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Electron Spin Resonance Studies of the Formation of Anion Radicals on γ-Irradiated Silica Gel

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The ESR spectra assigned to the anion radicals of SO_2^-, $(TCNE)^-$ (tetracyanoethylene), and O_2^- were obtained for, respectively, sulfur dioxide, TCNE, and oxygen when these gases were adsorbed on γ-irradiated silica gel. As regards sulfur dioxide, a characteristic change in the concentration of the SO_2^- radical was observed during the post-irradiation with high-energy UV light. In the case of carbon dioxide, the CO_2^- radical was produced only when UV post-irradiation was added to γ-irradiation. The assignments were principally made in comparison with the reported g-values. Especially, the identification of the CO_2^- radical was ascertained by using ^{13}C. The analyses of the g-factor for the O_2^- radical and of ^{13}C hyperfine constants for the CO_2^- radical gave information on the interaction of the radicals on a solid surface with the cations in the adsorption center. In view of the fact that each of these molecules possesses a different degree of electron affinity, the results described above indicate that the electrons trapped in the defects of the silica gel surface transfer to the adsorbed molecules and that UV light promotes the electron transfer.

The application of ESR spectroscopy to the study of the state of molecules adsorbed on solid surfaces has been of considerable interest since it permits an analysis of the radical species produced from the molecules. The radicals detected by this method are generally classified into two types by taking the properties of adsorbents into account: (1) neutral radicals adsorbed on insulators[1,2] and (2) anion radicals on n-type semiconductors.[3-5] In respect to the radicals of the first type, the adsorbent contributes mainly to the stabilization rather than to the formation of radicals. Those of the second type are produced as a result of electron transfer from the adsorbent to the adsorbate with a high electron affinity. However, Lunsford and Jayne[6,7] have recently found that such anion radicals as CO_2^- or O_2^- are produced even on UV-irradiated magnesium oxide, an insulator. They have concluded from their studies that the trapped electrons created by UV irradiation take part in the formation of the anion radicals. All the investigations using silica gel, which is also an insulator, have, however, dealt only with neutral radicals

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1) C. L. Gardner, *J. Chem. Phys.*, **46**, 2991 (1967).

2) V. B. Kazanskii, G. B. Pariiskii, I. V. Aleksandrov and G. M. Zhidomirov, *Fiz. Tverdogo Tela*, **5**, 649 (1963).

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4) A. I. Mashchenko, V. B. Kazanskii, G. B. Pariiskii and V. M. Sharapov, *ibid.*, **8**, 853 (1967).

5) I. D. Mikheikin, A. I. Mashchenko and V. B. Kazanskii, *ibid.*, **8**, 1363 (1967).

6) J. H. Lunsford and J. P. Jayne, *J. Phys. Chem.*, **69**, 2182 (1965).

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produced from the adsorbed-state molecules by γ- or UV-irradiation.[1,2]

In the present study, such anion radicals as SO_2^-, $(TCNE)^-$, and O_2^- were obtained from, respectively, sulfur dioxide, TCNE, and oxygen adsorbed on γ-irradiated silica gel. As for carbon dioxide, the CO_2^- radical was formed when UV post-irradiation was added to γ-irradiation.

Experimental

Materials. The method of the preparation of silica gel was described in the preceding paper.[8] Sulfur dioxide, oxygen, and carbon dioxide were purified by distillation under a vacuum. TCNE from the Wako Pure Chemical Co. was purified by sublimation.

Measurements. The silica gel was placed in a quartz tube fitted with a breakable seal and was outgassed in a vacuum of 10^{-5} Torr for 5 hr at 450—500°C. The tube was sealed off under a vacuum and then was irradiated at room temperature for *ca.* 15 hr with a ^{60}Co γ-source at a dose rate of 10^6 rad/hr. After the irradiation, the silica gel in a tube was exposed to sulfur dioxide, oxygen, carbon dioxide, or the vapor of TCNE through the breakable seal in a vacuum system. The ESR spectra were measured by a Japan Electron Optics Laboratory JES-3BS-X type ESR spectrometer operating at a cavity resonance frequency of 9400 Mc/sec with 100 kc modulation. The g-value was obtained by comparison with the value for DPPH. The error in g-value was estimated to be ± 0.0002.

A high-pressure mercury lamp equipped with a Toshiba UV-D25 or VY-42 filter and also a low-pressure mercury lamp were employed in order to examine the effects of UV irradiation. UV-D25 and VY-42 filters transmit the light between 2400 Å and 4000 Å, and that between 4200 Å and 6000 Å, respectively. Carbon dioxide containing 60.8 atom% $^{13}CO_2$ which had been obtained from the Ateledyne Co., was used to identify the radical species. The TCNE anion radical was confirmed by a study of the diffuse reflectance spectra in addition to ESR spectra.

Results and Discussion

The spectrum of silica gel irradiated at room temperature is shown in Fig. 1. It was previously identified as being due to the electrons trapped in the defects.[9,10] The g-value (2.0009) of the spectral line is smaller than that of the free spin, and this spectrum is apt to be saturated with microwave power. These results support the above assignment.

In view of the facts that the silica gel used here has a high surface area ($S=790$ m^2/g) and that the introduction of such a gas as sulfur dioxide results in the destruction of the defects, it seems reasonable that the electrons are trapped in the defects at the surface or its vicinity.

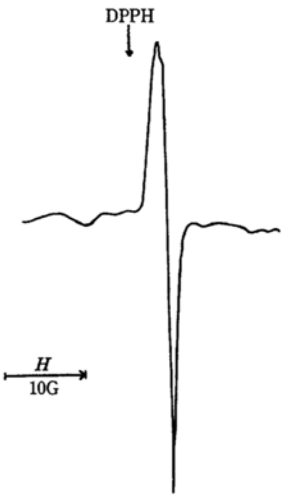

Fig. 1. ESR spectrum of γ-irradiated silica gel at room temperature.

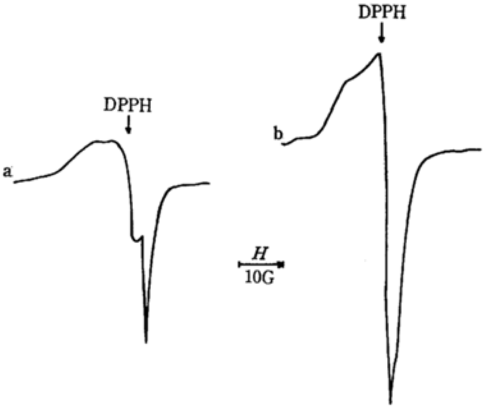

Fig. 2. (a) Spectrum recorded after sulfur dioxide was introduced at a pressure of 5 Torr to pre-irradiated silica gel, (b) spectrum recorded after sample (a) was irradiated with UV light for 5 min.

Sulfur Dioxide Adsorbed on Silica Gel. When sulfur dioxide was introduced into the silica gel at a pressure of 5 Torr, the gel, which had taken a faint violet color upon γ-irradiation, became colorless and a new ESR spectral line appeared, as is shown in Fig. 2a. This spectral line, however, did not appear on unirradiated silica gel. The values of $g_{\perp}=2.0018$ and $g_{//}=2.0079$ can be compared with those of the SO_2^- radical adsorbed on reduced titanium dioxide or zinc oxide.[3] On the basis of these results, the spectrum exhibited in Fig. 2a may be considered to be due to the SO_2^- radical. The formation of the SO_2^- radical on such semiconductors as titanium dioxide and zinc oxide has been interpreted as being due to the fact that the sulfur dioxide molecule, having a

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

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high electron affinity, easily accepts an electron from the adsorbents because of the narrow energy gap between the valence and conduction bands.[11] In the case of silica gel, therefore, it is probably the trapped electrons that transfer to the adsorbed sulfur dioxide molecules, since silica gel is a typical insulator.

The signal (g=2.0009) corresponding to the electron trapped in the defect still remains, though faintly, after the adsorption. However, post-irradiation with UV light leads to the disappearance of this signal and, at the same time, to an increase in the intensity of the ESR signal due to the SO_2^- radicals. The increment in SO_2^- radicals by UV light in two different ranges of wavelengths are presented in Fig. 3 as a function of the irradiation time.

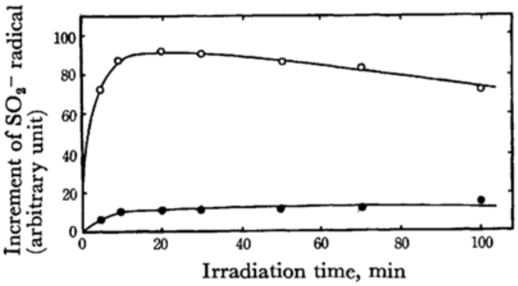

Fig. 3. The increment of SO_2^- radical by UV irradiation.

○: 2400—4000 Å (transmittance 60%)
●: 4200—6000 Å (transmittance 95%)

The illumination with light of wavelengths from 4200 Å to 6000 Å resulted in little increase in the radical. On the other hand, when light from 2400 Å to 4000 Å was used, the amount of the radical increased remarkably, though the short-wavelength light is more scattered than that of long wavelengths. Moreover, the increase in the radical reached a maximum after *ca.* 20 min and then decreased with the irradiation time. These results indicate that an energy higher than *ca.* 3 eV, which is equivalent to 4000 Å, is effective for the electron transfer. It has previously been reported that absorption spectra with peaks at 2.3, 4.1, and 5.6 eV appear on X-irradiated fused quartz,[12] the chemical composition of which is similar to that of silica gel. If these absorption bands are available to γ-irradiated silica gel, it should be mentioned, in view of the electron affinity of sulfur dioxide (2.8 eV), that even deeply-trapped electrons equivalent to 4.1 and 5.6 eV can migrate to the sulfur dioxide molecules on the surface upon UV illumination, supposing that the activation energy for the formation of the SO_2^- radical is overestimated.

The diminution in the radical concentration with the irradiation time can be interpreted if the following reactions are taken into consideration:

$$SO_2 + e^- \rightarrow SO_2^- \qquad (1)$$

$$SO_2^- \rightarrow SO_2 + e^- \qquad (2)$$

where e^- in Reaction (1) corresponds to an electron trapped in the defect, while that in Reaction (2) denotes an electron bleached. Namely, Reaction (2) should bring about a decrease in the radical concentration. Upon the illumination with the light from 4200 Å to 6000 Å, an appreciable increase in the radical amount was observed in the first stage, but it showed no change after *ca.* 20 min. It may be concluded from these facts that an energy less than *ca.* 3 eV contributes slightly to Reaction (1) through the transfer of the electrons trapped in the shallow potential at the first stage, but that it is inactive for Reaction (2).

TCNE Adsorbed on Silica Gel. When γ-irradiated silica gel was exposed to the vapor (10^{-2}—10^{-3} Torr) of TCNE for 10 hr, an ESR spectrum was obtained, as is shown in Fig. 4. On the other hand, no ESR signal was detected for unirradiated silica gel. The spectrum given in Fig. 4 is in good agreement with that of the TCNE anion radical formed when TCNE was adsorbed on alumina.[13] In order to identify the radical species further the reflectance spectrum of adsorbed TCNE was measured. The absorption band at *ca.* 420 mμ nearly corresponds to that of the TCNE anion radical in solution.[14] These results lead to the conclusion that the radical formed on silica gel is the TCNE anion. This is further supported by the characteristic features that TCNE has a high electron affinity and that the TCNE anion radical, as is well known, is stable even at room temperature. It seems reasonable that electron transfer is involved in the formation of the TCNE anion radical as in the case of the SO_2^- radical on silica gel. The spectral lines of the TCNE anion radical on silica gel are ill-resolved in contrast with those in solution, where four equivalent nitrogen atoms give nine lines as a result of interaction with the unpaired electron. This is explained by the fact that the anisotropy of the hyperfine structure arises from the lack of motional degrees of freedom. The signal due to the electrons trapped in the defects can scarcely be seen in Fig. 4, and the UV irradiation has no remarkable effect, different from the case of the SO_2^- radical.

Oxygen Adsorbed on Silica Gel. Oxygen was introduced at a pressure of 100 Torr to silica gel which had been irradiated by γ-ray at room temper-

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[11] V. B. Kazanskii and G. B. Pariiskii, 3rd International Congress on Catalysis, Amsterdam, 1964.

[12] R. Yokota, *J. Phys. Soc. Japan*, **7**, 316 (1952).

[13] K. Hirota, K. Kuwata and Y. Akagi, This Bulletin, **38**, 2209 (1965).

[14] W. D. Phillips, J. C. Rowell and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

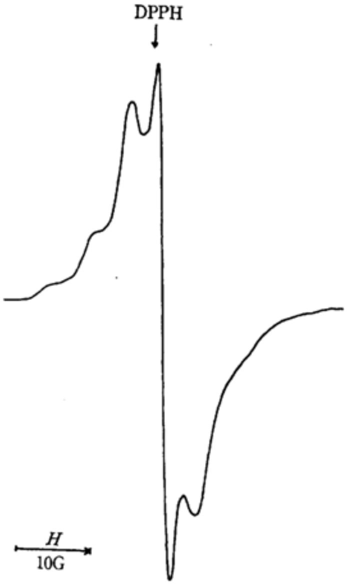

Fig. 4. Spectrum recorded after TCNE was introduced at a vapor pressure of 10^{-2}—10^{-3} Torr to pre-irradiated silica gel.

ature. A broad asymmetric spectrum appeared in addition to the signal responsible for the electrons trapped in the defects (Fig. 5a). The g-values of the new spectral line are $g_1=2.0250$, $g_2=2.0095$, and $g_3=2.0031$. Similar experiments have already been carried out by several investigators. Kazanskii *et al.*[10] showed that, for the sample outgassed at 200—300°C, the radicals formed by the cleavage of surface hydroxyl groups react with oxygens to produce the surface peroxide radicals ($g_1=2.025$, $g_2=2.002$, and $g_3=2.002$). In the case of the sample pre-treated at 500°C, however, they did not discuss the weak, different ESR spectrum formed by the introduction of oxygen to γ-irradiated silica gel. Since the present sample was outgassed at 450—500°C, the signal obtained here is considered not to be due to the surface peroxide radicals. As the matter of fact, the signal exhibited in Fig. 5a is identical with that observed under outgassing at 500°C by Kazanskii *et al.* Haul *et al.*[15] studied the effect of oxygen, nitrogen oxide, and a number of other gases on the ESR signal of irradiated silica under static and dynamic flow conditions. However, they did not find the new spectrum obtained here.

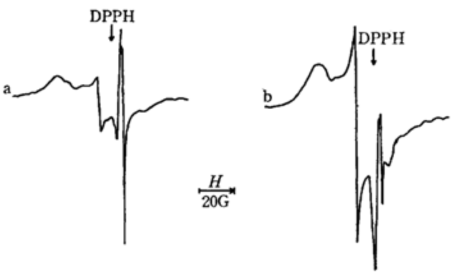

Fig. 5. (a) Spectrum recorded after oxygen was introduced at a pressure of 100 Torr to pre-irradiated silica gel, (b) spectrum recorded after sample (a) was irradiated with UV light for 30 min.

In order to elucidate the radical species corresponding to the asymmetric spectrum, a sample containing oxygen is irradiated by UV light for 30 min (Fig. 5b). The intensity of the spectral line is clearly enhanced. From these experiments and the assignment mentioned above for SO_2^- and $(TCNE)^-$, it may be concluded that the broad asymmetric spectrum is due to the O_2^- radical formed by the electron transfer from the solid to the adsorbed oxygen. This assignment is not necessarily inconsistent with the conclusions described above. The O^- radical may also be considered as a radical species. However, the g-values observed here are not suitable for the O^- radical reported,[16] and the energy required for the dissociation of O_2^- into

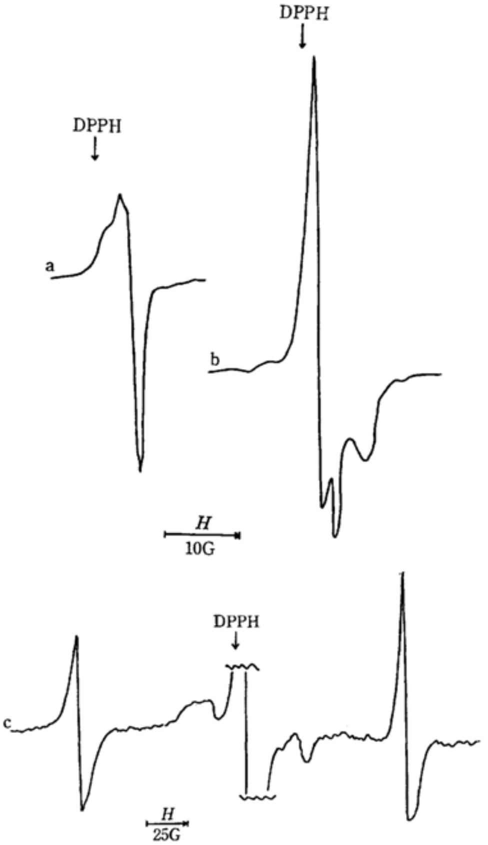

Fig. 6. (a) Spectrum recorded after $^{12}CO_2$ was introduced at a pressure of 100 Torr to the pre-irradiated silica gel, (b) spectrum recorded after sample (a) was irradiated with UV light for 30 min, (c) spectrum recorded at the similar condition to (b) with the exception of using the mixture of $^{13}CO_2$ 60.8 atom% and $^{12}CO_2$ 39.2 atom%.

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15) R. Haul, J. Karra and J. Turkevich, *J. Am. Chem. Soc.*, **87**, 2092 (1965).

$O+O^-$ is 4.1 eV,[17] an energy which is impracticable under the present experimental conditions. Therefore, the formation of the O^- radical should be excluded. After all, then, these discussions give strong evidence for our tentative identification.

Kazanskii *et al.*[5] pointed out, from their analysis of g-values, that the most probable state of the peroxide radical on silica gel and of O_2^- radicals on various solid surfaces is such that the O–O axis of these radicals is parallel to the surface. The analysis of the g-values obtained in the present case suggests that the O_2^- radical on silica gel is also adsorbed in such a situation.

Carbon Dioxide Adsorbed on Silica Gel. On the exposure of pre-irradiated silica gel to $^{12}CO_2$ gas at 100 Torr, the spectrum illustrated in Fig. 6a was observed. It is similar in shape to that of irradiated silica gel itself. With the UV irradiation, the shoulder grew, whereas the signal due to the electrons trapped in the defects was weakened (Fig. 6b). The g-values of the new spectral line ($g_1 = g_2 = 2.0024$ and $g_3 = 1.9975$) are in complete agreement with those of the CO_2^- radical reported in a preceding paper.[8] In this case, the UV light may contribute to the electron transfer since the electron affinity of carbon dioxide is much less than those of sulfur dioxide, TCNE, and oxygen. The spectrum, which was measured under the same conditions by using a mixture of 60.8 atom% $^{13}CO_2$ and 39.2 atom% $^{12}CO_2$, is illustrated in Fig. 6c. The ^{13}C hyperfine coupling constants evaluated from this spectrum are presented in Table 1, along with the values in the literatures. At the same time the experiment of Lunsford and Jayne[6] on the CO_2^- radical on magnesium oxide was repeated. The isotropic and anisotropic hyperfine constants obtained are almost identical with their results shown in Table 1, within the limits of experimental error. The values of a_s^2 and a_p^2, which give the unpaired electron density in the $2s$ and $2p$ orbitals respectively of the carbon atom, were calculated by analogy with Ovenall and Whiffen's article.[18] These values correspond to the isotropic and anisotropic parts of ^{13}C coupling.

Coulson[19] introduced the following formula for the bond angle of such molecules as CO_2^- and NO_2:

$$\cos\theta = -\lambda^2/(2+\lambda^2) \tag{3}$$

where θ denotes the OCO bond angle and λ, the ratio of a_s to a_p. The bond angle of the CO_2^- radical on γ-irradiated silica gel was determined by the use of Eq. (3). The value of the hyperfine splitting constant introduces some error (±8G) because of the overlapping of the anisotropies of g-factors and hyperfine constants. The bond angle of the CO_2^- radical on silica gel is much less than that on magnesium oxide, as is obvious from Table 1. The narrowing of the OCO bond angle of the CO_2^- radical on silica gel may be attributed to the characteristic adsorption: the separation of silicon atoms on the silica gel surface is smaller than that of magnesium atoms on the magnesium oxide surface. The narrowing of the OCO angle should also have an influence upon the molecular orbitals of the CO_2^- radical. The OCO angle of the CO_2^- radical may be expected to become narrow as the energy gaps between $3b_2$ and $4a_1$ and between $2b_1$ and $3b_2$ in the energy levels of the CO_2^- radical molecular orbital become large. Accordingly, the $4a_1 \leftarrow 3b_2$ and $2b_1 \leftarrow 3b_2$ promotions are reduced. The $4a_1 \leftarrow 3b_2$ and $2b_1 \leftarrow 3b_2$ contribute to the deviation of the values of g_1 and g_2 respectively from the value of free spin. Thus, the narrowing of the OCO angle results in the approach of g_1 and g_2 to the value of the free spin. The experimental result ($g_1 = g_2 = 2.0024$) is consistent with these considerations.

In conclusion, it was found that the anion radicals are formed by introducing such gases as sulfur dioxide, TCNE, and oxygen to γ-irradiated silica gel. As for the CO_2^- radical, it was formed by UV irradiation in addition to γ-irradiation because carbon dioxide has a low electron affinity. The O_2^- radical seems to be adsorbed in such a state that the O–O axis is parallel to the gel surface. In addition, the analysis of the ^{13}C hyperfine constants for the CO_2^- radical gave a closer OCO angle than that of the CO_2^- radical on magnesium oxide. This finding may be ascribed to the difference in the crystal radii of the cations on the solid surface.

TABLE 1. HYPERFINE COUPLING CONSTANTS AND PARAMETERS FOR CO_2^- RADICAL

	Hyperfine coupling constants (gauss)				Parameters			
	A_x	A_y	A_z	A_{iso}	a_s^2	a_p^2	λ^2	θ
$^{13}CO_2^-$ in NaCOOH[a)]	156	151	195	167	0.14	0.66	4.71	134°
$^{13}CO_2^-$ on MgO[b)]	184[c)]	…	230	199	0.17	0.73	5.21	132°
$^{13}CO_2^-$ on SiO_2	199[c)]	…	215	204 (Estd. error ±8)	0.17	0.26	1.53	116°

a) Ref. 18
b) Ref. 6
c) It is impossible to distinguish between A_x and A_y.

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16) M. J. Blandmer, L. Shields and M. C. R. Symons, *J. Chem. Soc.*, **1964**, 4352.

17) E. R. S. Winter, *Advan. Catalysis*, **10**, 196 (1958).

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

19) C. A. Coulson, Victor Henri Volume Commemoratif, Contribution à l'étude de la Structure Moléculaire (1948), p. 15.