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PHOTOCHEMICAL REACTIONS OF AROMATIC ALDEHYDES AND KETONES

Higher Triplet State Reactions and Radiationless Transitions

By SATOSHI HIRAYAMA*

Photoreduction and photoaddition reactions were investigated on those compounds, 9-CH₃CO-A, 9-CHO-A, 1-CH₃CO-A, 2-CH₃CO-A, 3-CH₃CO-P and 3-CHO-P, which are the carbonyl derivatives of anthracene (-A) or pyrene (-P). These compounds had the $\pi\pi^*$ state as their lowest triplet states. 9-CHO-A, 1-CHO-A, 3-CH₃CO-P and 3-CHO-P underwent the above photoreactions. The other compounds were not photoreactive at all. Quantum yields of the photoreactions on the photoreactive compounds were measured, and it was found that the value for 3-CHO-P was larger than that for 9-CHO-A. The relative photoreduction rates were also obtained in several solvents.

Most compounds were non-fluorescent in non-polar solvents but showed fluorescence in various degrees in polar media. In spite of the supposition that those phenomena reflected the natures of the excited states of the compounds, they had no relation to the photoreactivity. The typical examples were 1-CH₃CO-A and 1-CHO-A, both of which showed a similar solvent effect on fluorescence spectra but had a different photoreactivity; the former was non-reactive.

From these results and the temperature dependence of the lowest triplet state yield, the relative positions of the several excited states of these compounds were estimated. It was supposed that the magnitudes of the decay rate of the higher excited triplet state $T_{(\pi\pi^*)}$ determined the photoreactivity.

The lifetimes of the lowest triplet state $T_{1(\pi\pi^*)}$ were also measured on the above compounds. It was found that the compounds having the shorter lifetime of the lowest triplet state were photoreactive. Particularly the lifetime of photoreactive 9-CHO-A was much shorter than that of non-reactive 9-CH₃CO-A, which had a similar lifetime to anthracene. With the aid of the theories of Robinson and El-Sayed and the first order perturbation, it will be shown that this lifetime is correlated to the molecular structure which seems to have a close connection with the radiationless transition process and the photoreactivity of $T_{(\pi\pi^*)}$.

Introduction

The photochemical reactions of aromatic ketones and aldehydes have long been studied by many photochemists and even now one of the most interesting subjects. Especially, their photoreduction reactions are typical and suggestive for the studies of the photochemical reactivity and the reaction mechanism. With regard to them the following facts have been already recognized: i) The excited states of aromatic carbonyl compounds are divided into the $n\pi^*$, $\pi\pi^*$ and CT states. ii) Except for the intramolecular hydrogen abstraction reactions, when they are irradiated in the appropriate hydro-

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gen donating solvents, they undergo photoreduction and their reactive excited state is the lowest triplet $n\pi^*$ state. Solvents^{1,2)} and substituents^{3~5)} affect the electronic nature of the lowest triplet state. When changed from the $n\pi^*$ state to the $\pi\pi^*$ or CT state, they lose reactivity and some kinds of ketones do not undergo photoreactions at all. iii) Even if the lowest triplet state is of $\pi\pi^*$ character, using strongly reductive compounds, e.g. stannane, some ketones can be reduced photochemically. Stannane is such a strong reducing reagent that it is possible to measure the rate constants of photoreduction which range over many orders of magnitude, e.g. from the rate constant for acetone ($n\pi^*$)⁶⁾ to that for 9-acetylanthracene ($\pi\pi^*$)⁷⁾. In our laboratory much attention has been paid to iii) and interesting studies are now in progress^{7,8)}. iv) Carbonyl compounds which are reducible photochemically easily add to olefine (oxetane formation)^{9,10)}. The reactive excited state is also the triplet state $n\pi^*$.

The experimental facts ii) and iv) stated above are generally observed in aromatic ketones and aldehydes having the $n\pi^*$ state as the lowest triplet state. 9-Aldehydeanthracene, however, is found to undergo both photoreduction and photoaddition reactions in spite of the $\pi\pi^*$ character of its lowest triplet state.

Yang *et al.*^{9,11)} discovered in the studies of the Paterno-Büchi reaction that 9-aldehydeanthracene, which has the $\pi\pi^*$ lowest triplet state, gave quite a large quantum yield of the photoaddition reaction and that this reaction showed the wavelength dependence. When it was irradiated by the light shorter than 410 m μ , the oxetane formation mainly occurred and when by the light longer than 410 m μ , only the dimerization reaction proceeded. From these facts they concluded that in this reaction the excited triplet state $n\pi^*$ was the reactive one. They supposed that the reason why the excited triplet $n\pi^*$ state played a main role in this reaction was that the energy difference between the excited triplet $n\pi^*$ state and the lowest triplet $n\pi^*$ state was extraordinarily large compared with that of the ordinary carbonyl compounds, so that the internal conversion from the higher $n\pi^*$ state to the lowest triplet $\pi\pi^*$ state became slow enough for the lowest triplet state $\pi\pi^*$ to participate in photoreactions.

Porter and Suppan³⁾, studying the substituent effect on the photoreduction reaction of aromatic carbonyl compounds, observed that 9-aldehydeanthracene could abstract hydrogen atom from solvent ethanol even in the presence of O₂ and so concluded that the reactive excited state was not the lowest $n\pi^*$ triplet state but that the reaction occurred at the lowest excited singlet state. (The electronic state

- 1) P. Suppan, *Ber. Bunsenges. Physik. Chem.*, **72**, 321 (1968)
- 2) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965)
- 3) G. Porter and P. Suppan, *ibid.*, **62**, 3375 (1966)
- 4) J. N. Pitts, Jr., H. W. Johnson, Jr. and T. Kuwana, *J. Am. Chem. Soc.*, **66**, 2456 (1962)
- 5) N. J. Turro, G. S. Hammond, J. N. Pitts, Jr. and D. Valentine, Jr., "Annual Survey of Photochemistry", Vol. 1, p. 324, Interscience (1970)
- 6) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2503 (1967)
- 7) J. Osugi, S. Kusuhara and S. Hirayama, *Rev. Phys. Chem. Japan*, **36**, 93 (1966); 37, 94 (1967)
- 8) I. Fujihara, M. Okushima, S. Hirayama, S. Kusuhara and J. Osugi, *Bull. Chem. Soc. Japan*, **44**, 3495 (1971)
- 9) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964)
- 10) D. R. Arnold, R. L. Hinman and A. H. Glick, *Tetrahedron Letters*, **1964**, 1425
- 11) N. C. Yang, M. Nussin, M. J. Jorgerson and S. Murov, *ibid.*, **1964**, 3657

was not indicated.) Further, they stated that the wavelength dependency of the reaction was recognized.

In succession, Yang *et al.*¹²⁾ measured the quantum yields of the oxetane formation reaction of carbonyl compounds. In the case of benzaldehyde, using piperylene as a quencher, they obtained the linear Stern-Volmer plot. This was considered to indicate that the reaction originated from only one excited state. On the other hand, in the case of 9-aldehydeanthracene, using di-*t*-butylnitroxide as a quencher, non-linear Stern-Volmer plot was obtained. They supposed that this was because there were two kinds of reactive states, one being the excited singlet $n\pi^*$ state and the other the excited triplet $n\pi^*$ state. For the first case, they also thought, as in the case of the triplet $n\pi^*$ state, that the large energy difference between the excited singlet $n\pi^*$ state and the lowest triplet state made the radiationless transition from the former state slow enough for the excited singlet $n\pi^*$ state to participate in the reaction. Furthermore, in order to justify this conclusion, they measured the quantum yields of the photosensitized oxetane formation reaction using many sensitizers. But their results merely ensured the participation of the excited triplet $n\pi^*$ state¹³⁾.

Wells and Warwick¹⁴⁾ studied the wavelength dependence of the photoaddition reaction of 9-aldehydeanthracene and analyzed the reaction products in detail. From the effect of many quenchers on the quantum yield of the reaction they concluded that the reactive excited state was the triplet state which lay in the range of 58~64 kcal/mole above the ground state.

As is easily seen in the above summary, concerning the important points, *i.e.*, the nature of the reactive excited state and the existence of the wavelength dependence of the reaction, several opinions have been proposed and any decisive experiments have not yet been made. Even if the opinion that the excited triplet $n\pi^*$ state is the main reactive one is accepted, the details of the internal conversion or the intersystem crossing process from that state to the lower states are still unknown. In addition, some of the experimental results are dubious in the author's opinion. The reason why the author has investigated the photoreaction of aromatic carbonyl compounds including 9-aldehydeanthracene partly lies in these points.

As pointed out by Yang¹¹⁾, if it is true that 9-aldehydeanthracene reacts at the $n\pi^*$ triplet state owing to the slow internal conversion of $T_{(n\pi^*)} \rightarrow T_{1(n\pi^*)}$, what will go with 9-acetylanthracene which has probably the similar energy difference between $T_{(n\pi^*)}$ and $T_{1(n\pi^*)}$ as 9-aldehydeanthracene? How about other carbonyl compounds, whose energy difference between $T_{(n\pi^*)}$ and $T_{1(n\pi^*)}$ is as large as that of 9-aldehydeanthracene?

To answer these questions, the photoreactions and the solvent effects on absorption and emission spectra of some carbonyl derivatives of anthracene and pyrene were investigated. The quantum yields of the photoreactions and the triplet state lifetimes at 77°K were also measured. Combining these results with the radiationless transition theory of Robinson and of El-Sayed, the mechanisms of the excitation energy conversion to the lowest triplet state were discussed. It led to the conclusion that the rate of energy relaxation of $T_{(n\pi^*)}$ state, which is supposed to determine the photoreactivity of our compounds, changes largely depending on the presence or the absence of the excited triplet states

12) N. C. Yang, R. Loeschen and D. Mitchell, *J. Am. Chem. Soc.*, **89**, 5465 (1967)

13) N. C. Yang and R. L. Loeschen, *Tetrahedron Letters*, **1968**, 2571

14) D. A. Warwick and C. H. J. Wells, *ibid.*, **1968**, 4401

which lie close to $T_{(nn^*)}$. The energies of the excited states are affected by molecular structures, so the decay rate of $T_{(nn^*)}$ will change from molecule to molecule and compounds having the larger decay rate of $T_{(nn^*)}$ state will not be reactive. This will be the reason why some of the anthracene derivatives are photoreactive and the others are unreactive.

An interesting fact was also found that the compounds which had the shorter lifetimes of the lowest triplet state $T_1(\pi\pi^*)$, which were observed experimentally, were photoreactive. It is proposed that these lifetimes are closely correlated to the molecular structures and that the latter determines the processes of the excitation energy relaxation.

In summary, it is said that the molecules which contain hetero atoms, such as nitrogen and oxygen, have approximately further additional excited states compared with their parent hydrocarbon compounds, so that without taking account of the whole energy transfer process containing these new excited states, to say nothing of their electronic property, it is difficult to determine the reactive excited state. To do this, as done by El-Sayed, the semiquantitative estimation of the internal conversion rate as well as of the intersystem crossing rate is quite helpful and is hoped to become more quantitative. The investigations of the photoreactions at the higher excited triplet state reported here have been done at the aim of answering this problem to some extent. The detailed discussions will be done in the section of discussions.

Experimental

Materials

The aromatic carbonyl compounds, 9-acetylanthracene¹⁵⁾ (in the following abbreviated as 9-CH₃CO-A and as to the numbering of the position of substitution, see Fig. 1), 9-aldehydeanthracene (9-CHO-A)¹⁶⁾, 1-acetylanthracene (1-CH₃CO-A)¹⁵⁾, 2-acetylanthracene (2-CH₃CO-A)¹⁵⁾, 1-carboxylanthracene (1-COOH-A)¹⁷⁾, 1-aldehydeanthracene (1-CHO-A)¹⁸⁾, 3-acetylpyrene (3-CH₃CO-P)¹⁹⁾ and 3-aldehydepypyrene (3-CHO-P), were synthesized by the usual methods cited in the literatures. 3-CHO-

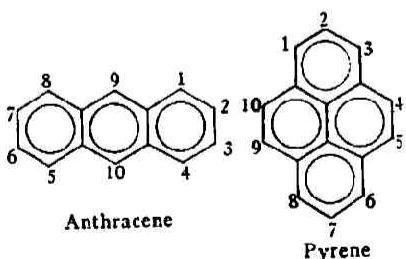


Fig. 1 Numbering of the positions of substitution

- 15) E. C. E. Hawkins, *J. Chem. Soc.*, 1957, 3858
 16) L. F. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.*, **60**, 2555 (1938)
 17) C. Graebe and S. Blumenfeld, *Ber.*, **30**, 1115 (1897); Edward de Barry Barnett, J. W. Cook and H. H. Grainger, *Ber.*, **57**, 1775 (1924)
 18) P. H. Gore, *J. Chem. Soc.*, 1959, 1617

P was synthesized analogously to 9-CHO-A and recrystallized from ethanol. There are several other synthetic methods of 1-CHO-A which was a little tedious to synthesize. 9-CH₃-A was a commercially available one (Nakarai Chem. Co. Ltd. extra pure grade) and used as received. 9-Cl-A was synthesized according to the literature. Identification of the synthesized materials was done by comparing the melting point and UV absorption spectrum with the reported data.

The plastic matrix used for the measurements of the triplet state lifetimes was made of distilled MMA (methylmethacrylate) monomer, which was thermally polymerized. The initiator of polymerization was BPO (benzoylperoxide). The solvents used for the photoreduction and the measurements of the absorption and the fluorescence spectra were, except for *m*-xylene, trichloroacetic acid, mesitylene and acetic acid, of spectro grade and were used without further purification. Pentene-2 (*cis* and *trans* mixture), a reactant of oxetane formation, was obtained from Tokyo Kasei Chem. Co. Ltd. and was used after distillation *in vacuo*. When evacuation was necessary, freeze-pump-thaw cycles were performed.

Measurements of absorption and fluorescence spectra

The UV absorption and fluorescence spectra were recorded on the Shimadzu SV 50 spectrophotometer. The fluorescence spectra were measured in the concentration range of *ca.* 10⁻⁵ mole/l. Correction was not made for the wavelength dependence of the sensitivity of the photomultiplier. The absorption spectra were shown in terms of optical density. Such a representation may not be suitable for the study of the solvent effects on spectra. But the variation of ϵ was assumed to be fairly small and the optical densities in different solvents were adjusted to be equal as nearly as possible. The shifts of the absorption maxima were measured. The results are shown in Figs. 3 to 8, 14 and 15.

Flash photolysis

Employing the previously reported apparatus of flash photolysis⁷⁾, the energy transfer from the higher excited triplet states of the carbonyl compounds of anthracene and pyrene to the quenchers and the participation of the higher excited triplet states in the oxetane formation were examined.

Measurements of *T-T'* absorption spectra at 77°K

Mounting a quartz Dewar vessel with four optically flat windows (Fig. 2) on the flash photolysis apparatus, measurements on the *T-T'* absorption spectra were done. At first, EPA (by volume of ether, isopentane, and ethanol 5:5:2) was used as a matrix at 77°K, but it was not suitable for measurement at room temperature because the path length could not be made longer than 1 cm in the present equipments used. Therefore, for the measurement on the variation of the triplet state yields at room temperature and at 77°K, plastic matrix was used. This plastic matrix was adjusted as follows. In a glass tube (10mm id.) MMA solution of a sample (10⁻⁴~5×10⁻⁵ mole/l) and BPO (0.1 w%) was poured and degassed. After sealing it was polymerized at first at *ca.* 70°C and then at 95°~100°C. The polymer formed was cut to a piece of 3cm length, whose edges were polished as flat as possible. It was immersed in the Dewar vessel as shown in Fig. 2. First, without filling the Dewar vessel with

liquid nitrogen, the $T-T'$ absorptions at room temperature were measured. Then filling the Dewar vessel with liquid nitrogen and cooling the plastic piece to 77°K, the $T-T'$ absorption measurement at 77°K was carried out. Liquid nitrogen in the path of the monitoring beam sometimes makes trouble for measurements on account of bubbling caused by flash. The triplet state lifetimes in plastic, however, were so long that such a strong exciting light as caused bubbling was not necessary. Lowering the irradiation energy of the flash lamp, it was possible to carry out the measurement without any disturbance by bubbling. In the two runs the irradiation energy was kept constant as much as possible. The plastic matrix, therefore, made it possible to know the temperature effect on the lowest triplet state yield by comparing the $T-T'$ absorption intensities at room temperature and at 77°K with one another. The lowest triplet state lifetimes in our cases are longer than 1 msec, so the ratio of the triplet state yields at two temperatures can be considered to be equal to the ratio of the $T-T'$ absorption intensities measured at time zero (or at such a short time as compared with 1 msec) at the two corresponding temperatures. The lifetimes of the lowest triplet states of our compounds at both temperatures were also calculated from the $T-T'$ absorption intensity changes.

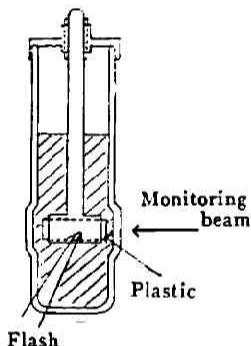


Fig. 2 Dewar vessel used for the measurement of the lifetimes of the triplet state at 77°K

BPO used as the initiator of polymerization did not disturb the measurements. The reaction between solvent MMA and solute molecules did not seem to occur. (However, as the degassed MMA solution of 9-CHO-A, when irradiated, easily polymerizes, caution must be taken when MMA plastic matrix is used.)

Photochemical reactions

The quantum yields of the photoreduction reaction and the oxetane formation reaction of carbonyl compounds of anthracene and pyrene were determined. As to the former reaction the relative rate in various solvents were measured. For the irradiation, a 300 w high pressure mercury lamp was used. The interference filter ($\lambda_{\text{max}}:366 \text{ m}\mu$) was employed for the measurement of the quantum yields. The reaction cell was made of quartz, 3 cm in length and 3 cm in diameter, and had a side arm for evacuation. The solutions were degassed by repeating a freeze-pump-thaw cycle six times. The optical densities of

19) C. A. Parker, *Proc. Roy. Soc. (London)*, A220, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid.*, A235, 518 (1956)

the solutions were in the range of 3.0 (3 cm in path length) so it was assumed that the exciting light was completely absorbed. The amount of photons absorbed was measured using the solution of potassium ferrioxalate¹⁹⁾. The solution filter (naphthalene 1 mole/l in ethanol, 2 cm in path length) was used for the determination of the relative reduction rates. The relative photoreduction rates in several solvents were determined from the relative amounts reacting when the same amount of photon was absorbed. For these purposes the optical densities in different solvents were adjusted to be equal as nearly as possible. In these experiments the amounts of molecules reacted were determined spectrophotometrically.

Results

Anthracene derivatives

Absorption and fluorescence spectra: The absorption and fluorescence spectra of 9-CH₃CO-A, 9-CHO-A, 1-CH₃CO-A, 1-CHO-A, 1-COOH-A and 2-CH₃CO-A are shown in Figs. 3~8. Acetic acid and isopropanol as polar solvents and cyclohexane as a non-polar solvent were used. In the case of 1-COOH-A, however, benzene was used instead of cyclohexane.

(1) 9-CH₃CO-A : Fig. 3 shows an absorption spectrum which is quite similar to the *p*-band of anthracene, though it shifts a little to the longer wavelength. This band hardly changes in cyclohexane, isopropanol and acetic acid. In the longer wavelength region, no absorption band assignable to the *nπ** transition was found. Compared with the other anthracene derivatives studied here, 9-CH₃CO-A exhibits the absorption band due to *ππ** transition at the shortest wavelength so that the *nπ** band was expected to be easily observed. In reality, however, neither the *nπ**-like band nor the solvent effect on the absorption spectrum was found. 9-CH₃CO-A does not exhibit fluorescence²⁰⁾.

If this non-fluorescent property, as is admitted for other compounds containing carbonyl group or nitrogen atom, is due to the situations that the lowest excited singlet state is the *nπ** state and that the energy gap between the *nπ** singlet state and the *ππ** singlet state is too small for each band to be discerned in the absorption spectrum, 9-CH₃CO-A should emit fluorescence strongly in the polar solvents²¹⁾. Contrary to this supposition, not only in isopropanol but also in such a quite protic solvent as trichloroacetic acid no fluorescence was observed²¹⁾. Therefore, the lowest excited singlet state should be assigned to the *ππ** state and the cause of non-fluorescent property must be sought else-

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- *1) For the purpose of ascertaining whether the non-fluorescent property of 9-CH₃CO-A is due to the flexibility of the freely rotating acetyl group at the excited state²¹⁾, fluorescence in the medium of PMMA was investigated. No fluorescence was observed at room temperature, but a weak fluorescence was seen at 77°K. We easily understand that the non-fluorescent property originates from its acetyl group, observing the fact that the chemical reduction of 9-CH₃CO-A by LiAlH₄ makes it fluorescent strongly. For further investigations see T. Matsumoto, M. Sato and S. Hirayama, *Chem. Phys. Letters*, 13, 13 (1972)
 - 20) T. M. Vember, L. A. Kiyanskaya and A. S. Cherkasov, *J. General Chem. USSR (English Transl.)*, 33, 2281 (1963)
 - 21) D. M. Hercules, "Fluorescence and Phosphorescence Analysis", Tokyo University International Edition (1966)

where (see Discussions).

(2) 9-CHO-A (Fig. 4): The absorption band corresponding to the *p*-band of anthracene shifts to the red in the polar solvents. Even at much higher concentrations, no band due to $n\pi^*$ transition could be found in the longer wavelength region.

Naphthaldehyde shows the $n\pi^*$ absorption band at *ca.* 27,000 cm^{-1} ²²⁾. In order that the lowest excited singlet state of 9-CHO-A may be $n\pi^*$, it should shift further by the amount of *ca.* 3,000 cm^{-1} to the lower energy compared with that of naphthaldehyde if it is taken into account that the longest absorption band of 9-CHO-A lies near 415 $\text{m}\mu$ (24,100 cm^{-1}). This value seems to be too large to be explained from the variation of the π -system alone.

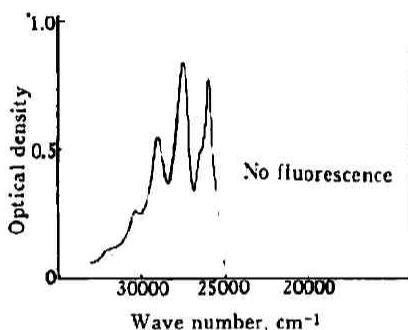


Fig. 3 The absorption spectrum of 9-
 $\text{CH}_3\text{CO-A}$ in isopropanol
It shows no fluorescence at room
temperature.

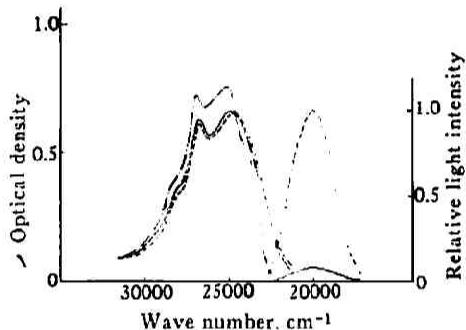


Fig. 4 The absorption and fluorescence
spectra of 9-CHO-A
— in isopropanol
--- in acetic acid
- - - in cyclohexane

There are a few investigations concerning the nature of the electronic state of the first excited singlet state of 9-CHO-A. Nurmukhametov²²⁾ has assigned it to $\pi\pi^*$ state from its absorption spectrum and solvent effect. In the study of the interactions between the electronic states, Hochstrasser and Marzzacco²³⁾ stated that if 9-CHO-A had the $n\pi^*$ singlet state which lay below the singlet $\pi\pi^*$ state as the lowest excited singlet state, the latter band, namely *p*-band, would have become much broader and they finally concluded that the lowest excited singlet state of 9-CHO-A was the $\pi\pi^*$ state. The present author also assumes it the $\pi\pi^*$ state. 9-CHO-A is practically non-fluorescent in non-polar solvents. So is the case with isopropanol, but in acetic acid in which the absorption spectrum is nearly the same as in isopropanol the strongly enhanced fluorescence is found. This cause will be discussed later, being related to the relative positions of the excited states.

(3) 1-CH₃CO-A, 1-CHO-A (Figs. 5, 6): 1-CH₃CO-A and 1-CHO-A are practically non-fluorescent in cyclohexane, but they exhibit very large fluorescence activation²⁴⁾. Being different in magnitude, both derivatives show broadening in their absorption spectra. However, their absorption maxima do

22) R. N. Nurmukhametov, *Optics and Spectroscopy*, 23, 209 (1967)

23) R. M. Hochstrasser and C. Marzzacco, *J. Chem. Phys.*, 49, 971 (1968)

24) S. A. Cherkasov, *Optics and Spectroscopy*, 9, 285 (1960)

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not shift. 1-CHO-A has an absorption spectrum with the well resolved vibrational structures, whose longest wavelength band lies at $420\text{ m}\mu$. At the wavelength longer than this, no $n\pi^*$ band is expected from the same reasons stated already in the case of 9-CHO-A. So it is concluded that the lowest excited singlet state is the $\pi\pi^*$ state in both compounds.

(4) 2-CH₃CO-A (Fig. 7): The absorption spectrum shows some broadening in polar solvents but its maximum does not shift. In the longest wavelength region there is only the vibrational bands of *p*-band and no $n\pi^*$ band is found. The fluorescence intensity does not greatly change with solvents^{25,26)}. From these the lowest excited singlet state is thought to be the $\pi\pi^*$ state.

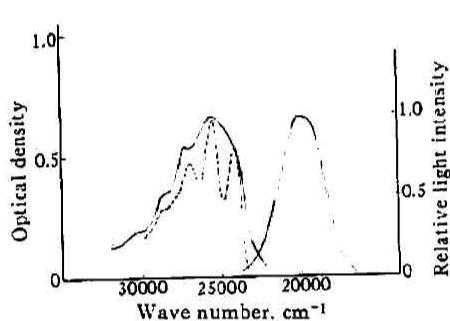


Fig. 5 The absorption and fluorescence spectra of 1-CHO-A
— in isopropanol
- - in cyclohexane

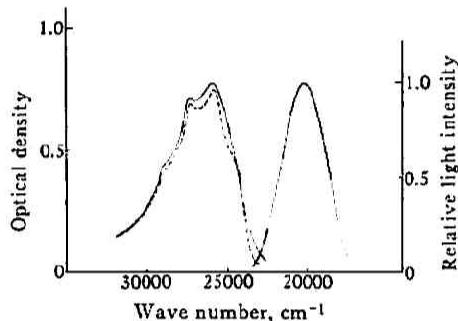


Fig. 6 The absorption and fluorescence spectra of 1-CH₃CO-A
— in isopropanol
- - in cyclohexane

(5) 1-COOH-A (Fig. 8): Instead of cyclohexane, benzene was used as a solvent. Except for a little different behavior of the absorption spectrum compared with the other derivatives stated above^{*2)}, in both isopropanol and benzene it fluoresces strongly and shows little intensity variation. Therefore,

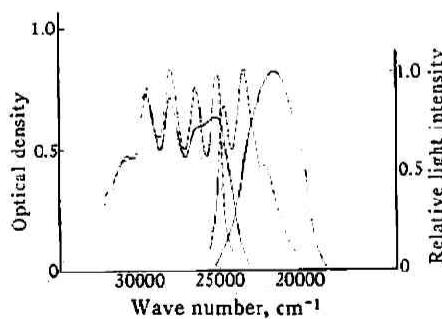


Fig. 7 The absorption and fluorescence spectra of 2-CH₃CO-A
— in isopropanol
- - in cyclohexane

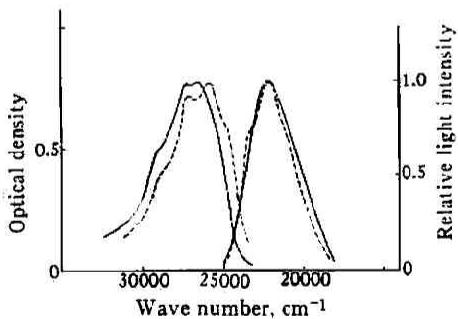


Fig. 8 The absorption and fluorescence spectra of 1-COOH-A
— in isopropanol
- - in benzene

*2) Hercules has explained this unusual behavior in relation to the change in its molecular structure in the excited state.

25) A. S. Cherkasov and G. I. Dragneva, *Optics and Spectroscopy*, **10**, 238 (1960)

26) J. C. Werner and D. M. Hercules, *J. Phys. Chem.*, **74**, 1040 (1970)

the lowest excited singlet state can be assigned to the $\pi\pi^*$ state.

In summary, what can be deduced from the results on the absorption and fluorescence spectra and their solvent effects are as follows: The lowest excited singlet states of the anthracene carbonyl compounds are the $\pi\pi^*$ state. The fluorescence intensity change with solvents does not seem to be caused by the exchange of the relative positions of the singlet $n\pi^*$ state and the singlet $\pi\pi^*$ state.

According to El-Sayed's theoretical treatment on spin-orbit interaction^{27~29}, the intersystem crossing efficiency between a singlet state and a triplet state is greater for $n\pi^* \leftrightarrow \pi\pi^*$ than for $\pi\pi^* \leftrightarrow \pi\pi^*$ or $n\pi^* \leftrightarrow n\pi^*$ by ca. 10³. Plotnikov³⁰ showed that these results were realized also for carbonyl compounds. Using these facts and our experimental results, it is quite reasonable to assume that the solvent effect on the fluorescence intensities is caused by the relative position exchange of triplet $n\pi^*$ state and the lowest excited singlet $\pi\pi^*$ state near which the former lies. As the intersystem crossing occurs isoenergetically, the radiationless transition of $S_{(n\pi^*)} \rightarrow T_{(n\pi^*)}$ becomes slower when the singlet $\pi\pi^*$ lies below the triplet $n\pi^*$ state than when the former lies above the latter. In the polar solvents the $n\pi^*$ state shifts to the higher energy and as the result, if the singlet $\pi\pi^*$ state becomes lower in energy than the triplet $n\pi^*$ state, the intersystem crossing rate becomes slower and it comes to have the rate of the same order as the radiative process. Consequently, fluorescence becomes observable.

It is interesting to know what will happen for the compounds with a substituent which makes the $n\pi^*$ state shift to the higher energy. As is generally recognized and as has been also shown by Nagakura³¹, in the compounds where carbonyl carbon atom is substituted by the hydroxy group, the amino group, or halogen atom, the $n\pi^*$ state is thought to shift considerably to the higher energy. Accordingly, in 1-COOH-A the $n\pi^*$ state is thought to shift to higher frequency, and it is expected to fluoresce, irrespective of solvents. In fact, fluorescence was observed even in hydrocarbon solvents. Besides this, the fact that 9-COOH-A³², different from 9-CH₃CO-A and 9-CHO-A, emits fluorescence confirms the supposition that the relative position of the $n\pi^*$ triplet state which lies near the lowest excited singlet $\pi\pi^*$ state plays a dominant role in the relaxation process of the excitation energy.

Of course the above mentioned facts could be interpreted in another way as has been done by Förster *et al.*³³ if it was admitted that the lowest excited singlet state was the $n\pi^*$ state. In this case, the change in the relative position of this state and the singlet $\pi\pi^*$ state with solvents would cause the fluorescence activation. In reality such a mechanism may have well explained the fluorescence activation process of some kinds of compounds, but in the present case the most reasonable interpretation is that stated above, which can explain consistently the results of the temperature effect on the yield of the lowest triplet state and the photochemical reactions stated in the following sections as well

27) M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2934 (1963)

28) M. A. El-Sayed, *ibid.*, **41**, 2462 (1964)

29) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966)

30) V. G. Plotnikov, *Optics and Spectroscopy*, **22**, 401 (1967)

31) S. Nagakura, *Bull. Chem. Soc. Japan*, **25**, 164 (1952)

32) J. C. Werner and D. M. Hercules, *J. Phys. Chem.*, **73**, 2005 (1969)

33) K. Bredebeck, T. Förster and H. G. Oesterlin, "Molecular Luminescence of Organic and Inorganic Materials", p. 164, ed. by H. Kallmann and G. M. Spruch, Wiley New York (1962)

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as the fluorescence activation.

Temperature effect on the intensity of $T-T'$ absorption

The lowest triplet state lifetimes at room temperature and 77°K, the wavelengths where the $T-T'$ absorption was measured, and the temperature variation of the lowest triplet state yield (at room temperature and 77°K) are shown in Table 1 about anthracene, 9-Cl-A, carbonyl derivatives of anthracene and others.

Although there is no doubt that the transient absorptions measured by the flash photolysis are due to the $T-T'$ absorptions, the especially detailed examinations were done on 9-CHO-A to make it sure. They are as follows: In the air saturated liquid solution, this transient absorption disappears. It is quenched by perylene (36 kcal/mole) and not by α -acetonaphthone (56 kcal/mole)*3). When 9-CHO-A has been completely photoreduced in isopropanol, this absorption disappears and instead of this the

Table 1 The lifetimes and the temperature effect on the yields of the lowest triplet states of aromatic aldehydes and ketones

Substance	Lifetime (msec)			$T-T'$ absorption (m μ)	Temp. effect on the intensity of $T-T'$ absorption
	77°K (in PMMA)	Room temp. (in PMMA)	Literature		
Anthracene	34.7		45 ^{a)}	424	no change
9-CH ₃ CO-A	28.2	13.1		430	no change
9-CHO-A	1.6	0.75		450	no change
9-Cl-A		~10		427	(~0) ^{b)}
1-CH ₃ CO-A	15.3	8.6		500	no change
1-CHO-A	9.6	5.9		500	no change
1-COOH-A		16.4		500	1/3 ^{b)}
2-CH ₃ CO-A		15.2		440	1/3 ^{b)}
Pyrene	not obs.		500 ^{a)}		(-0) ^{b)}
3-CH ₃ CO-P	29.9	19.7		430	no change
3-CHO-P	20.1	11.9		425	no change
Naphthalene			2.4 sec ^{a)}		
2-CH ₃ CO-N			970 ^{c)}		
2-CHO-N			350 ^{c)}		
Benzene			16 sec ^{a)}		
Acetophenone			1.6 ^{d)}		
Benzaldehyde			1.5 ^{d)}		

a) Reference 37, p. 44

b) The value of zero means that the triplet state yield at 77°K is nearly zero and the value of 1/3 means that at 77°K it decreases to one third of the yield at room temperature.

c) V. L. Ermolaev and A. N. Terenin, *J. Chim. Phys.*, **55**, 698 (1958)

d) S. P. McGlynn, T. Azumi and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall (1969)

*3) This result is consistent with that of Warwick³⁴⁾ who estimated the triplet state energy of 9-CHO-A as 43.5 kcal/mole from the position of the $S-T$ absorption obtained by the oxygen perturbation method.

34) D. A. Warwick and C. H. J. Wells, *Spectrochim. Acta*, **24A**, 589 (1968)

$T-T'$ absorption of the substituted anthracene corresponding to the reduced 9-CHO-A appears. In plastic matrix the decay lifetimes of the transient absorption of 9-CHO-A is about 1 msec. These experimental facts ensure the present assignment. About other compounds, the observed transient absorptions are also considered reasonably to be those due to the $T-T'$ absorption.

In Table 1, in the column denoting the temperature effect, the variations of the lowest triplet state yields with temperature are shown. As can be seen from the Table, not only anthracene but also 9-CHO-A, 1-CH₃CO-A, and 1-CHO-A, all of which exhibit the fluorescence activation, yield the lowest triplet state invariantly at both temperatures. The triplet state yield is not altered either in non-fluorescent 9-CH₃CO-A. On the other hand, in both compounds, 2-CH₃CO-A which shows quite a little fluorescence activation and 1-COOH-A which hardly shows the fluorescence activation, the lowest triplet state yield at 77°K decreases to one third of those at room temperature. 9-Cl-A and 9-CH₃-A do not yield the lowest triplet state at 77°K as already described. The fact that the yield of the lowest triplet state has decreased indicates that the radiationless transition of $S_1 \rightarrow T$ includes the temperature dependent process.

On anthracene it is well known that its energy levels can be depicted as shown in Fig. 9(a)³⁵⁾. The process to produce the lowest triplet state is $S_1 \rightsquigarrow T_2 \rightsquigarrow T_1$ and the direct radiationless process of $S_1 \rightarrow T_1$ hardly occurs. This is well substantiated by the fact that in the molecular crystal of anthracene where S_1 lies below T_2 , no triplet state is produced³⁶⁾. On account of such an energy level arrangement the rate of the radiationless transition of $S_1 \rightsquigarrow T_2$ scarcely alters^{*4)} though the temperature is lowered from room temperature to 77°K. Contrary to this the *meso* derivatives of anthracene give no triplet state at 77°K and at this temperature the fluorescence quantum yield becomes to unity. This is because the energy level arrangement of the *meso* derivatives of anthracene is as shown in Fig. 9(b)^{38~40)}. Namely, as the process of $S_1 \rightarrow T_2$ needs the thermal activation, it can be neglected at 77°K compared

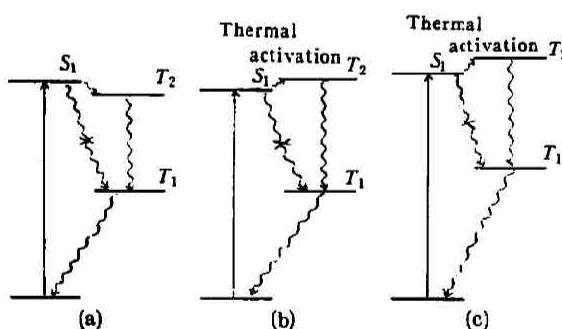


Fig. 9 The energy level diagrams of anthracene, its *meso* derivatives and pyrene
 (a) anthracene
 (b) *meso* derivative
 (c) pyrene

*4) Anthracene belongs to what is called the category "Big Molecule"³⁷⁾, so its radiationless transition is independent of media and does not need activation energy when S_1 is higher than T_2 .

- 35) R. Kellogg, *J. Chem. Phys.*, **44**, 411 (1956)
- 36) J. Adolph and D. F. Williams, *ibid.*, **46**, 4248 (1967)
- 37) G. W. Robinson, "The Triplet State", p. 213, ed. by A. B. Zahlan, Cambridge University Press (1970)
- 38) E. J. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959)
- 39) R. G. Bennett and F. J. McCartin, *J. Chem. Phys.*, **44**, 1969 (1966)
- 40) E. C. Lim, Joseph D. Laposa and J. M. H. Yu, *J. Mol. Spectr.*, **19**, 412 (1966)

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with the fluorescence radiative process. So it may be assumed that from the temperature variation of the lowest triplet state yield of the carbonyl compounds studied here new informations will be given about the energy level arrangement.

The energy level arrangements which are thought to be most reasonable from the results on the solvent effects on the absorption and fluorescence spectra stated in the preceding section and the results on the temperature dependence of the triplet state yield described in this section are displayed in Fig. 10(a) to 10(f).

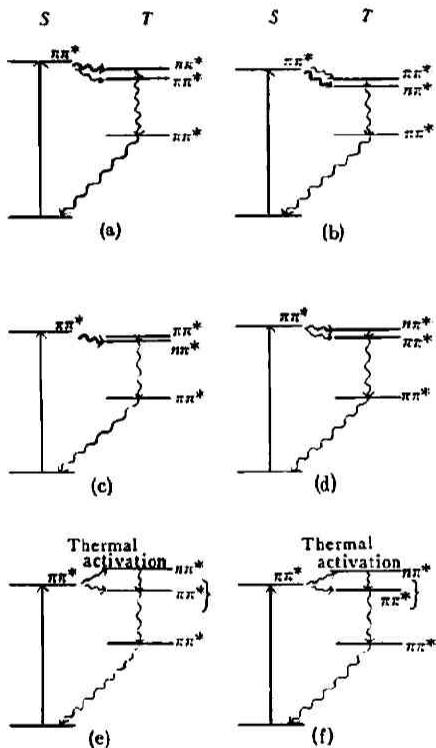


Fig. 10 The estimated energy level diagrams of the carbonyl derivatives of anthracene

- a) 9-CH₃CO-A
- b) 9-CHO-A
- c) 1-CHO-A
- d) 1-CH₃CO-A
- e) 1-COOH-A
- f) 2-CH₃CO-A

The thick wavy lines indicate the main radiationless process. } signs show the uncertainty in the position of the excited state.

Photoreduction and photoaddition

The compounds which undergo photochemical reactions (photoreduction and photoaddition) are only 9-CHO-A and 1-CHO-A. The fact that the other compounds do not undergo reactions is important to deduce what state the reactive excited state is. This problem will be discussed later.

The absorption spectra of the photo-products of 9-CHO-A are shown in Figs. 11(a), (b) and those of 1-CHO-A in Figs. 12(a), (b). In each case, as the reaction proceeds, the structureless broad band at the initial stage changes into the band with the pronounced vibrational structures characteristic to the ρ -band.

These two reactions proceed easily even in the presence of oxygen. In Fig. 13 the behaviors of the photoreduction of 9-CHO-A in both the presence and the absence of oxygen are shown.

In order to investigate the difference between the photoreduction of 9-CHO-A and 1-CHO-A and

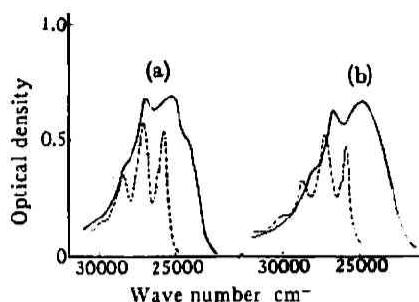


Fig. 11 The absorption spectra of the products of photoreactions of 9-CHO-A
 (a) photoaddition (in pentene-2)
 (b) photoreduction (in isopropanol)

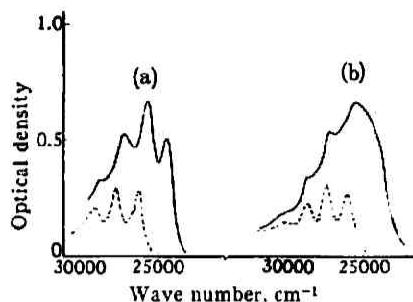


Fig. 12 The absorption spectra of the products of photoreactions of 1-CHO-A
 (a) photoaddition (in pentene-2)
 (b) photoreduction (in isopropanol)

that of benzophenone whose reactive state is believed to be the $n\pi^*$ triplet state, the relative rates of photoreduction in several solvents were measured for 9-CHO-A and 1-CHO-A. The results are shown in Table 2. In each case the rate in isopropanol is normalized to 9.7, that is, the value reported for benzophenone⁴¹⁾ in isopropanol. As is shown the behavior of 9-CHO-A is similar to that of

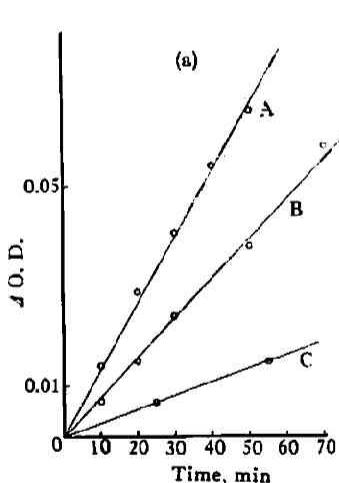


Fig. 13 The photoreduction rates in the degassed and air saturated solutions

(a) 9-CHO-A

A : in degassed isopropanol

B : in air saturated isopropanol

C : in degassed isopropanol-acetic acid 1 : 1 mixed solution

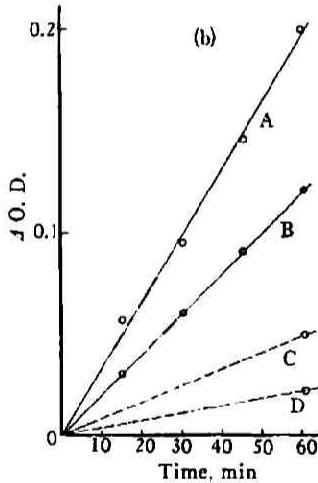
(b) 3-CHO-P

A : in degassed isopropanol } measured at 393 m μ

B : in air saturated isopropanol }

C : in degassed mesitylene }

D : in air saturated mesitylene } measured at 395 m μ



41) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, 87, 3361 (1965)

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Table 2 Relative reduction rates

Solvent	Benzophenone ⁴¹⁾	9-CHO-A	1-CHO-A	3-CHO-P
Isopropanol	9.7*	9.7*	9.7*	9.7*
Ethanol	—	6.9	—	—
Methanol	—	1.4	—	—
Mesitylene	5.6	5.4	34.4	5.9
<i>m</i> -Xylene	2.9	1.9	—	—
Cyclohexane	2.2	0.6	—	—
Benzene	~0.0	~0.0	—	—
Acetic acid	~0.0	~0.0	—	—

*) The relative rates are all normalized to 9.7, the value obtained for benzophenone in isopropanol by Walling and Gibian⁴¹⁾, in order to make comparison with benzophenone easier.

benzophenone but 1-CHO-A behaves differently.

In Table 3 the values of the quantum yields of the photoreduction and photoaddition are listed. The quantum yield of photoaddition of 9-CHO-A is greater than the value reported in the literature^{13,14)}. This is probably because pentene-2 (bulk) was used instead of 2-methyl 2-butene (mixed solvent) and further the reported value was obtained under the condition where the concentration of 9-CHO-A was much higher (0.1 mole/l) than that we employed (*ca.* 10⁻⁴ mole/l).

Table 3 Quantum yields of photoreactions

Substance	Photoaddition	Photoreduction
9-CHO-A	3.2×10^{-2} (1×10^{-2}) ^{a)}	1.4×10^{-3} (1.6×10^{-3}) ^{b)}
1-CHO-A	1.3×10^{-2}	—
3-CHO-P	4.4×10^{-2}	6.5×10^{-3}
3-CH ₃ CO-P	2.5×10^{-3}	very small

a) Reference 14,

b) Reference 3

Carbonyl derivatives of pyrene

The reactivity of carbonyl derivatives of anthracene seems to be determined by the efficiency of the population of $T_{(nn^*)}$ and the rate of the internal conversion from it. If this is correct, the compounds which satisfy such conditions as anthracene derivatives fulfill will undergo photoreactions. Pyrene derivatives belong to such compounds.

In Fig. 9(c) the energy level diagram of pyrene is shown. On account of the large energy gap between $S_{(nn^*)}$ and $T_{1(nn^*)}$, the intersystem crossing process passes through the process of $S_{(nn^*)} \rightarrow T_{2(nn^*)}$. But $S_{(nn^*)}$ lies below $T_{2(nn^*)}$ so that the intersystem crossing process requires the thermal activation. For that reason at 77°K the triplet state is not produced^{37,42)}.

42) B. Stevens, M. F. Thomaz and J. Jones, *J. Chem. Phys.*, **46**, 405 (1967)

In carbonyl derivatives of pyrene the energy gap between $T_{1(\pi\pi^*)}$ and newly added $T_{(n\pi^*)}$ is supposed to be large enough to slow down the radiationless transition from $T_{(n\pi^*)}$ and to give it a chance to react. Further, the higher triplet state $T_{2(\pi\pi^*)}$ probably locates above $T_{(n\pi^*)}$. Consequently $T_{2(\pi\pi^*)}$ would not play a role in determining the radiationless transition rate from $T_{(n\pi^*)}$, differing from the status in 9-CH₃CO-A. Therefore, both acetyl and aldehyde derivatives of pyrene are expected to react. To ascertain this, the similar experiments have been done on 3-CH₃CO-P and 3-CHO-P as on anthracene derivatives and will be described below.

Absorption and fluorescence spectra

3-CHO-P exhibits the intensity change of vibrational structures with the change of solvent from a non-polar to a polar one but has not the band attributable to the $n\pi^*$ band in the longest wavelength region. Admitting this fact, Förster *et al.*³³⁾ pointed out the possibility that the $n\pi^*$ band existed in the longest wavelength region because the extinction coefficient ϵ was so small that the $n\pi^*$ band might be hidden under the strong $\pi\pi^*$ band. 3-CH₃CO-P shows little change of absorption spectrum in polar and non-polar solvents. Of course no $n\pi^*$ band was found in the longest wavelength region.

Both compounds emit no (or very weak) fluorescence in non-polar solvents but strongly fluoresce in polar solvents. These results are shown in Figs. 14 and 15.

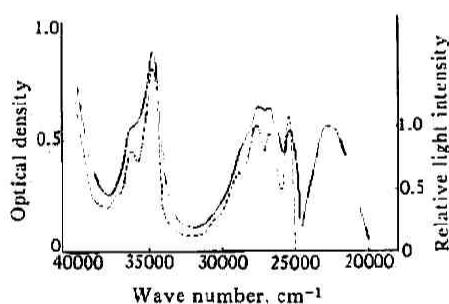


Fig. 14 The absorption and fluorescence spectra of 3-CHO-P
 — in isopropanol
 in cyclohexane
 Fluorescence was measured at the concentration $\text{ca. } 5 \times 10^{-5}$ mole/l.

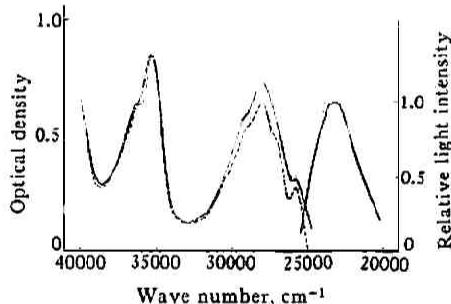


Fig. 15 The absorption and fluorescence spectra of 3-CH₃CO-P
 — in isopropanol
 in cyclohexane
 Fluorescence was measured at the concentration $\text{ca. } 5 \times 10^{-5}$ mole/l.

Temperature effect on the intensity of $T-T'$ absorption

The temperature variation of the triplet state yields at room temperature and 77°K were measured in the same way as in the case of anthracene derivatives. Pyrene itself has an energy level arrangement shown in Fig. 9(c) and at 77°K does not produce the triplet state and its fluorescence quantum yield is reported to approach to unity as temperature decreases⁴²⁾.

On the other hand, 3-CHO-P and 3-CH₃CO-P investigated here showed no change in the yield at both temperatures. The results are shown in Table 1. From this and the results in the preceding section,

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such energy level diagrams as presented in Fig. 16(a), (b) were deduced for 3-CHO-P and 3-CH₃CO-P. (Of course from the above experiments alone cannot be eliminated a possibility that $T_{2(\pi\pi^*)}$ lies below $T_{(\pi\pi^*)}$.)

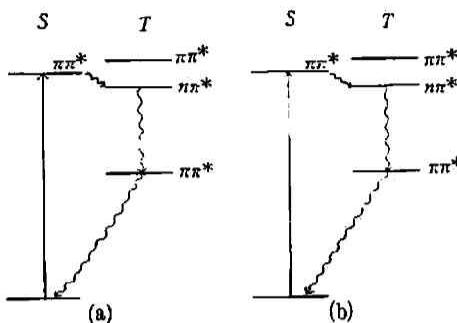


Fig. 16 The estimated energy level diagrams of 3-CH₃CO-P (a) and 3-CHO-P (b)
The thick wavy line indicates the main radiationless process.

Photoreduction and photoaddition reactions

Both 3-CHO-P and 3-CH₃CO-P undergo photoreduction and photoaddition reactions in the presence of oxygen. Time *vs* the optical density change of 3-CHO-P in isopropanol is plotted in Fig. 13(b) and its relative rates in two solvents are listed in Table 2. The quantum yields are given in Table 3.

The photoreaction products were ascertained to be the corresponding alcohols by comparing their absorption spectra with those of alcohols obtained by reducing chemically 3-CHO-P and 3-CH₃CO-P⁴³ (Figs. 17 and 18). In the case of photoaddition reaction, the products were not studied. However, the fact that the quantum yields are larger than those of photoreduction by an order is considered to show that the reaction in pentene-2 is a photoaddition.

So far the carbonyl derivatives of the aromatic compounds which have large π -system, such as pyrene, have been simply believed to have the lowest triplet states characterized as $\pi\pi^*$ and therefore

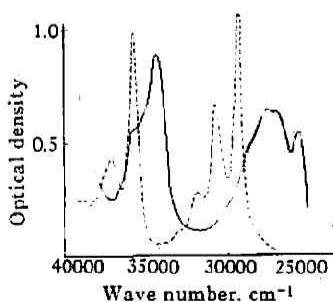


Fig. 17 The absorption spectrum of the photoreduction product (broken line in isopropanol) of 3-CHO-P

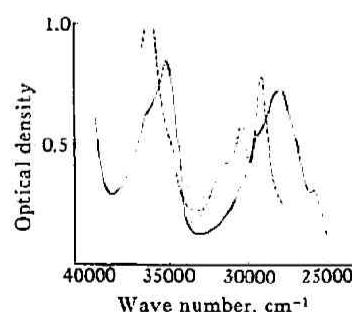


Fig. 18 The absorption spectrum of the photoreduction product (broken line in isopropanol) of 3-CH₃CO-P

to be non-reactive. In reality, however, as shown in this article, both 3-CHO-P and 3-CH₃CO-P undergo photoreduction and photoaddition, though their lowest triplet states are $\pi\pi^*$. Furthermore it has been suggested that it is the slow radiationless transition rate of $T_{(nn^*)} \rightarrow T_{1(\pi\pi^*)}$ that enables $T_{(nn^*)}$ to have a sufficient long lifetime to react. This also gives another experimental support to the interpretation proposed by Yang *et al.*¹¹⁾ for the reaction of 9-CHO-A.

Studies by flash photolysis

The intensities of the $T-T'$ absorption of 9-CHO-A and 3-CHO-P were measured in pentene-2 and found to decrease to one third and three fourths of that observed for benzene solution of the same concentration, respectively. But the decay rates did not change. Less reactive 3-CH₃CO-P hardly showed the intensity change. Probably this is because in pentene-2 there arises a new process, namely the photoaddition reaction which competes with the radiationless transition process of $T_{(nn^*)} \rightarrow T_{1(\pi\pi^*)}$ and to that extent the internal conversion of $T_{(nn^*)} \rightarrow T_{2(\pi\pi^*)}$ is retarded. As a result the yield of $T_{1(\pi\pi^*)}$ and the intensity of $T-T'$ absorption have decreased. This may be considered to be a direct evidence to show that the higher excited triplet state is a reactive one.

Discussions and Considerations

Energy level diagrams

In this section the energy level arrangement which are thought to be most reasonable from the present results will be explained.

(1) 9-CH₃CO-A does not fluoresce so that the intersystem crossing is considered to occur quite efficiently. Therefore the process should be $S_{(\pi\pi^*)} \rightarrow T_{(nn^*)}$. $S_{(nn^*)}$ must have higher energy than $T_{(nn^*)}$ because there is not the temperature effect on the yield of the lowest triplet state within experimental errors. The relative positions of $T_{(nn^*)}$ and the second excited triplet state $T_{2(\pi\pi^*)}$ could not be known by the physical methods alone. However, in order to explain the results of the photochemical reactions found here most reasonably, $T_{(nn^*)}$ was placed higher than $T_{2(\pi\pi^*)}$. The reasonings are as follows: When the energy of $T_{(nn^*)}$ is greater than that of $T_{2(\pi\pi^*)}$, the energy gap between $T_{(nn^*)}$ and $T_{2(\pi\pi^*)}$ is so small that the internal conversion of $T_{(nn^*)} \rightarrow T_{2(\pi\pi^*)}$ must be quite rapid²³⁾. On the other hand, when the energy of $T_{(nn^*)}$ is smaller than that of $T_{2(\pi\pi^*)}$ the internal conversion from $T_{(nn^*)}$ occurs only to $T_{1(\pi\pi^*)}$ and this rate must be slow because of the large energy gap between $T_{(nn^*)}$ and $T_{1(\pi\pi^*)}$. In the former case, the chance that the $T_{(nn^*)}$ state can take part in reactions is kinetically so small that the inactiveness of 9-CH₃CO-A can be explained in this way. For further discussions on the intersystem crossing process in 9-carbonyl derivatives of anthracene, see the author's recent work⁴⁴⁾.

(2) 9-CHO-A (Fig. 10 (b)) shows fluorescence activation. Its triplet state yield does not change with temperature. These facts are considered to indicate that there is $T_{(nn^*)}$ state which lies lower than $S_{(nn^*)}$ and the energy gap between these states is small enough to exhibit fluorescence acti-

44) T. Matsumoto, M. Sato and S. Hirayama, *Chem. Phys. Letters.*, **13**, 13 (1972)

vation. The second triplet state $T_{2(n\pi^*)}$ is assumed to have the higher energy in order to explain the photochemical reactivity. (Here the relative position of $S_{(n\pi^*)}$ and $T_{2(n\pi^*)}$ is not discussed.)

(3) Figs. 10(c) and 10(d) are for 1-CHO-A and 1-CH₃CO-A, respectively.

(4) 1-COOH-A has no tendency to activate fluorescence²⁶⁾. At 77°K the lowest triplet state yield decreases to one third of that at room temperature. The hydroxy group increases the energy of the $n\pi^*$ state. The energy level diagram in Fig. 10(e) expresses these facts well.

(5) 3-CH₃CO-P and 3-CHO-P hardly fluoresce in non-polar media and show fluorescence activation. The $T-T'$ absorption intensities of these compounds did not decrease at both room temperature and 77°K within experimental errors. So the intersystem crossing process will not be dependent on temperature. If we admit that the lowest excited singlet states of these compounds are $\pi\pi^*$ states, such energy level diagrams as depicted in Figs. 16(a) and 16(b) will be conceivable. $T_{2(n\pi^*)}$ states are placed higher than $S_{1(n\pi^*)}$ states because $T_{2(n\pi^*)}$ state of pyrene is higher than its $S_{1(n\pi^*)}$.

Reactive excited states

In this section it is discussed whether there exist any other reactive excited states than $T_{(n\pi^*)}$.

Hitherto, the results of the photochemical reactions have been interpreted in terms of the reactive $T_{(n\pi^*)}$ state and the deduced plausible energy level arrangements for the carbonyl derivatives of anthracene. Then the same reasoning has been applied to 3-CHO-P and 3-CH₃CO-P and has been ascertained to be consistent with the experimental results. Nevertheless, if it is taken into account that the extinction coefficient ε of the $n\pi^*$ band is so small that it may be hidden under the strong $\pi\pi^*$ band, it is possible to consider, as Förster *et al.* did for aromatic aldehydes³³⁾, that the fluorescence activation occurs as the result of the change in the relative positions of the lowest excited singlet states with solvents, that is in polar solvents the lowest excited singlet state becomes $\pi\pi^*$ and the rate of radiative process increases and finally fluorescence becomes observable. In this case at least in non-polar solvents the first excited singlet state is the $n\pi^*$ state and this state should be considered to be a reactive one, so not only 9-CHO-A but also all compounds which show fluorescence activation are anticipated to undergo photoreactions. Contrary to this supposition, 1-CH₃CO-A which shows fluorescence activation does not react at all. It is not reasonable to consider that only the lifetime of $S_{(n\pi^*)}$ of 1-CH₃CO-A is too short to participate in the reaction and the lifetimes of $S_{(n\pi^*)}$ states of other compounds are long enough.

Considering from the measurement on the intensity of $T-T'$ absorption, it is understood that 9-CH₃CO-A yields the lowest triplet state quite efficiently. It is due to an efficient intersystem crossing process that 9-CH₃CO-A does not fluoresce. If the non-fluorescent property of 9-CH₃CO-A is caused by the situation that the lowest excited singlet state is $n\pi^*$, it can not be understood why 9-CH₃CO-A is unreactive.

In order to assign the lowest excited singlet state as $n\pi^*$ state, it is necessary to find the $n\pi^*$ absorption band. But none was found in all the compounds which showed fluorescence activation.

From these reasons it is concluded that it is improbable that the lowest excited singlet state is the $n\pi^*$ state and that this $n\pi^*$ state is the main reactive excited state.

Another possible case is that the lowest excited singlet state is $\pi\pi^*$ and slightly above it the singlet $n\pi^*$ state exists, which is directly or thermally excited to take part in the photochemical reactions.

We first examine the possibility of the direct excitation. The extinction coefficient, ϵ , of the $n\pi^*$ band is so small that the amount of the light absorbed by the $n\pi^*$ band is at most $1/100 \sim 1/1,000$ of the total amount absorbed in the region where the strong $\pi\pi^*$ band superposes the $n\pi^*$ band. Such a small fraction can not be compatible with the values of the quantum yields, even if the probability of the reaction of the excited state is taken to be nearly one.

Next we must examine the possibility that the higher excited singlet $n\pi^*$ state which is populated by the thermal activation of the lowest excited singlet $\pi\pi^*$ state becomes a reactive excited state. In this case the efficiency to produce $n\pi^*$ state could become high, even if the efficiency by direct excitation due to light absorption is low. If this is admitted, the non-fluorescent property must be explained by considering the efficient intersystem crossing process of $S_{(n\pi^*)} \rightsquigarrow T_{(n\pi^*)}$ according to El-Sayed^{27~29)*5)}. Then the mechanism to produce the lowest triplet state becomes $S_{(n\pi^*)} \rightsquigarrow S_{(n\pi^*)}$ (thermal activation) $\rightsquigarrow T_{2(n\pi^*)} \rightsquigarrow T_{1(n\pi^*)}$ and needs thermal activation. This conclusion is contradictory to the fact that 9-CHO-A, 1-CHO-A, 3-CHO-P and 3-CH₃CO-P yield efficiently the lowest triplet state independent of temperature. Furthermore when $S_{(n\pi^*)}$ can be thermally populated, the energy difference between $S_{(n\pi^*)}$ and $S_{(n\pi^*)}$ is so small, as is calculated from Boltzmann factor, that the reaction which proceeds by this mechanism is thought to be quite sensitive to the polarity of solvents. This is not the case, however, because 9-CHO-A and 3-CHO-P show a tendency similar to that of benzophenone for which thermal activation is not necessary. Thus it is understood that the reaction mechanism including the thermal activation is not supported by the experimental facts and it is reasonable to exclude it from the possible reaction mechanisms.

It is concluded that the most appropriate reactive excited state is $T_{(n\pi^*)}$. The reasons why $T_{(n\pi^*)}$ can participate in the photoreactions investigated here, as is clear from the above discussions are as follows:

- i) The efficient intersystem crossing process of $S_{(n\pi^*)} \rightsquigarrow T_{(n\pi^*)}$ can produce the reactive excited state $T_{(n\pi^*)}$ at the quantum yield close to unity. This is the most remarkable difference compared with the case where the higher excited singlet state whose extinction coefficient is small is the reactive one.
- ii) The internal conversion process of $T_{(n\pi^*)} \rightsquigarrow T_{1(n\pi^*)}$ is slow enough for the former to take part in the reactions.

The tendency not to fluoresce or a good yield of the lowest triplet state substantiates the reason i). The position of $T_{2(n\pi^*)}$ becomes important concerning the reason ii).

Reactivity and the lowest triplet state lifetime—relation to molecular geometry

Hitherto the author has considered what excited states of 9-CHO-A, 1-CHO-A, 3-CHO-P and 3-CH₃CO-P take part in the reactions. Next it will be discussed what endows them with such a reactive excited state. It will be noted in Table 1 that all of the reactive compounds have remarkably shorter

5) Here the state $T_{(n\pi^)}$ is not taken into account at all, because another appropriate mechanism is being searched for without trusting to $T_{(n\pi^*)}$.

lowest triplet lifetimes compared with the parent compounds from which they are derived and that the aldehyde derivatives have shorter ones than the acetyl derivatives. (This is also true for benzene and naphthalene derivatives.) It will be asserted that the lifetime of the lowest triplet state has the intimate relation with the molecular structure—coplanarity of the aromatic ring and the carbonyl group $\text{C}=\text{O}$ and that this molecular geometry exactly makes the compounds studied here have the energy level arrangements shown in Figs. 10(a)~(f). Here the author will discuss about these.

The intramolecular radiationless transition processes are in principle divided into i) the internal conversion and ii) the intersystem crossing. Both processes have been studied by many workers. Using some empirical relations, Robinson^{45,46)} has shown theoretically that the radiationless transition rate constant can be expressed generally by the following equations

$$k = 2\hbar^{-2} \tau_{\text{vib}} \beta_{\text{el}}^2 \langle \phi''/\phi' \rangle^2_{\text{tot}}, \quad (1)$$

$$\log \langle \phi''/\phi' \rangle^2_{\text{tot}} \approx -0.1096 \Delta E^{0.4332}, \quad (2)$$

The meaning of the notations should be referred to the original paper. $\langle \phi''/\phi' \rangle^2_{\text{tot}}$ is what is called the Franck-Condon factor and ΔE is the electronic energy difference between the states where the radiationless transition occurs. In the case of i), if it holds that τ_{vib} and β_{el} do not change significantly from transition to transition, the magnitude of ΔE will determine the rates of radiationless transition. The internal conversion of $T_{(\pi\pi^*)} \rightarrow T_{(\pi\pi^*)}$ discussed above corresponds to this case.

Taking 9-CHO-A as an example, when $T_{(\pi\pi^*)}$ is the lower triplet state $T_{1(\pi\pi^*)}$, ΔE is about 18 kcal/mole and when $T_{(\pi\pi^*)}$ is the higher triplet state $T_{2(\pi\pi^*)}$, ΔE is at most about 5 kcal/mole, so the ratio of the individual radiationless transition rate is calculated to be about one hundred. (The energy difference of 5 kcal/mole lies in the range where the uncertainty in the calculated value of the Franck-Condon factor is fairly large⁴⁶⁾, but it is assumed that eq. (2) still holds.) This enables one to understand that when $T_{2(\pi\pi^*)}$ lies just below $T_{1(\pi\pi^*)}$, the latter can not participate in the reactions since the internal conversion of $T_{(\pi\pi^*)} \rightarrow T_{2(\pi\pi^*)}$ is quite rapid.

In the case of ii), assuming that ΔE is of the same magnitude, the value of β_{el} determines the order of the transition rates. Expressing the wave function of the excited singlet state by Ψ_S and that of the triplet state by Ψ_T , then β_{el} is given by

$$\beta_{\text{el}} = \langle \Psi_S | \mathbf{H}_{\text{S.O.}} | \Psi_T \rangle, \quad (3)$$

where $\mathbf{H}_{\text{S.O.}}$ is the operator of spin-orbit interaction⁴⁵⁾. According to the theoretical treatment by El-Sayed *et al.*^{27~29)} the spin-orbit interaction of $n\pi^* \leftrightarrow n\pi^*$ is greater than that of $n\pi^* \leftrightarrow n\pi^*$ or $\pi\pi^* \leftrightarrow \pi\pi^*$ by the factor of $10^2 \sim 10^3$ (as the value of the square of β_{el}). This criterion has been used in this paper to interpret the fluorescence activation.

Since the lifetime of the lowest triplet state is determined by the efficiency of the intersystem

*6) The triplet state lifetime of anthracene is determined not by a radiative process (~ 30 sec) but by a radiationless process⁴⁷⁾.

45) G. W. Robinson and R. P. Frosh, *J. Chem. Phys.*, 37, 1962 (1962)

46) G. W. Robinson and R. P. Frosh, *ibid.*, 38, 1187 (1963)

47) W. Siebrand, *ibid.*, 47, 2411 (1967)

crossing process from the lowest triplet state to the ground state^{*6)}. β_{el} for that process is given by eq. (4) instead of eq. (3).

$$\beta_{el} = \langle \Psi_T | \mathbf{H}_{S,O} | \Psi_O \rangle \quad (4)$$

where Ψ_O is the wave function of the ground state.

If Ψ_T is purely expressed by the $\pi\pi^*$ state, since the state given by Ψ_O is, so to speak, the $\pi\pi$ state, by symmetry prohibition β_{el} can only have a small value^{*8)}. If this were the case, the carbonyl compounds treated in this article would have quite longer triplet state lifetimes. On that account it is assumed that $T_{1(\pi\pi^*)}$ is mixed with $T_{1(\pi\pi^*)}$ by the first order perturbation. Then eq. (5) is obtained for the wave function of the lowest triplet state,

$$\Psi_T \approx \Psi_{T_1(\pi\pi^*)} + \frac{\langle \Psi_{T_1(\pi\pi^*)} | \mathbf{H}' | \Psi_{T(\pi\pi^*)} \rangle}{E_{T_1(\pi\pi^*)} - E_{T(\pi\pi^*)}} \Psi_{T(\pi\pi^*)}, \quad (5)$$

where \mathbf{H}' is the perturbation Hamiltonian^{*7)}.

Accordingly β_{el} can be written as

$$\beta_{el} \approx \frac{\langle \Psi_{T_1(\pi\pi^*)} | \mathbf{H}' | \Psi_{T(\pi\pi^*)} \rangle \langle \Psi_{T(\pi\pi^*)} | \mathbf{H}_{S,O} | \Psi_O \rangle}{E_{T_1(\pi\pi^*)} - E_{T(\pi\pi^*)}}. \quad (6)$$

Since $\mathbf{H}_{S,O}$ is the one electron operator generally expressible by $\sum_i A_i \mathbf{L}_i \mathbf{S}_i$, where $\mathbf{L}_i, \mathbf{S}_i$ is the orbital and spin angular momentum operator of the i th electron^{*9)}, respectively, for the component of $S_z=1$, eq. (6) can be rewritten as

$$\langle \Psi_{T(\pi\pi^*)} | \mathbf{H}_{S,O} | \Psi_O \rangle \propto \langle \bar{n}\pi^* | h_{S,O} | \bar{n}n \rangle = \langle \bar{\pi}^* | h_{S,O} | n \rangle. \quad (7)$$

The upper bar refers to α -spin and $h_{S,O}$ to the spin-orbit interaction operator for one electron. The excited molecular orbital π^* is represented by L.C.A.O., then

$$\pi^* = \sum_i C_i^* \phi_i + C_o^* \phi_o, \quad (8)$$

where i is summed over for all carbon atoms and the p -atomic orbital of the oxygen atom is denoted by ϕ_o and its coefficient by C_o^* . Then eq. (8) becomes

$$\langle \bar{\pi}^* | h_{S,O} | n \rangle \approx C_o^* \zeta_{\pi^* \bar{n}n} \quad \zeta_{\pi^* \bar{n}n} = \langle \bar{\phi}_o | h_{S,O} | n \rangle. \quad (9)$$

From eqs. (1), (6), (8) and (9), is finally obtained the result that the lifetimes of the lowest triplet state are inversely proportional to the square of the coefficient of the atomic orbital of the oxygen in the

7) It might be thought that when the triplet $\pi\pi^$ state is mixed with a $\pi\pi^*$ state, it gains reactivity in proportion to the extent of mixing. But it depends on the relative importance of the term existent at the beginning and the other term added by mixing. The spin-orbit interaction between the triplet $\pi\pi^*$ state and the ground state is so small that even only a bit of $\pi\pi^*$ state character is mixed, it causes a great change in the lifetimes of the triplet state. Contrary to this, since the reactivity is completely determined by the inactive $\pi\pi^*$ state, a small amount of $\pi\pi^*$ character mixed has no effect on reactivity. In other words, the addition of a small value to zero has a remarkable effect but when a small value is added to a large value, its effect will be obscured.

48) D. S. McClure, *J. Chem. Phys.*, 20, 682 (1952)

49) H. F. Hameka, "The Triplet State", ed. by A. B. Zahlan, Cambridge University Press (1967)

π^* -molecular orbital*8).

The small value of the coefficient C_o^* is thought to correspond to the situation that the conjugation between the carbonyl group $\text{C}=\text{O}$ and the aromatic ring is small. And this is caused mainly by the two reasons mentioned below.

i) The aromatic ring and the carbonyl group are not in coplanar, but twisted through some angle*9).

ii) The position of substitution of the carbonyl group is not suitable for conjugation.

Accordingly, that the lifetime of the lowest triplet state of the carbonyl derivatives is long (as long as that of anthracene or pyrene) shows that the carbonyl group and the aromatic ring are twisted through a significant angle or that the position of substitution is not suitable for conjugation.

The substitution positions of anthracene is considered first. Contribution to conjugation from the carbonyl group should decrease in the order of 9, 1 and 2⁵²⁾. Therefore, as far as the steric effect is of the same magnitude for the carbonyl derivatives of anthracene, the lifetimes of the lowest triplet state of these compounds will increase in the order of 9, 1 and 2. In contrast to this, if the circumstance is not so different among the three substitution positions, the steric effect, which becomes larger in the order of 2, 1 and 9, will solely determine the lifetimes and they will increase in that order. In actual these two effects superpose each other. Compared with the acetyl group, the aldehyde group is less sterically hindered, so it is expected that the substitution positions determine the lifetimes of the aldehyde derivatives and they increase in the order of 9, 1 and 2. This expectation is compatible with the experimental results found for 9-CHO-A and 1-CHO-A.

On the other hand, the acetyl group in 9-CH₃CO-A is, owing to its methyl group, sterically hindered by peri-hydrogen atoms to a significant extent, so the carbonyl group, making nearly a right angle with the anthracene ring, is hardly conjugated with anthracene ring. On account of this, the lifetime of 9-CH₃CO-A is nearly the same as that of anthracene.

X-ray analysis by Trotter substantiates these things. For 9-CHO-A, the angle is 27°⁵³⁾, and for 9-NO₂-A, 85° (crystal state)⁵⁴⁾ is reported. Besides these compounds for 9-COOH-A⁵²⁾ and 9-Vinyl-A⁵⁵⁾, the nearly right angle is expected.

8) A different approach is also possible. First consider the spin-orbit interaction between S_{orb} and $T_{(\pi,\pi^)}$ and then the perturbation Hamiltonian, which does not contain the spin-orbit interaction term and causes a radiationless transition. In this case the lowest triplet state lifetime will be reciprocally proportional to the square of the coefficient of the *p*-orbital of the oxygen atom in the highest filled π -orbital. And yet the following discussion will hold without significant modification. Recently Hunter⁵⁰⁾ proposed a similar idea. A paper by Baba and Takemura⁵¹⁾ should also be consulted.

*9) Although a change in a molecular geometry accompanying with excitation is in itself an important problem, it is not taken into consideration in the present treatments.

50) T. F. Hunter, *Trans. Faraday Soc.*, **66**, 300 (1970)

51) H. Baba and T. Takemura, *Bull. Chem. Soc. Japan*, **40**, 2215 (1967)

52) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Chap. 10, John Wiley and Sons, New York (1963)

53) J. Trotter, *Acta Cryst.*, **12**, 922 (1959)

54) J. Trotter, *ibid.*, **12**, 237 (1959)

55) A. S. Cherkasov and K. G. Volodkina, *Izvest. Akad. Nauk SSSR, Ser. Fizicheskaja*, **27**, 628 (1963)

1-CH₃CO-A, which is preferred to 2-CH₃CO-A in conjugation, is expected to have the shorter lifetime than the latter. This is also consistent with the experimental result. (For 1-CH₃CO-A the angle of 46° is reported⁵⁶⁾.)

As to pyrene derivatives such a remarkable steric hindrance as is found for 9-CH₃CO-A is not conceivable⁵⁷⁾. As a matter of fact the absorption bands of 3-CH₃CO-P and 3-CHO-P shift in a similar manner to the red, indicating the similar conjugation effect for both compounds. As is expected both have much shorter lifetimes than pyrene.

It is also to be noted that the aldehyde derivatives always have the shorter lifetimes than the acetyl derivatives.

The detailed discussions so far have made clear the relation between the molecular structure and the lifetime of the lowest triplet state. The matter of the greatest interest for us, however, is to know what relation exists between the reactivity and the molecular structure, *i.e.*, the lifetime of the lowest triplet state. The following discussion will be relevant.

The greater the conjugating attitude of the carbonyl group to the aromatic π -system is, the lower the energy of the $n\pi^*$ state is expected to become. (Its variation may be small since the $n\pi^*$ state is characterized by a comparatively local excitation.) As a result of this, the energy of $T_{(n\pi^*)}$ happens to become lower than that of the second excited triplet state $T_{2(n\pi^*)}$. Its extent is, as is known from the results on the fluorescence activation, greater for 9-CHO-A which fluoresces only in such a strong protic solvent as acetic acid than for 1-CHO-A. On the other hand, on account of the less preferable position of substitution or non-coplanarity, in 9-CH₃CO-A, 1-CH₃CO-A and 2-CH₃CO-A the energy of $T_{(n\pi^*)}$ is higher than that of $T_{2(n\pi^*)}$. Of course since the substitution of a carbonyl group affects not only the energy of the $n\pi^*$ state but also that of the $\pi\pi^*$ state, the above discussion may be only qualitatively correct. Although the present discussion may lack rigidity, the conclusion is drawn that the compounds having the shorter lifetime of the lowest triplet state are more reactive, which agrees with the tendency mentioned above.

On the other hand, as frequently referred to, the second triplet state $T_{2(n\pi^*)}$ of pyrene lies above the lowest excited singlet state, and therefore either in 3-CHO-P or in 3-CH₃CO-P its $T_{(n\pi^*)}$ is expected to lie below $T_{2(n\pi^*)}$ and the necessary conditions for reaction, *i.e.*, the good yield and the long lifetime of the reactive excited state are satisfied. In this consequence in both compounds photochemical reactions have been observed. (As to the reactions in the ground state it is generally known that the aldehyde compounds are more reactive than the acetyl compounds⁵⁸⁾ and yet as far as the present experiments may be concerned, it is not certain that the difference in the reactivity of 3-CH₃CO-P and 3-CHO-P originates either from the intrinsic reactivity difference in $T_{(n\pi^*)}$ of each compound or from the difference in its lifetime.)

56) P. H. Gore, J. A. Hoskine, C. K. Thadani, R. J. W. LeFevre, L. Radom and G. L. D. Ritchie, *J. Chem. Soc.*, B1969, 426

57) R. Norman Jones, *J. Am. Chem. Soc.*, 67, 2127 (1945)

58) L. P. Hammet, "Physical Organic Chemistry", Chap. 11, McGraw-Hill, New York (1940)

Prediction of the photochemical reactivity of the aromatic carbonyl compounds

Up to now, for many kinds of aromatic aldehydes and ketones the change of the photochemical reactivity caused by the alternation in the electronic states has been discussed by many photochemists. In this article the author has investigated the same problem from a different point of view, that is, in terms of intramolecular radiationless transition the photochemical reactivity has been elucidated.

Then, which compounds are expected to be reactive? In Fig. 19 are shown the energies of the lowest excited singlet $\pi\pi^*$ state and the lowest excited triplet state $\pi\pi^*$ state (solid lines) of aromatic compounds and the lowest excited singlet $n\pi^*$ state and the lowest triplet $n\pi^*$ state (broken lines) of acetophenone. As the first approximation the energies of the $n\pi^*$ states of the carbonyl compounds shown on the abscissa in Fig. 19 are taken to be the same as those of acetophenone. Then Fig. 19 predicts, though intolerable to a rigorous discussion, that naphthalene derivatives, whose lowest triplet state is probably $\pi\pi^*$ state in the ordinary condition, decrease reactivity compared with benzene derivatives. The upper $n\pi^*$ triplet state does not matter because in this case the internal conversion from the $n\pi^*$ state to the lower $\pi\pi^*$ state is quite rapid (small ΔE). The same is true for phenanthrene derivatives. In anthracene and pyrene derivatives, however, the internal conversion rate from the higher triplet $n\pi^*$ state to the lowest $\pi\pi^*$ triplet state becomes slow enough for them to recover photochemical reactivity. Chrysene derivatives will show the intermediate behavior. Studies on tetracene and chrysene derivatives have not been carried out, so nothing proves the validity of the prediction. However, so far as the present experiments are concerned, Fig. 19 predicts a qualitative tendency and shows what determines the reactivity.

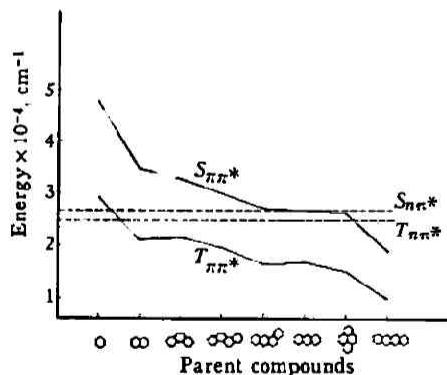


Fig. 19 The diagram showing the approximate relative positions of the excited $n\pi^*$ and $\pi\pi^*$ states of the aromatic carbonyl compounds

The solid lines show the energies of the parent aromatic compounds and the broken lines show the energies of the singlet and triplet $n\pi^*$ states of acetophenone.

Hitherto, the author has discussed about the photochemical reactions of aromatic carbonyl compounds, emphasizing the importance of the energy relaxation or the radiationless transition processes. The real radiationless transition processes in themselves are still complicated and ambiguity is so great that the author's treatments may have been inadequate. Since it cannot be said that the photochemical reaction mechanisms have completely been known unless the relaxation processes of the excitation energy have completely been elucidated, it is hoped that the studies on photochemical reactions will be carried out in future, taking account of the energy relaxation process or the radiationless process.

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