Phosphorescence lifetime of naphthalene and phenanthrene in aggregated aromatic molecule—β-cyclodextrin—precipitant complexes

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Aggregated aromatic molecule—β-cyclodextrin—precipitant complexes exhibit long-lived phosphorescence at room temperature in water after the chemical binding of oxygen. The temperature dependences of the phosphorescence lifetimes of naphthalene-h_8, naphthalene-d_8, and phenanthrene in the aggregates were measured. For example, the phosphorescence lifetimes of naphthalene-d_8 aggregated with β-cyclodextrin and cyclohexane are equal to 25.1, 17.6, and 6.8 s at 77, 276, and 347 K, respectively, and that of phenanthrene aggregated with isooctane and β-cyclodextrin are 3.24, 3.06, and 1.26 s at 268, 274, and 335 K, respectively. The temperature dependences of the phosphorescence lifetimes at room temperature are determined by the rate constants of the radiative and nonradiative transitions from the triplet state of an aromatic molecule.

Key words: triplet state; water, β-cyclodextrin, naphthalene-d_8, naphthalene-h_8, phenanthrene, complexes; precipitant, cyclohexane, hexane, chloroform, isooctane, decalin; temperature dependence, phosphorescence at room temperature, quenching.

It has been found recently that complexes of aromatic molecules (AM) with β-cyclodextrin (β-CD) in water exhibit phosphorescence at room temperature (room temperature phosphorescence, RTP) not only in the presence of an "internal" [1] or "external" heavy atom,[2] but also when precipitants containing no heavy atoms (such as cyclohexane, benzene,[3] decalin, and isooctane[4]) are added. The RTP is also observed when chloroform is added, and its lifetime increases as the concentration of $CHCl_3$ increases (see Ref. 5).

It has been established that the appearance of the long-lived (≥1 s) RTP in water is associated with the formation of macrostructures (aggregates) in which the AM is separated from the surrounding medium by molecules of β-CD and precipitant, which initiate the formation of the aggregate.[4—6] The absence of a heavy atom in the AM and precipitant favors an increase in the lifetime of RTP. The effect of the complex formation and formation of aggregates with cyclodextrin on the lifetime of the RTP of aromatic molecules is poorly studied.

The phosphorescence of a bromosubstituted AM with a lifetime of 3.5 ms observed[7] in an aqueous solution containing CD at room temperature and at an oxygen pressure equal to 1 atm was explained by the formation of a 1 : 2 AM—γ-CD complex. A similar molecule, 1-bromonaphthalene, in a diethyl ether—isopentane—ethanol (5 : 5 : 2) mixture at 77 K exhibits phosphorescence with a lifetime of 18 ms due to the effect of the heavy atom. The lifetime of the RTP (3.5 ms) obtained by the authors of Ref. 7 is evidence for a decrease in the efficiency of the quenching of the phosphorescence by oxygen due to complex formation with CD.

The three-component complex and its aggregate may not be less efficient in this respect. This is indicated by the existence of RTP in their aqueous solutions from which oxygen has not been removed.[2,3] However, the authors of Refs. 2 and 3 do not present the lifetimes of the RTP.

The data on the lifetimes of RTP for systems in which AM are adsorbed on the surface of the CD—NaCl mixture in a nitrogen atmosphere are available.[8—10]

In this work, the temperature dependences of the lifetimes of the RTP of naphthalene, deuterated naphthalene, and phenanthrene in aggregates containing AM surrounded by CD and precipitant molecules in water have been studied.

Experimental

The purity of phenanthrene and naphthalene (-h_8 and -d_8) samples was monitored by their absorption and fluorescence spectra in ethanol; chloroform was purified by distillation; hexane (analytical purity grade), β-CD (Aldrich), and Na_2SO_3 (analytical purity grade) were used without additional purification. Decalin was purified by prolonged multiple treatments with concentrated H_2SO_4 at 50 °C until the coloring of the acidic layer stopped. Then it was dried over $CaCl_2$, distilled, and chromatographed several times on freshly calcined silica gel until the absorption at $\lambda > 230$ nm disappeared. Isooctane (2,2,4-trimethylpentane) and cyclohexane were purified by

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distillation and chromatography in the same manner as decalin. Freshly prepared bidistilled water was used as the solvent.

Sample preparation. Samples of AM and β-CD were dissolved in water in a test tube. The solution was separated from the atmosphere by ground-glass stoppers and heated on a water bath until boiling. At the concentrations used ([naphthalene] = 10^{-4} mol L^{-1}, [β-CD] = $5 \cdot 10^{-3}$ mol L^{-1}), these compounds easily form a two-component complex, which, however, is very unstable. Bubbling the solution (3 mL) with argon at a velocity of 1 mL s^{-1} for 5 min results in the almost complete disappearance of naphthalene from the solution and the decomposition of the complex. Therefore, the oxygen was bound only chemically by Na_2SO_3 (see Ref. 11). Weighted samples of phenanthrene (taken in such amounts that the concentrations were $5 \cdot 10^{-5}$ mol L^{-1}) do not dissolve completely in water at room temperature; therefore, the completeness of complex formation (more exactly, the absence of phenanthrene microcrystals in the solution) was monitored by the fluorescence spectrum which has a form typical of microcrystals after heating on a water bath and the addition of β-CD.

The solutions of the two-component complexes obtained were placed in quartz tubes with ground-glass stoppers, and the three-component complexes were prepared by the addition of precipitants, hexane, decalin, chloroform, isooctane, or cyclohexane. These complexes were condensed to aggregates and formed a precipitate, which phosphoresced brightly during UV irradiation after the oxygen was removed by sodium sulfite. The amount of the precipitant was 0.2—10.0 μL per mL of solution of the two-component complex. After the precipitant and Na_2SO_3 were added, the solutions were shaken vigorously for 20 min. Suspensions whose precipitation times were considerably greater than the duration of the measurements were also used in the work.

Measurement of lifetimes. Decaying phosphorescence was observed after the sample was irradiated with the light from an ISK-25 xenon lamp through a UFS5-5 light filter, which transmits light at $\lambda \le 410$ nm. A ZhS17-3 light filter, which transmits light at $\lambda \ge 480$ nm, and an IF-525 interference light filter with a transmission maximum at $\lambda = 529$ nm and a band of ±5.5 nm were placed in the observation channel behind a FEU-79 photomultiplier. The number of points measured in the signal was 125, and the number of levels of the signal after processing in an analog-digital converter (the time of the transformation of one point was 10 μs) was 255. The decreases in the phosphorescence were processed on an IBM PC by a specially developed program. The error of the measurement of the lifetime was not greater than 2%.

Results and Discussion

The studies performed showed that in the samples studied the intensity of the phosphorescence (I_{ph}) of AM normed to unity is always described by the dependence

$$I_{ph} = a\exp(-t/\tau) + b\varphi(t),$$

where $a + b = 1$, $\varphi(0) = 1$, and $\varphi(t)$ decreases much faster than $\exp(-t/\tau)$.

By varying the conditions of the formation of the aggregates (time, temperature, and concentration of the precipitant), the ratio between the long-lived and short-lived components of the phosphorescence (*i.e.*, coefficients a and b) can be varied. However, the lifetime of the long-lived phosphorescence is independent of the experimental conditions and is reproduced with high accuracy. The concentration of the precipitant was chosen in such a way that the a coefficient would be maximum. Almost in all cases the inequality $0.5 \le a \le 1$ was fulfilled, and the value of τ was accepted as the lifetime of the phosphorescence.

Table 1. Temperature dependences of the lifetimes of the phosphorescence (τ/s) of AM in aggregated AM—β-CD—precipitant complexes in water ([naphthalene-h_8] = [naphthalene-d_8] = 10^{-4} mol L^{-1}, [β-CD] = $5 \cdot 10^{-3}$ mol L^{-1}, [*cyclo*-C_6H_{12}] = $9 \cdot 10^{-2}$ mol L^{-1}, [*iso*-C_8H_{18}] = $6 \cdot 10^{-2}$ mol L^{-1}, [Na_2SO_3] = $4 \cdot 10^{-2}$ mol L^{-1})

T /K	Naphthalene-d_8 + *cyclo*-C_6H_{12}	Naphthalene-d_8 + *iso*-C_8H_{18}	Naphthalene-h_8 + *cyclo*-C_6H_{12}	Naphthalene-h_8 + *iso*-C_8H_{18}
77	25.1	24.0	2.60	2.60
276	17.6	16.2	2.15	2.10
284	16.6	14.6	2.05	2.00
301	15.4	11.9	1.96	1.75
315	13.7	9.8	1.82	1.53
331	10.3		1.67	
338	8.8		1.55	
347	6.8		1.49	

The temperature dependences of the lifetimes of RTP of the complexes of naphthalene-h_8, napthalene-d_8, and phenanthrene containing β-CD and various precipitants are presented in Tables 1 and 2.

The measurements were carried out when a constant temperature over the volume of the sample was achieved. The aggregates in the sample were quasi-stable at high temperatures. Their stability depended first of all on the precipitant used and restricted the possibilities of taking measurements at high temperatures. The lifetime of the aggregate at all temperatures considerably exceeded the lifetime of the phosphorescence, which was evidenced by the reproducibility of the amplitude of the phosphorescence signal and its lifetime for repeated measurements of the same sample.

When there are no external effects on the efficiency of triplet-singlet transitions (in particular, in the absence of "external" heavy atoms), the complete rate constant (k) of the deactivation of the triplet state of AM includes three components

$$k = k_r + k_{nr} + k_q[O_2], \tag{1}$$

where k_r and k_{nr} are the intramolecular rate constants of radiative and nonradiative transitions, respectively, and k_q is the rate constant of the external quenching of the triplet states by oxygen. When the curve of the decay of the triplet states is exponential, the lifetime of the phosphorescence (τ), taking into account Eq. (1), is determined by the expression

$$1/\tau = k = k_r + k_{nr} + k_q[O_2]. \tag{2}$$

Table 2. Temperature dependences of the lifetimes of the phosphorescence (τ/s) of AM in the aggregated phenanthrene—β-CD—precipitant complexes in water ([phenanthrene] = $5 \cdot 10^{-5}$ mol L^{-1}, [β-CD] = $5 \cdot 10^{-3}$ mol L^{-1}, [C_6H_{14}] = $8 \cdot 10^{-2}$ mol L^{-1}, [$CHCl_3$] = $1.2 \cdot 10^{-2}$ mol L^{-1}, [*cyclo*-C_6H_{12}] = $9.2 \cdot 10^{-2}$ mol L^{-1}, [decalin] = [*iso*-C_8H_{18}] = $6 \cdot 10^{-2}$ mol L^{-1}, [Na_2SO_3] = $4 \cdot 10^{-2}$ mol L^{-1})

C_6H_{14}		Decalin		$CHCl_3$		*cyclo*-C_6H_{12}		*iso*-C_8H_{18}	
T/K	τ/s	T/K	τ/s	T/K	τ/s	T/K	τ/s	T/K	τ/s
						77	4.44	77	3.9
276	2.62	275	2.61	274	2.32	274	2.99	268	3.24
287	2.47	284	2.47	282	2.10	277	3.06	274	3.06
293	2.0	302	2.21	291	1.95	283	2.74	277	2.96
304	1.66	333	1.85	295	1.82	295	2.60	282	2.91
				305	1.50	301	2.64	283	2.75
				310	1.17	304	2.44	291	2.70
				317	0.96	313	2.25	295	2.41
						318	2.22	301	2.42
						324	2.22	303	2.33
								313	1.93
								318	1.87
								324	1.54
								329	1.57
								335	1.26

The results presented in Tables 1 and 2 can reflect the temperature dependences of both k_r and/or k_{nr} and $k_q[O_2]$ ($[O_2]$ is the residual concentration of oxygen after the addition of Na_2SO_3 to the samples).

The rate constants of diffusionally limited bimolecular reactions are fairly high at room temperature, and the phosphorescence of naphthalene in an aqueous solution is completely quenched by oxygen. However, for the aggregated three-component complexes of naphthalene-d_8 and -h_8 with cyclohexane at 274 K the phosphorescence was also observed without the addition of Na_2SO_3. In both cases, the lifetimes of RTP are almost the same (Table 3). The addition of Na_2SO_3 increases this lifetime by one order of magnitude for naphthalene-h_8 and by two orders of magnitude for naphthalene-d_8. Therefore, the values of $k_q[O_2]$ in Eq. (2) coincide for these molecules in the aggregated complexes. If the temperature dependences were determined only by the concentration of the residual oxygen, the change in the rate constants of the phosphorescence decay would be the same for naphthalene-d_8 (k_d) and naphthalene-h_8 (k_h), and the difference ($k_h - k_d$) would be temperature independent. From the data in Table 1 at 276, 284, 301, 315, and 331 K, using Eq. (2), the following values are obtained: $k_h = 0.465$, 0.488, 0.510, 0.549, and 0.598 s^{-1} and $(k_h - k_d) = 0.408$, 0.427, 0.445, 0.476, and 0.502 s^{-1}, respectively. Therefore, in the aggregated complexes, after the oxygen dissolved in water is bound by sodium sulfite, the temperature dependences of the lifetimes and the lifetimes of the RTP of the AM themselves are entirely determined by the intramolecular constants of the radiative and nonradiative transitions from the triplet state. The contributions of these processes to the value of the lifetime of the phosphorescence can be separated, if the quantum yield of the phosphorescence is known. However, the great error of the measurement of the phosphorescence quantum yield in the light-scattering sample, which is comparable to the effects observed, does not allow one to solve this problem.

At 276 K, in the aggregates in water, the achieved lifetimes of the phosphorescence of AM are very close to those obtained in homogeneous solutions frozen to 77 K: 22 and 2.3 s for naphthalene-d_8 and -h_8, respectively.[12a,13]

No break is observed on the temperature dependence of τ at the freezing point of water for the aggregate containing phenanthrene, β-CD, and isooctane. The huge increase in the viscosity of the solvent during freezing does not result in a sharp change in the lifetime of the phosphorescence, which also confirms the ab-

Table 3. Lifetimes of the phosphorescence (τ/s) of AM in various media at 77 and 274 K ([naphthalene-d_8] = [naphthalene-h_8] = 10^{-4} mol L^{-1}, [β-CD] = $5 \cdot 10^{-3}$ mol L^{-1}, [*cyclo*-C_6H_{12}] = $9.2 \cdot 10^{-2}$ mol L^{-1} in the three-component complex)

System	77 K		274 K	
	without O_2	with O_2	without O_2	with O_2
Naphthalene-d_8 + Et_2O		21.7	**	**
Naphthalene-d_8 + *cyclo*-C_6H_{12}		20.5	**	**
Naphthalene-d_8 + β-CD*	23.9	22.8	**	**
Naphthalene-d_8 + β-CD + + *cyclo*-C_6H_{12}*	25.1	24.8	18.6	0.118
Naphthalene-h_8 + β-CD + + *cyclo*-C_6H_{12}*	2.7	2.66	2.15	0.124

* In water. ** No phosphorescence.

sence of quenching of the phosphorescence by admixtures in water and a high degree of screening of AM in the aggregate from the solvent.

The value τ = 25.1 s obtained for the naphthalene-d_8—β-CD—*cyclo*-C_6H_{12} aggregate at 77 K (see Table 3) is greater than the maximum phosphorescence lifetime known to date (22 s) and its theoretical limit (20 s)[12] for this AM. The data in Table 3 testify that at 77 K oxygen exerts almost no effect on the lifetime of the phosphorescence of AM in the aggregated complexes, while at $T > 273$ K its action becomes determining.

In the homogeneous solutions frozen to 77 K, the lifetimes of the phosphorescence of phenanthrene are 3.3—3.7 s.[12,13] These values are close to those for the RTP (see Table 2), but they are lower than the lifetime obtained for the aggregated phenanthrene—β-CD—*cyclo*-C_6H_{12} complex at 77 K (4.44 s). When chloroform is used as the precipitant, the lifetimes of the RTP of phenanthrene are noticeably lower, which can be explained by the effect of the heavy Cl atom.

The differences in the lifetimes of the RTP (see Table 2) for complexes with different hydrocarbon precipitants at the same temperature are likely related to the structures of the aggregates formed, which has not yet been elucidated.

Thus, for naphthalene-d_8, naphthalene-h_8, and phenanthrene in the aggregated three-component AM—β-CD—*cyclo*-C_6H_{12} complexes in water from which oxygen has been chemically removed, the lifetimes of the phosphorescence at 77 K are greater than the values known to date, and at room temperature they are comparable with the lifetimes of the phosphorescence of these molecules in homogeneous frozen solutions at 77 K. The temperature dependences of the phosphorescence lifetimes for these complexes are determined only by intramolecular radiative and nonradiative transitions from the triplet state of AM.

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