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Nature of the Acid Sites on the Surface of Silica-alumina. II. The Relation between the Acid Property of the Sites and the Photo-ionization of Polyacenes Adsorbed on the Surfaces

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The ESR and diffuse reflection spectra of the polyacenes adsorbed on the surfaces of silica gel, alumina, and silica-alumina were measured. The amount of the cation radicals generated on the surfaces was enhanced upon irradiation with UV light. This was interpreted in terms of the photo-ionization accomplished *via* a charge-transfer state by an absorption of $h\nu_{CT}$, which was expected to vary with the strength of the Lewis-acid sites. The rate of the radical formation was not the first order, and that of the annihilation was the second order only in the initial stage. These phenomena are discussed in connection with the heterogeneity of the acid properties on the surfaces.

It is well known that such polyacenes as anthracene and perylene cause an electron transfer and a proton transfer on the surface of silica-alumina, even in the absence of ultraviolet (UV) irradiation. This phenomenon is interpreted in terms of the interaction of these polyacenes with the strong Lewis-acid sites and the Brönsted-acid sites on the surface of silica-alumina. A number of studies of the acidity, activity, and structure of the acid sites have been done in connection with catalysis by such techniques as infrared, ESR, diffuse reflection, and gas adsorption.[1-4] From these studies, we know that some strong acid sites on the surface interact with the polyacenes even in the ground state;

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1) E. P. Parry, *J. Catalysis*, **2**, 371 (1963); G. Fabbri and G. Farne, *Ann. Chim.* (Rome), **56**, 309 (1966).

2) D. N. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, **86**, 749 (1964); G. M. Muha, *J. Phys. Chem.*, **71**, 633 (1967); B. R. T. Garrett, I. R. Leith, and J. J. Rooney, *Chem. Commun.*, **1969**, 222.

3) A. N. Terenin, V. A. Barachevskii, E. I. Kotov, and V. Kholmogorov, *Spectrochim. Acta*, **19**, 1797 (1963).

4) A. J. de Rosset, C. G. Finstron, and C. J. Adams, *J. Catalysis* **1**, 244 (1962).

the cation radical is formed by an electron transfer from the polyacenes to the surface, and the carbonium ion is generated by a proton transfer from the surface to the polyacenes. Terenin and his co-workers have found that the formation of the cation radical on the surface is enhanced by UV irradiation.[5] This may show that the electron transfer occurs even on the weaker acid sites upon irradiation with UV light. As has previously been reported,[6] the acid properties of silica-alumina, alumina, and silica gel have been fairly well revealed. It is, therefore, of great interest to study the photo-ionization of polyacene adsorbed on the surfaces in connection with their acid properties.

The polyacene adsorbed on the surface can be regarded as a surface complex. We take into consideration the charge-transfer state in order to explain the transition from a nonbonding type, D···A, to a cation and anion type, $D^{+}+A^{-}$, by UV irradiation, where D and A are a donor and an acceptor respectively. It is significant that the energy corresponding to the charge-transfer absorption band, $h\nu_{CT}$, caused by the interaction of the polyacene with the acid site varies with the strength of the acid site. The purpose of this work is to reveal; (1) the relation between the radical formation by UV irradiation and the acid property of the surface, and (2) the mechanism of the annihilation of the radical.

Experimental

Naphthalene and anthracene were purified by the sublimation method. Guaranteed perylene obtained from the Tokyo Kasei Co. was used without further purification. *n*-Hexane was purified by distillation, with several pieces of metallic sodium added to remove any moisture. The 12% silica-alumina, alumina, and silica gel were the same as those used in the preceding work.[6]

The polyacenes were adsorbed from their vapor phases or from the oxygen-free *n*-hexane solutions onto the surfaces of the silica-alumina, alumina, and silica gel. The source of UV light was an 1-kW high-pressure mercury arc. The ESR spectra were obtained by using a spectrometer described elsewhere.[7] The rate of the radical formation was determined from the increase in the relative intensity of the ESR signal on UV irradiation. The diffuse reflection spectra were measured by using a Hitachi-Perkin-Elmer 139 spectrophotometer, equipped with an attachment to measure diffuse reflection.

Results

ESR Spectra. When the surface coverage of polyacene was low and the coloration was just discernible, an ESR spectrum with nine well-resolved peaks was observed, as may be seen in Fig. 1; the hyperfine coupling constant and the *g*-value of the spectrum were 3.4 gauss and 2.0025 respectively. The spectrum was the same as that of the cation radical of polyacene, as was found by comparing the spectrum with that measured in a strongly oxidizing reagent.[8]

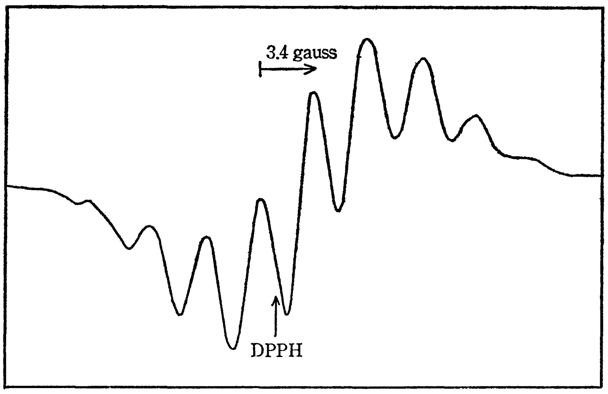

Fig. 1. ESR spectrum of the perylene cation radical adsorbed on the surface of 12% silica-alumina.

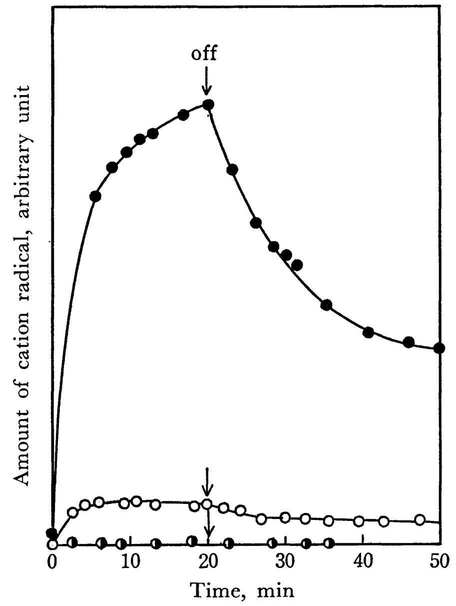

Fig. 2. Rates of the radical formation from naphthalene adsorbed on the surfaces of silica-alumina, alumina, and silica gel with UV irradiation.

●: 12% silica-alumina (G 320)
○: alumina (G 1400)
◑: silica gel (G 1400)

Figure 2 shows the rate of the radical formation from the naphthalene adsorbed on the surfaces of the silica-alumina, alumina, and silica gel which were treated at 300°C for 8 hr *in vacuo*. In the absence of UV irradiation, the cation radical of the naphthalene was formed only on the surface of the silica-alumina. Upon UV irradiation, the cation radical was generated also on the surface of the alumina, though it was not formed on the surface of the silica gel. The rates of radical formation by UV irradiation and its annihilation on the surface of the silica-alumina were faster than those on the alumina. The rate of the radical annihilation was considerably slower than that of the radical formation. The rates of the formation and annihilation of the radicals from the anthracene and perylene are

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[5] V. A. Barachevskii and A. N. Terenin, *Opt. i Spectroskopiya*, **17**, 304 (1964).

[6] M. Miura, Y. Kubota, T. Iwaki, K. Takimoto, and M. Muraoka, This Bulletin, **42** 1476, (1969).

[7] A. Hasegawa and M. Miura, *ibid.*, **40**, 2553 (1967).

[8] W. I. Aalbergsberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3055.

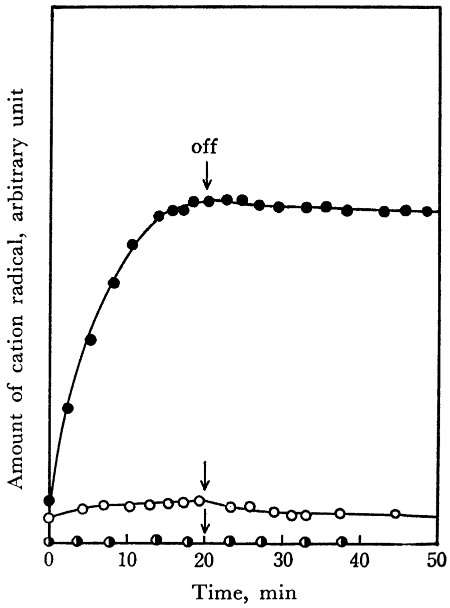

Fig. 3. Rates of the radical formation from anthracene adsorbed on the surfaces of silica-alumina, alumina, and silica gel with UV irradiation.
●: 12% silica-alumina (G 140)
○: alumina (G 1400)
◑: silica gel (G 1400)

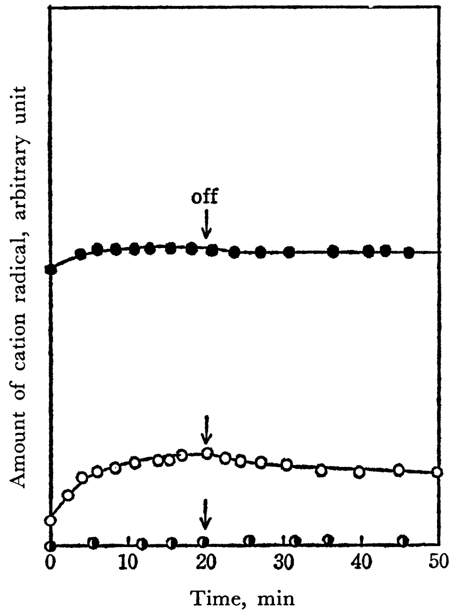

Fig. 4. Rates of the radical formation from perylene adsorbed on the surfaces of silica-alumina, alumina, and silica gel with UV irradiation.
●: 12% silica-alumina (G 10)
○: alumina (G 1400)
◑: silica gel (G 1400)

shown in Figs. 3 and 4 respectively. The formation rates of the radicals of these two polyacenes were faster than that of naphthalene. However, the ratios of the rates of the annihilation to those of the formation were small in comparison with that of naphthalene.

Diffuse Reflection Spectra. Figure 5 shows the diffuse reflection spectrum of the naphthalene adsorbed on the surface of the silica-alumina. Intense visible

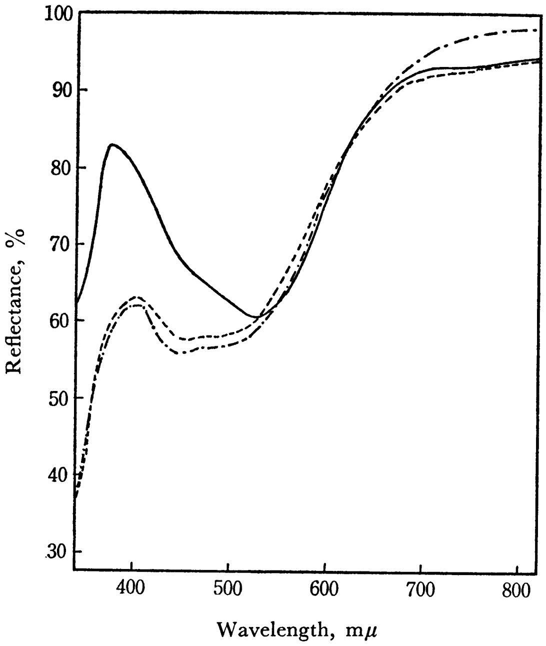

Fig. 5. Diffuse reflection spectra of naphthalene adsorbed on the surface of 12% silica-alumina.
—— in the absence of UV irradiation
---- UV irradiation for 30 min
•—• keeping in a dark room for a day after UV irradiation

bands at 440 and about 530 mμ, and a feeble band at 760 mμ were observed. Upon UV irradiation for 30 min, the absorption band at 440 mμ was remarkably enhanced, while the bands at 530 and 760 mμ scarcely changed. According to several authors,[9] the band at 430 mμ, corresponding to that at 440 mμ in this work, is to be ascribed to the carbonium ion, naphthalene$\cdot$H$^+$. On the other hand, the band at 530 mμ arises from the cation radical, naphthalene$^+$. The band at 760 mμ is attributable to the anion radical, naphthalene$^-$, which, in theory, must have the same band as that of the cation radical.[10] The structured bands below 320 mμ belong to physically-adsorbed naphthalene molecules. After the sample had been allowed to stand in a dark room for a day, the absorption maxima at 440 and 530 mμ increased a little, while the bands at wavelengths longer than 680 mμ slightly decreased.

The spectrum of the anthracene adsorbed on the surface of silica-alumina is shown in Fig. 6. The absorption bands appeared at 420, 560, 620, 660, and 720 mμ. The absorption maxima at 420 and 720 mμ may be assigned to the carbonium ion and the cation radical of the anthracene respectively.[9] The species for the weak absorption bands at 560, 620, and 660 mμ are not certain. The structured bands below 380 mμ arise from physically-adsorbed anthracene molecules. The absorption spectrum of the perylene adsorbed on the surface of the silica-alumina is shown in Fig. 7. The absorption bands are situated at 540, 610—620, and 730 mμ. After UV irradiation, the

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[9] V. Gold and F. D. Type, *J. Chem. Soc.*, **1952**, 2172.

[10] H. Kon and M. S. Blois, *J. Chem. Phys.*, **28**, 743 (1958).

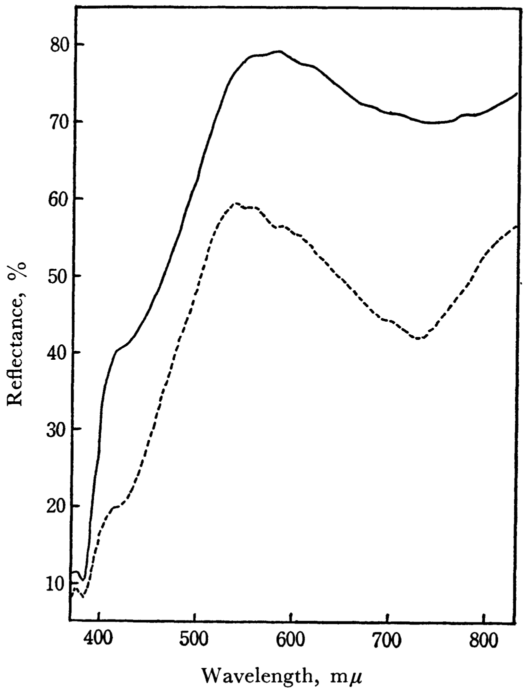

Fig. 6. Diffuse reflection spectra of anthracene adsorbed on the surface of 12% silica-alumina.
—— in the absence of UV irradiation
---- UV irradiation for 30 min

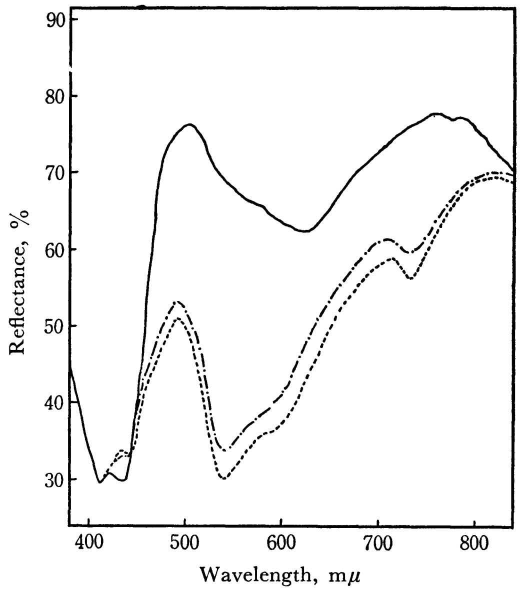

Fig. 7. Diffuse reflection spectra of perylene adsorbed on the surface of 12% silica-alumina.
—— in the absence of UV irradiation
---- UV irradiation for 30 min
·—· keeping in a dark room for a day after UV irradiation

maximum at 540 mμ increased significantly, while that at 730 mμ did so fairly much. These bands may be ascribed to the perylene cation radical. The bands below 450 mμ are due to physically-adsorbed perylene molecules.

Discussion

According to Mulliken's theory,[11] the wave functions of a surface complex may be represented by the following formulas:

$$\Psi_{\mathrm{G}}{}^{(i)} = a^{(i)}\phi_{\mathrm{D}\cdots\mathrm{A}}{}^{(i)} + b^{(i)}\phi_{\mathrm{D}^+\cdots\mathrm{A}^-}{}^{(i)}$$

$$\Psi_{\mathrm{E}}{}^{(i)} = a^{*(i)}\phi_{\mathrm{D}\cdots\mathrm{A}}{}^{(i)} + b^{*(i)}\phi_{\mathrm{D}^+\cdots\mathrm{A}^-}{}^{(i)}$$

where $\Psi_{\mathrm{G}}{}^{(i)}$ and $\Psi_{\mathrm{E}}{}^{(i)}$ are the *i*th wave functions in the ground state and the excited state respectively, and $\phi_{\mathrm{D}\cdots\mathrm{A}}{}^{(i)}$ and $\phi_{\mathrm{D}^+\cdots\mathrm{A}^-}{}^{(i)}$ are the *i*th wave functions of the nonbonding type and the charge-transfer type respectively, among many wave functions of the complex which result from the heterogeneity in the strength of the Lewis-acid site on the surface.

When a polyacene was adsorbed on the surface of silica-alumina, the cation radical was formed even in the absence of UV irradiation. This indicates the presence of a considerable amount of the surface complex, whose coefficient, $|b^{(i)}|$, in $\Psi_{\mathrm{G}}{}^{(i)}$ is much larger than $|a^{(i)}|$. In other words, a large number of the strong Lewis-acid sites are present on the surface of silica-alumina. As the ionization potential of polyacene decreases, the amount of the cation radical generated on the surface in the ground state increases, as may be seen in Figs. 2, 3, and 4. This is due to an increase in the number of the charge-transfer-type functions, accompanied by a decrease in the ionization potential of polyacene.

The charge-transfer band corresponding to the transition from Ψ_{G} to Ψ_{E} could not be detected. This may be due to the band-broadening caused by the fact that the coefficients, $|a|$ and $|b|$, in Ψ_{G} can take various values. The energy of the charge transfer, $h\nu_{\mathrm{CT}}$, decreases as the electron affinity of the Lewis-acid site increases and as the ionization potential of polyacene decreases. The photo-ionization of the polyacene adsorbed on the site, the electron affinity of which has a low value as compared with that of the ionization potential of the polyacene, may be accomplished *via* a charge-transfer state by the absorption of $h\nu_{\mathrm{CT}}$. Thus, when polyacene adsorbed on the surface of silica-alumina was irradiated with UV light, the cation radical was formed even in the weak-acid site on the surface where it could not be produced in the absence of UV irradiation.

In the case of the alumina, the perylene and naphthalene adsorbed on the strong Lewis-acid sites are ionized by the transfer of the electron to the surface, while those adsorbed on the comparatively weak acid sites are also ionized *via* a charge-transfer state by means of UV irradiation. The amount of the radicals formed by the photo-ionization is, however, affected by the acid property of the surface. The difference between the amounts of the radicals produced on the surfaces of the alumina and the silica-alumina results not from the difference in the distribution of the acid sites, but from that in their number.[6,12] On the other hand, the naphthalene and perylene adsorbed on the surface of the silica gel were scarcely

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11) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952); *J. Amer. Chem. Soc.*, **74**, 811 (1958); *J. Chim. Phys.*, **61**, 20 (1963).

12) M. R. Basila, J. R. Kantner, and K. H. Rhee, *J. Phys. Chem.*, **68**, 3197 (1964).

ionized even with UV irradiation. This may be due to the lack of Lewis-acid sites on the surface.

When the energy level of a nonbonding type, D···A, rises to over the barrier or a charge-transfer state, the cation radical is generated. Its stability becomes higher as the electron affinity of the Lewis-acid site increases because the photo-ejected electron is stabilized on the site.

The rate of the radical formation was not the first order. However, the rate of the formation may be expected to be the first order, since the radical is formed by UV irradiation through the following process:

$$\mathrm{D\cdots A} \xrightarrow{h\nu} \mathrm{D^+\cdots A^-} \xrightarrow{\text{stabilization}} \mathrm{D^+ + A^-}$$

The deviation of the formation rate from the first order may be caused by the heterogeneity of the surface. The sites on the surface have a wide range of acidity and acid strength. Such a distribution of the acid sites may complicate the rate of the radical formation.

On the other hand, when the UV light was put off, the annihilation of the radical occurred. Two mechanisms for the annihilation may be considered:

$$(1)\quad \mathrm{D^+ + A^-} \xrightarrow{\text{reaction}} \text{other products}$$

$$(2)\quad \mathrm{D^+ + A^-} \xrightarrow{\text{recombination}} \mathrm{D\cdots A} + h\nu$$

When the sample was kept for a day after UV irradiation and again irradiated, the amount of the radical was restored almost to the initial value. Hence, the (2) mechanism seems to be predominant. The rate of the annihilation was the second order in the initial stage, while it became the first order in the later stage. The annihilation rate seems to be the second order, since the recombination of the cation radical with the trapped electron predominantly contributes to the rate process. The fact that the rate of the radical annihilation in the later stage is apparently the first order may be due to the distribution of the Lewis-acid sites. That is, the rate constant of the recombination may be different according to the strength of the Lewis-acid sites; the rate of the recombination of the radical with the photo-ejected electron becomes faster as the Lewis-acid site is weaker, and also as the ionization potential of polyacene is higher. As a result, the rate of the annihilation seems to deviate from the second order as the reaction proceeds. This may also explain why the rate of the annihilation of the radical is slow in comparison with that of the formation, and why the ratio of the rate of the annihilation to that of the formation is least for perylene among these three polyacenes.

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