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Excited Triplet State of a UV-B Absorber, Octyl Methoxycinnamate

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The lowest excited triplet (T_1) state of the most widely used UV-B absorber, octyl methoxycinnamate (OMC), has been studied through measurements of phosphorescence and electron paramagnetic resonance spectra in rigid solutions at 77 K. The energy level and lifetime of the T_1 state of OMC were determined. The observed T_1 lifetime and zero-field splitting parameter suggest that OMC possesses mainly a $^3\pi\pi^*$ character in the T_1 state.

Recently, awareness of the detrimental effects of UV radiation has increased, as a result, there is an increasing need for safe and effective sunscreens. To be ideal UV absorbers in skin-care sunscreens, it is essential that the absorbed UV energy is harmlessly transformed into vibrational energy with minimal impact to epidermal and dermal tissues. The photophysical and photochemical processes of organic UV absorbers are under active investigation.[1]

In most sunscreens, at least two UV absorbers are used in formulations to cover a wide range of wavelengths, especially 280–400 nm. Two widely used representatives of organic UV absorbers are butylmethoxydibenzoylmethane (BM-DBM, avobenzone) for the UV-A region and octyl methoxycinnamate (OMC, 2-ethylhexyl *trans*-4-methoxycinnamate) for the UV-B region. However, BM-DBM is well-known for its photoinstability. The photostability of the mixtures of BM-DBM, OMC, and other UV absorbers has attracted considerable interest for many years since there may be stabilizing and destabilizing interactions in UV absorber combinations.[2]

It is especially important to determine the energy levels of the lowest excited triplet (T_1) state of individual UV absorbers because triplet–triplet energy transfer is possible provided the energy levels are suitable. Recently, the energy levels of the T_1 states of the keto and enol forms of BM-DBM have been determined through measurements of phosphorescence in rigid solutions at 77 K.[3] On the other hand, to the best of our knowledge, the phosphorescence spectrum of OMC has not been reported. The only the literature datum concerning the T_1 energy of OMC is the value of T_1 energy estimated through the oxygen-enhanced absorption spectrum of OMC in carbon tetrachloride.[4]

In the present study, we observed the phosphorescence spectrum of OMC in ethanol–ethyl iodide (EtOH–EtI, 4:1 by volume) at 77 K by using external heavy atom effects.[5] We obtained the lifetime and zero-field splitting (ZFS) parameter of the T_1 state of OMC through the measurements of electron paramagnetic resonance (EPR) spectra in EtOH at 77 K by using benzophenone as a triplet sensitizer. The nature of the T_1 state of OMC is discussed.

OMC (Wako EP grade, >95%), EtOH (Wako Super Special grade), and EtI (Tokyo Kasei GR grade) were used without further purification. The sample solutions were prepared at a concentration of 3×10^{-3} mol dm^{-3} for the UV absorption, phosphorescence, and EPR measurements and 3×10^{-5} mol dm^{-3} for fluorescence, fluorescence–excitation, and phosphorescence–excitation measurements.

The UV absorption spectra were measured with a JASCO V-550 spectrometer and a Hitachi U-3210 spectrometer. Details of UV absorption measurements at 77 K have been described previously.[3,6] The fluorescence and phosphorescence–excitation spectra were measured with a JASCO FP-6500 spectrofluorometer. For the phosphorescence and EPR measurements, an Ushio 500 W Hg lamp or a Canrad-Hanovia 1 kW Xe–Hg lamp with an Asahi Technoglass UV-D33S glass filter (transmits the wavelength 250–400 nm), 5 cm of nonfluorescent water, and a Copal DC-494 electromechanical shutter were used as an exciting light source. The experimental setup for the phosphorescence and EPR measurements is the same as that reported previously.[7]

The UV absorption, fluorescence, and fluorescence–excitation spectra of OMC were measured at 298 K and at 77 K, as shown in Figures 1 and 2. The fluorescence spectrum observed in EtOH–EtI is similar to that observed in EtOH, although the former spectrum shows somewhat blurred vibronic bands. This fact shows that the external heavy atom effect of EtI on the energy level of the lowest excited singlet (S_1) state of OMC is small. The S_1 energy of OMC in EtOH was estimated to be 29900 cm^{-1} from the intersection point of UV absorption and fluorescence spectra.[8] The fluorescence–excitation spectrum observed in EtOH is similar to the UV absorption spectrum observed in EtOH. On the other hand, the fluorescence–excitation spectrum observed in EtOH–EtI is somewhat different. This is due to the long wavelength absorption edge of EtI

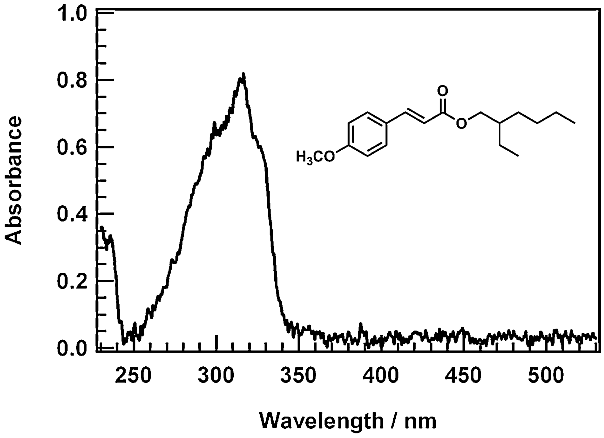

Figure 1. UV absorption spectrum of OMC in EtOH at 77 K.

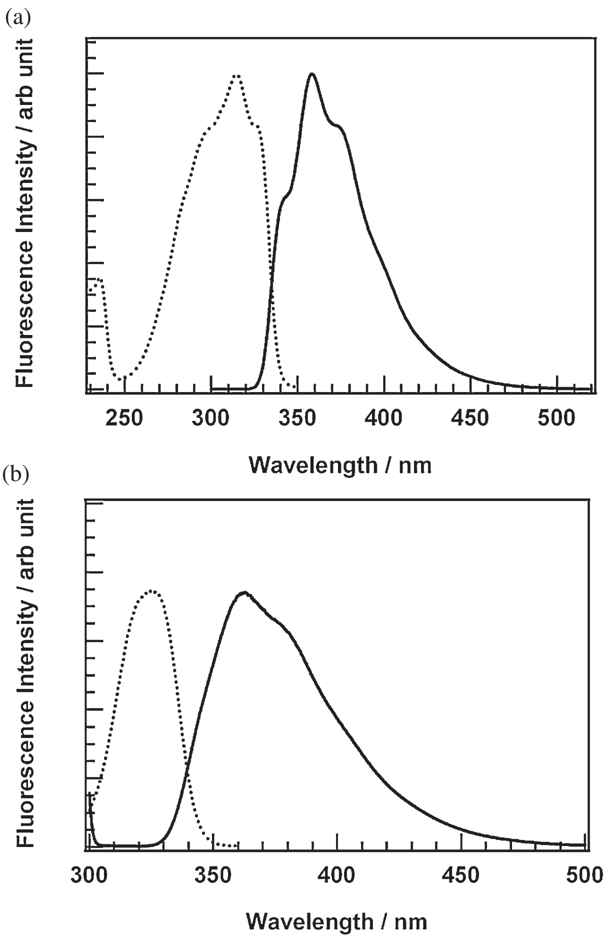

Figure 2. (a) Fluorescence (full line, $\lambda_{\mathrm{exc}} = 290\,\mathrm{nm}$) and fluorescence–excitation (dotted line, $\lambda_{\mathrm{obs}} = 358\,\mathrm{nm}$) spectra of OMC in EtOH and (b) fluorescence (full line, $\lambda_{\mathrm{exc}} = 290\,\mathrm{nm}$) and fluorescence–excitation (dotted line, $\lambda_{\mathrm{obs}} = 380\,\mathrm{nm}$) spectra of OMC in EtOH–EtI (4:1 by volume) at 77 K.

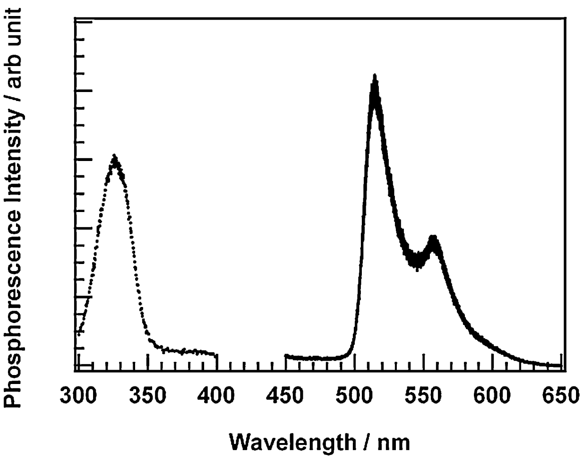

Figure 3. Phosphorescence (full line) and phosphorescence–excitation (dotted line, $\lambda_{\mathrm{obs}} = 512\,\mathrm{nm}$) spectra of OMC in EtOH–EtI (4:1 by volume) at 77 K.

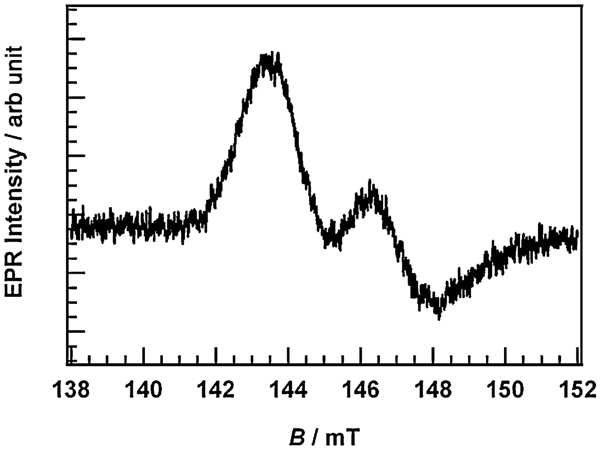

Figure 4. EPR spectrum observed for the ternary solution containing OMC ($3 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$) and benzophenone ($3 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) in EtOH at 77 K. The microwave frequency was 9211 MHz.

because the concentration of EtI was extremely high under our experimental conditions.

Figure 3 shows the phosphorescence and phosphorescence–excitation spectra of OMC observed in EtOH–EtI at 77 K. As is clearly seen in Figures 2b and 3, the phosphorescence–excitation spectrum is similar to the fluorescence–excitation spectrum of OMC in EtOH–EtI. This shows that the phosphorescence observed in EtOH–EtI is reasonably assigned to the phosphorescence of OMC enhanced by the external heavy atom effects of EtI. It should be noted here that we can safely assume that the external heavy atom effect of EtI on the T_1 energy of OMC is small, as is observed for the S_1 state mentioned above. The energy level of the T_1 state of OMC was estimated to be $19500\,\mathrm{cm^{-1}}$ from the first peak of phosphorescence. The T_1 energy thus obtained is close to that estimated through the oxygen-enhanced absorption spectrum, $19950\,\mathrm{cm^{-1}}$.[4] The present work shows that the T_1 energy of OMC is lower than that of BM-DBM (keto form), $24400\,\mathrm{cm^{-1}}$, and that of BM-DBM (enol form), $20400\,\mathrm{cm^{-1}}$.[3] OMC may be useful as a triplet acceptor of photolabile BM-DBM. The triplet energy transfer experiments for a ternary solution containing OMC and BM-DBM in EtOH are currently in progress.

The EPR signals of OMC in the T_1 state are too weak to be observed in EtOH at 77 K. To observe the EPR signals, the excitation of our choice is triplet energy transfer. Benzophenone was chosen as a sensitizer in this work. The EPR spectrum of the T_1 state of OMC was measured for a ternary solution containing OMC and benzophenone in EtOH at 77 K, as shown in Figure 4. As is clearly seen in Figure 4, there are two T_1 species in EtOH at 77 K. In this paper the species which gives lower-field B_{min} signal is denoted as *A*-OMC and the species which gives higher-field B_{min} signal is denoted as *B*-OMC. Although the molecular structures of *A*-OMC and *B*-OMC remain uncertain, one possible explanation arises from a consideration of the *trans–cis* photoisomerization of OMC. The photoisomerization quantum yields are found to be fairly high in solutions.[9]

The values of ZFS parameter D^* of the T_1 states of *A*-OMC and *B*-OMC were found to be 0.1282 and $0.1196\,\mathrm{cm^{-1}}$, respectively, from the observed resonance fields of B_{min} signals with Kottis and Lefebvre's correction.[10] The g value was assumed to be equal to the free-electron value. The lifetimes of the T_1 states of A-OMC and B-OMC obtained from the decay of the EPR B_{min} signal are 141 and 144 ms, respectively. These facts show that the T_1 state of OMC possesses mainly a $^3\pi\pi^*$ character. The distribution of the two unpaired electrons is sensitive to the molecular conformation for the $^3\pi\pi^*$ state. Therefore the ZFS parameters are very sensitive to the molecular conformations of OMC because these parameters are elucidated by taking the electron spin dipole–dipole interactions into consideration. On the other hand, the energy levels of the S_1 states of *trans*-OMC and *cis*-OMC have been reported to be nearly identical.[1c,9a] The lifetimes of the T_1 states of A-OMC and B-OMC are the same as mentioned above. It may be difficult to assign the observed phosphorescence spectrum to A-OMC or B-OMC or to the mixture of the two species if the energy levels of A-OMC and B-OMC are nearly identical in the T_1 states as in the S_1 states. The values of D^* of the T_1 states of 4-methylanisole, 4-fluoroanisole, ethylene, and formaldehyde were estimated to be 0.1547, 0.1560, 0.4310, and 0.43 cm^{-1}, respectively.[11] Since the observed D^* values of A-OMC and B-OMC are fairly smaller than those of methoxyphenyl, ethylenic, and carbonyl fragments, the two unpaired electrons localize on neither the methoxyphenyl, nor the ethylenic, nor the carbonyl fragment. The delocalized character of the unpaired electrons has been observed for cinnamic acid and *p*-methylcinnamic acid.[12]

In EtOH at 77 K, OMC is fluorescent but nonphosphorescent or very weakly phosphorescent. The EPR signals of OMC in the T_1 state are too weak to be observed, whereas they were observed using the triplet sensitizer. These facts show that the quantum yield of $S_1 \rightarrow T_1$ intersystem crossing (ISC) is small and the deactivation processes are predominantly fluorescence and internal conversion to the ground state. Further detailed studies including luminescence and ISC quantum yields are currently in progress to elucidate the deactivation processes of the photoexcited states of OMC.

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