Experimental

A Jeol FX-90Q spectrometer (89.95 MHz for ^{1}H) was used for kinetic measurements. Chemical shifts were measured in $CDCl_3$ at 27 °C relative to HMDS as the internal standard with an accuracy of 0.01 ppm, and the accuracy of measurement of the integral intensity was 5%.

General procedure for the preparation of the starting 2-alkylthiopropenals by the retro-Diels—Alder reaction of 2,5-dialkylthio-3,4-dihydro-2*H*-pyran-2-carbaldehydes. A dimer of 2-alkylthiopropenal (3 g) was heated *in vacuo* to 180 °C. The fraction with b.p. 110—140 °C (1 Torr) was collected in a receiver cooled with liquid nitrogen. According to the ^{1}H NMR spectral data, the obtained mixtures of monomer **1** and dimer **2** contained from 25 to 80% of α-alkylthioacrolein (**1**).

Kinetic measurements were carried out in a tube of an NMR spectrometer in $CDCl_3$ at 27 °C, using freshly distilled mixtures of the monomer and dimer of 2-alkylthiopropenal (C = 0.15—0.9 mol L^{-1}). The calculation of k was performed by monitoring the decrease in time of the relative integral intensity of singlets of protons of the aldehyde group of the monomer. Dimerization constants of 2-alkylthiopropenals were calculated as the average of six to nine values. It is noteworthy that the anamorphoses of the kinetic curves obtained fall well on straight lines (correlation coefficients $r > 0.9845$).

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Long-lived phosphorescence of aqueous solutions of β-cyclodextrin complexes with naphthalene and its derivatives at room temperature

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A long-lived phosphorescence at room temperature (lifetime >1 s) of aqueous solutions of β-cyclodextrin complexes with naphthalene and its derivatives was found. The phosphorescence is observed for aggregated complexes that form in water a light-scattering suspension, and its low intensity is due to predomination of 2 : 2 complexes with efficient excimer fluorescence. Complexes containing isolated aromatic molecules are assumed to be the centers of fluorescence.

Key words: complex, cyclodextrin, naphthalene, long-lived phosphorescence, excimer fluorescence.

It has previously been shown that phosphorescence at room temperature (RTP) of complexes of aromatic molecules with cyclodextrins (CD) occurs only when a third compound (ethanol,[1] dibromoethane,[2] acetonitrile,[3] saturated hydrocarbons,[4—6] and others) is added to an aqueous solution of the complex. The addition of hydrophobic compounds is usually accompanied by the formation of aggregated complexes and appearance of light-scattering microparticles (microcrystals) whose sizes are comparable with wavelengths of visible light, *i.e.*, of an order of one micron. When water-soluble (to some extent) compounds are added, smaller particles are

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formed, and correspondingly, a weaker light scattering is observed. It has previously been shown[7] that the formation of light-scattering microparticles and the appearance of long-lived RTP are related to each other.

Long-lived RTP with lifetime of an order of several seconds has not previously been observed in aqueous solutions of two-component complexes of aromatic molecules with CD. These solutions were thought to be transparent and not exhibit RTP,[7] but in this work we showed that this is not true. It is known that CD in aqueous solutions form CD concentration-dependent aggregates whose sizes are sufficiently large (210—300 nm for β-CD) to scatter light.[8] Perhaps, β-CD with naphthalene incorporated in its cavity also can form aggregated complexes in the absence of the third component, and this may be a prerequisite for the appearance of long-lived phosphorescence of the substrate. In this work, we studied long-lived RTP in aqueous solutions of two-component complexes of β-CD with naphthalene and its derivatives.

Experimental

Samples were prepared by the addition of 10 mL of an aqueous solution of β-CD with a concentration of 10^{-2} mol L^{-1} into a quartz tube containing such an amount of a substrate that its concentration in the solution was 10^{-4} mol L^{-1}. The hermetically closed tube with the resulting solution was heated at 70 °C for 1 h on a water bath and then cooled slowly to room temperature. Naphthalenes-h_8 and -d_8 and 1,6-, 2,7-, and 2,3-dimethylnaphthalenes were studied as substrates. Three-component complexes were prepared for comparison by the addition of cyclohexane (CH) to solutions of two-component complexes until [CH] = 0.04 mol L^{-1} was achieved. The substances were purified by recrystallization. 1,6-Dimethylnaphthalene was purified by distillation. β-CD (Cyclolab Co., Hungary) was used without additional purification.

Freshly prepared samples at first were transparent, but 1 day later opalescence appeared, and a precipitate was formed after several days. Prior to measurements, Na_2SO_3 was added to the sample for binding dioxygen.

Phosphorescence was excited by a pulse of nonfiltered light of an ISK-25 xenon lamp (flash energy 110 J), and the screen in the front of a photoelectron amplifier (used for detection of phosphorescence) was removed 0.1 s after the flash. Luminescence reached the photoelectron amplifier through a ZhS-12 light filter (λ > 450 nm).

Results and Discussion

The long-lived RTP was observed for all samples both visually and on a setup for measuring lifetimes,[6] but its intensity was by ~2 orders of magnitude lower than that observed for the three-component complexes. This prevented us from measuring the RTP spectrum.

The results of measuring the lifetimes of RTP at 293 K are presented in Table 1. The measurement error did not exceed 15%.

Table 1. Lifetimes (s) of RTP of AC complexes with CD and CH at 293 K

AC	AC+β-CD	AC+β-CD+CH
Naphthalene-d_8	9.6	16[6]
Naphthalene-h_8	1.7	2[6]
1,6-Dimethylnaphthalene	1.3	1.6
2,7-Dimethylnaphthalene	1.4	1.6
2,3-Dimethylnaphthalene	1.0	1.5

Note. AC is aromatic compound.

It was found that in all cases, RTP in aqueous solutions of the complexes is associated with the appearance of light scattering. Several days later, a precipitate was formed in the two-component solutions, and RTP could be observed visually only for the precipitate. Therefore, as for the three-component complexes, RTP is observed only for the aggregated complexes of β-CD with naphthalene or its derivatives.

Our experiments showed that the absorption spectrum of the two-component "naphthalene—β-CD" complex is additive with respect to the spectra of individual components at a concentration of naphthalene of $1 \cdot 10^{-4}$ mol L^{-1} and β-CD concentrations within $1 \cdot 10^{-3}$—$1 \cdot 10^{-2}$ mol L^{-1}. A solution of β-CD a week after its preparation was used in experiments, because β-CD aggregates were formed in the solution over this time, which was observed by the characteristic increase in the absorption of β-CD in the UV region. The additivity of the spectra indicates that the formation of the two-component complexes of β-CD with naphthalene at its concentration of 10^{-4} mol L^{-1} does not result in additional aggregation of β-CD.

A decrease in the concentration of β-CD to $1 \cdot 10^{-3}$ mol L^{-1} results in a decrease in light scattering and a decrease in the RTP intensity of the "naphthalene-h_8—β-CD" complex, but the lifetime of RTP remains unchanged.

A low intensity of phosphorescence of the two-component complexes at both room temperature and 77 K[9] is due, most likely, to the formation of 2 : 2 complexes rather than 1 : 1 complexes. Under these conditions, excimer fluorescence appears,[10,11] which competes with phosphorescence. In fact, when the concentration of naphthalene-h_8 increases to $5 \cdot 10^{-3}$ mol L^{-1}, the luminescence of the precipitate at room temperature corresponds to excimer fluorescence, and RTP is not observed (a weak phosphorescence was observed only at 77 K). This hypothesis is also favored by the fact that the addition of cyclohexane to the two-component complex even in the presence of dioxygen results in a sharp increase in the RTP intensity with a simultaneous decrease in the excimer fluorescence. The equilibrium constant of formation of the 1 : 1 "naphthalene—β-CD" complex is sixfold lower than the equilibrium constant of aggregation of these complexes into the 2 : 2 complex, in which efficient excimer fluorescence is observed and phosphorescence is virtually absent.[11] Previous calculations[12] showed that the formation of the 2 : 2 complexes is energetically favorable.

Thus, long-lived RTP belongs, most likely, to isolated molecules of naphthalene or its derivatives in the 1 : 2 "AC—β-CD" complex, which contributes to larger light-scattering aggregates of β-CD.

For methyl derivatives of naphthalene, the formation of 1 : 2 complexes is probably due to steric hindrances to the formation of a dimeric structure. In addition, the methyl substituents can play, to some extent, the same role as hydrocarbon precipitating agents (hexane, cyclohexane, and others) in the appearance of RTP. In fact, for 1,6-dimethylnaphthalene, RTP with a lifetime of 0.4 s was observed even when sodium sulfite was not added to the solution.

The decrease in the lifetime of RTP of the two-component complexes as compared to that of the aggregated three-component complexes (see Table 1) is due to an increase in the rate of nonradiative transition of AC from the T_1 state to S_0.

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