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Anomalous Phosphorescence of *p*-Methylacetophenone in Nonpolar Solvent at 77 K

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Absorption and phosphorescence spectra were studied for *p*-methylacetophenone in 3-methylpentane–isopentane mixed solvent at low temperature. From the concentration and temperature dependencies of the absorption spectrum, it is concluded that the monomer-dimer equilibrium exists in the solution of the *p*-methylacetophenone at low temperature. The phosphorescence of *p*-methylacetophenone in the mixed solvent at low temperature was found to be composed of two components, with lifetimes of 23 and 42 ms at 77 K. They are ascribed to the π,π^* triplet states of the monomer and dimer, respectively.

A number of aromatic carbonyl compounds exhibit anomalous phosphorescence with non-exponential decay.[1-9] Yang and Murov[1] studied phosphorescence for a series of aromatic carbonyl compounds and found that 1-indanone exhibits two phosphorescences with different lifetimes at 77 K, the short-lived one being assigned to the n,π^* triplet state, but the assignment of the long-lived one was open to question. They reported that simple aryl alkyl ketones like acetophenone and propiophenone also show a similar phenomenon.

Callis and Wilson[5] studied the absorption and emission spectra of Michler's ketone in glassy solutions at 77 K. They concluded that, in most commonly used glasses, the solute molecules are surrounded by two or three different types of environments and consequently anomalous luminescence appears. Wagner, May, and Haug[6] analyzed the viscosity dependence of dual phosphorescence of phenyl alkyl ketones at 77 K and ascribed the higher and lower frequency emissions to the n,π^* triplet state of the rigidly held molecule and to that of the conformationally relaxed one, respectively.

Griffin[4] explained anomalous phosphorescence of some acetophenone derivatives in terms of coexistent n,π^*, π,π^*, and charge-transfer triplet states. This explanation, however, is doubtful in view of the fact that, since the molecular relaxation time is of the order of 10^{-12} s,[10] a thermal equilibrium among the nearby triplet states is established within their decay and their phosphorescence decay times must be equal to each other, as was formulated by Mao and Hirota.[11a]

The mechanism of the anomalous phosphorescence observed with aromatic carbonyl compounds is still open to question. Hirota[12] found that the phosphorescence of *p*-methylacetophenone shows non-exponential decay and its apparent decay time changes with the concentration of the solution. In the present study, we have undertaken a study of the mechanism of the anomalous phosphorescence observed with this molecule in nonpolar solvent.

Experimental

p-Methylacetophenone (Tokyo Kasei, EP Grade) was purified with a Perkin-Elmer F21 gaschromatograph. Isopentane and 3-methylpentane were treated with active alumina column, dried with calcium chloride, and finally distilled over sodium metal. 3-Methylpentane–isopentane (1:6 volume ratio) mixed solvent (hereafter abbreviated to 3MP–P solvent) was used as nonpolar solvent.

Low temperature absorption spectra were measured with a Cary spectrophotometer model 14, quartz cells of 1 and 10 mm light-path lengths being used. Temperatures between 97 and 300 K were obtained by controlling a flow of cold nitrogen gas from an evaporation vessel containing liquid nitrogen.

Phosphorescence excitation spectra (PE spectra) were measured at 77 K with a phosphoroscope by exciting samples at various wavelengths with the aid of a 500 W xenon lamp and a Spex 1700-II monochromator. In order to eliminate the effect of stray light, an interference filter ($\lambda_{\max}=422$ nm, transmittance 30%) was set in front of an EMI 6256S photomultiplier used as a detector.

Phosphorescence spectra were measured at 77 K with the Spex monochromator by exciting samples with an Avco Everett model C950 pulsed nitrogen gas laser. The excitation-wavelength dependence of phosphorescence was observed with an Avco Everett model 1000 tunable wavelength laser as a monochromatized excitation source and a PAR model 121 lock-in amplifier. Time-resolved phosphorescence spectra and phosphorescence decay times were measured with a combination of the pulsed nitrogen gas laser and a PAR model 160 boxcar integrator.

Results and Discussion

Absorption Spectra. Three absorption bands were observed with *p*-methylacetophenone in 3MP–P solvent; the n,π^* transition band at ~360 nm, the π,π^* transition band at ~290 nm corresponding to the α band of benzene, and the π,π^* transition band with the charge-transfer character (the CT transition band) at ~260 nm.

Figure 1 shows the absorption spectra in the 290 nm region measured at 100 K with solutions of various concentrations of *p*-methylacetophenone. Since 3MP–P solvent is not rigid at 100 K, the system can rapidly attain equilibrium. For the solution with a concentration of 2.7×10^{-4} M, a band maximum appears at 288.1 nm. With increasing concentration of the solution its intensity decreases and a new band appears at 291.2 nm. The intensity of the new band increases with increasing concentration and isosbestic points appear at 287.5 and 288.7 nm.

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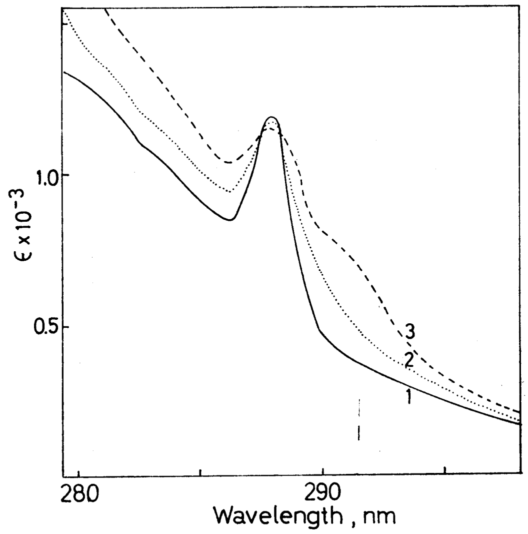

Fig. 1. Absorption spectra (280 nm—300 nm) observed at 100 K with 3MP-P solutions with various concentrations of *p*-methylacetophenone: the concentrations of *p*-methylacetophenone are 2.7×10^{-4}, 5.4×10^{-4}, and and 1.1×10^{-3} M for curves 1, 2, and 3, respectively.

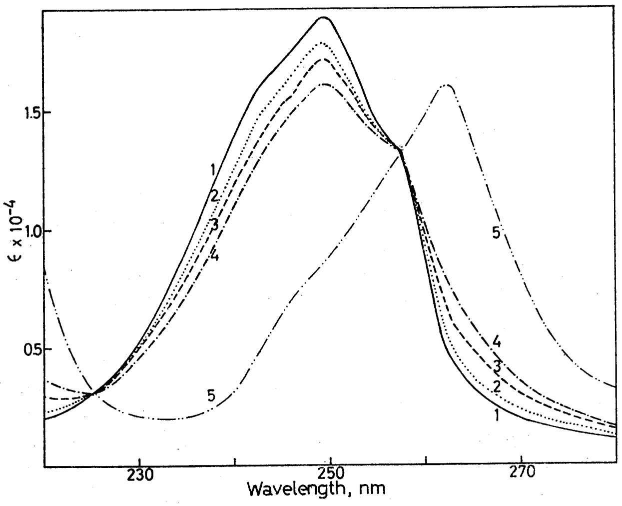

Fig. 2. Absorption spectra (220 nm—280 nm) observed at various temperatures with the 3MP-P solution of *p*-methylacetophenone (5.4×10^{-4} M): curve 1 at 120 K; curve 2 at 110 K; curve 3 at 107 K; curve 4 at 97 K. In this figure, the absorption spectrum of the dimer obtained with the aid of the observed spectrum at 97 K and the equilibrium constant is shown for the purpose of comparison (curve 5).

Figure 2 shows the temperature effect on the absorption spectrum in the range 280—220 nm observed for the solution with a concentration of 5.4×10^{-4} M. The spectra shown in this figure were observed in the temperature range 120—97 K.[13] The intensity of the band at 249 nm decreases with decreasing temperature. On the other hand, the absorption intensity at ~263 nm increases with decreasing temperature and isosbestic points appear at 225 and 258 nm.

The n,π* transition band at ~360 nm was obtained through the PE spectrum. Figure 3 shows the observed concentration dependence of the band. *p*-Methylacetophenone has a band maximum at 360 nm in the solution with a concentration of 1×10^{-5} M. With increasing concentration of the solution, the intensity of the 360 nm band decreases, and a new band at 357 nm gradually grows.

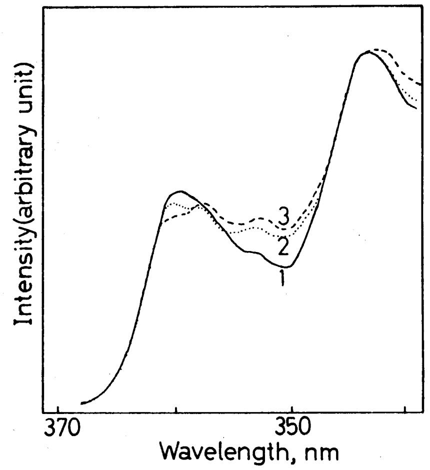

Fig. 3. The phosphorescence excitation spectra (340 nm —370 nm) of *p*-methylacetophenone observed at 77 K in 3MP-P solutions: the concentrations of *p*-methylacetophenone are 1.0×10^{-5}, 1.0×10^{-4}, and 1.0×10^{-3} M for curves 1, 2, and 3, respectively.

The results show that an equilibrium exists between the monomer and associated species and the new bands at 357, 291.2, and ~263 nm which appear in the relatively concentrated solutions are due to the associated species, most probably the dimer.

From the results shown in Fig. 2, we tried to obtain the monomer-dimer equilibrium constant and the enthalpy (ΔH) and entropy (ΔS) changes for the dimer formation. In view of the fact that the isosbestic points appear at 225 and 258 nm and that the absorption spectrum of the dimer has a peak at about 261—264 nm and its intensity increases with decreasing wavelength below 225 nm, we assumed that the apparent molar extinction coefficient of the dimer around 240 nm is equal to that at the isosbestic point at 225 nm. We further assumed that the absorption spectrum measured at 120 K is entirely due to the monomer. This might be reasonable since the intensity of the monomer band remains constant above this temperature, while below this temperature it increases with a

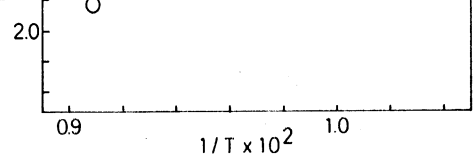

Fig. 4. Temperature dependence of the monomer-dimer equilibrium constant (K) of *p*-methylacetophenone.

rise in temperature. Thus we achieved a rough estimate of the concentrations of the monomer and dimer, C_M and C_D, and the equilibrium constant $K=C_D/C_M^2$ from the absorption intensity around 240 nm observed with a solution of a fixed concentration of *p*-methylacetophenone.[14] In actuality, K was obtained at 242.5, 240.0, and 237.5 nm. The values obtained at these wavelengths are in good agreement with each other at a fixed temperature. The logarithm of the average value of K's obtained at the three wavelengths is plotted against the reciprocal of temperature ($1/T$) in Fig. 4. From this plot, we obtained ΔH and ΔS to be -2 kcal/mol and -10 e.u., respectively. These values are very rough but reasonable for weak association.[15]

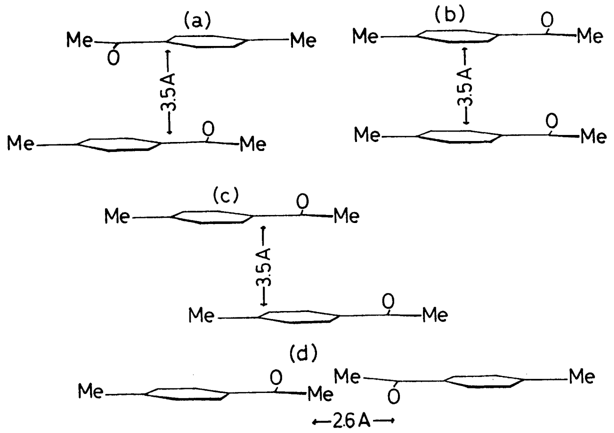

Fig. 5. Geometries of the *p*-methylacetophenone dimer taken for the CNDO/2 calculation.

Let us consider the geometry of the dimer. Using the MO's evaluated by the CNDO/2 method,[16] we calculated the band shifts due to the dimer formation considering interaction between permanent dipole moments in both the ground state and the appropriate excited states and also interaction between transition dipoles.[17] Figure 5 shows the dimer conformations which were used. Figure 5(a) shows the geometry of the dimer which best reproduces the observed band shifts. The experimental observation that the π,π^* and CT bands showed red shift by dimer formation while the n,π^* band showed blue shift can be explained qualitatively by this dimer conformation. This geometry may be reasonable in view of the fact that the stabilization due to the dipole-dipole interaction in the ground state of the dimer is conceivably large for this conformation.

Phosphorescence Spectra. Figures 6(a) and 6(b) show the integrated and time-resolved phosphorescence spectra of *p*-methylacetophenone in 3MP–P solvent at 77 K. The integrated phosphorescence has band maxima at 393.8, 420.8, and 451.8 nm, and the phosphorescence shows non-exponential decay. The time resolved spectra measured 1 and 70 ns after the excitation by the nitrogen gas laser have peaks at 393.0, 420.3, and 450.8 nm, and at 395.8, 420.9, and 453.2 nm, respectively. Thus, we interpret the phosphorescence spectrum as having two components: the band maxima for the longer-lived component lie at slightly lower energy. The phosphorescence decay curve observed at 420 nm at 77 K is shown in Fig. 7. From the analysis of this curve, the lifetimes of the short- and long-lived components were determined to be 23 and 42 ms, respectively. This indicates that two kinds of molecular species exist in the 3MP–P solution of *p*-methylacetophenone at 77 K.

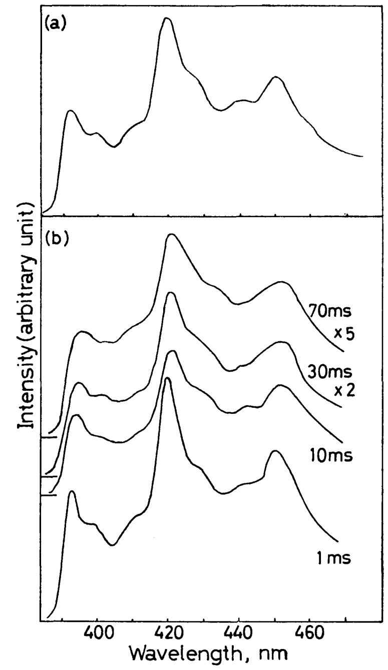

Fig. 6. Integrated (a) and time-resolved (b) phosphorescence spectra observed at 77 K with the 3MP–P solution of *p*-methylacetophenone (1.4×10^{-3} M).

It is reasonable to ascribe the short- and long-lived phosphorescences to the monomer and dimer of *p*-methylacetophenone, which exist in equilibrium in solution as concluded from the absorption measurement.

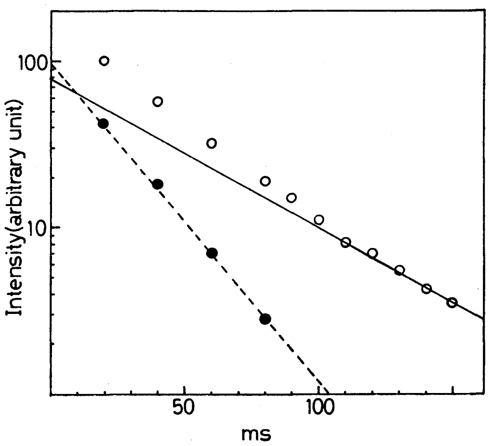

Fig. 7. Analysis of the phosphorescence (420 nm) decay curve observed at 77 K with the 3MP–P solution of *p*-methylacetophenone (8.4×10^{-4} M):

○; the observed decay curve

—; the long-lived component with the lifetime of 42 ms

●; the short-lived component, the difference between the observed decay curve and the long-lived component.

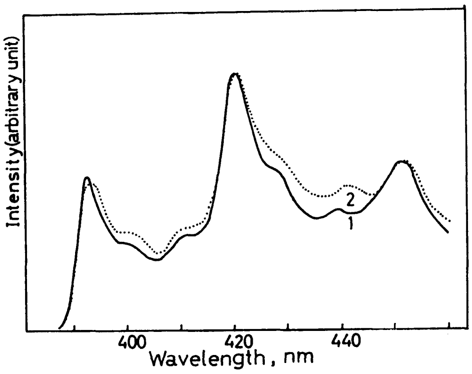

Fig. 8. Phosphorescence spectra observed at 77 K with the 3MP–P solution of *p*-methylacetophenone (1.4×10^{-3} M): excitation was made at 360 nm for curve 1 and at 357 nm for curve 2.

This is supported by the fact that the phosphorescence decay with the short- and long-lived components can be observed only in the low temperature region in which a considerable amount of the dimer exists in solution.[18]

In order to check this mechanism of the anomalous phosphorescence observed with *p*-methylacetophenone and also to determine which of the long-lived and short-lived components corresponds to the monomer or dimer, we measured the excitation-wavelength dependence of the phosphorescence spectrum.

Figure 8 shows the phosphorescence spectra obtained by the excitation at 360 and 357 nm at which the absorptions of the monomer and dimer mainly occur, respectively (Fig. 3). Although both spectra are similar to each other, the band maxima of the spectrum excited at 360 nm appear at slightly higher frequencies than the corresponding maxima of the spectrum excited at 357 nm. It is therfore, concluded that the dimer phosphorescence appears in lower frequencies than the monomer one. Combining this result with the time-resolved phosphorescence, we are led to the conclusion that the higher frequency phosphorescence with the lifetime of 23 ms and the lower energy one with the lifetime of 42 ms are ascribed to the monomer and dimer, respectively. The assignment is supported by the observed tendency that the band positions in the phosphorescence spectrum observed with *p*-methylacetophenone in 3MP–P shift to longer wavelengths with decreasing temperature in the range 90—80 K and also with increasing concentration of *p*-methylacetophenone.[19]

The phosphorescent states of the monomer and dimer of *p*-methylacetophenone may be regarded as π,π^* triplet states, since both lifetimes are too long to be ascribed to the n,π^* triplet state.[11b]

Cheng and Hirota[11b] presented a linear relationship between $k_z^{1/2}$ and ΔE_T^{-1} for aromatic carbonyl compounds. Here, k_z and ΔE_T are the decay rate constant of the T_z sublevel and the energy difference between the n,π^* and π,π^* triplet states, respectively. Since $1/\tau=k=\sum_i n_i k_i$, we can calculate the ΔE_T from the observed lifetime, if we assume $k_x=k_y=0$.[20] Here, τ and k are the mean lifetime and the mean decay rate constant, respectively, and k_i and n_i the decay rate constant and population fraction of the T_i sublevel, respectively. At 77 K $n_i=1/3$ is used. Thus, ΔE_T's are calculated to be 348 and 475 cm^{-1} for the monomer and dimer, respectively.

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13) The spectrum measured at room temperature does not cross the isosbestic points and the absorption peak shifts slightly toward shorter wavelengths. This shift may be due to the difference in the environment between room temperature and ~100 K.

14) We determined the *K* value roughly on the assumption that the molar extinction coefficient of the dimer band at 291.2 nm is equal to that of the monomer band at 288.1 nm. The value thus obtained is 200 M^{-1} l at 100 K—almost half the corresponding value 400 M^{-1} l at 102 K obtained by the method given in the text. This discrepancy seems to be unavoidable because of the roughness of both methods, in particular the method mentioned here. Importance should be attached to the fact that both methods give values of the same order of magnitude.

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18) By extrapolating the straight line in Fig. 4, we can estimate the equilibrium constants at 90 and 80 K to be 1280 and 5480 M^{-1} l, respectively. By the use of these values, the concentration ratio of the dimer to the monomer is evaluated for the *p*-methylacetophenone solution of 1×10^{-3} M to be 3: 5 and 4: 3 at 90 and 80 K, respectively. Furthermore, considering the fact that the lifetimes of the two components are rather close to each other, we may explain the observation that the phosphorescence decay of

the 3MP–P solution containing 8.4×10^{-4} M *p*-methylacetophenone fits considerably well into a single exponential curve at 87 K but deviates from it at 77 K.

[19] The phosphorescence of *p*-methylacetophenone in 3MP–P is weak, particularly above 90 K. It is therefore difficult to measure its intensity in a wide temperature range accurately enough for the monomer-dimer equilibrium and the temperature dependence of the phosphorescence intensity to be treated quantitatively.

[20] This assumption is reasonable since k_x for most aromatic carbonyl compounds is predominantly large among the three decay rate constants.[11b]