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Thermodynamic and Kinetic Parameters Concerning Complex Formation between 3-Hydroxy- and 1-Aminopyrene and Pyridine

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Systems formed by the pyrene derivatives 3-hydroxypyrene and 1-aminopyrene with pyridine were studied. The thermodynamic and kinetic parameters of the systems were calculated using the changes in the absorption and emission spectra which occur due to hydrogen bond or complex formation. The decrease of the formation rate constant in the series methylcyclohexane, benzene, and o-chlorotoluene may be due to a more difficult formation of the hydrogen bond complex due to the increase of the dielectric constant in the solvent series.

Introduction

Photoexcitation of molecules leads to a significant change in their electronic structure and reactivity. Photochemically induced proton transfer is extremely convenient for the investigation of the general characteristics of the reactions of electronically excited states. Recently much attention has been paid to the excited state characteristics exhibited by polycyclic aromatic hydrocarbons (PAHs) in photochemical processes. This is partly because PAHs have acute biological activity such as 'carcinogenicity. In particular, 3-hydroxypyrene is of considerable significance in terms of the environment and human health[1]. For this reason, the 3-hydroxypyrene and 1-aminopyrene systems were chosen for study.

The investigation of proton donor-acceptor and electron donor-acceptor systems of aromatic compounds was first carried out by Förster in 1950. He investigated the reactions of aromatic hydroxy compounds which occur protolitically. Subsequently Weller determined the rate constant of these reactions in water[2]. Nagakura and Baba studied the absorption spectra of 1:1 hydrogen bond complexes of phenols with suitable bases[3]. Absorption and fluorescence spectra of purine and cytosine systems were studied in aqueous solution[4]. The fluorescence of hydrogen-bonded complexes was first observed by Mataga et al. for complexes of 2-naphthol with acetates in hexane[5]. Mataga et al. derived an equation to determine the complex formation equilibrium constant in the excited state showing the concentration dependence of the fluorescence[6]. Proton transfer reactions involving electronically excited aromatic molecules have been examined, and the

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methods for the determination of the acidities of aromatic molecules in the excited state have been discussed and compared[7]. The complex formation rate constants in the excited state have been outlined from the fluorescence intensity differences of hydrogen bonded complexes[8].

The stabilization of the hydrogen bond interaction of the 3-hydroxypyrene-3,5-dimethylpyridine system in the ground state and the bimolecular rate constant of the fluorescence quenching reaction in hexane have been compared with those in acetonitrile solution[9]. Absorption and fluorescence spectra of the 3-hydroxypyrene-triethylamine system have been recorded in n-hexane, benzene and acetonitrile solutions and the decrease of the free 3-hydroxypyrene fluorescence intensity due to ground-state hydrogen bond complex formation has been investigated[10].

Proton transfer reactions in the excited singlet state of 1-aminopyrene in the presence of protons in H_2O (or D_2O) –acetonitrile mixtures have been investigated by spectrofluorometric methods[11]. Excited state proton transfer complexes of 1-aminopyrene and α-napthol with cyclodextrins in an ethanol-water mixture have been studied by time-resolved spectroscopy[12]. Aminopyrene-methyl-substituted pyridine pairs in hexane at room temperature have been investigated by spectroscopic methods[13]. The complexes of the 1-aminopyrene-pyridine system and the N,N-dimethyl-1-aminopyrene-pyridine system have been compared, and the quenching by pyridine in hexane solution has been monitored by diffusion controlled reactions.

Studies concerning the solvent effects on fluorescence spectra have generally been carried out in aqueous and polar solutions. However, although limited work on the spectroscopic investigations of 3-hydroxypyrene and 1-aminopyrene with some acceptors has been carried out in aprotic solvents, spectroscopic investigation at different temperatures has not been conducted. In addition, there is little information available regarding the thermodynamic and kinetic parameters of these systems. As a result, when their biological significance was taken into consideration, we decided it was important to examine both 3-hydroxypyrene-pyridine and 1-aminopyrene-pyridine systems. They were investigated in methylcyclohexane, benzene and o-chlorotoluene solution.

Experimental

The properties of the donor and acceptor systems used are as follows: 3-hydroxypyrene (99% , Aldrich), 1-aminopyrene (97% , Aldrich, recrystallized), and pyridine (99%, for analysis Veb Petrolchemisches Kombinat Schedt). The solvent systems chosen are methylcyclohexane (99%, Aldrich, spectroscopic grade), benzene (99%, Aldrich) and o-chlorotoluene (99%, Aldrich).

All absorbance measurements were taken using a Hitachi U2000 Spectrophotometer at various temperatures. Steady-state measurements were performed using a Shimadzu RF 5000 at different temperatures. The temperature was controlled in all experiments by an FP40 thermostat.

Fluorescence lifetimes were measured at room temperature according to the Pulse-Sampling Method. For pulsed light, an N_2 Laser ($\lambda = 337$ nm) of the Firm Laser 2000 (Model ILEE-NN100) was used. During measurements of fluorescence intensities and lifetimes, nitrogen gas was used to remove the dissolved oxygen in the solution so that the quenching effect due to the presence of oxygen was diminised. The thickness of the quartz cuvette was 1 cm.

Results and Discussion

The investigation of the fluorescence and absorption spectra involves the use of very dilute solutions in order to minimize self-absorption effects. The optimum concentrations of 3-hydroxypyrene and 1-aminopyrene were found to be $5x10^{-5}$ M and $4x10^{-5}$ M respectively. 3-hydroxypyrene and 1-aminopyrene complexes formed with pyridine were measured at different temperatures (10 - 44°C) and solvents. As an example, the effects of the addition of pyridine on the ground state absorption spectrum of 3-hydroxypyrene in the solvents examined show typical characteristics of spectral change due to a 1:1 complex formation. This spectral change can be analyzed by equation 1 based on 1:1 hydrogen bonding

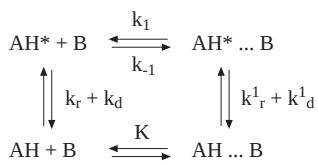
$$\frac{1}{\Delta A} = \frac{1}{\Delta A_{\max}} + \frac{1}{K\Delta A_{\max}} x \frac{1}{C_a} \tag{1}$$

where ΔA is the change in optical density of the donor in the presence of the acceptor having concentration of C_a^{14}. ΔA_{max} is the maximal change in absorbance when all the donor is in the form of the complex and K is the association constant of the ground state. The graph of $1/\Delta$A vs $1/C_a$ gives a linear change in which K and ΔA_{max} can be found from the slope and intercept value.

The absorption spectra of a series of 1-aminopyrene-pyridine solutions having different pyridine concentrations ($4x10^{-3}$- $2.4x10^{-1}$ M) were examined. Absorption spectra for these systems were recorded in methylcyclohexane, benzene and o-chlorotoluene at different temperatures (10 - 42^0C).

It was observed that the spectral shifts of the 3-hydroxypyrene-pyridine system were larger than those of the 1-aminopyrene-pyridine system. These shifts depend on the ionization potential of the substituent. The smaller the ionization potential of the substituent, the easier its proton interacts with the acceptor. The ionization potential of oxygen in 3-hydroxypyrene is smaller than that of nitrogen in 1-aminopyrene. Hence, the shifts in the 3-hydroxypyrene-pyridine system are larger than in the 1-aminopyrene-pyridine system. The ground-state equilibrium constant, K, of the 3-hydroxypyrene-pyridine system is greater than that of the 1-aminopyrene-pyridine system in the same solvent depending on the donor characteristics. The ground-state equilibrium constants of the 3-hydroxypyrene-pyridine complex in o-chlorotoluene and benzene solution are three and/or four times smaller than that of the complex in methylcyclohexane; however, this ratio is two in the 1-aminopyrene-pyridine system (Tables 1 and 2). These shifts also depend on the dielectric constant of the solvents and the acceptor strength.

The interaction of aromatic hydroxy- and amino-compounds (AH) with acceptor (B) in the ground state results in the formation of hydrogen bonded complexes. As in the ground state, there is a possibility of the formation of excited hydrogen-bonded complexes in the excited state. The general mechanism of the processes occurring in the ground and excited states in aprotic solvents can be represented as follows[7]:



where k_r and k_r^1 are the fluorescence rate constants, and k_d and k_d^1 are the rate constants for the non-radiative deactivation of the free form of the fluorescent species and the excited hydrogen-bonded complex respectively. K is the equilibrium constant for the formation of the hydrogen-bonded complex.

Fluorescence spectra for 3-hydroxypyrene were recorded in different solvents and at temperatures (10 and 44°C). The successive decrease in intensity of the fluorescence bands with increasing concentration of pyridine ($2\times10^{-3}-2\times10^{-2}$ M) may be attributed to the depletion of free 3-hydroxypyrene by the formation of hydrogen bonded 3-hydroxypyrene in the excited state. As an example, the fluorescence spectra of the system having different pyridine concentrations in methylcyclohexane solution at 20°C are shown in Figure 1.

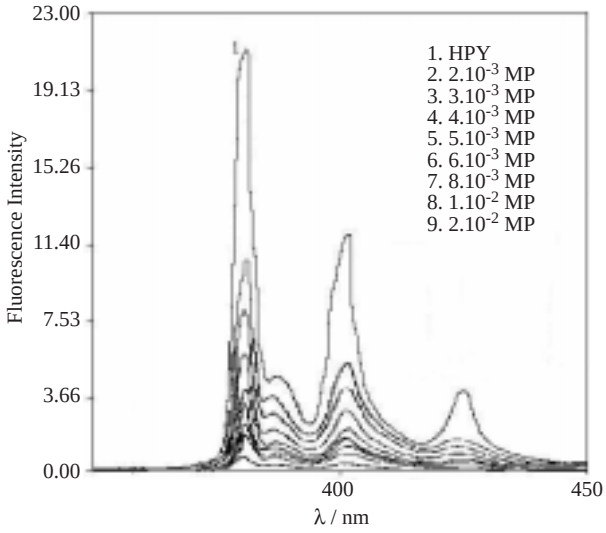


Figure 1. Effects of the addition of pyridine on the fluorescence spectra of 5x10^{-5} M 3-hydroxypyrene in methylcyclohexane solution at 20°C.

Mataga et al.[6] derived the following equation, which shows the relation between concentration and fluorescence intensity:

$$\frac{\frac{I}{I_0}-1}{[C_a]} = \alpha K* - K*\frac{I}{I_0} \tag{2}$$

Here, I and $I_0$are the intensities of emissions from the complex form and free form respectively and α is the ratio of the quantum efficiencies of fluorescence for the excited state complex (ϕ_c) and excited proton donor (ϕ) respectively, $\alpha = \phi_c/\phi$. The graph drawn of $[(I/I_0)-1]/[Ca]$ vs I/I_0 gives a straight line and the equilibrium constant for the excited state, K*, can be found from the slope. The excited state equilibrium constant can also be calculated from the difference of wavenumbers at half the maximal height ($\Delta\nu_h$) of the absorption measurements with the assumption of equal reaction entropies in the ground and excited states ($\Delta S = \Delta S^*$)[15]:

$$pK^* = pK + \frac{0.625}{T}\Delta\nu_h(cm^{-1}) \tag{3}$$

When the K* values obtained through the calculation of eq. 2 and eq. 3 for 3-hydroxypyrene-pyridine system are compared, they are determined to be consistent with each other.

As recorded for the 3-hydroxypyrene-pyridine system, fluorescence quenching has been observed by the formation of hydrogen-bonded 1-aminopyrene in the excited state by an increase in pyridine concentration (3x10^{-3} – 3.5x10^{-2}). The optimum concentration for the 1-aminopyrene solution was determined to be

$2.5x10^{-5}$ M. Figure 2 shows the fluorescence spectra of the 1-aminopyrene-pyridine system in methylcyclohexane solution. The fluorescence spectra of the system in o-chlorotoluene and benzene were also recorded. Tables 1 and 2 show thermodynamic values for 3-hydroxypyrene-pyridine and 1-aminopyrene-pyridine systems respectively.

Table 1. The ground and excited thermodynamic parameters of the 3-hydroxypyrene-pyridine system in different solvents and at different temperatures.

in methylcyclohexane						
T ^{0}C	K /M^{-1}	K* /M^{-1}	-ΔG /kJ mole^{-1}	-ΔG* /kJ mole^{-1}	-ΔH /kJ mole^{-1}	-ΔH* /kJ mole^{-1}
10	356	1125	13.9	16.5		
15		883		16.2		
20	218	799	13.1	16.3		
20	[1](220)	[1](980) [2]994			37.4 ±0.8	41.1±0.8
28	136	538	12.3	15.7		
34	104	501	11.9	15.9		
44	66	446	11.0	16.0		
					$\Delta\nu_h$ /cm^{-1} : 309 (20^{0}C)	
in benzene						
T^{0}C	K /M^{-1}	K* /M^{-1}	-ΔG /kJ mole^{-1}	-ΔG* /kJmole^{-1}	-ΔH /kJ mole^{-1}	-ΔH* /kJ mole^{-1}
12		347		13.9		
15	80	322	10.5	13.8		
20	57	274	9.8	13.6	23.8 ±0.5	27.5 ±0.5
20	[1](58)	[1](270) [2]268				
25	56	241	9.9	13.6		
30	53	235	10	13.7		
35	37		9.2		$\Delta\nu_h$ /cm^{-1} : 315 (20^{0}C)	
in o-chlorotoluene						
T^{0}C	K /M^{-1}	K* /M^{-1}	-ΔG /kJ mole^{-1}	-ΔG* /kJ mole^{-1}	-ΔH /kJ mole^{-1}	-ΔH* /kJ mole^{-1}
10	145		11.2			
15	113	437	11.3	14.6		
20	79	416	10.6	14.7	31.9 ±0.7	35.9 ±0.7
20	[1](78)	[1](430) [2]402				
25		320		14.3		
30	60	293	10.3	14.3		
					$\Delta\nu_h$ /cm^{-1} : 331 (20^{0}C)	

[1] From reference 8.
[2] Calculated according to equation 3.

Table 2. The ground and excited state thermodynamic parameters of the 1-aminopyrene-pyridine system at 20°C.

Solvent	K /M^{-1}	K* /M^{-1}	-ΔG /kJ mole^{-1}	-ΔG* /kJ mole^{-1}	-ΔH /kJ mole^{-1}	-ΔH* /kJ mole^{-1}
in methylcyclohexane	3.2	91	2.8	11	18.6	21.7
in benzene	1.29	29	0.62	8.2	9.4	10.6
in o-chlorotoluene	1.6	31.9	1.14	8.4	15.3	17.6

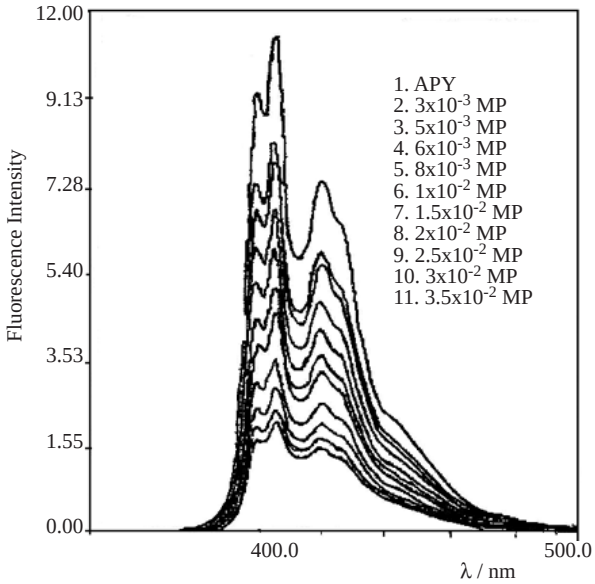


Figure 2. Effects of the addition of pyridine on the fluorescence spectra of $2.5x10^{-5}$ M 1-aminopyrene in methylcyclohexane solution at 20°C.

In all systems, K and K* values decrease with increasing temperature as expected due to exothermic hydrogen bond formation reactions. It has been seen that hydrogen bond complex formation becomes weaker with increasing temperature. The shifts for the systems 3-hydroxypyrene-pyridine and 1-aminopyrene-pyridine in methylcyclohexane, benzene and o-chlorotoluene solutions have not been observed since the systems were not fluorescent. The association constant, K*, has been calculated using equation (2). The large K* values in both the 3-hydroxypyrene-pyridine and 1-aminopyrene-pyridine systems show the increasing acidity in the excited state (Table 1 and 2), since the mesomeric effect in the excited state is stronger than in the ground state. Hence, ionization energy is smaller in the excited state and the substituent may have a stronger effect as an electron donor.

The diffusion step determines the rate of hydrogen bonding in the excited state.

$$\underset{}{AH^* + B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{I}{AH^* \ldots B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{II}{A^{*-}\ldots HB^+} \tag{4}$$

At first, diffusion, and then hydrogen bond formation were observed in a system in which AH is the donor and B is the acceptor:

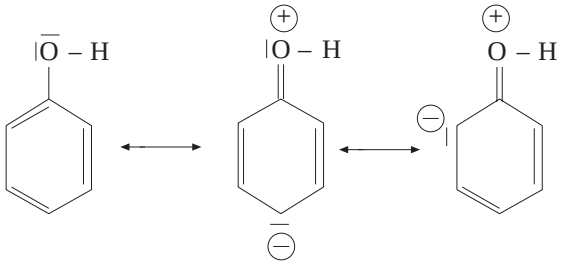
$$AH^* + B \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} (AHB^*) \overset{k_r}{\rightleftharpoons} AH^*\ldots B \tag{5}$$

In the second step, the proton is bound to acceptor B and the formation of equilibrium is fairly fast ($<10^{-11}$ sec).

Hydrogen bond formation occurs in the 3-hydroxypyrene-pyridine system in methylcyclohexane, benzene and o-chlorotoluene solution according to the equilibrium I in the excited state. It is known that a

hydrogen bond is formed using triethylamine as an acceptor in the 3-hydroxypyrene-triethylamine system in methylcyclohexane according to the equilibrium I in eq. 4. However, an ion-pair was formed according to the equilibrium II in eq. 4 in benzene and o-chlorotoluene solution[16]. Similar to the 3-hydroxypyrene-pyridine system, hydrogen bond formation was also seen for the 1-aminopyrene-pyridine system in all three solvents in the excited state.

It has been observed that K* constants in the 1-aminopyrene-pyridine system are smaller than that in the 3-hydroxypyrene-pyridine system (Table 1 and 2). This shows that the 3-hydroxypyrene-pyridine system makes a stronger hydrogen bond in the excited state. Therefore, mesomeric forms could also be present in the excited state according to (a) and (b) as shown below:



(a) (b)

K and K* values for the 3-hydroxypyrene-pyridine and 1-aminopyrene-pyridine systems in methylcyclohexane are larger than the values in o-chlorotoluene and benzene in the ground and excited state. This situation arises from stronger hydrogen bond formation in the aliphatic solvents according to the equilibrium given below:

$$\mathrm{AH \ldots L + B} \rightleftharpoons \mathrm{AH \ldots B + L} \tag{6}$$

Thus, aromatic solvent (L) competes with the donor due to its structure (π-electrons) prior to complex formation, and therefore hydrogen bond formation would be more difficult[17]. A similar case was observed in the 1-aminopyrene-pyridine system.

The enthalpy changes ΔH accompanying hydrogen bond formation can be obtained by the Van't Hoff equation

$$\Delta H = -R[d \ln K/d(1/T)] \tag{7}$$

The value of ΔH is obtained by the least squares method from the curve drawn by lnK versus 1/T. The enthalpy change derived in this way is of course to be associated with the ground state of a given molecule. In general, the enthalpy change of the hydrogen bond in the excited state is different from that in the ground state, and the former will therefore be denoted by ΔH*.

$$\Delta \mathrm{H} - \Delta \mathrm{H}^* (\mathrm{kcal/mole}) = 2.86 \times 10^{-3} \Delta\nu(\mathrm{cm}^{-1}) \tag{8}$$

Equation (8) can be obtained from an electronic transition on the basis of the Franck-Condon principle[18]. Here, $\Delta\nu(\cong \Delta\nu_h)$ represents the wavenumber which is equal to $\Delta\nu = \nu_b - \nu_f$. ν_f and ν_b denote the wavenumbers of the absorption maxima for free and bonded molecules, respectively.

For the 3-hydroxypyrene-pyridine and 1-aminopyrene-pyridine sytems, ΔH and ΔH^* were calculated according to equation (7) and equation (8), respectively. As expected, ΔH^* values were found to be larger than ΔH values for both systems (Table 1 and 2).

The enthalpy change for the 3-hydroxypyrene-pyridine system was found to be between -5.7 and - 8.9 kcal/mole in different solvents in the ground state while it was found to be between -2.2 and -4.5 kcal/mole for the 1-aminopyrene-pyridine system. The hydrogen bond energies OH-N (in the range -1.5 _ -9 kcal/mole) and NH-N (in the range -1.5 _ -5 kcal/mole)[19] further support these results. As a result, it was thought that the hydrogen bond formation in the 3-hydroxypyrene-pyridine system was stronger than the hydrogen bond formation in the 1-aminopyrene-pyridine system.

Table 3 shows the kinetic parameters for all the systems. The k_1 rate constant can be calculated according to the following equation given for the free form. The complex forms give the same absorbance intensity at the excitation wavelength:

$$\frac{1-\delta}{I/I_0} = 1 + k_1\tau_0 C_a \tag{9}$$

where 1-δ refers the fraction of the free molecule which is totally excited and τ_0 is the actual lifetime of the free molecule and $C_a$is the donor concentration as molarity[16].

Examining k_1 rate constants (Tables 3 and 4), small k_1 values of 3-hydroxypyrene-pyridine and 1-aminopyrene-pyridine systems in aromatic solvents (o-chlorotoluene and benzene) show the hindrance of hydrogen bond formation due to the solvation effects in these solvents. Since hydrogen bond complex formation is diffusion controlled, quenching depends on solvent viscosity. The k_1/η value in o-chlorotoluene is smaller than that in benzene and methylcyclohexane (Tables 3 and 4).

Table 3. Kinetic constants of the 3-hydroxypyrene(HPY) -pyridine systems in different solutions.

Solvent $^{20}n_D$: refractive index ε: dielectric constant	k_l /η η: solvent viscosity (cP)	τ_0 /ns	$k_1\tau_0$ /L mole^{-1}	k_1 /L mole^{-1}sec^{-1}
Solvent: Methylcyclohexane				
$^{20}n_D$: 1.4231 ε: 2.07	2.11 x10^{10} η: 0.734 cP	23	356 (380)	1.55x10^{10} (1.65x10^{10})
Solvent: Benzene				
$^{20}n_D$: 1.5011 ε: 2.28	1.34 x10^{10} η: 0.649 cP	22	193	0.87 x10^{10}
Solvent: o-chlorotoluene				
$^{20}n_D$: 1.5268 ε: 4.45	0.66 x10^{10} η: 1.02 cP	[1](30)	[1](200)	[1](0.67 x10^{10})

[1] From reference 8.

Table 4. Kinetic constants of the 1-aminopyrene(APY) -pyridine systems in different solutions.

	k_1 / η η: solvent viscosity (cP)	τ_0 /ns	$k_1\tau_0$ /L mole^{-1}	k_1 /L mole^{-1}sec^{-1}
Solvent: Methylcyclohexane				
$^{20}n_D$: 1.4231 ε: 2.07	1.38x10^{10} η: 0.734 cP	7.2	73	1.01x10^{10}
Solvent: Benzene				
$^{20}n_D$: 1.5011 ε: 2.28	0.64x10^{10} η: 0.649 cP	5.8	23	0.39x10^{10}
Solvent: o-chlorotoluene				
$^{20}n_D$: 1.5268 ε: 4.45	0.33x10^{10} η: 1.02 cP	5.5	19	0.34 x10^{10}

The radiative lifetime (τ_r) of 3-hydroxypyrene in methylcyclohexane was calculated to be 0.25x10^{-7} sec by the Strickler and Berg Equation[20] as shown below:

$$\frac{1}{\tau_r} = 2.88 \times 10^{-9} n^2 \langle \nu_f^{-3} \rangle_{AV}^{-1} \int \frac{\varepsilon(\nu) d\nu}{\nu} \tag{10}$$

where $< \nu_f^{-3} >_{AV}^{-1}$ is the reciprocal of the wavenumber mean value of ν^{-3} over the fluorescence spectrum, n is the refractive index for the solvent, $\varepsilon(\nu)$ is the molar extinction coefficient and the integral is over the absorption line or band.

The fluorescence quantum efficiency of 3-hydroxypyrene was known to be 0.60 (Φ_f)[17] and the actual lifetime was measured to be 23 ns. Using these values, the experimental radiative lifetime was found to be 0.38x10^{-7} s ($\tau_r = \tau_0/\Phi_f$). As a result it could be suggested that the calculated and experimental values of radiative lifetimes were the same.

Acknowledgements

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