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PRESSURE-INDUCED REVERSIBLE PHOTO-REACTION OF PYRENE IN ALCOHOL SOLUTIONS

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Irradiation of alcohol solutions of pyrene under high pressure led to the formation of photoproduct which shows absorption and fluorescence bands similar to those of 3-hydroxypyrene. The photoproduct disappeared and absorption bands of pyrene recovered completely when the pressure was removed.

In the course of the study of effects of external high pressure on the behavior of the hydrocarbon-amine exciplex, we have found out a peculiar effect of external high pressures on the irradiation of alcohol solutions of pyrene.

The high-pressure optical cell was the same one as described before,$^{1)}$ and the applied pressure was ca. 5000 atm for all examined solutions. The solutions were irradiated at 337 nm ('La band). Light source was a Ushio 500 W Xe lamp. The monochromatic exciting light was taken out by a 250 mm Baush-Lomb monochromator. The absorption spectra were measured by means of a Cary 15 spectrometer. The fluorescence spectra were measured with an Aminco-Bowman spectrophotometer.

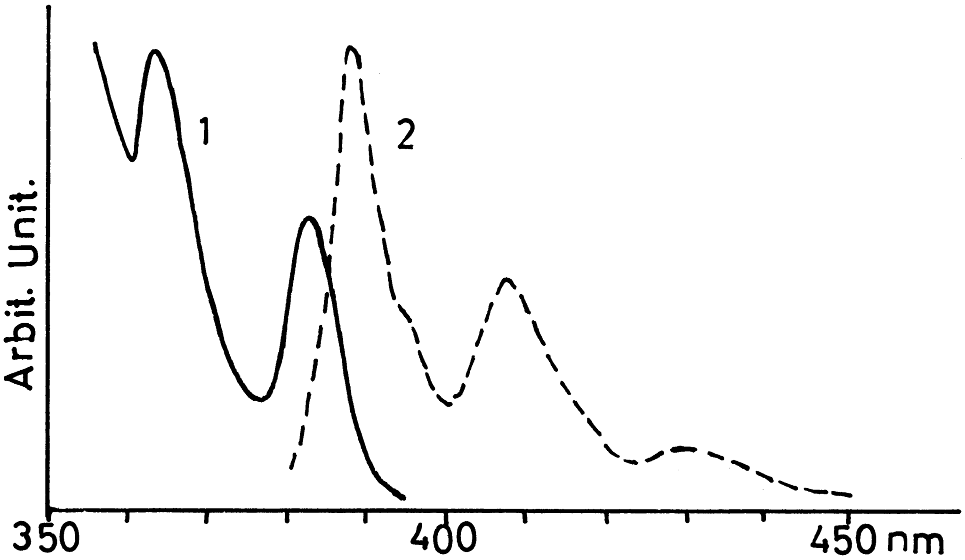

Fig.1. Absorption and fluorescence spectra of photoproduct in ethanol.
1. Absorption 2. Fluorescence

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Typical absorption and fluorescence spectra obtained in the case of the ethanol solution are shown in Fig.1, where the concentration of pyrene was 1.6x10^{-5}M. The solution for the absorption measurement was flushed with a nitrogen gas stream and irradiated at 337 nm for ca. 130 minutes while that for the fluorescence measurement was deaerated by the freeze-pump-thaw cycles and irradiated for 153 minutes, and the fluorescence of the photoproduct was excited at 365 nm. Although we deaerated these solutions, small amounts of dissolved oxygen remaining in the solution seem to be indispensable for the formation of the photoproduct since we have confirmed that the formation of the photoproduct is accerelated when the quantity of the dissolved oxygen is increased. On the other hand , we could not observe the formation of the photoproduct in n-hexane solution. Therefore, not only the dissolved oxygen but also alcohol appears to be playing an important role for the formation of the photoproduct. The observed spectra of irradiated solutions consist of both bands due to pyrene and photoproduct. The spectra indicated in Fig.1 were obtained by subtracting the bands due to pyrene from the observed spectra. At any rate, one can see that spectra in Fig.1 are rather similar to those of 3-hydroxypyrene.2)

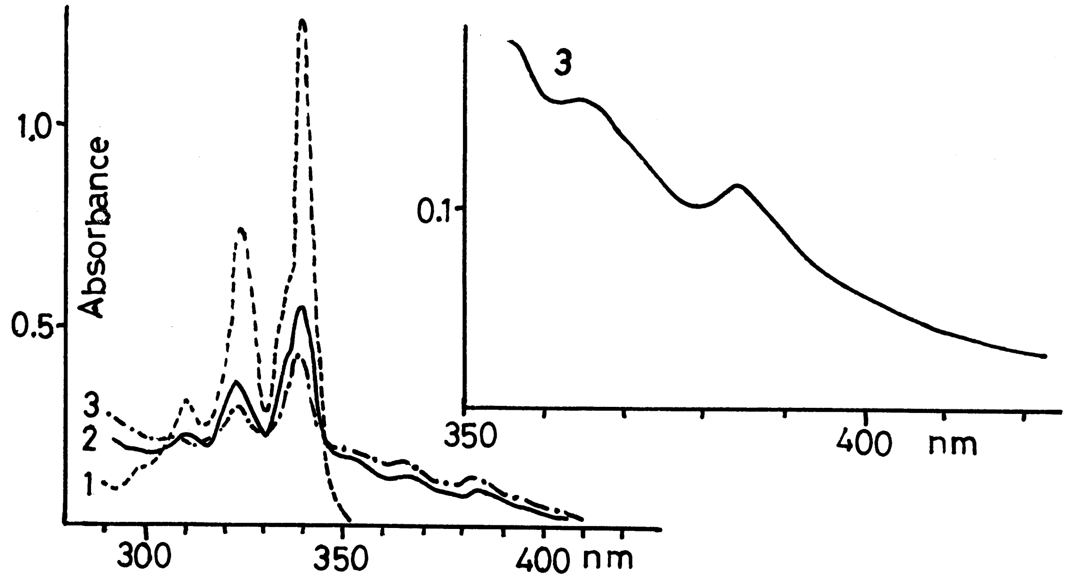

Fig.2. Absorption spectra of isoamylalcohol solution.
Irradiation time. (1) 0, (2) 30 min. (3) 50 min.

In Fig.2, the change of the absorption spectra of iso-amylalcohol solution caused by the irradiation is indicated. Although these spectra of the photoproduct are a little broadened compared to the spectra in Fig.1, the positions of the absroption peaks are the same. We can see clearly the isosbestic point at ca. 345 nm in Fig.2. Accordingly, there is a 1:1 correspondence between pyrene and the photoproduct.

The photoproduct is rather stable since its absorbance does not show any appreciable decrease when the irradiated solution is left in the dark under high pressure. However, the absorption bands due to the photoproduct disappears and those of pyrene recovers completely when the pressure is removed. Thus, the photoproduct is stable only under the high pressure.

The nature of the photoproduct is not very clear at the present stage of the investigation. It might be peroxide ROOH substituted at 3-position.

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1) Y. Torihashi, Y. Furutani, K. Yagii, N. Mataga and A. Sawaoke, Bull. Chem. Soc. Japan, 44, 2985 (1971).

2) See for example, R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, New York (1951) for the absorption spectra of 3-hydroxypyrene and, H. Beens, K. H. Grellmann, M. Gurr and A. Weller, Discuss. Farad. Soc., 39, 183 (1965), for its fluorescence spectra.

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