic acid was confirmed by gas chromatography. In view of the strong interaction of the formic acid monomer with the surface by means of the hydrogen bond,[12] it may be said that both the C–H bond and the O–H bond of the adsorbed acid were ruptured by γ-irradiation.

The formation of the CO_2^- radical was further studied as follows. Carbon dioxide was introduced to γ-irradiated silica gel. The ESR measurement was done while the sample was being irradiated with UV light.[*1] The spectrum was in complete agreement with that shown in Fig. 2c. Our results on the g-value for CO_2^- radical are summarized in Table 1, along with those obtained by other authors.[3,11]

TABLE 1. SUMMARY OF g-VALUES FOR CO_2^- RADICAL

	g_x	g_y	g_z
CO_2^- on MgO[a]	2.0029	1.9974	2.0017
CO_2^- in NaCOOH[b]	2.0032	1.9975	2.0014
CO_2^- on SiO_2	2.0024	1.9978	2.0024

a) Ref. 3 b) Ref. 11

γ-Irradiated Acetic Acid on Silica Gel. Acetic acid irradiated at −196°C gave a doublet with splitting of *ca.* 30 gauss (Fig. 3a). As the temperature was raised from −196°C, this doublet gradually changed into a quartet (Fig. 3b). The coupling constant of the quartet was *ca.* 15 gauss. These results are in good agreement with those reported by Miyagawa *et al.*[10] The doublet has

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9) H. W. Kohn, *J. Chem. Phys.*, **33**, 1588 (1960).

10) I. Miyagawa and W. Gordy, *J. Am. Chem. Soc.*, **83**, 1036 (1961).

11) D. W. Ovenall and D. H. Whiffen, *Mol. Phys.*, **4**, 135 (1961).

12) B. Imelik, J. Francois-Rassetti and P. Sigli, *J. Chim. Phys.*, **56**, 1048 (1959).

[*1] The details of this study will be reported later.

been assigned by them to the radical, $CH_3\dot{C}\begin{matrix}\diagup OH\cdots\\ \diagdown OH\cdots\end{matrix}$ or $CH_3\dot{C}\begin{matrix}\diagup OH\cdots\\ \diagdown O^-\cdots\end{matrix}$. The change in the spectrum may be due to the rotational motion of the methyl group of the radical at higher temperatures.

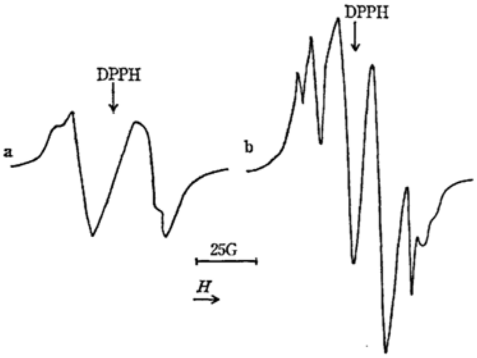


Fig. 3. Spectra of γ-irradiated acetic acid (a) at $-196°C$ and (b) at $-160°C$.

The spectrum of the irradiated acetic acid on silica gel (Fig. 4a) consists of a quartet superimposed on a broad doublet. Since the quartet has the coupling constant of *ca.* 23 gauss, it is assigned to the methyl radical. The formation of the methyl radical indicates that the cleavage of the C–C bond occurred on the adsorbed acetic acid. The intensity ratio of the methyl radical spectrum at the coverage $\theta=1$ was $1:4.3:4.7:1.3$, where θ is the fraction of the surface covered by the adsorbate. In comparison with the usual binominal coefficient ratio, the intensities of the central two components are too large. The central two components became sharp with a decrease in the coverage (Fig. 4b). The intensity ratios were $1:5.1:5.9:1.7$ at $\theta=0.15$ and $1:6.0:6.2:2.0$ at $\theta=0.04$. The abnormality in the intensity ratio suggests that the methyl radical interacts with the silica gel surface.

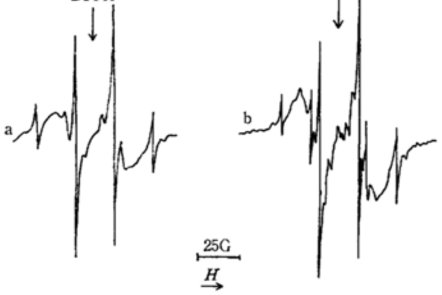
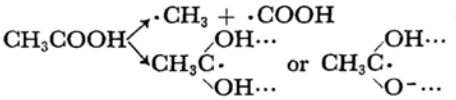


Fig. 4. Spectra of γ-irradiated acetic acid on silica gel (a) at $\theta=1$ and (b) at $\theta=0.15$.

In addition to the quartet and doublet, a signal due to the defects in the silica gel begins to appear with a decrease in the coverage. The spectrum of the ·COOH radical was not observed. The difference between the spectra in the frozen and adsorbed states might be explained as follows. It is well-known that acetic acid forms a dimer by means of the hydrogen bond. However, when the acetic acid was adsorbed on silica gel, the three hydrogens of the methyl group as well as the carboxylic hydrogen may interact considerably with the surface.[13] According to this view, the transfer of the electron from the carboxyl group to the surface and the reduction of the inductive effect of the methyl group due to the interaction with the surface would lead to the weakness of the C–C bond. If this effect is taken into account, the breakage of the C–C bond can be understood. The appearance of the quartet and doublet shows that the acetic acid adsorbed on the silica gel decomposes through the following two simultaneous processes:



$$CH_3COOH \begin{cases} \rightarrow \cdot CH_3 + \cdot COOH & (1)\\ \rightarrow CH_3\dot{C}\begin{matrix}\diagup OH\cdots\\ \diagdown OH\cdots\end{matrix} \text{ or } CH_3\dot{C}\begin{matrix}\diagup OH\cdots\\ \diagdown O^-\cdots\end{matrix} & (2)\end{cases}$$

The process (2) is considered to arise from the acetic acid, which interacts weakly with the surface.

In order to investigate the stability of the methyl radical, ESR measurements were made at various temperature. As the temperature was raised from $-196°C$, the intensity ratio of the quartet approached the binominal ratio. The radical continued to be present up to about $-60°C$. From these results it can be concluded that the methyl radical is initially fairly-well stabilized on the surface of silica gel but becomes mobile with a rise in the temperature.

γ-Irradiated Propionic Acid on Silica Gel. In the spectrum observed from the γ-irradiated

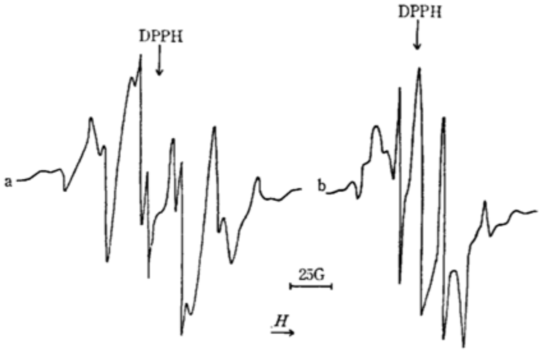


Fig. 5. (a) Spectrum of γ-irradiated propionic acid, (b) spectrum of γ-irradiated propionic acid on silica gel.

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[13] M. Shimizu and I. Higuchi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **81**, 1501 (1960).

propionic acid on silica gel (Fig. 5b), the singlet signal in the center seems to be due to the defects. With the exception of this singlet, this spectrum has a close resemblance to that of γ-irradiated propionic acid alone (Fig. 5a). The formation of the ethyl radical on the adsorbed state may be explained in the same way as in the case of acetic acid. However, because of the disappearance of the outer two components of the spectrum due to the ethyl radical on silica gel and the superposition of other radicals, it is impossible to discuss the adsorbed state of the ethyl radical.

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