Phosphorescence of aromatic molecules in complexes with crystalline β-cyclodextrin at room temperature

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The rate constants for the quenching by oxygen of triplet states of aromatic molecules (naphthalenes-d_8 and -h_8, phenanthrene) forming inclusion complexes with crystalline β-cyclodextrin in water at 290 K are equal to 900—1300 L mol^{-1} s^{-1}.

Key words: phosphorescence, triplet state, lifetime, quenching; oxygen, naphthalene, phenanthrene, microcrystal, inclusion complex.

It is known that complexes of organic compounds with cyclodextrin (CD) in solutions can demonstrate bright phosphorescence at room temperature.[1—6] This requires that the rate constant of the radiative transition k_{ph} be greater than the sum of the rate constants of the nonradiative process k_{nr} and of quenching by oxygen $k_q \cdot [O_2]$, and, hence, that the phosphorescence yield from the triplet state

$$q_{ph} = k_{ph}/(k_{ph} + k_{nr} + k_q \cdot [O_2])$$

and the phosphorescence lifetime

$$\tau_{ph} = 1/(k_{ph} + k_{nr} + k_q \cdot [O_2]) \qquad (1)$$

be rather high. These conditions can be met by either suppressing channels of nonradiative deactivation and quenching of the triplet state or increasing the rate constant of the radiative process. The latter route usually occurs through the introduction of a heavy atom into the system, but the phosphorescence lifetime simultaneously decreases.

Under real conditions, dissolved molecular oxygen is the most efficient quencher of the phosphorescence of aromatic molecule—cyclodextrin (AM—CD) complexes in solution. The deactivation of the triplet state by oxygen can be decreased either by the complete or partial removal of oxygen from the solution or by the creation of a molecular shell that prevents oxygen from getting within quenching distance of a phosphorescent molecule.

In liquid solutions, the rate of quenching of the triplet state of an aromatic molecule by oxygen is equal to $\alpha \cdot K_{dif} \cdot [AM] \cdot [O_2] = k_q \cdot [O_2]$ and decreases as the concentration of oxygen in solution decreases, the diffusion constant of oxygen K_{dif} decreases (which is achieved, in particular, by increasing the viscosity by freezing the solution), and the probability of quenching α decreases. The latter reflects the possibility of an oxygen molecule

getting to within quenching distance of a phosphorescent molecule (triplet-triplet energy transfer).

In an aqueous solution of 1-bromonaphthalene, the $k_q \cdot [O_2]$ value can be estimated inserting $k_q = 5 \cdot 10^8$ L mol^{-1} s^{-1} [1] and $[O_2] = 2.65 \cdot 10^{-4}$ mol L^{-1}.[7] Under these conditions, the phosphorescence is almost quenched, which means $k_{ph} << k_q \cdot [O_2]$ and $\tau_{ph} \approx 1/k_q \cdot [O_2] = 20$ μs. The degree of protection from quenching of triplet states by oxygen in molecular-organized systems can be estimated by comparing the phosphorescence lifetimes in complexes involving CD with the value obtained above for a homogeneous solution.

The model that is most frequently used for kinetic calculations suggests that AM can be present both within the complex and in the bulk of a solution.[1,3,4] An equilibrium state occurs and determines the time that AM exists in the complex. Since the efficiencies of deactivation of the triplet state of AM in the complex and in the solution differ, the formation of a complex between AM and CD should result in a decrease in α. The published data confirm this assumption. The complex of 4-bromonaphthalene with γ-cyclodextrin (1) in an aqueous solution at room temperature exhibits a biexponential decrease in phosphorescence.[5] It was assumed[5] that the long-lived phosphorescence ($\tau = 3.9$ ms) belongs to a 1 : 2 complex that provides reliable protection of the molecule in the triplet state from quenching by oxygen, and the short-lived phosphorescence with a lifetime of 506 μs belongs to a 1 : 1 complex that exhibits phosphorescence only in a degassed solution.

When oxygen is not removed, the phosphorescence in the three-component AM—β-CD—dibromoethane system is quenched only partially.[4] It is assumed that the fraction of nonquenched phosphorescence is proportional to the time during which AM exist in the complex. The fraction of nonquenched phosphorescence increases from 8.9% to 28.9% on going from naphtha-

lene to 1-methylnaphthalene. The same effect is observed for AM with a lower solubility in water.[8] These data indirectly confirm the hypothesis suggested.

The addition of various alcohols to an aqueous solution of the 1-bromonaphthalene—modified β-CD complex results in the formation of triple 1 : 1 : 1 complexes and in the observance of phosphorescence in a solution containing oxygen.[1] The appearance of the phosphorescence is associated with the ability of alcohols in a triple complex to shield a 1-bromonaphthalene molecule from oxygen. This ability increases in the series butan-1-ol > propan-1-ol > propan-2-ol > butan-2-ol > *tert*-butanol and cyclohexanol. In this series, cyclohexanol is the exception: the equilibrium constant of the formation of the complex with cyclohexanol is the smallest one, while the quantum yield of phosphorescence is the maximum. The constant of quenching of phosphorescence by oxygen, which was determined from the Stern—Volmer dependence, is two orders of magnitude lower in the case of cyclohexanol than for butan-1-ol. The phosphorescence lifetimes are rather large: 3.9 and 4.6 ms when cyclohexanol and *tert*-butanol, respectively, are added.

In several cases, when the ability of the complexes to prevent quenching of phosphorescence of molecules entering into the complex was studied, the solutions were degassed, and quenchers of triplet states ($NaNO_2$[3,9] or $Co(NH_3)_6^{3+}$ ions[5,10]) were introduced into the solutions to measure the Stern—Volmer dependence.

Phosphorescence and delayed fluorescence were observed in an aqueous suspension of AM microcrystals, but more detailed data were not presented.[11]

In almost all cases studying phosphorescence, the complex contained a heavy atom: in AM,[1,3,5] in CD,[12] or in a third compound added to the system.[4,9,13] The presence of a heavy atom results in an increase in the rate constant of the radiative transition, and the yield and lifetime of phosphorescence depend to a lesser extent on quenchers. Therefore, a heavy atom should be removed from the complex and the solution to elucidate the intrinsic ability of complexes with CD to shield an aromatic molecule from quenchers.

Long-lived (seconds) phosphorescence was obtained in three-component aggregated complexes containing no heavy atom after oxygen was chemically bound.[6,14] When oxygen is not removed, the lifetime of phosphorescence of naphthalene-d_8 in the complex with β-CD and cyclohexane as a precipitating agent (third compound) is equal to 110 ms, and after removing oxygen, it increases to 18.6 s.[6] It was shown that in this system, the method used for binding oxygen completely rules out an effect of the residual oxygen on the phosphorescence.

This work is aimed at studying quenching of phosphorescence of aromatic molecules by oxygen in organized systems: a) in an aqueous suspension of microcrystals with a characteristic size of ~1 μm formed after cyclohexane is added as a precipitating agent to a solution of the AM—β-CD complex (the less exact term

"aggregated complex" has been used[6] for this system) and b) in an aqueous suspension of microcrystals formed from a supersaturated solution of the AM—β-CD complex.

Experimental

Results and Discussion

The problem of revealing the intrinsic possibility of protecting phosphorescence of AM from quenching by oxygen in a molecular-organized system is similar in many respects to the problem of determining the inherent lifetime of phosphorescence of AM when the removal of oxygen from the sample results in an increase in the lifetime.[16] In our case, oxygen is present in the sample, lifetimes on an order of magnitude of several seconds are considered, and the most insignificant changes in the structure of the complex and of the microcrystals associated with the procedure of preparation of the sample can cause considerable scatter in the absolute values of the lifetimes of the phosphorescence. However, relative changes for the same series of samples have a small error (not greater than 5%)[6] and allow one to see some regularities.

As in the previous work,[6] in the general case, the decay of phosphorescence was not exponential, and the maximum value, which characterizes not less than 50% AM in the sample, was accepted to be the lifetime.

Table 1 presents the temperature dependences of the phosphorescence lifetime of a three-component complex in which the concentrations of β-CD, phenanthrene, and naphthalene-d_8 in an aqueous solution were $2 \cdot 10^{-3}$, $5 \cdot 10^{-5}$, and $1 \cdot 10^{-4}$ mol L^{-1}, respectively, and cyclohexane was added in an amount of 0.5 μL per milliliter of the solution (which is an order of magnitude lower than that in the previous study[6]).

It can be seen that in this system, AM are fairly well isolated from oxygen, since the lifetimes of phosphorescence are greater than 1.5 s. It has been assumed[2] that

Table 1. Temperature dependences of the phosphorescence lifetime (τ_1/s) of AM—CD—cyclohexane complexes

AM	T/K				
	253	264	274	291	290
Phenanthrene	3.0	3.0	2.0	1.7	3.0*
Naphthalene-d_8	12.4	10.4	3.8	2.7	14.2*

* Na_2SO_3 was added to the solution.

Table 2. Temperature dependences of the phosphorescence lifetime (τ_2/s) of AM—CD complexes

AM	T/K		
	274	290	291
Naphthalene-d_8	3.7	2.4	10.8*
Naphthalene-h_8	1.27	1.05	1.78*
Phenanthrene	1.94	1.36	2.4*

* Na_2SO_3 was added to the solution.

Table 3. Quenching rate constants (k_q/L mol^{-1} s^{-1}) obtained from Eq. (2)

AM	Type of complex	
	AM—β-CD—cyclohexane	AM—CD
Naphthalene-d_8	1000	1140
Naphthalene-h_8	—	1340
Phenanthrene	890	1070

oxygen and water are displaced from the β-CD cavity by cyclohexane and AM, which can explain the appearance of phosphorescence at room temperature. There is no proof for this assumption, because the structure of the complex and of the microcrystals formed after the addition of cyclohexane have not yet been established exactly.

The temperature dependence of the phosphorescence lifetime jumps when the solution is frozen. This is more pronounced for naphthalene-d_8, whose inherent lifetime of phosphorescence is 6 times greater than that of phenanthrene. It is evident that freezing of the solution decreases the diffusion of oxygen, but the effect caused by this decrease is comparable to the effect of the molecular-organized system. A comparable effect is achieved by the addition of sodium sulfite to the solution to chemically bind oxygen.

The phosphorescence lifetimes in two-component complexes with naphthalenes, $1 \cdot 10^{-4}$ mol L^{-1}, phenanthrene, $5 \cdot 10^{-5}$ mol L^{-1}, and β-CD, $2.4 \cdot 10^{-2}$ mol L^{-1} are presented in Table 2.

A comparison of the data in Tables 1 and 2 shows that rather efficient shielding from oxygen is also achieved in the two-component system when AM exists in the CD cavity and CD is organized as a microcrystal.

When the proved[6] statement that the addition of Na_2SO_3 to the solution completely rules out the effect of oxygen on the phosphorescence lifetime is used, for the systems studied $k_q \cdot [O_2]$ can be calculated from Eq. (1). Then phosphorescence lifetimes in three- (τ_1) and two-component systems (τ_2) for each compound, using Eq. (1) can be described by:

$$1/\tau_1 = k_{ph} + k_{nr} + k_q \cdot [O_2]$$

and $1/\tau_2 = k_{ph} + k_{nr}$.

Subtracting the second expression from the first one, we obtain

$$k_q \cdot [O_2] = 1/\tau_1 - 1/\tau_2. \qquad (2)$$

The k_q values at 290 K calculated (error 15%) from this formula assuming[7] that $[O_2] = 2.9 \cdot 10^{-4}$ mol L^{-1} are presented in Table 3.

The obtained k_q values for all compounds are similar and reflect the high degree of protection of triplet states of AM in CD crystals obtained by different methods from quenching by molecular oxygen.

References

1. A. Ponce, P. A. Wong, J. J. Way, and D. G. Nocera, *J. Phys. Chem.*, 1993, **97**, 11137.
2. W. Jin, Y. Wei, A. Xu, C. Liu, and S. Zhang, *Spectrochim. Acta*, 1994, **50A**, 1769.
3. N. J. Turro, J. D. Bolt, Y. Kuroda, and I. Tabushi, *Photochem. Photobiol.*, 1982, **35**, 69.
4. S. Scypinski and L. J. Cline Love, *Anal. Chem.*, 1984, **56**, 322.
5. N. J. Turro, G. S. Cox, and X. Li, *Photochem. Photobiol.*, 1983, **37**, 149.
6. V. B. Nazarov, V. I. Gerko, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2225 [*Russ. Chem. Bull.*, 1996, **45**, 2109 (Engl. Transl.)].
7. S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973, 89.
8. S. Scypinski and L. J. Cline Love, *Anal. Chem.*, 1984, **56**, 331.
9. S. Hamai, *J. Am. Chem. Soc.*, 1989, **111**, 3954.
10. N. J. Turro, T. Okubo, and C.-J. Chung, *J. Am. Chem. Soc.*, 1982, **104**, 1789.
11. R. Weinberger and L. J. Cline Love, *Spectrochim. Acta*, 1984, **40A**, 49.
12. R. A. Femia and L. J. Cline Love, *J. Phys. Chem.*, 1985, **89**, 1897.
13. A. M. Delapena, I. Duran-Meras, and F. Salinas, *Anal. Chim. Acta*, 1991, **255**, 351.
14. V. B. Nazarov, V. I. Gerko, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1014 [*Russ. Chem. Bull.*, 1996, **45**, 969 (Engl. Transl.)].
15. V. B. Nazarov, V. I. Gerko, and T. G. Vershinnikova, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1966 [*Russ. Chem. Bull.*, 1995, **44**, 1886 (Engl. Transl.)].
16. S. McGlynn, T. Azumi, and M. Kinoshita, *Molecular Spectroscopy of the Triplet State*, Prentice-Hall, Englewood Cliffs (USA), 1969.