BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (6), 1816—1818 (1979)

Solvent Effects and Hyrogen-bonding Interactions on Absorption and Fluorescence Spectra of 1-Methyl-2-pyridone

Akira FUJIMOTO and Kozo INUZUKA*

Department of Applied Science, Faculty of Technology, Tokyo Denki University, Kanda, Chiyoda-ku Tokyo 101

(Received December 21, 1978)

The electrostatic solvent effects and hydrogen-bonding interactions on IR and UV absorption and fluorescence spectra of 1-methyl-2-pyridone has been investigated. It was found that the UV absorption and fluorescence bands of 1-methyl-2-pyridone shifted towards the shorter-wavelength region with increasing solvent polarity and that these bands exhibited a blue shift on hydrogen bond formation with alcohols and chloroform. The excited-state dipole moment of 1-methyl-2-pyridone, and the equilibrium constants in the ground and excited states and enthalpy change in the ground state for hydrogen-bond formation between 1-methyl-2-pyridone and ethanol have been determined from the spectroscopic studies.

Kimura *et al.*[1] have suggested from fluorescence data, that the lowest excited singlet state of 1-methyl-2-pyridone (abbreviated to MPD) is π-π^* in character in alcoholic solution. It was not reported that the fluorescence band characterized by the π-π^* transition shifted towards the shorter-wavelength region with increasing solvent polarity and that the band exhibited a blue shift on hydrogen bond formation with alcohols.

As part of this study[2] on the electronic spectra of heterocyclic compounds, the solvent effects and hydrogen-bonding interactions on UV absorption and fluorescence spectra of MPD in isooctane (2,2,4-trimethylpentane) have been investigated. The presence of an intermolecular hydrogen bond between MPD and ethanol has been confirmed by IR analysis.

Experimental

MPD was purified by vacuum distillation to give a sample of boiling point 103.0—103.5 °C/930 Pa. The solvents used were commercially available and further purified by distillation. IR spectra were measured using a Hitachi Model 260-30 infrared spectrophotometer; measurements were conducted at ambient temperature, a cell of 0.5 mm path length being used. Measurements of UV absorption and fluorescence were conducted with the spectrophotometers reported previously.[2a] The temperature of the UV absorption cells (10 mm) was regulated by a Komatsu-Yamato Model CTR-120 electronic cooling circulator within the temperature range 8 to 50 °C.

Results and Discussion

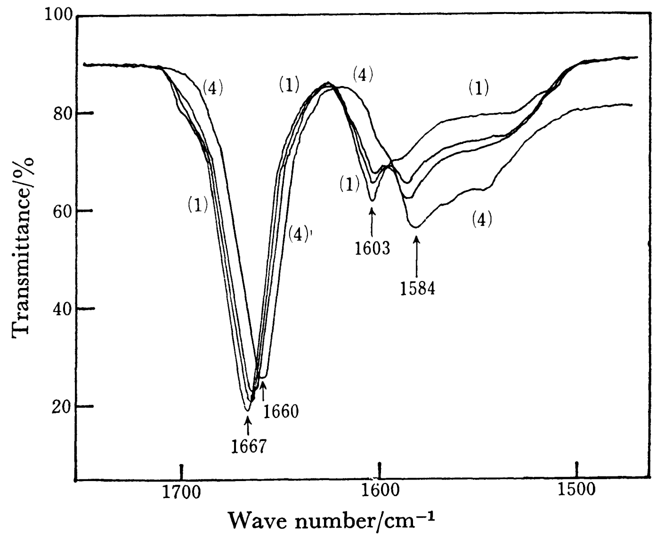
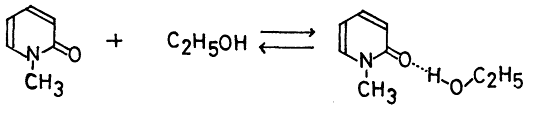


Fig. 1. IR spectra of the MPD–ethanol–carbon tetrachloride system. Concentration of MPD: 8.26×10^{-3} mol dm^{-3}. Concentrations of ethanol (mol dm^{-3}): (1) 0, (2) 8.8×10^{-2}, (3) 1.76×10^{-1}, (4) 2.14.

The C=O absorption bands of MPD observed in the several solvents at room temperature are given in Table 1. As may be seen the C=O band shifted to the lower-frequency region with increasing polarity of the solvents; notably the frequency shift of the corresponding band is appreciably larger in alcohols and chloroform than in other solvents. As Fig. 1 illustrates remarkable changes are produced in the IR spectra of MPD by the addition of ethanol to the carbon tetrachloride solution: the C=O streching band of MPD was observed at 1667 cm^{-1} in CCl_4, while the corresponding band shifted to the lower-frequency region with increasing ethanol concentration (1660 cm^{-1}, ethanol concentration=2.14 mol dm^{-3}). A similar frequency-shift was observed on the addition of chloroform to a carbon tetrachloride solution of MPD. Such frequency-shifts in alcohol and chloroform may be attributed to intermolecular hydrogen bonding between the C=O group of MPD and alcohol, and between the C=O group of MPD and chloroform. The hydrogen bond between MPD and ethanol is represented by the following equilibrium:



(1)

Here MPD acts as a proton acceptor and ethanol as a proton donor. In Fig. 1, the absorption band at 1603 cm^{-1}, corresponding to the ring streching vibration of MPD[3] disappeared, while a new band maximum was observed at 1584 cm^{-1}, attributed to the redistribution of the ring electrons as a result of hydrogen-bond formation with the OH group of ethanol.

The solvent effects on the electronic spectra of organic compounds have been studied by many workers: Lippert,[4] Mataga *et al.*,[5] and McRae[6] proposed the following equation (Eq. 2) for the evaluation of the difference in the dipole moments of the excited and ground states, *i.e.* $\Delta\mu = \mu_e - \mu_g$.

$$hc\Delta\sigma = \text{const} + 2F(D, n)(\Delta\mu)^2/a^3, \tag{2}$$

where

$$\Delta\sigma = \sigma_a^m - \sigma_f^m$$

and

$$F(D, n) = \left(\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1}\right).$$

In Eq. 2 σ_a^m and σ_f^m represent the wave number of the peak of the UV absorption band and the fluorescence band maximum, respectively. D and n represent the dielectric constant and refractive index of the solvent and a represents Onsager's reaction radius of the solute molecule.

Table 1. Wave numbers of the C=O band maxima (ν), UV absorption maxima (σ_a^m), and fluorescence band maxima (σ_f^m) of MPD measured in solvents of different polarity at room temperature

No.	Solvent	$F(D,n)$	$\dfrac{\nu}{\text{cm}^{-1}}$	$\dfrac{\sigma_a^m}{\text{cm}^{-1}}$	$\dfrac{\sigma_f^m}{\text{cm}^{-1}}$
1	Isooctane	0.000	1677	32410	26700
2	Benzene	0.002	1667	32440	26700
3	Carbon tetrachloride	0.010	1667	32440	26700
4	Dioxane	0.020	1666	32420	26700
5	Chloroform	0.185	1660	32840	26800
6	Ethyl acetate	0.202	—[a)]	32570	26700
7	Dichloromethane	0.218	1665	32680	26800
8	Ethanol	0.298	1660	32950	26800
9	Acetonitrile	0.304	1664	32790	26800
10	Methanol	0.308	1659	33000	26800

a) The C=O band of MPD was hidden by the intense absorption band of the C=O group of ethyl acetate.

The observed values of σ_a^m and σ_f^m are given in Table 1, together with the values of $F(D,n)$.[4,5] It may be seen that the UV absorption and fluorescence band maxima tend to shift towards the shorter-wavelength region with increasing solvent polarity and the blue shift of the UV absorption band maximum is much larger than that of the fluorescent counterpart. A similar phenomenon has been observed for the UV absorption and fluorescence spectra of pyridine N-oxide in several solvents.[7] In analogy with pyridine N-oxide the above experimental facts indicate that the π-electron transfer from the oxygen atom to the pyridine ring is much larger in the excited state than in the ground state. Accordingly, the dipole moment appears to be larger in the ground state than in the excited state, $\mu_g > \mu_e$. In Fig. 2 the $\Delta\sigma$ has been plotted against $F(D,n)$ and as can be seen there is a linear relationship between $\Delta\sigma$ and $F(D,n)$ except for alcohols and chloroform. The linear relationship between $\Delta\sigma$ and $F(D,n)$ corresponds to Eq. 2 and may be approximately represented as follows:

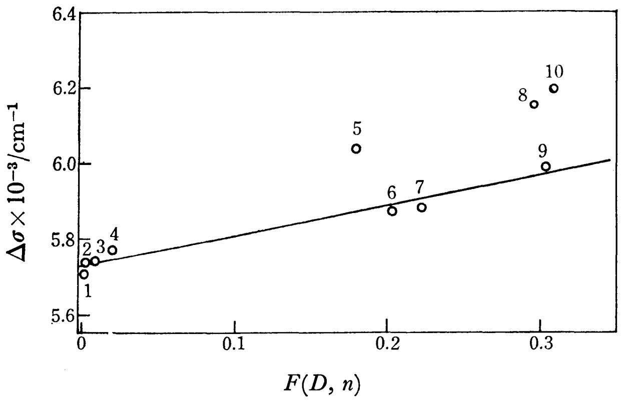


Fig. 2. The plot of $\Delta\sigma$ *vs.* $F(D, n)$.

$$\Delta\sigma = 5730 + 770F(D, n). \tag{3}$$

From this equation, the $\Delta\mu$ value for MPD has been evaluated as -1.1 D, assuming 2.5 Å for a. μ_e has been estimated to be 2.94 D, using the values $\Delta\mu$ and μ_g (4.04 D) determined by Krackov *et al.*[8] In Fig. 2 the solvents such as alcohol and chloroform cause a large deviation and this has been attributed to hydrogen-bonding as described in the experimental section.

The equilibrium constant in the ground state (K_g),

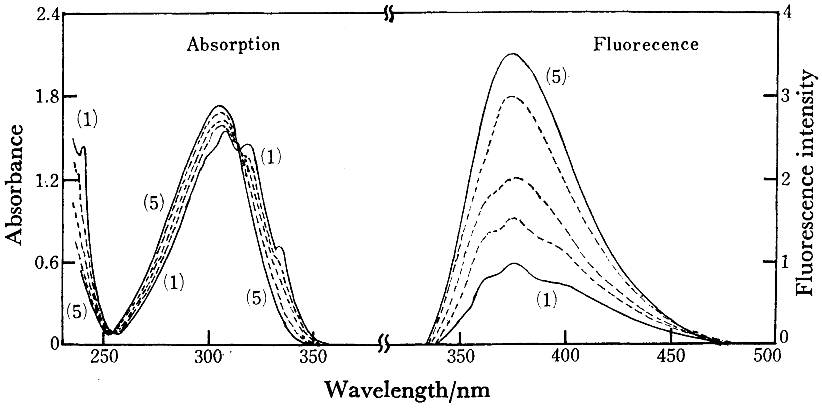


Fig. 3. UV absorption and fluorescence spectra of the MPD–ethanol–isooctane system at ambient temperature. Concentration of MPD: 4.2×10^{-4} mol dm^{-3}. Concentrations of ethanol (mol dm^{-3}): (1) 0, (2) 7.0×10^{-2}, (3) 1.5×10^{-1}, (4) 5.0×10^{-1}, (5) 2.0. Excitation wavelength: 300 nm.

enthalpy change ($-\Delta H$), and entropy change ($-\Delta S$) due to hydrogen-bond formation have been obtained by UV spectroscopy.[9] As shown in Fig. 3, considerable changes are produced in the UV spectra of MPD by the addition of ethanol to the isooctane solution. In order to eliminate the interference of the ordinary solvent effect, a three-component system was employed.[9] Consequently, it may be assumed that the spectral changes are due to the formation of a hydrogen-bonded complex between MPD and ethanol. It has been found that the UV absorption spectra, characterized by the π-π^* transition[1] exhibits a large blue-shift and an increase in total absorption intensity with increasing ethanol concentration. The values, 5.91 mol^{-1} dm^3 for K_g, 18 kJ mol^{-1} for $-\Delta H$, and 45.6 J K^{-1} mol^{-1} for $-\Delta S$ which were interpolated at 25.0 °C, were obtained from the UV spectra of the MPD–ethanol–isooctane system.

The fluorescence spectra of the MPD–ethanol–isooctane system are presented in Fig. 3. A blue shift of the fluorescence band maximum is evident and the intensity of the fluorescence band increases with increasing concentration of ethanol. The degree of spectral shift of the band maximum caused by hydrogen bonding is smaller in the fluorescence spectrum than in the absorption one. Experimentally it has been established that the addition of ethanol to the isooctane solution of MPD does not change either the fluorescence or absorption spectra when the concentration of ethanol is more than 2.0 mol dm^{-3}. From the fluorescence and absorption band spectra and the concentration of ethanol being 2.0 mol dm^{-3}, the fluorescence and absorption band maxima wave numbers were found to be 26800 and 32950 cm^{-1}, respectively. These values agree with the values of σ_f^m and σ_a^m in ethanol, respectively (Table 1).

The equilibrium constant of the hydrogen-bond formation in the excited state (K_e) may be related to K_g using the UV absorption and fluorescence spectral data in Eq. 4:[10]

$$\log K_e = \log K_g - 0.625\,\delta\sigma/T, \tag{4}$$

where

$$\delta\sigma = (\delta\sigma_a + \delta\sigma_f)/2.$$

$\delta\sigma_a$ (540 cm^{-1}) is the difference between the UV absorption band maxima of MPD in isooctane and ethanol, and $\delta\sigma_f$ (100 cm^{-1}) corresponds to the difference between the fluorescence band maxima in the above two solvents and T is the absolute temperature. The value of K_e at 25.0 °C has been estimated to be 1.3 mol^{-1} dm^3 from Eq. 4. The equilibrium constant in the excited state may also be obtained *via* Eq. 5.[11]

$$[1-(f_0/f_m)(d_m/d_0)]/[\mathrm{D}] = -K_e + \alpha K_e (f_0/f_m)(d_m/d_0) \tag{5}$$

$$\alpha = \Phi_a/\Phi_c,$$

where f_m and f_0 correspond to the fluorescence intensities with and without the addition of donor, and d_m and d_0, the absorbances at a definite wavelength with and without the addition of donor, respectively. Φ_c and Φ_a correspond to the quantum yields of fluorescence of the acceptor and hydrogen-bonded complex, respectively, and [D] is the concentration of donor. The analysis of the fluorescence intensities is shown in Fig. 4 where it may be seen that K_e is approximately 1.8 mol^{-1} dm^3. This value is in reasonable agreement with the K_e value obtained by Eq. 4. Both K_e values are smaller than the K_g value indicating that the hydrogen-bonding is weaker in the excited state than in the ground state.

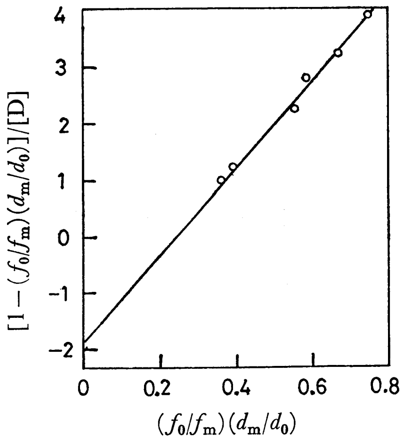


Fig. 4. The plot of $[1-(f_0/f_m)(d_m/d_0)]/[\mathrm{D}]$ *vs.* $(f_0/f_m)(d_m/d_0)$. From the observed change of fluorescence intensity at 375 nm, the equilibrium constant of hydrogen bond formation in the excited state (K_e) was obtained.

This work was supported by grants from the Tokyo Denki University Research Fund.

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