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Surface Oxidation of the Thin Films of Polycyclic Aromatic Hydrocarbons Studied by X-Ray Photoelectron Spectroscopy

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The oxidation of the surfaces of thin films of perylene, pentacene, violanthrene, and mesonaphthodianthrene on exposure to oxygen or to the air was studied by means of X-ray photoelectron spectroscopy. A perylene film was found to be the least reactive toward oxygen among the above four hydrocarbons. In the cases of pentacene and violanthrene films, a single, broad O 1s peak grew up with time over the period of a few months as the exposure to the air was prolonged. On exposure to oxygen, a mesonaphthodianthrene film exhibited the O 1s spectrum which apparently consisted of two peaks located at the binding energies, 531.0 and 532.9 eV respectively, and the peak at 532.9 eV reduced its intensity irreversibly on heating the film in a high vacuum, suggesting that it was the one associated with a loosely bound oxygen.

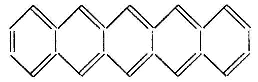
Semiconductive and photoconductive behavior of organic solids are often influenced considerably by the oxygen adsorption on the surface.[1] It is well known that the photoconductivity of anthracene crystal is significantly affected by oxygen.[2,3] In the cases of large polycyclic aromatic hydrocarbons such as mesonaphthodianthrene[4] and quaterrylene,[5]* their evaporated films were reported to exhibit quite different semiconductive behavior in the ordinary atmosphere as compared with those measured in a high vacuum. Generally, the surfaces of organic molecular crystals are rather unreactive to oxygen, so that one could consider that the oxygen species formed on their surfaces by the interaction with ambient oxygen would be primarily the oxygen molecules loosely bound on the crystal surface by physical adsorption. In effect, most of the observed oxygen effects on electrical properties of organic solids were found to vary reversibly depending on the ambient oxygen pressure. However, in some cases, the effects were not entirely reversible,[5] suggesting the formation of strongly-bound oxygen species or surface oxides.

Although a considerable amount of experimental results have been accumulated on the phenomena related to the influence of ambient oxygen on the electrical properties of organic solids,[1] little is known about the actual reactivities of the surfaces of organic crystals toward oxygen. In the present study, we have investigated the oxygen adsorption, or the surface oxidation of the thin films of polycyclic aromatic hydrocarbons by means of X-ray photoelectron spectroscopy.

Experimental

X-Ray photoelectron spectra were measured with McPherson ESCA 36 electron spectrometer employing Al K_α (1486.6 eV). The sample films were prepared by sublimation onto aluminum plates set inside the sample chamber of the spectrometer, which was kept at a vacuum of about 10^{-7} Torr by using a turbomolecular pump and a cryogenic pump. On each sample, the experiments were carried out according to the following steps. First, the C 1s and O 1s regions of Al K_α photoelectron spectrum were recorded immediately after the preparation of the sample film. A wide-scan spectrum was also recorded in order to see if the film was free from any impurity, and if the film was thick enough to prevent the appearance of any spectrum due to the substrate. After the above measurements, the cryogenic pump was switched off prior to the introduction of oxygen into the sample chamber. This inevitably caused a release of gases, including oxygen, from the cryopanel in the sample chamber. Thus, the C 1s and O 1s spectra were recorded again after this operation to examine the effects of the released gases. Then, the oxygen gas of a few hundred Torr was introduced into the sample chamber. After the sample film having been kept in this oxygen gas for 30 min, the oxygen gas was pumped out from the sample chamber to measure Al K_α photoelectron spectrum. In some cases, oxygen was again introduced into the sample chamber, and the film was continuously kept in the oxygen atmosphere for a night before the next measurement of the spectrum. After those experiments, the sample film was taken out of the spectrometer, and kept at a dark place in the ordinary atmosphere to examine the effect of prolonged exposure to the air. The C 1s and O 1s spectra of the sample film were observed occasionally over the period of a few months. Finally, a small amount of gold was deposited onto the sample surface for calibration of binding energies by use of Au $4f_{7/2}$ (84.0 eV) peak as the standard.

Experiments were done on four polycyclic aromatic hydrocarbons; pentacene(**1**), violanthrene(**2**),** perylene(**3**), and mesonaphthodianthrene(**4**).***



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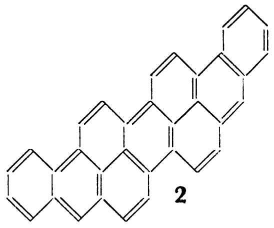

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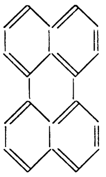

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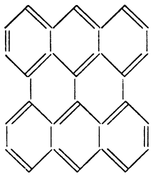

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Results and Discussion

It is well known that pentacene, $C_{22}H_{14}$, is quickly oxidized in the solution by the interaction with the oxygen dissolved in the solvent, particularly under the

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* Benzo[1,2,3-*cd*: 4,5,6-*c′d′*]diperylene.

** Dinaphtho[1,2,3-*cd*: 3′,2′,1′-*lm*]perylene.

*** Phenanthro[1,10,9,8-*opqra*]perylene.

action of visible light, to form a transannular peroxide.[6] However, it is quite stable in the crystalline state, so that the crystalline powder of pentacene can be kept in the ordinary atmosphere without significantly suffering the oxidation. The oxygen effect on the photoconductivity of a pentacene film was studied some years ago by one of the present authors.[7] It was observed that, when a pentacene film was exposed to an oxygen gas, the photocurrent through the film under a fixed light intensity gradually increased with time to the stationary-state value which was dependent on the pressure of the ambient oxygen. This oxygen effect was found to be almost reversible, suggesting that it was primarily associated with the oxygen molecules loosely bound on the surface.

The Al K_α photoelectron spectrum of a pentacene film before being exposed to the oxygen gas, did not exhibit any O 1s peak, showing only a strong and sharp C 1s peak (with the FWHM of about 1.7 eV) accompanied by weak satellite bands. When the film was exposed to the oxygen gas for about 30 min, a weak O 1s peak appeared in the photoelectron spectrum, and the intensity of this peak did not decrease at all even by keeping the film in a high vacuum (about 10^{-7} Torr) for a night. This fact indicates that, although the oxygen effect on photoconductivity is mostly reversible,[7] there are some oxygen species which can not be removed by a prolonged pumping from the surface of the pentacene film which has been once exposed to the oxygen gas.

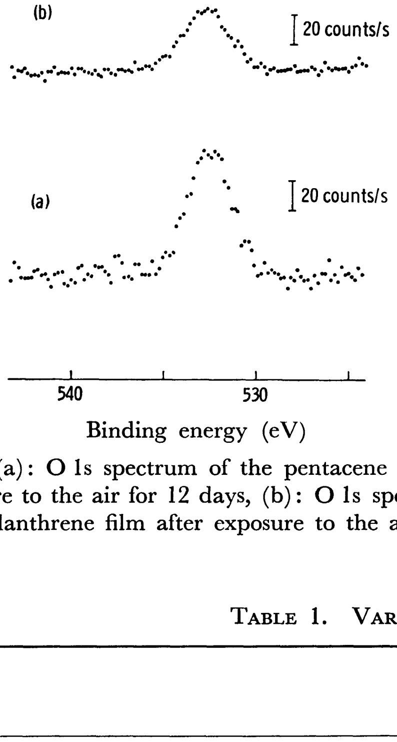

Fig. 1. (a): O 1s spectrum of the pentacene film after exposure to the air for 12 days, (b): O 1s spectrum of the violanthrene film after exposure to the air for 10 days.

On keeping the pentacene film in the air, the O 1s peak further grew up slowly with time. As shown in Fig. 1(a), the FWHM of this O 1s peak was 2.9 eV while a sample containing only a single kind of oxygen would give an O 1s peak with the FWHM of less than 2.0 eV under the same experimental conditions.[8] Thus the broadness of the observed O 1s peak is likely to indicate that there are more than one chemical states of oxygen atoms in the surface region of the pentacene film. In the photoelectron spectrum taken after 38 days' exposure to the air, the ratio of integrated intensity of the O 1s peak to that of the C 1s peak was found to be 0.099, which corresponds to the atom ratio, one oxygen atom per 22 carbon atoms,[9] in other words, one oxygen atom per one pentacene molecule. Since the escape depth of photoelectrons is of the order of two or three molecular layers of pentacene, the above results would possibly mean that every pentacene molecule on the surface is in the state bound with one oxygen molecule. The intensity ratios, O 1s/C 1s, obtained for the pentacene film at different stages of oxygen exposure are summarized in Table 1 together with the data concerned with other hydrocarbon films.

In the case of violanthrene, $C_{34}H_{18}$, the observed behaviors were a little different from those of a pentacene film. When a violanthrene film was exposed to the gases evolved from the cryopanel on turning off the cryogenic pump, there appeared a weak O 1s peak in the photoelectron spectrum of the film, but thereafter its intensity did not detectably increase on keeping the film in the oxygen gas for a night. The growth of the O 1s peak was so slow that we had to keep the film in the air for several days in order to attain an appreciable increase of its intensity. After the 38 days' exposure to the air, the intensity of O 1s peak relative to that of C 1s peak became 0.047, which corresponds to 0.7 oxygen atom per one violanthrene molecule. As in the case of a pentacene film, the observed O 1s peak was broad with the FWHM of about 3 eV as shown in Fig. 1(b).

The film of perylene, $C_{20}H_{12}$, was found to be the least reactive toward oxygen. Any O 1s peak did not appear in the photoelectron spectrum after the 10 min

Table 1. Variation of the intensity ratio, O 1s/C 1s

	Pentacene I_O/I_C[a]	Violanthrene I_O/I_C[a]	Mesonaphthodianthrene I_O/I_C[a]
(Fresh film)			(0.026)
After the cryogenic pump was switched off	0.006	0.013	0.030
After exposure to O_2 for 30 min	0.015	0.014	0.038
After exposure to O_2 for a night	not tried	0.017	0.055
After exposure to the air	12 days 0.062	10 days 0.035	17 days 0.090
	38 days 0.099	38 days 0.047	67 days 0.101

a) Ratio of the integrated intensity of the O 1s peak to that of the C 1s peak.

exposure to the oxygen gas. Even after having been kept in the air for six months, only a very weak O 1s peak appeared in the spectrum, its intensity relative to that of the C 1s peak being only 0.017.

The results described above demonstrate that the films of pentacene, violanthrene, and perylene are markedly different from each other as regards the reactivity toward oxygen. This difference seems to be closely related to the reactivity of the free molecule of each hydrocarbon. As it has been already mentioned, a pentacene molecule in the solution easily forms a transannular peroxide by the interaction with an oxygen molecule.[6)] But a transannular peroxide will not be so easily formed in the bulk of a pentacene crystal since its formation requires a large distortion of crystal lattice. This is likely to be the reason why the pentacene crystal can be stably kept in the ordinary atmosphere. However, the situation can be different for the crystal surface, where the change of molecular arrangement can occur more easily than in the bulk. Thus one could consider that the oxygen-containing species formed on the surface of the film on exposing to the oxygen gas is the transannular peroxide of pentacene. One could also consider the formation of other oxides of pentacene such as a quinone or hydroxy compounds. But the observed O 1s peak is too broad to be attributed to any one of these oxides. Possibly, several different kinds of oxides coexist on the surface. In the case of violanthrene, a model like the transannular peroxide is hard to be considered because of the molecular geometry. Possibly, a quinone and/or hydroxy compounds would be the chemical species formed on the surface of the violanthrene film.

An interesting behavior was observed in the case of mesonaphthodianthrene, $C_{28}H_{14}$, which is also known to be very reactive to oxygen.[10)] In the photoelectron spectrum of a fresh film, which was measured immediately after the preparation without breaking the vacuum, there appeared a weak O 1s peak at the binding energy of 531.0 eV (see the spectrum(a) of Fig. 2). This must be due to some impurity that originally existed in the powder of mesonaphthodianthrene. The above impurity is likely to be some stable oxide of mesonaphthodianthrene such as mesonaphthodianthrone.**** On exposure to oxygen, a new peak appeared on the higher binding-energy side (at 532.9 eV) of the first peak, as shown in the spectrum(b) of Fig. 2. This new O 1s peak can be attributed to the oxygen-containing species formed on the surface. The intensity of this new peak increased as the film was further exposed to the oxygen gas. However, at the same time, the intensity of the 531.0 eV peak increased by a larger extent, so that, after the 17 days' exposure to the air, the film showed the O 1s spectrum consisting of a strong peak at 531.0 eV and a shoulder at 532.9 eV (see the spectrum(d) of Fig. 2). After the 67 days' exposure to the air, the integrated intensity of the O 1s peak relative to that of the C 1s peak became 0.101 which corresponds to 1.3 oxygen atoms per one mesonaphthodianthrene molecule.

The O 1s spectrum of a mesonaphthodianthrene film once exposed to oxygen was found to vary with time. This behavior is illustrated by the spectra shown in Fig. 3. The spectrum(a) was obtained just after the exposure to oxygen for a night. The intensity of the 532.9 eV peak decreased when the film was kept in a high vacuum for 90 min, while that of the 531.0 eV

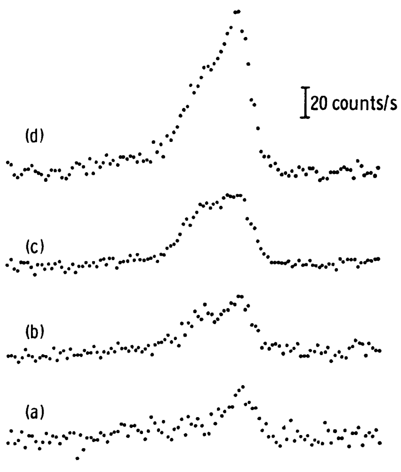

Fig. 2. Variation of the O 1s spectrum of the mesonaphthodianthrene film as exposures to oxygen or to the air were repeated.
(a): Immediately after preparation.
(b): After exposure to oxygen for 30 min.
(c): After exposure of (b) to oxygen for a night.
(d): After exposure of (c) to the air for 17 days.

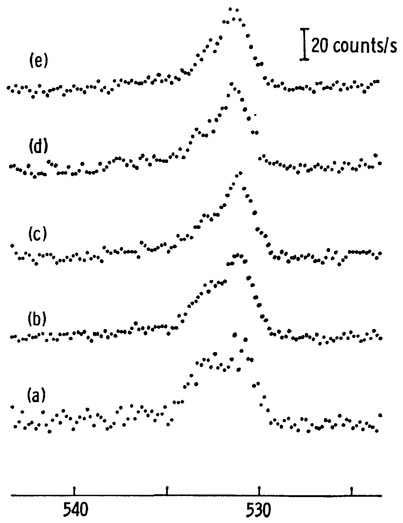

Fig. 3. Variation of the O 1s spectrum of the mesonaphthodianthrene film by heating it in the high vacuum of the sample chamber.
(a): The first recording at room temperature after exposure to oxygen for a night.
(b): Recorded at room temperature after standing (a) for 90 min.
(c): Recorded at about 60 °C.
(d): Recorded at about 100 °C.
(e): Reocrded again at room temperature.

**** Phenanthro[1,10,9,8-*opqra*]perylene-7,14-dione.

peak remained almost the same. This change became faster on elevating the temperature of the film to 60 °C and settled in the state which gave the spectrum(c). Thereafter, the O 1s spectrum did not further change on heating the film to 100 °C (the spectrum(d)), nor on cooling down it to room temperature (the spectrum (e)).

From the observation described above, we can conclude that there are at least two different kinds of oxides; the first is the species responsible for the O 1s peak at the binding energy of 532.9 eV, and the second is the one responsible for the 531.0 eV peak. Possibly the former is a metastable surface oxide where an oxygen molecule is rather loosely bound to a mesonaphthodianthrene molecule, and the latter is a stable oxide of mesonaphthodianthrene. The semiconductivity of a mesonaphthodianthrene film is known to be influenced by the oxygen adsorption.[4] It was observed that the electrical conductivity gradually increased with time in the oxygen gas, and decreased when the ambient oxygen gas was removed. These changes were found to be very slow at room temperature. Matsunaga reported that a sharp ESR signal appeared as the mesonaphthodianthrene powder was exposed to the air, and the intensity of this ESR signal increased slowly with time over the period of a few days.[11] It is most likely that the metastable surface oxide detected by X-ray photoelectron spectroscopy has some connection with the phenomena mentioned above. But, at present, it is hard to derive a definite conclusion as regards the true nature of this oxide.

References

1) F. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York (1966), pp. 197—214.

2) A. G. Chynoweth, *J. Chem. Phys.*, **22**, 1029 (1954).

3) A. Bree and L. E. Lyons, *J. Chem. Soc.*, **1960**, 5179.

4) H. Kuroda and E. A. Flood, *Can. J. Chem.*, **39**, 1475 (1961).

5) Y. Maruyama and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **39**, 1418 (1966).

6) E. Clar, "Polycyclic Hydrocarbons," Academic Press, Vol. 1, London (1964), p. 425.

7) H. Kuroda and E. A. Flood, *Can. J. Chem.*, **39**, 1981 (1961).

8) The evaporated film of hydroquinonc (cooled to about −50 °C) exhibited an O 1s peak with the FWHM of 1.9 eV under the same experimental conditions.

9) The relative sensitivity of detection for carbon and oxygen is taken as 0.46 : 1.00. This value was derived from gas-phase measurements of nitromethane, acetone, and phenol with the same instrument.

10) H. Kuroda, *J. Chem. Phys.*, **33**, 1586 (1960).

11) Y. Matsunaga, *Can. J. Chem.*, **38**, 323 (1960).