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Photooxidation of the Evaporated Films of Polycyclic Aromatic Hydrocarbons Studied by X-Ray Photoelectron Spectroscopy

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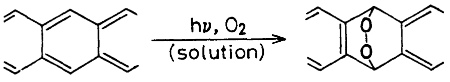
Photooxidations of the evaporated films of rubrene, naphthacene, and pentacene were investigated by means of X-ray photoelectron spectroscopy. A rubrene film was found to be photooxidized far more easily than a naphthacene film although the molecules of rubrene and naphthacene in solution are known to be almost equally reactive for photooxidation. Although pentacene is photooxidized very easily in solution, the oxidation rate of a pentacene film was little enhanced by the light irradiation. Discussion is given on these behaviors of the evaporated films by considering the molecular packing in the solid state and the mechanism of photooxidation.

Photoconductivities of polycyclic aromatic hydrocarbons are known to be influenced more or less by the presence of oxygen in the ambient atmosphere.[1] Frankevich and his collaborators investigated the magnetic field effect on the photoconductive behaviors of evaporated films of rubrene (5,6,11,12-tetraphenylnaphthacene)[2] and naphthacene[3] in the oxygen atmosphere.

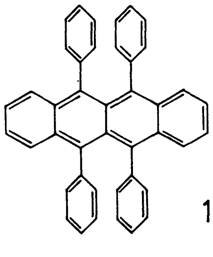
On the other hand, the photochemical reactions of polycyclic aromatic hydrocarbons with oxygen in solution have been extensively studied.[4,5] Polyacenes such as naphthacene and pentacene are rapidly converted to their transannular peroxides when their aerated solutions are irradiated with light.[4–6] Therefore one could expect that photooxidation will take place more or less when the photoconduction experiments are done on the solids of these hydrocarbons in the atmosphere containing oxygen.



However, little is known so far about the solid-state photooxidation of above-mentioned hydrocarbons except for rubrene.[7] This lack of information is largely due to the situation that, even if the photooxidation occurs in the solid state, it proceeds very slowly from the surface to the bulk in most organic solids, hence it is hard to follow the progress of oxidation by means of conventional experimental methods.

A variety of surface-sensitive techniques such as electron spectroscopies have developed since 1970's. However, they have scarcely been utilized in the studies of the reactions at the surfaces of organic molecular solids. Harada, Ohno and their collaborators examined the photooxidation of evaporated films of rubrene and naphthacene by ultraviolet photoelectron spectroscopy (UPS) and by Penning ionization electron spectroscopy (PIES).[8,9] They observed spectral changes due to photooxidation, and reported that a rubrene film is more easily photooxidized than a naphthacene film.

X-Ray photoelectron spectroscopy (XPS) is one of the most suitable techniques in such studies, because it can reveal non-destructively the elemental composition near the surface of molecular solids. We have previously studied the oxidation which proceeds in the dark, on the surfaces of the evaporated films of polycyclic aromatic hydrocarbons, by means of XPS.[10] In the present paper, we will report the results obtained on the photooxidation of the evaporated films of rubrene (**1**), naphthacene (**2**), and pentacene (**3**).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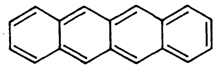
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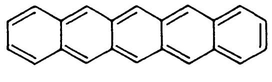
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Experimental

Rubrene and naphthacene were commercially obtained and purified by sublimation in vacuo. Pentacene which had already been purified, was kindly supplied by Professor H. Inokuchi, Institute for Molecular Science.

X-Ray photoelectron spectra were measured with a McPherson ESCA 36 photoelectron spectrometer by using Mg $K\alpha$ (1253.6 eV) as the stimulating radiation. The sample chamber of the spectrometer was a little modified for the purpose of the present study. The layout of the modified sample chamber is illustrated in Fig. 1(a).

On each hydrocarbon, we carried out experiments with the following sequence. With the setup shown in Fig. 1(a), the

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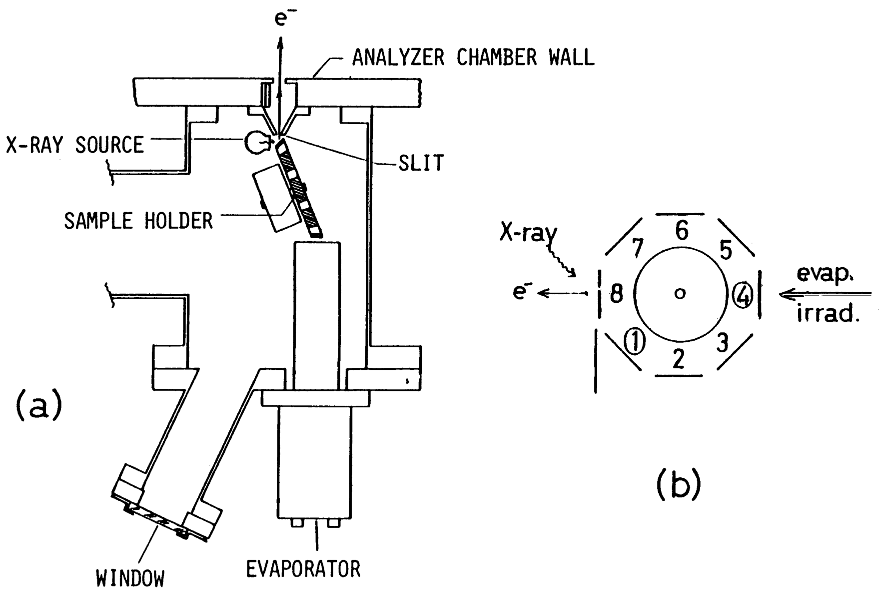

Fig. 1. (a) Layout of the sample chamber arranged for a photooxidation experiment, and (b) the side view of the 8-position sample holder. Sample films are prepared at the positions No. 1 and No. 4.

sample was deposited by sublimation in vacuo onto the substrates (aluminum or quartz plates) at the two different positions (No. 1 and No. 4 in Fig. 1(b)) of the 8-position rotatable sample holder, successively, and the first XPS measurement was done immediately. Then, the sample evaporator was quickly replaced with a Pyrex glass window while purging the sample chamber continuously with nitrogen. Since the oxidation of the sample film proceeds very slowly in the dark,[10] the above-mentioned procedure is allowable for the purpose of the present study even though we cannot completely avoid the contact of the sample film with oxygen. After the replacement of the evaporator with the window, the sample chamber was evacuated and the second XPS measurement was carried out. Next, we introduced oxygen to a desired pressure into the sample chamber, and one of the two sample films was irradiated with the light from a 500 W incandescent lamp through the window. During this procedure, the other sample film was sheltered from the light behind the sample holder. After the sample films were kept under the above-mentioned conditios for an appropriate period, the sample chamber was evacuated to carry out XPS measurement. Thereafter a similar procedure was repeated with different oxygen pressure and with different light irradiation time. The light irradiation was given to the two sample films alternately.

For each film, the binding energies, E_B's, were referenced to the Cls line (284.3 eV).[11]

Results

In the XPS spectra which were measured immediately after the preparation of the sample films under a high vacuum, all three hydrocarbons exhibited only a strong and sharp Cls peak, with the FWHM (full width at half maximum) of 1.5—1.7 eV.

Figure 2 illustrates the growth of the Ols peak in the spectrum of rubrene films at successive experimental stages. After the replacement of the evaporator with the window, both of rubrene films gave a weak Ols peak (see Fig. 2(b)). Figure 2(c) shows the Ols peaks measured after the films were kept in the oxygen of 1.5 kPa for 17 min, during which one film (at position

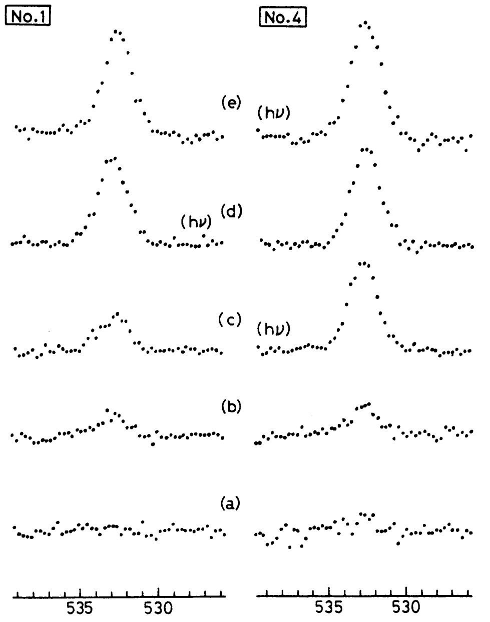

Fig. 2. Growth of the Ols peaks from two evaporated films of rubrene. "($h\nu$)" indicates the irradiated film at each stage. (a) Freshly evaporated films. (b) After replacement of the evaporator with the window. (c) After exposure to 1.5 kPa oxygen for 17 min, No. 4 irradiated for 10 min. (d) After exposure to 1.6 kPa oxygen for 19 min, No. 1 irradiated for 11 min. (e) After exposure to 5.7 kPa oxygen for 69 min, No. 4 irradiated for 60 min.

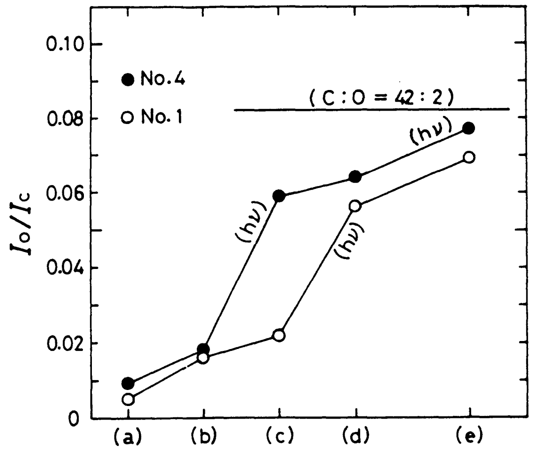

Fig. 3. Variation of the intensity ratios, I_O/I_C, for two evaporated films of rubrene. "(*hν*)" indicates the irradiated film at each stage. The line designated by "C:O=42:2" indicates the ratio expected for the transannular peroxide of rubrene. Note that the ordinate is expanded twice as compared to those in Figs. 4 and 5. (a)—(e) on the abscissa correspond to (a)—(e) in Fig. 2.

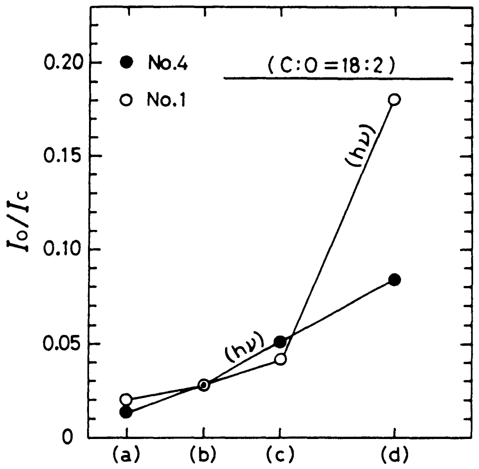

Fig. 4. Variation of the intensity ratios, I_O/I_C, for two evaporated films of naphthacene. (a) Freshly evaporated films. (b) After replacement of the evaporator with the window. (c) After exposure to 5.1 kPa oxygen for 67 min, No. 4 irradiated for 61 min. (d) After exposure to 12.9 kPa oxygen for 620 min, No. 1 irradiated for 605 min.

No. 4 of the sample holder) was irradiated with light for 10 min. Note that a pronounced intensity increase occurred in the case of the irradiated film, while the Ols peak of the nonirradiated film increased little. In the next stage, the films were kept in the oxygen of 1.6 kPa for 19 min, and the film (at position No. 1) which had not been irradiated in the previous oxygen exposure, was irradiated with light for 11 min. Then the Ols peak of the irradiated film appreciably increased its intensity, and the intensity of Ols peak became almost equal between the two sample films as shown in Fig. 2(d). These results clearly demonstrate that the oxidation of a rubrene film is markedly enhanced by the light irradiation. Figure 2(e) shows the spectra measured after an exposure to the oxygen of 5.7 kPa for 69 min, during which one film (at position No. 4) was irradiated with light for 60 min. As compared with Fig. 2(d), the change of Ols spectrum is very little both with and without the light irradiation. Seemingly the intensity of Ols peak had nearly saturated already in the preceding stage.

The ratio of the integrated intensity of the Ols peak to that of the Cls peak, I_O/I_C, was determined from the spectrum measured at each experimental stage. The results are plotted in Fig. 3, where the horizontal line designated by "C:O=42:2" represents the value expected for the transannular peroxide of rubrene under the assumption that the relative sensitivity of detection for carbon and oxygen is 0.58 : 1.00.[12] Note that the ratio obtained in the final stage is close to the value mentioned above.

The corresponding data for naphthacene and pentacene films are shown in Figs. 4 and 5, respectively.

In the case of a naphthacene film, the I_O/I_C ratio was far below the value for the transannular peroxide even after the 61 min light irradiation in the oxygen of 5.1 kPa. It approached to the latter ratio when a film was irradiated for about 10 hours in the oxygen of 12.9 kPa. Thus markedly severer conditions seem to be necessary to photooxidize a naphthacene film as compared with a rubrene film.

The behavior of a pentacene film is very different from those of naphthacene and rubrene films. As can be seen from Fig. 5, the oxidation of a pentacene film is enhanced only little by the light irradiation, and the I_O/I_C ratio was still about half of the value expected for the transannular peroxide even if the film had been irradiated with light for 9 hours in the oxygen of 14.4 kPa. It is hard to make a quantitative comparison of

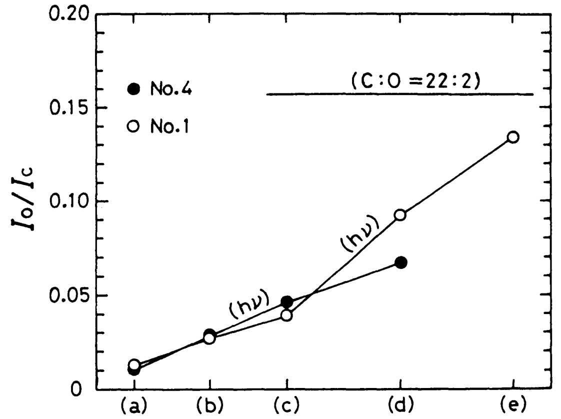

Fig. 5. Variation of the intensity ratios, I_O/I_C, for two evaporated films of pentacene. (a) Freshly evaporated films. (b) After replacement of the evaporator with the window. (c) After exposure to 4.4 kPa oxygen for 146 min, No. 4 irradiated for 135 min. (d) After exposure to 14.4 kPa oxygen for 555 min, No. 1 irradiated for 540 min. (e) After kept in the air (dark) for 12 days.

photooxidation activities of three hydrocarbons from the results of the present study. But we may safely conclude that a pentacene film is far less reactive for photooxidation than rubrene and naphthacene films.

For the three hydrocarbons studied here, the binding energies of their C1s peaks are expected to be almost the same.[11] Furthermore, they will change little under our experimental conditions since, as seen in Figs. 3—5, less than two atoms among 18—42 carbon atoms in a molecule may be directly bound to oxygen atom in their oxidation products. Therefore, we utilized the C1s peak (284.3 eV) as the reference for the binding energy scale.

The observed binding energies, E_B's, and FWHM's of O1s peaks from oxidized hydrocarbon films are summarized in Table 1 together with the corresponding values of polycyclic carbonyl compounds. Note that the O1s binding energy is 532.5—532.7 eV in the case of the photooxidation products while it is 530.6—530.9 eV in the case of carbonyl compounds. This fact shows that carbonyl compounds are not the predominant products of photooxidation. In effect, the photooxidation product of rubrene in the solid state is considered to be the transannular peroxide[2,7–9] as is the case with photooxidation in solution.

The main photooxidation product is likely to be the transannular peroxide also in the case of a naphthacene film since the observed O1s binding energy is equal to the one observed of a rubrene film. But it is conceivable that some other oxidized species coexist in the case of a naphthacene film because the observed O1s peak is appreciably broader than that of a rubrene film. Probably, a part of the transannular peroxide is further transformed to more stable species. The O1s peak from an oxidized pentacene film is similar in position and width to that from a photooxidized naphthacene film. Some oxygen-containing species (including the transannular peroxide) may coexist on the surface of a pentacene film.

Table 1. Binding Energies and FWHM's of the O1s Peaks from Photooxidized Hydrocarbons and Polycyclic Carbonyl Compounds[a]

Compound	E_B/eV	FWHM/eV
Rubrene	532.7	2.3
Naphthacene	532.6	2.7
Pentacene	532.5	2.7
Anthraquinone	530.9[b]	1.7
Anthrone	530.9[b]	1.8
Mesonaphthodianthrone[c]	530.6[b]	1.7

a) Mg$K\alpha$ spectra of carbonyl compounds were obtained from the films freshly deposited in the sample chamber. b) The binding energy was referenced to the main C1s line, whose binding energy was assumed to be 284.3 eV. c) Phenanthro[1,10,9,8-*opqra*]perylene-7,14-dione.

Discussion

As we have already mentioned, the three hydrocarbons studied here form the transannular peroxides by the photooxidation in solution. The following scheme has been proposed for the self-sensitized photoperoxidation of aromatic hydrocarbons.[13,14]

$$M(S_0)+h\nu\rightarrow M^*(S_1) \tag{1}$$

$$M^*(S_1)\rightarrow M^*(T_1) \tag{2}$$

$$M^*(S_1)+O_2(^3\Sigma)\rightarrow M^*(T_1)+O_2(^3\Sigma) \tag{3}$$

$$M^*(T_1)+O_2(^3\Sigma)\rightarrow M(S_0)+O_2{}^*(^1\Delta) \tag{4}$$

$$M(S_0)+O_2{}^*(^1\Delta)\rightarrow MO_2\,[\text{peroxide}] \tag{5}$$

where $M(S_0)$, $M^*(S_1)$, and $M^*(T_1)$ are the hydrocarbon molecules in the ground, singlet excited and triplet excited state, respectively, and $O_2(^3\Sigma)$ and $O_2{}^*(^1\Delta)$ are the oxygen molecules in the ground and singlet excited state (0.98 eV above the ground state),[15] respectively. Recently, it was established that $O_2{}^*(^1\Delta)$ can be generated also by the following process.[16]

$$M^*(S_1)+O_2(^3\Sigma)\rightarrow M^*(T_1)+O_2{}^*(^1\Delta) \tag{6}$$

In an aerated solution, $M^*(S_1)$ is quenched by oxygen via the process (3) or (6) with a diffusion controlled rate,[13] the rate constant being of the order of 10^{10} dm^3 mol^{-1} s^{-1}. The process (4) which produces the singlet oxygen $O_2{}^*(^1\Delta)$ by the energy transfer from $M^*(T_1)$, is also known to proceed rapidly with a rate constant of about one-ninth of the diffusion controlled value provided that the triplet state of the hydrocarbon, $M^*(T_1)$, has an energy in the range of 1.2—1.9 eV (e.g., naphthacene and anthracene).[13,17] Thus once $M^*(T_1)$ is formed, $O_2{}^*(^1\Delta)$ is produced with a yield of about unity via the process (4) in an air-saturated solution. On the other hand, the rate constant of the process (5) which gives the transannular peroxide by the reaction between $M(S_0)$ and $O_2{}^*(^1\Delta)$ is significantly lower than the diffusion controlled value except for extremely reactive hydrocarbons such as pentacene: It has been reported to be 4.2×10^7, 1.2×10^7, and 4.2×10^9 dm^3 mol^{-1} s^{-1} for rubrene, naphthacene and pentacene, respectively.[18] Therefore, the overall photooxidation rate will be primarily determined by the rate constant of the process (5), and consequently, pentacene will be the most reactive, and the reaction rate will be comparable between naphthacene and rubrene.

However, the results described in the preceding section, show that the situation is quite different in the solid state: the photooxidation takes place most easily in a rubrene film, and least in a pentacene film.

If we take an analogy to the above-mentioned scheme of the photooxidation in solution, we can consider that the solid-state photooxidation proceeds by the interaction of a hydrocarbon molecule with a singlet oxygen, $O_2{}^*(^1\Delta)$, which is formed by the energy transfer to an oxygen molecule either from a triplet exciton or from a singlet exciton of the hydrocarbon solid.

It is known that triplet excitons are produced with high efficiency in a naphthacene crystal via the fission of a singlet exciton into two triplet excitons.[19] The same process takes place also in a rubrene crystal.[20] In the case of a naphthacene crystal, the interaction of a triplet exciton with oxygen[21] will occur only on the crystal surface, because naphthacene molecules are closely packed in the crystal,[22] so that it is difficult for oxygen molecules to diffuse into the bulk. It is well known that a transannular peroxide has a folded configuration whereas its parent hydrocarbon is planar. Close packing of molecules will hinder such large change of molecular shape, and consequently, retard the photooxidation. Therefore the oxidation will proceed only very slowly from the surface to the bulk. On the other hand, rubrene molecules are loosely packed in the crystal because of the four bulky, noncoplanar, substituents.[23] Thus oxygen molecules can easily diffuse into the bulk, and the formation of $O_2^*(^1\Delta)$[21] as well as that of the peroxide can occur not only on the crystal surface but also in the bulk. Furthermore, the distortion of the crystal lattice accompanying the formation of the transannular peroxide will easily take place in the bulk. Seemingly, these differences arising from the molecular packing in the crystal, are the origin of the significant difference in photooxidation reactivity between a naphthacene film and a rubrene film.

The fission of a singlet exciton to two triplet excitons can also take place in a pentacene crystal.[24] But, the energy of the triplet exciton[24] is lower than 0.98 eV and insufficient to produce a singlet oxygen by the energy transfer. Under this situation, a singlet oxygen $O_2^*(^1\Delta)$ is probably formed via the energy transfer from a singlet exciton to oxygen. This will primarily occur on the crystal surface since pentacene molecules are closely packed in the crystal to prevent the diffusion of oxygen into the bulk.[25] However, there will not be much probability that a singlet exciton reaches the crystal surface since the fission of the singlet exciton efficiently takes place in the bulk. Seemingly this explains why the oxidation of a pentacene film is little enhanced by the light irradiation though, in solution,[26] pentacene is photooxidized rapidly.

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