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Direct observation of the intermolecular triplet–triplet energy transfer from UV-A absorber 4-*tert*-butyl-4′-methoxydibenzoylmethane to UV-B absorber octyl methoxycinnamate

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ABSTRACT

Triplet energy transfer (TET) is an important photostabilization process for organic UV absorbers, such as 4-*tert*-butyl-4′-methoxydibenzoylmethane (BM-DBM) and octyl methoxycinnamate (OMC). To characterize interactions between UV absorbers as TET the interactions between BM-DBM and OMC have been studied through measurements of EPR and time-resolved phosphorescence spectra. The EPR B_{min} signals and the phosphorescence of OMC were observed through the selective excitation of BM-DBM at 365 nm in EtOH at 77 K. These results indicate that the intermolecular TET occurs from BM-DBM to OMC. This is the first report of the experimental evidence of the TET between the organic UV absorbers.

1. Introduction

Over the last few years, the increasing awareness, among the general population, of the risks associated with solar exposure on human skin has resulted in an increase in the use of sunscreens because the decrease of the ozone layer results in an increase of UV reaching the surface of the earth. There is an increasing need for safe and efficient sunscreens to prevent harmful effect of UV radiation on human skin. Although the ideal UV absorbers in skin-care sunscreens should remain unchanged after UV irradiation and the absorbed UV energy is harmlessly transformed into vibrational energy, most UV absorbers exhibit some photoreactivity.

In most sunscreens, at least two UV absorbers are combined to prevent UV radiation. Photochemical stability is an important characteristic that an effective and safe UV absorber should possess because the UV-induced photoreactivity of the UV absorber not only reduces its UV protection effectiveness but can also generate potentially toxic species. The combination of different UV absorbers usually leads to synergism concerning both the effectiveness and photostability of the sunscreen, or the other way their decomposition if a photoreaction occurs between the different UV absorbers. In order to improve of sunscreen photostability, photochemical and photophysical properties of UV absorbers and have been studied by many researchers [1–21]. A significant volume of research has focused on the intermolecular interactions between a UV-A (320–400 nm) absorber, 4-*tert*-butyl-4′-methoxydibenzoylmethane (BM-DBM, Scheme 1) and another UV absorbers [3–11,14]. The combination of BM-DBM and the UV-B (290–320 nm) absorber, octyl methoxycinnamate (OMC, Scheme 1), provides an effective protection throughout the whole UV range (290–400 nm). However, the combination of BM-DBM and OMC is known to be photoinstable. The photochemical and photophysical properties of the BM-DBM–OMC combination have been discussed for efficacy and safety of UV absorber combinations [3–12,14]. In general principles, energy transfer occurs between UV absorbers through relaxation processes when several UV absorbers coexist. Although the possibility of the triplet–triplet energy transfer between UV absorbers has been proposed by many studies, up to now, the direct evidence has not been shown [1,4,12]. It is important to demonstrate the experimental evidence of the pathways of UV absorber interactions between UV absorbers in UV absorber combinations.

In our previous works, the energy levels and lifetimes of the lowest excited triplet (T_1) states of the keto and the enol forms of BM-DBM and that of OMC were determined through the measurements of phosphorescence and electron paramagnetic resonance (EPR) spectra in rigid solutions at 77 K [20,21]. The BM-DBM–OMC combination can be useful for examining the interaction between UV absorbers, because the energy level of the T_1 state of OMC is lower than that of BM-DBM and the T_1 lifetime of OMC is longer than that of BM-DBM [20,21]. OMC may be useful as a triplet quencher of photoinstable BM-DBM. To our best knowledge, the conclusive evidence of the intermolecular triplet–triplet energy transfer between UV absorbers such as BM-DBM and OMC has not been reported. In the present study, we observed the intermolecular triplet–triplet energy transfer from BM-DBM to OMC by measuring phosphorescence and EPR spectra in EtOH at 77 K.

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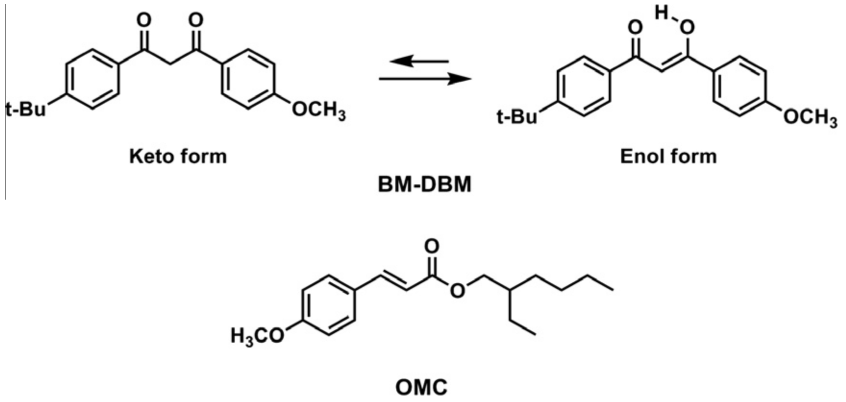

Scheme 1. Molecular structures of BM-DBM and OMC.

2. Experimental

BM-DBM (Wako first grade), OMC (Wako EP grade, >95%), EtOH (Kanto for fluorometry), benzophenone (Wako first 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} or 6×10^{-3} mol dm^{-3} for the UV absorption, phosphorescence, and EPR measurements.

The UV absorption spectra were measured with Hitachi U-3210 spectrometer. Details of UV measurements at 77 K have been described previously [19–21]. For the phosphorescence and EPR measurements, a Keyence UV-400 UV-LED radiator (365 nm) equipped with a UV-50H radiation head and an Ushio 500 W 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. For the phosphorescence measurements, the emissions from a sample were passed through a Jobin Yvon H-20VIS spectrometer and detected by an EMI 9789QB photomultiplier tube. The EPR spectra were measured with a JEOL JES-FE1XG spectrometer with 100 kHz magnetic field modulation at microwave frequency close to 9.2 GHz. The static magnetic field was calibrated with an Echo Electronics EFM-2000AX proton NMR gauss meter. The experimental setup for the phosphorescence and EPR measurements is the same as that reported previously [19–21]. All measurements were carried out at 77 K in EtOH.

3. Results and discussion

Figure 1 shows the UV absorption spectra of BM-DBM and OMC. The observed UV absorption spectrum of BM-DBM shows strong absorption bands in the UV-A region (Figure 1a) and is attributed to the enol form because BM-DBM exists mainly as the enol form in solutions [13]. On the other hand, OMC absorbs strongly at wavelengths shorter than 340 nm, as presented in Figure 1b [15–18,21]. In general, the T_1 states of a molecule is longer-lived than the corresponding lowest excited singlet (S_1) state of the same molecule [22–26].Triplet–triplet energy transfer is likely for intermolecular energy transfer because of the long lifetime of T_1 states in rigid solutions at low temperature. To investigate triplet–triplet energy transfer between UV absorbers, a convenient experimental condition is that the energy level of the S_1 state of the donor lies below that of the acceptor but the T_1 energy level of the donor lies above that of the acceptor. Under such condition, singlet–singlet energy transfer is unlikely because of the unfavorable energetic positions of the donor and the acceptor. The selective excitation of the donor in the presence of the acceptor is possible by employing exciting radiation which is totally absorbed by the donor [22–28]. To provide a certain insight as to whether the triplet energy transfer is taking place intermolecularly, a desirable condition is that the lifetime of the triplet state of the donor molecule must be shorter than that of the acceptor molecule. The BM-DBM–OMC combination satisfies the necessary and desirable conditions because the energy level of the T_1 state of BM-DBM ($E_{T1,\ enol} = 20\,400$ cm^{-1} and $E_{T1,\ keto} = 24\,400$ cm^{-1}) lie above that of OMC ($E_{T1} = 19\,500$ cm^{-1}) and the S_1 state of BM-DBM ($E_{S1,\ enol} = 25\,400$ cm^{-1}) lies below that of OMC ($E_{S1} = 29\,900$ cm^{-1}) [20,21]. The lifetime of the T_1 state of BM-DBM ($\tau_{phos,\ enol} = 30$ ms) is shorter than that of OMC ($\tau_{phos} = 140$–144 ms) [20,21].

The EPR spectrum of the ternary solution containing BM-DBM (3×10^{-3} mol dm^{-3}) and OMC (3×10^{-2} mol dm^{-3}) in EtOH at 77 K was observed through the UV-LED selective excitation of the enol form of BM-DBM at 365 nm, as shown in Figure 2a. As presented in Figure 2b, the only one B_{min} signal was observed for the T_1 state of the enol form of BM-DBM with the UV-LED excitation in the binary solution of BM-DBM in EtOH. The T_1 state of the keto form of BM-DBM gives no EPR signals with the UV-LED excitation. Although the EPR signals of the T_1 state of OMC are too weak to be observed with the 365 nm UV-LED and Hg-Xe lamp excitations, the two EPR B_{min} signal, 144 mT and 148 mT, of OMC were observed for the ternary solution containing OMC and benzophenone with Hg-Xe lamp excitation, as is clearly seen in Figure 2c [21]. Since singlet–singlet energy transfer is energetically prohibited, these results clearly show that the intermolecular triplet–triplet energy transfer from BM-DBM to OMC for the ternary solution was observed in EtOH at 77 K.

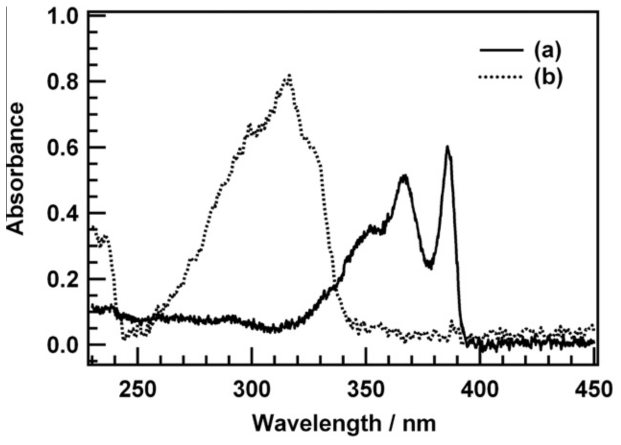

Figure 1. UV absorption spectra of (a) BM-DBM and (b) OMC in EtOH at 77 K.