Room Temperature Phosphorescence of Aromatic Hydrocarbons in SDS Rodlike Micelles

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Room temperature phosphorescence (RTP) of aromatic hydrocarbons has been investigated in deoxgenated SDS micelles and in the presence of a hydrophobic heavy-atom containing species. No RTP was observed in spherical or sub-rodlike micelles. In the presence of a heavy-atom containing species, a tremendous increase in phosphorescence intensity was observed during the sphere-to-rod transition induced by the addition of a strong electrolyte. The increased microviscosity and the incorporation of more heavy atoms during the micellar elongation will lead to an increase in the rate of intersystem crossing and a decrease in the rates of nonradiative processes, favoring the observation of RTP. At high temperatures, the phosphorescence intensity is reduced dramatically probably because of the decrease in rigidity and aggregation number of the micelle with less heavy atoms incorporated. Various heavy-atom containing species induce RTP to a different extent. Iodoethane exhibits the most prominent heavy atom effect. 1,2-Dibromoethane, 1-bromopropane, and bromobenzene are about 40% as efficient as iodoethane in inducing RTP, while long-chain 1-bromoalkanes and polar species are much less efficient. This study demonstrates the feasibility of detecting RTP in deoxygenated SDS rodlike micelles using a suitable hydrophobic heavy-atom containing species.

INTRODUCTION

The successful observation of room temperature phosphorescence (RTP) in fluid solutions is usually accomplished by incorporating the luminophores in the completely deoxygenated organized media (e.g., micelles,[1,2] cyclodextrin,[3,4] proteins[5]) and in the presence of a heavy-atom containing species. A heavy-atom containing species, such as silver or thallium salts,[1] 1,2-dibromoethane,[3] or 2-bromoethanol,[6] is commonly introduced into the solution to enhance the rate of intersystem crossing through a large spin-orbit coupling. The removal of oxygen, which is an efficient quencher of phosphorescence, in solution is usually achieved by purging with nitrogen, and adding enzymes[5] or Na_2SO_3.[7] Deoxygenation with hydrogen gas and carbon dioxide produced by the reactions Zn/HCl and Na_2CO_3/HCl in the measuring media has also been reported.[8] The heterogeneous nature of the micellar assembly offers several advantages for the observation of RTP such as screening the luminophores from external quenchers, bringing heavy atoms and luminophores into close proximity,[9] preventing triplet-triplet annihilation,[10] decreasing the rate of nonradiative decay due to orientational constraints,[11] and increasing the phosphorescence quantum yield due to the enhanced rigidity and favorable environments.

We have reported the observation of RTP of 2-bromonaphthalene in deoxygenated SDS (sodium dodecyl sulfate) rod-like micelles.[12] No RTP of 2-bromonaphthalene was observed in spherical micelles. At high surfactant concentration and/or in the presence of a strong electrolyte, the surfactant molecules first aggregate to form a spherical micelle then transform into a rigid rod, a flexible rod, and then entangle with each other.[13] The sphere-to-rod transition of micellar assembly is usually accompanied by dramatic increases in hydrophobicity,[14] rigidity,[15] and aggregation number.[15,16] This provides further advantages for the rodlike micelles over the spherical micelles in decreasing the rate of nonradiative decay to facilitate the observation of RTP. For luminophores with no intrinsic heavy atoms, the addition of external heavy-atom containing species is essential for the successful observation of RTP. In this paper, we have demonstrated the feasibility of detecting RTP of selected aromatic hydrocarbons (naphthalene, acenaphthene, and pyrene) in SDS rod-like micelles in the presence of various heavy-atom containing species (iodoethane, bromobenzene, brominated alkanes). We have also studied the effects of temperature and concentration of salt on the phosphorescence intensities of these luminophores.

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EXPERIMENTAL SECTION

Acenaphthene, 1-bromopropane, pyrene, naphthalene, SDS, 1-bromohexane, bromobenzene, iodoethane, 2-bromoethanol, 6-bromohexane-1-ol were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Bromoethane, 1-bromobutane, 1-bromodecane, 1,2-dibromoethane, sodium chloride, and sodium sulfite were from E. Merk (Darmstadt, Germany). All reagents are of the highest grade of purity. Deoxygenation was achieved by adding a sufficient amount of sodium sulfite (> 0.01 M) to the aqueous solution containing SDS, NaCl, the luminophore, and the heavy atom containing species in a quartz cuvette. The solution was then stirred for 20 min to remove the dissolved oxygen. Fluorescence and phosphorescence spectra were measured on a Hitachi F-4500 fluorescence spectrometer (Hitachi, Japan) equipped with a circulating water bath for temperature control. This instrument can be operated either in the fluorescence or in the phosphorescence mode.

RESULTS AND DISCUSSION

Effect of Salt Concentration on RTP

RTP in deoxygenated spherical SDS micelle has been observed in the presence of a heavy metal ion such as Tl^+ or Ag^+ adsorbed on the micellar surface.[1,2] Addition of NaCl to the Tl-SDS system to induce the sphere-to-rod transition causes the replacement of Tl^+ by Na^+ leading to a gradual disappearance of RTP (data not shown). To detect RTP in rodlike micelle, a hydrophobic external heavy-atom containing species such as 1,2-dibromoethane (DBE) was employed. Fig. 1 shows the phosphorescence spectra of 1.0×10^{-5} M acenaphthene, naphthalene, and pyrene in 0.05 M SDS, 0.5 M NaCl, 0.05 M Na_2SO_3, 0.2 M DBE solution at 30 °C. All three phosphorescence spectra show well-resolved vibrational structures. The effect of the concentration of NaCl on the phosphorescence intensities of these three luminophores is illustrated in Fig. 2. No phosphorescence was observed when the concentration of NaCl is below 0.2 M (or 0.3 M of Na^+ including the contribution of Na^+ from 0.05 M Na_2SO_3). The concentration of SDS (0.05 M) is well above its critical micelle concentration (cmc, which is 8.3 mM in aqueous solution and decreases dramatically as the concentration of NaCl increases[16]) indicating the absence of RTP in spherical or sub-rodlike micelles. When the concentration of NaCl is above 0.2 M, RTP starts to appear and its intensity increases rapidly with increasing concentration of NaCl. Shielding of the charged head groups of the surfactant molecules by counter ions upon

addition of strong electrolytes reduces their repulsion, leading to the formation of the rod-like micelles. The sphere-to-rod transition is usually accompanied by dramatic increases in microviscosity, hydrophobicity, and aggregation number. The increased compactness and rigidity of the rodlike micelles tend to decrease the rate of nonradiative decay. Moreover, the increase in hydrodynamic volume during the micellar elongation will lead to an accommodation of more DBE molecules in the micelle. This will increase the possibility of close contact for the heavy atoms and the luminophore, giving rise to an enhanced rate of intersystem crossing. All these factors favor the observation of RTP in rodlike micelles. The three luminophores exhibit similar variations (relatively) in phosphorescence intensities during the sphere-to-rod transition (Fig. 2).

Upon further addition of NaCl, the phosphorescence intensities of acenaphthene and pyrene change only slightly (Fig. 2a and 2b), while that of naphthalene decreases dramatically (Fig. 2c). It is known that continuing elongation on both sides of the rodlike micelles upon further addition of NaCl
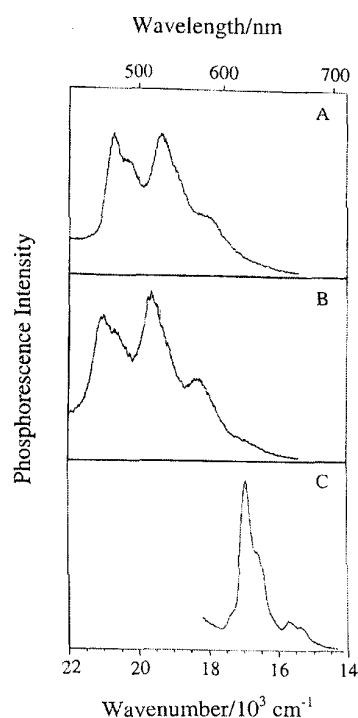
Wavelength/nm

Fig. 1. Uncorrected phosphorescence spectra of 1.0×10^{-5} M acenaphthene (A), naphthalene (B), and pyrene (C) in 0.05 M SDS, 0.5 M NaCl, 0.05 M Na_2SO_3 and 0.2 M DBE solution at 30 °C. λ_{ex} = 290, 280, and 334 nm for acenaphthene, naphthalene, and pyrene, respectively.

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gives rise to flexible rods. The increased micellar flexibility is unfavorable for the observation of RTP.[12] However, this effect is somewhat offset by an increased intersystem crossing rate due to the accommodation of more DBE molecules with increasing micellar size. The change in phosphorescence intensity of a luminophore at high concentration of salt is thus determined by the relative magnitudes of these two opposing effects. The effect of micellar flexibility on RTP intensity depends strongly on the location of the luminophore in the micelle. Luminophores located closer to the micellar surface will experience a larger microflexibility. Luminophores with high rigidity and hydrophobicity, such as acenaphthene and pyrene, are probably located near the micellar interior, giving rise to a slight change in RTP intensity (Fig. 2a and 2b). Naphthalene is probably located near the micellar surface and thus experiences a large microfluidity, leading to a decreased RTP intensity at high salt concentration (Fig. 2c).

The microviscosity and aggregation number of micelles are strongly dependent on the temperature. It is therefore important to examine how the temperature affects RTP of luminophores during the micellar elongation. Fig. 3 shows the temperature dependence of the phosphorescence intensities of 1.0×10^{-5} M pyrene, naphthalene, and acenaphthene in 0.05 M SDS, 0.05 M Na_2SO_3, 0.2 M DBE, 0.36 M NaCl solution. The phosphorescence intensities of all three luminophores decrease significantly with increasing temperature. Extremely weak RTP was observed at a temperature above 60 °C. As temperature increases, the aggregation number and rigidity of the micelle are expected to decrease dramatically.[16] Moreover, less DBE molecules will be incorporated into the
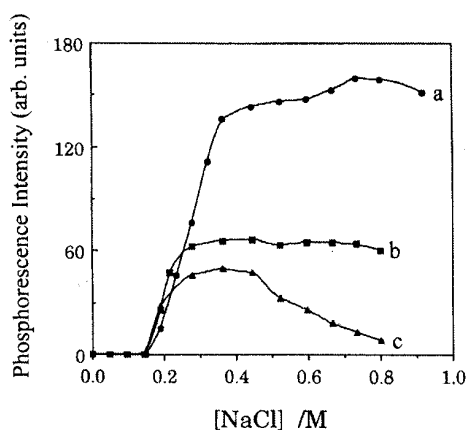
smaller micelle. These are all unfavorable for the observation of RTP, leading to a decrease in RTP intensity with increasing temperature.

Fluorescence is a powerful means in probing the change in microenvironment of the liminophore and the efficiency of the quenching effect during micellar elongation. The variation in fluorescence intensities of 1.0×10^{-5} M naphthalene in SDS micelle in the presence and absence of 0.2 M DBE upon continuing addition of NaCl is illustrated in Fig. 4. The fluorescence intensity increases dramatically in the absence of DBE (Fig. 4a) and changes only slightly in the presence of 0.2 M DBE (Fig. 4b). The increase in rigidity upon micellar elongation causes a decrease in the rates of nonradiative pro-
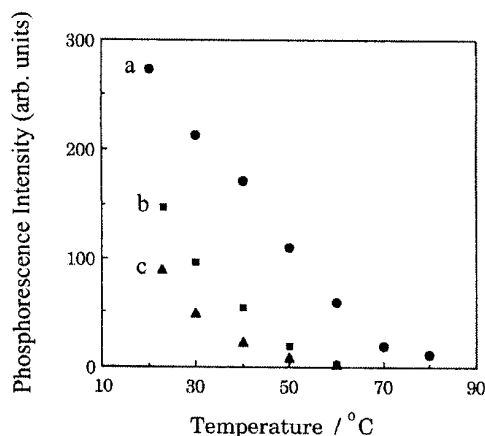

Fig. 3. The variations in phosphorescence intensities of 1.0×10^{-5} M pyrene (a), naphthalene (b), and acenaphthene (c) in 0.05 M SDS, 0.05 M Na_2SO_3, 0.2 M DBE, 0.36 M NaCl solution as a function of temperature.
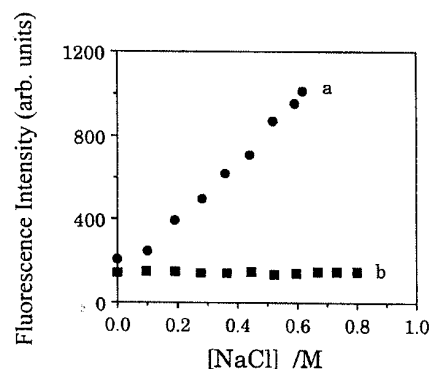

Fig. 2. The effect of NaCl concentration on the phosphorescence intensities of 1.0×10^{-5} M pyrene (a), acenaphthene (b), and naphthalene (c) in 0.05 M SDS, 0.05 M Na_2SO_3 and 0.2 M DBE solution at 30 °C.

Fig. 4. The effect of NaCl concentration on the fluorescence intensity of 1.0×10^{-5} M naphthalene in 0.05 M SDS, 0.05 M Na_2SO_3 solution at 30 °C in the absence (a) and presence (b) of 0.2 M DBE.

cesses, which will enhance the fluorescence intensity. On the contrary, incorporation of more DBE molecules in the micelle during its elongation will give rise to a reduction in fluorescence intensity due to a Stern-Volmer type of quenching effect. The two opposing effects may offset one another, leading to nearly a constant fluorescence during the sphere-to-rod transition with the presence of a quencher (Fig. 4b).

Effect of Different Heavy-atom Containing Species on RTP

In order to investigate the effect of various heavy-atom containing species on the intensity of RTP, we have measured the phosphorescence intensity of 1.0×10^{-5} M pyrene in 0.05 M SDS, 0.05 M Na_2SO_3, 0.6 M NaCl solution at 30 °C and in the presence of various heavy-atom containing species. The variation in phosphorescence intensity of pyrene upon continuing addition of DBE is demonstrated in Fig. 5A. The in-
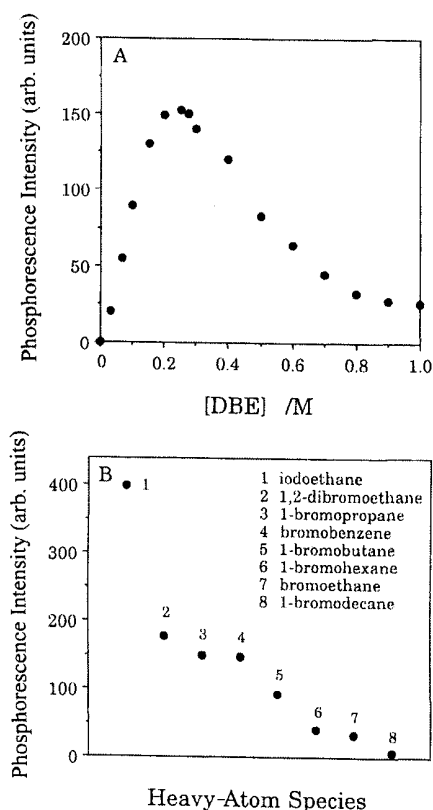
tensity first increases rapidly until a maximum is reached at 0.23 M DBE, then drops sharply at high concentration. The results suggest that the presence of DBE facilitates the observation of RTP, whereas high concentration of DBE leads to quenching of the phosphorescence. Similar variations in phosphorescence intensities were also observed for other heavy-atom containing species. The optimal concentration of heavy-atom containing species for RTP measurements varies from 0.1 M to 0.3 M. The maximal phosphorescence intensities obtainable by different heavy-atom containing species are shown in Fig. 5B. Iodoethane exhibits the most prominent heavy atom effect. DBE, 1-bromopropane, and bromobenzene are about 40% as efficient as iodoethane in inducing RTP. For a series of straight-chain 1-bromoalkanes, 1-bromopropane is the most efficient heavy-atom containing species. Long 1-bromoalkanes are expected to show large hydrophobic interactions with surfactant molecules leading to a reduction in their mobility in the micelle. This results in a less frequent contact between the heavy-atom containing species and the luminophores and hence a diminishing heavy atom effect. No RTP was observed for the polar heavy-atom containing species, including 2-bromoethanol and bromohexane-1-ol.

CONCLUSION

The detection of RTP for selected aromatic hydrocarbons is feasible in deoxgenated SDS rodlike micelles and in the presence of a hydrophobic heavy-atom containing species. No RTP was observed in spherical or sub-rodlike micelles. In the presence of a heavy-atom containing species, the phosphorescence intensity increases tremendously, while the fluorescence intensity changes only slightly during the sphere-to-rod transition. At high temperatures, the phosphorescence intensity decreases dramatically because of the decreased micellar rigidity and heavy atom effect. Different heavy-atom containing species induces RTP to a different extent with iodoethane exhibiting the most prominent effect. This study demonstrates the feasibility of detecting RTP in deoxygenated SDS rodlike micelles using a suitable hydrophobic heavy-atom containing species.

Fig. 5. (A) The effect of DBE concentration on the phosphorescence intensity of 1.0×10^{-5} M pyrene in 0.05 M SDS, 0.05 M Na_2SO_3, 0.6 M NaCl solution at 30 °C. (B) The effect of heavy-atom containing species on the maximal phosphorescence intensities of pyrene.

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