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PRESSURE EFFECTS ON FLUORESCENCE AND PHOTODIMERIZATION OF ANTHRACENE AND 9-METHYLANTHRACENE IN SOLUTION

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The relative values of photodimerization yields Φ_f and fluorescence yields Φ_f with anthracene and 9-methylanthracene were measured in *n*-hexane at room temperature under pressures up to 3,000 kg/cm². In anthracene where Φ_f has a slight pressure dependence, the apparent first order rate constant k_{obs} for photodimerization yield was approximately inversely proportional to the viscosity of the solvent. On the other hand, in 9-methylanthracene where Φ_f increases steeply with increasing pressure, k_{obs} did not decrease with pressure so much as predicted from the increase of the viscosity of the solvent. Considering the changes of Φ_f as the changes of lifetime τ_f of the lowest excited singlet state S_1 , the pressure dependences of photodimerization rate constants k_r were obtained according to the relation $k_{obs} = k_r \cdot \tau_f$. In 9-methylanthracene as well as anthracene k_r were nearly inversely proportional to the viscosity of the solvent. The remarkable effects of pressure on fluorescence yields also were discussed in view of the intersystem crossing from the S_1 state to the second triplet state T_2 .

Introduction

The effects of high pressure on the chemical reactions and the relaxation processes of excited molecules have been studied by several workers. With chemical processes, the pressure effects on the formation and dissociation of excimer in the lowest excited singlet state S_1 have been exclusively examined by fluorescence measurements¹⁻⁴). The effect of pressure on the rates for both formation and dissociation of excimer have been explained from the increase of the viscosity of the solvent due to increase of pressure^{2,4}). These results are qualitatively consistent with the prediction that bimolecular reactions in the S_1 state would be controlled by diffusion. The pressure effects on the relaxation processes from the S_1 state and the lowest triplet state T_1 have been investigated with various organic compounds in rigid solutions by measurements of lifetimes⁵⁻⁸). The decreases of lifetimes were observed in most of studied compounds with increasing pressure. But these interesting observations have

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not been explained completely.

The authors have been interested in the pressure effects on the photochemical reactions in solution⁹⁾. The present work concerns the pressure effects on the bimolecular reaction in the excited singlet state in relation to the influence of high pressure on its lifetime. It is confirmed that the photodimerizations of anthracene and its derivatives occur between an excited singlet molecule and a ground state molecule, and the reaction rates are controlled by diffusion^{10,11)}. The photodimerization yield at the low concentration is written by

$$\Phi_r = \frac{k_r[c]}{k_r + k_{ic} + k_{is}} = k_r \tau_f [c] = k_{obs}[c],$$

where k_r , k_f , k_{ic} and k_{is} are the rate constants for photodimerization, radiative process of fluorescence, internal conversion to the ground state and intersystem crossing to the triplet state, respectively, and τ_f is the average lifetime of the excited singlet state, and $[c]$ is the concentration of solution. It is predicted that k_r is approximately inversely proportional to the viscosity of the solvent according to a simple theory on the diffusion-controlled reaction. But because an apparent rate constant k_{obs} for photodimerization yield contains lifetime τ_f besides k_r , the pressure effect on τ_f must be made clear in order to obtain the pressure dependence of k_r . To know the influence of pressure on τ_f , the fluorescence spectra were measured under high pressure. The fluorescence yield at the low concentration where photodimerization is negligible is given by

$$\Phi_f = \frac{k_f}{k_f + k_{ic} + k_{is}} = k_f \tau_f.$$

If k_f is invariable with pressure, the change of Φ_f is equal to that of τ_f . Indeed, though k_f may be varied, for instance, by the increase of refractive index of the solvent with increasing pressure, its change is small in the pressure range up to 3,000 kg/cm² in this experiment, and the assumption that k_f is constant will not cause a large error. With anthracene and 9-methylanthracene k_{obs} and Φ_f were measured as relative values in *n*-hexane at room temperature at pressures up to 3,000 kg/cm² and pressure dependences of k_r were obtained. The result on fluorescence measurements showed that Φ_f increased very steeply with pressure in 9-methylanthracene, while it increased slightly in anthracene. The changes of Φ_f are also discussed in view of the pressure effect on the intersystem crossing k_{is} .

Experimental

Apparatus

The apparatus reported previously was improved⁹⁾. The cell for photochemical reactions and fluorescence measurements is shown in Fig. 1. The cell made of stainless steel is provided with three quartz windows and a teflon piston. In the case of fluorescence measurements, one sapphire window of

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the high pressure optical vessel⁹⁾ gave place to a coil of manganin wire for the direct measurement of pressure. As all of three sapphire windows are necessary for following the photochemical reaction yields spectrophotometrically, pressure cannot be measured simultaneously. In this case the correction for the Bourdon gauge was done. Silicone oil was used as pressure transmitting medium.

Materials

Commercial anthracene for scintillation and *n*-hexane of spectroscopic quality (Nakarai Chemicals, Ltd.) were used without further purification. 9-Methylanthracene was synthesized by the known method¹²⁾ and purified by recrystallization, column chromatography and sublimation.

Measurement of relative yield of photodimerization

The yields of photodimerizations were determined by following the disappearance of the typical absorption band at the longer wave length in anthracene and 9-methylanthracene. Reactions were carried out under practically total absorption, with the exciting light from 300 m μ to 400 m μ which was

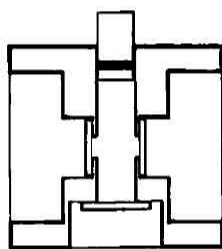


Fig. 1 The cell for photochemical reactions and fluorescence measurements

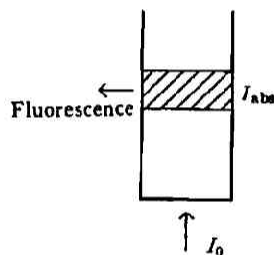


Fig. 2 I_0 : Intensity of incident exciting light
 I_{abs} : The amount of absorbed light in the shaded part

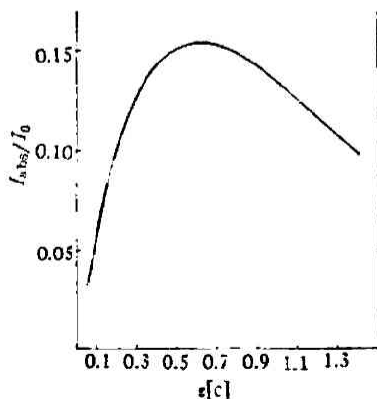


Fig. 3 The relation between I_{abs} and c

12) A. Sieglitz and R. Marx, *Ber.*, **56**, 1619 (1923)

isolated from ultra high pressure mercury lamp by using CoSO_4 solution filter. The initial concentrations of reaction solutions are 10^{-3}mol/l for anthracene, $5 \times 10^{-3}\text{mol/l}$ for 9-methylanthracene, respectively. Solutions were degassed by several freeze-thaw cycles and put into the cell under a stream of nitrogen gas.

Measurement of fluorescence spectrum

The sample solutions were irradiated by $366\text{m}\mu$ light isolated from high pressure mercury lamp with the interference filter and the fluorescence passed through a monochromator was detected by the photomultiplier and the recorder. Though the amount of absorbed light must be constant at each pressure to get the relative values of the fluorescence intensity, it may be changed because of the pressure-induced red shifts of absorption spectra and the concentration changes caused by the volume contraction. It is necessary to find the condition where the amount of absorbed light I_{abs} is nearly constant at the part of the cell available to detect fluorescence (shaded part in Fig. 2). The relation between I_{abs} and $\epsilon[c]$ (ϵ : extinction coefficient at $366\text{m}\mu$, $[c]$: concentration of solute) was plotted taking account of the shape of the cell.

As shown in Fig. 3, even if ϵ and $[c]$ change in the range from 0.5 to 0.8 for $\epsilon[c]$, the amount of absorbed light is kept nearly constant. Under such a condition the fluorescence measurements were carried out: $[c]=2.5 \times 10^{-4}\text{mol/l}$ for anthracene, $[c]=7 \times 10^{-5}\text{mol/l}$ for 9-methylanthracene. Oxygen was excluded from solutions by the same method as for photodimerization.

Results

The photodimerization yield was proportional to the concentration at each pressure in both compounds. In Fig. 4, apparent rate constants k_{obs} versus pressure are shown at the ratio to the values at the normal pressure. The reciprocals of viscosity of *n*-hexane also are shown¹³⁾. In anthracene k_{obs} is nearly inversely proportional to the viscosity of the solvent. On the other hand, in 9-methylanthracene

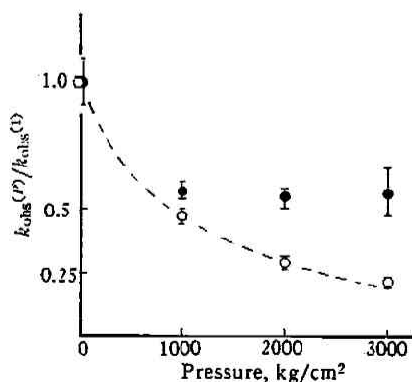


Fig. 4 The change of apparent rate constant for photodimerization yield with pressure
○: Anthracene, ●: 9-Methylanthracene
The broken line shows reciprocal of relative viscosity of *n*-hexane ($\eta(1)/\eta(P)$)

13) D. W. Brazier and G. R. Freeman, *Can. J. Chem.*, 47, 893 (1969)

the discrepancy between k_{obs} and the reciprocal of the viscosity of solvent become larger with increasing pressure.

The fluorescence spectra are described in Figs. 5 and 6. The spectra show the monotonous red shifts with increasing pressure, but apparently the shapes of spectra are scarcely changed in both compounds. The most remarkable pressure effect on the fluorescence spectra is a large increase of intensity in 9-methylantracene, while the effect is small in anthracene. The spectra described in the figures are uncorrected for the sensitivities of the monochromator and the photomultiplier, and for the changes of refractive indexes of solvent and pressure medium. But considering that changes in refractive indexes at pressures up to 3,000 kg/cm² are small and that red shifts are small, the shapes of spectra would be practically invariable, so the ratio of the fluorescence intensities at peaks could be regarded as the ratio of fluorescence yields. The change of fluorescence yields with pressure are shown in Fig. 7. From the relation $\Phi_f = k_f \tau_f$ and the assumption that k_f is invariable with pressure, the following relation is derived:

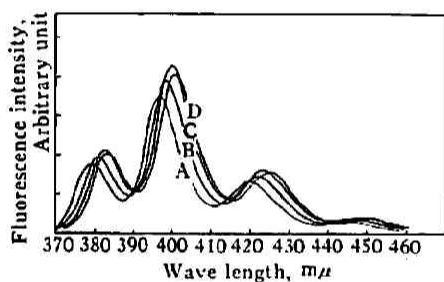


Fig. 5 The uncorrected fluorescence spectra of anthracene in *n*-hexane at each pressure
The concentration at 1 atm is 2.5×10^{-4} mol/l
A: 1 atm, B: 1,000 kg/cm²
C: 2,000 kg/cm², D: 3,000 kg/cm²

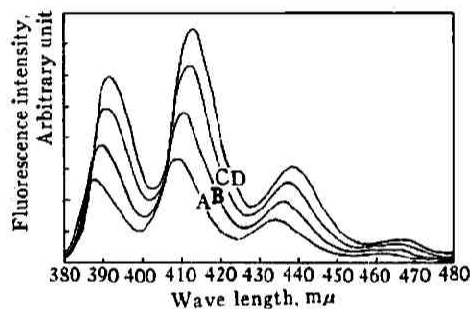


Fig. 6 The uncorrected fluorescence spectra of 9-methylantracene in *n*-hexane at each pressure
The concentration at 1 atm is 7×10^{-5} mol/l
A: 1 atm, B: 1,000 kg/cm²
C: 2,000 kg/cm², D: 3,000 kg/cm²

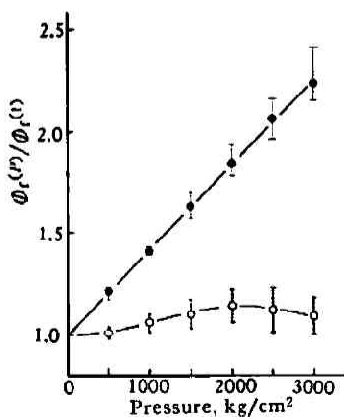


Fig. 7 The change of relative fluorescence yield with pressure
○: Anthracene
●: 9-Methylantracene

$$\frac{\phi_f(P)}{\phi_f(1)} = \frac{\tau_f(P)}{\tau_f(1)}.$$

τ_f increases strikingly with increasing pressure in 9-methylanthracene, while τ_f is not so sensitive to pressure in anthracene.

Discussion

Photodimerization rate

It is expected that the pressure effect on the rate of diffusion-controlled reaction appears as the viscosity effect^{2,14-16}. The bimolecular reaction rates in the excited singlet state are frequently controlled by diffusion because reactions occur during the short lifetime of excited singlet molecules. The photodimerizations of anthracene and 9-methylanthracene that have large rate constants $10^8 \sim 10^9 \text{ mol}^{-1} \cdot \text{sec}^{-1}$ also are considered to be diffusion-controlled reactions^{11,17}.

The obtained results indicate that in anthracene where τ_f has a slight pressure dependence, the correspondence of k_{obs} to a reciprocal of the viscosity of solvent is fairly good, but in 9-methylanthracene where τ_f shows a remarkable increase by pressure, k_{obs} become larger than expected by the change of viscosity as pressure increase. Considering this reaction as a simple bimolecular reaction between an excited singlet state molecule and a ground state molecule, the reaction yield at the low concentration as in this case is described in the following form:

$$\phi_f = k_r \cdot \tau_f [C] = k_{\text{obs}} [C].$$

Therefore $k_{\text{obs}} = k_r \cdot \tau_f$.

The pressure dependences of reaction rates k , with anthracene and 9-methylanthracene were obtained from the relative values for k_{obs} and for τ_f (ϕ_f). As shown in Fig. 8, k_r are approximately inversely proportional to the viscosity of solvent in 9-methylanthracene as well as anthracene. That is, the photodimerization rates are controlled by the diffusion in both compounds and the unexpected behavior of apparent rate constant k_{obs} for 9-methylanthracene is due to the increase of the lifetime τ_f with pressure.

Now, the existence of excimers has often been considered in anthracene and its derivatives and indeed excimer fluorescence has been observed in 9-methylanthracene^{17,18} though not observed in anthracene. And it was also suggested that the photodimerizations occurred via the excimer states¹⁹.

The present results cannot elucidate the role of excimer in the photodimerization. In the case of dimer formation via excimer, the process of excimer formation may be considered to be rate determining and diffusion-controlled.

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19) Th. Förster, *Angew. Chem.*, **81**, 364 (1969)

Moreover, the results on 9-methylantracene suggest that when the pressure effects on the photochemical reaction yields are investigated, the influences of pressure on other competitive rate processes as well as on the concerned reaction rates are important factors.

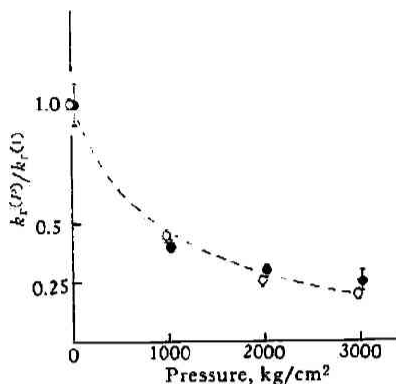


Fig. 8 The change of rate constant for photodimerization with pressure
○: Anthracene
●: 9-Methylantracene

Fluorescence yield

The fluorescence yield of 9-methylantracene became higher with increasing pressure. Now, the reason of the changes of fluorescence yields should be considered. Bowen and Sahu reported that the fluorescence yields of 9-substituted anthracenes increased with the decrease of temperature and the increase of the viscosity of solvent, while side-substituted anthracenes did not show such an effect²⁰. Thereafter, many studies on the temperature dependences were carried out by the measurements of fluorescence yield, lifetime and T - T absorption²¹⁻²³. The results obtained have indicated that the internal conversions k_{ic} are negligible and the radiative rates k_f are practically invariable with temperature and the intersystem crossing rates k_{is} from singlet state to triplet state increase with increasing temperature in the derivatives which have temperature dependences of fluorescence yield.

Neglecting k_{ic} , Φ_f is written by

$$\Phi_f = \frac{k_f}{k_f + k_{is}}$$

Assuming that k_f are invariable with pressure and that the changes of Φ_f are only due to k_{is} , the pressure dependences of k_{is} for anthracene and 9-methylantracene are obtained from the absolute values at normal pressure ($\Phi_f=0.36$ for anthracene²¹, 0.33 for 9-methylantracene²⁰) and the measured relative values at each pressure for Φ_f (Fig. 9). As pressure increases, k_{is} shows large decrease for 9-methylantracene and the decrease is smaller for anthracene.

The temperature dependences of k_{is} have been explained by Fig. 10^{23, 24}. Anthracene and side-substituted derivatives in which the lowest excited singlet state S_1 lies above T_2 , where T_2 is the second

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24) R. E. Kellog, *ibid.*, **44**, 411 (1966)

triplet state near to S_1 , do not need the activation energy for the intersystem crossing $S_1 \rightarrow T_2$. In contrast to those, the intersystem crossing $S_1 \rightarrow T_2$ for 9-substituted anthracenes in which S_1 lies below T_2 is the activation process and consequently exhibits temperature dependence.

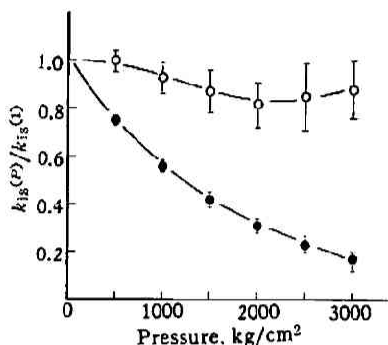


Fig. 9 The change of intersystem crossing rate with pressure
○: Anthracene
●: 9-Methylanthracene

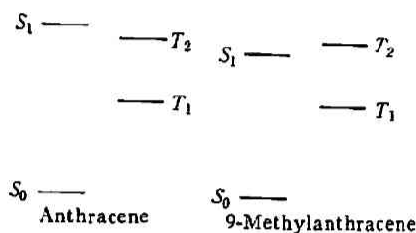


Fig. 10 The diagram showing relative positions of electronic states

The pressure effects also may be explained from the difference of energy between S_1 and T_2 . As clear from the observed red shifts of fluorescence spectra (roughly $1 \sim 2 \text{ m}\mu/\text{kbar}$), pressure lowers the energy level for S_1 . Generally, in nonpolar solute-nonpolar solvent system, absorption and fluorescence spectra are shifted to the longer wave length by pressure²⁵⁻²⁷. These red shifts occur because the solute-solvent interaction is stronger in S_1 owing to its larger polarity than in the ground state and the increase of the interaction by pressure also is larger in S_1 . Considering that the polarities in T_1 are probably smaller than in S_1 ²⁸ in anthracene derivatives where both the S_1 state and the T_1 state are L_a state^{29,30} and that transition moments in $T_1 \rightarrow T_2$ absorption are very small^{23,24}, it may be expected that polarities in T_2 are smaller than in S_1 and hence the lowering of T_2 by pressure is also smaller. If it is true, the energy gap in $S_1 \rightarrow T_2$ for 9-methylanthracene increases with pressure, so its intersystem crossing rate is retarded because of the larger activation energy. On the other hand, the energy gap should be smaller with increasing pressure in anthracene and it seems contradictory to the so-called energy gap law because the fluorescence yield of anthracene still increases with pressure though the increment is small.

Although it may be insignificant at this stage to discuss the small change of Φ_f , Johnson and Offen³¹ have observed that the intersystem crossing of anthracene was retarded by pressure and pro-

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- 29) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956)
- 30) H. B. Klevens and J. R. Platt, *ibid.*, **17**, 470 (1949)
- 31) P. C. Johnson and H. W. Offen, *Chem. Phys. Letters*, **6**, 505 (1970)

hibited completely at about 20 kbar at 77°K in matrix. Further, it has been suggested³²⁾ that the rate for intersystem crossing between the approximately degenerate states has not a simple relation to the difference of energy between those states. Recently, the "inverse deuterium effect" also has been observed with anthracene³³⁾. In such a case the state density in the final state may give an important contribution to the Franck-Condon factor of the intersystem crossing rate³⁴⁾. That is, as the energy gap becomes smaller with increasing pressure, the number of vibronic states in T_2 which are degenerate with the lowest vibronic level in S_1 is diminished and hence the Franck-Condon factor may be smaller. But the influences of pressure on the factors other than energy gap, e. g. the effect of viscosity which Bowen and Sahu pointed out, could not be either excluded at the present stage. Anyhow, the intersystem crossing on anthracene derivatives are not yet clear in many points. Further studies are being done in view of the pressure effects.

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