BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2231—2233(1972)

The Nature of Acid Sites on the Surface of Silica-alumina. III. The Mechanism of the Photo-ionization of Perylene and Anthracene Adsorbed on the Surface of Silica-alumina

Kazuto TAKIMOTO and Masaji MIURA
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

(Received August 13, 1971)

The photo-ionization of various aromatic compounds has been extensively studied in solid matrices and solutions.[1–3] However, hardly no work on the dynamic behavior or the mechanism for the photo-ionization on solid surfaces has been done, although the identification and structure of the radicals generated on the surfaces by UV irradiation have been widely investigated.[4] The purpose of this work is to reveal the mechanism of the photo-ionization of polyacenes adsorbed on the surface of silica-alumina with Lewis-acid sites of various strengths.

Experimental

Anthracene, perylene, and 40% silica-alumina were used; they were the same as those used in our preceding work.[5] The polyacenes were adsorbed from their vapor phase on a silica-alumina surface pretreated at 500°C for 3 hr in a vacuum of 5×10^{-5} mmHg. The increase in the amount of the cation radical under irradiation of UV light was continuously measured by fixing the magnetic field at one of the peaks of the ESR spectrum. UV light was supplied from a 1-kW high-pressure mercury lamp or a 1-kW, point-source, superhigh-pressure mercury arc. The light intensity was controlled by means of nets of various meshes. The filters used were Toshiba UVD-25, UV-39, VY-42, and VY-46, while a Shimadzu-Bausch-Lomb Model 33-86-01 Mono-

---

[1] H. Tsubomura, *Nippon Kagaku Zasshi*, **89**, 1 (1967).

[2] W. A. Gibbons and G. Porter, *Nature*, **206**, 1355 (1965).

[3] G. E. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **44**, 3179 (1966).

[4] A. Terenin, *Advan. Catal.*, **15**, 227 (1964).

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

chromator was also used. The ESR spectra and diffuse reflection spectra were obtained by using, respectively, the spectrometer and spectrophotometer described previously.[6]

Results and Discussion

When perylene was adsorbed on the surface of silica-alumina from the vapor phase, an ESR spectrum with nine well-resolved peaks was observed. On the other hand, the diffuse reflection spectrum showed the absorption maxima at 540, 600, and 700 mμ.[4,6] These spectra are due to the cation radical of perylene. The increment of the cation radical with the irradiation time is shown in Fig. 1. The initial rate of the radical formation was approximately proportional to the intensity of the exciting light which includes wavelengths longer than 320 mμ, as may be seen in Fig. 2. In the case of anthracene, the situation was the same. These phenomena suggest that the photo-ionization of these two polyacenes proceeds through a single-photonic process on the silica-alumina surface.

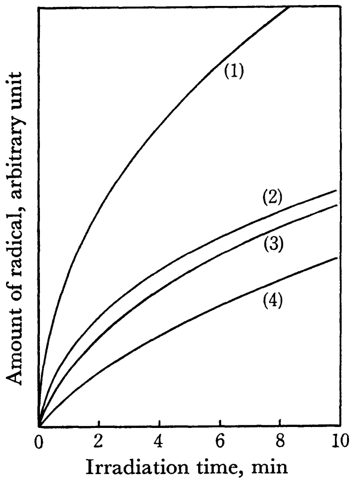

Fig. 1. Rates of the radical formation of perylene adsorbed on the 40% silica-alumina. Transmittancy of net (%): (1) 100, (2) 42.2, (3) 37.0, and (4) 14.0.

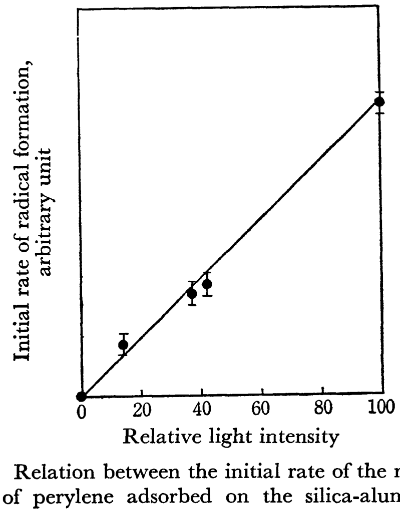

Fig. 2. Relation between the initial rate of the radical formation of perylene adsorbed on the silica-alumina and the intensity of exciting light.

Silica-alumina has Lewis-acid sites with various strengths; the strong acid sites exist in the range of $-3.0>H_0>-8.0$, while the weak ones exist in the range of $H_0>+3.0$.[5] The cation radical and the trapped electron are formed on the strong Lewis-acid sites even in the absence of UV irradiation and are stabilized on the surface.[6] A sort of charge-transfer complex with polyacene is formed on the weak Lewis-acid site even in the ground state.[6] Physically-adsorbed perylene which possesses absorption maxima at 410 and 430 mμ is present on much weaker Lewis-acid sites.[4,6]

The cation radicals of polyacenes were not formed in a sulfuric acid solution of 48 weight-percent, which corresponds to $H_0=-3.0$; the cation radicals are formed only in the range of $H_0<-3.0$ in the absence of UV irradiation. In addition, the amount of the cation radicals decreased markedly with an increase in the value of the ionization potential in the absence of UV light.[6] It may be considered, therefore, that the critical acid strength of the Lewis-acid sites required for the ionization of these polyacenes is situated in the range of $-3.0>H_0>-8.0$. The charge-transfer complexes and the physically-adsorbed polyacenes are presumably generated on the Lewis-acid site with an acid strength weaker than the critical value.

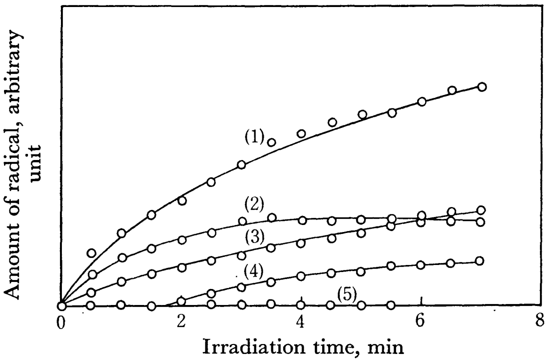

Fig. 3. Filter effect on the radical formation of perylene adsorbed on the silica-alumina: (1) full line, (2) UV-39, (3) UVD-25, (4) VY-42, and (5) VY-46.

The effect of the energy of the photon on the photoionization of the perylene adsorbed on the silica-alumina surface is shown in Fig. 3. The increment of the cation radical by using the VY-42 ($\lambda>420$ mμ) filter and a high-pressure mercury lamp was smaller than those caused by the use of the UV-39 ($\lambda>390$ mμ) and UVD-25 ($250<\lambda<400$ mμ) filters. When the VY-46 ($\lambda>460$ mμ) filter was employed during the irradiation of UV light from the same light source, no increase was observed. However, an increase was observed when the 1-kW, point-source, superhigh-pressure mercury lamp and the VY-46 filter were used. The VY-42 and VY-46 filters transmit the light of wavelengths longer than those absorbed by the physically-adsorbed perylene. The charge-transfer bands ($\lambda>480$ mμ) which are situated at wavelengths longer than those ($400<\lambda<450$ mμ) of the perylene physically adsorbed on much weaker Lewis-acid sites may exist even in the ground state, although they can not usually be observed because of the band-broadening

---

6) K. Takimoto and M. Miura, This Bulletin, **44**, 1534 (1971).

due to the broad distribution of the acid strength of the Lewis-acid sites on the silica-alumina surface.[6) These phenomena may indicate that the photo-ionization is caused by the absorption of photons with an energy corresponding to $h\nu_{\mathrm{CT}}$. On the other hand, the light of wavelengths absorbed only by the physically-adsorbed perylene was separated by the use of a monochromator. An increase in the amount of the cation radical was also observed here, though it was appreciable only with difficulty because of the low transmittancy of the monochromator. The cation radical was formed on the surface even by exciting the physically-adsorbed perylene which may be present on much weaker Lewis-acid sites.

The photo-ionization of polyacenes can possibly occur through the following two processes.1) In the case of the single-photonic process, the amount of the cation radical generated is proportional to the intensity of the exciting light, I, while in the case of the two-photonic process it is proportional to I^2. When a charge-transfer complex has been formed on the surface, the photo-ionization is accomplished through a single-photonic process. For the photo-ionization of these physically-adsorbed polyacenes, the following two processes may be considered: one through the triplet state as an intermediate (two-photonic process), and the other through the formation of a charge-transfer complex *via* a first excited singlet state of these polyacenes, resulting in the formation of the cation radical and the trapped electron (single-photonic process). The photo-ionization of these physically-adsorbed polyacenes probably takes place through the latter process, since the amount of the cation radical formed is approximately proportional to I.