Photoinduced α-Cleavage of α-Acyl-4-phenylphenols in Highly Excited Triplet States Studied by Stepwise Two-Color Laser Photolysis

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Absorption and phosphorescence spectra of phenyl acetate and Phenyl benzoate

Figure S1 shows absorption spectra of phenyl acetate and phenyl benzoate (PA and PB) in acetonitrile at 295 K and phosphorescence spectra in ethanol at 77 K.

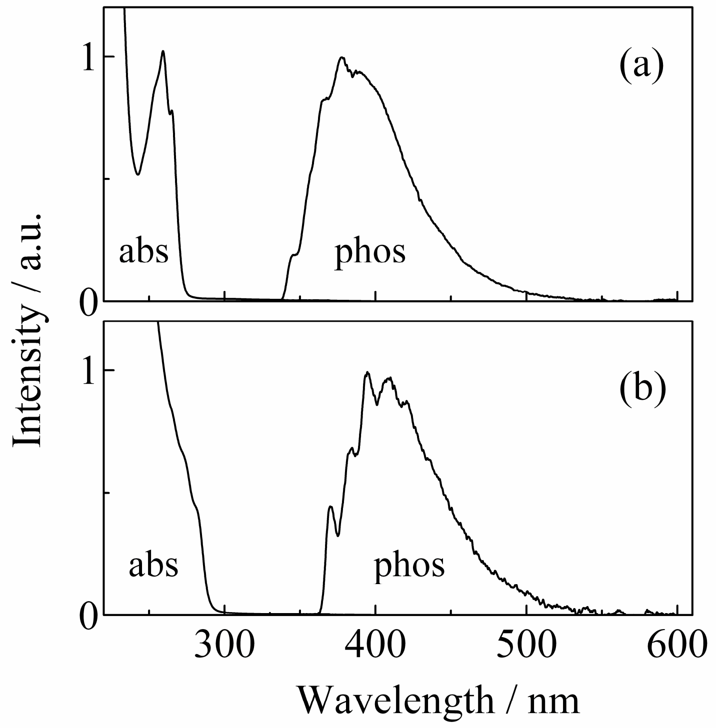

Figure S1 Absorption spectra of PA (a) and BA (b) in ACN at 295 K, and phosphorescence spectra in ethanol at 77 K.

Fluorescence from PA and BA was absent at 295 K. From the 0-0 origins of the phosphorescence spectra, the triplet energies, E_T were determined to be 82.9 kcal mol^{-1} for PA and 77.3 kcal mol^{-1} for

BA whereas the lifetimes (τ_p) of phosphorescence at 77 K were 2.2 s for PA and 2.0 s for PB. From the τ_p values, it is inferred that the electronic configuration of the T_1 state of PA and PB is of π,π^*.

Absorption spectrum changes upon 254-nm steady-state photolysis of R-ODP

Stationary photolysis of R-ODP in CH was carried out using 254-nm light from a low-pressured mercury lamp. Figure 2 shows absorption spectrum changes during photolysis of R-ODP at 295 K.

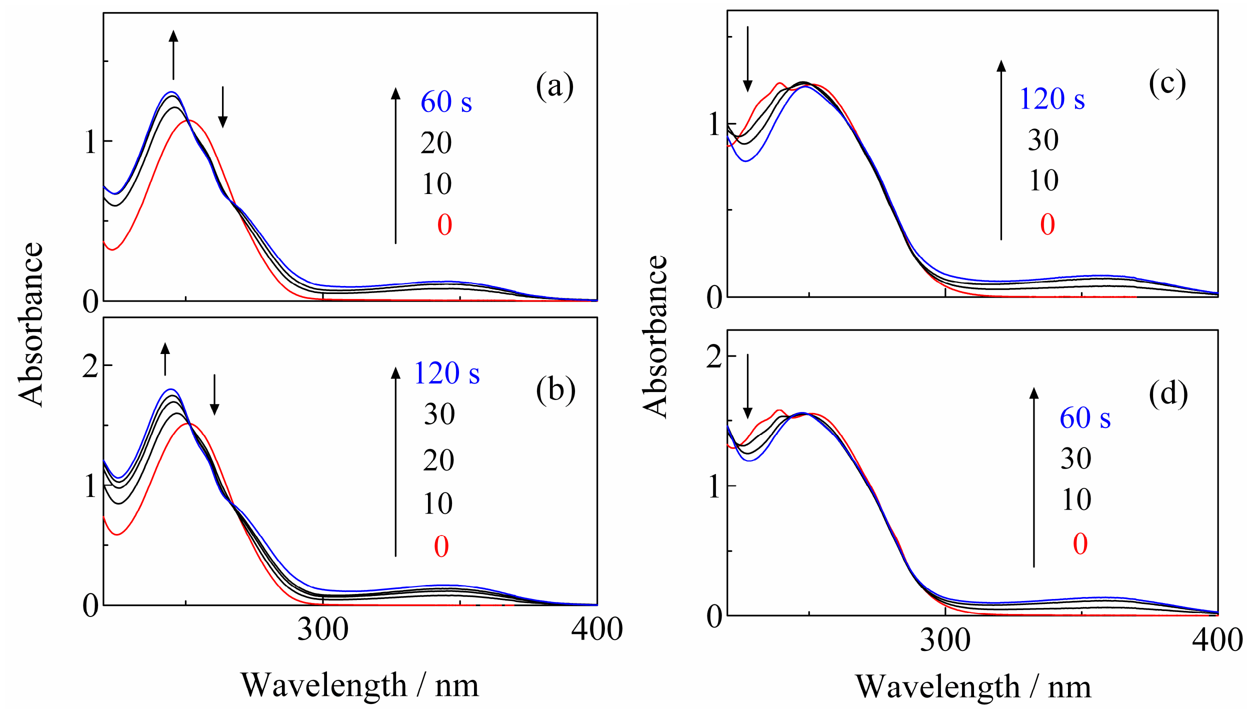

Figure S2 Absorption spectrum changes during 254-nm photolysis of Me-ODP in the degassed (a) and aerated CH (b), and Ph-ODP in the degassed (c) and aerated CH (d) at 295 K.

Isosbestic points can be seem during the absorption spectrum changes, which indicates a definite photochemical reaction proceeds to form the corresponding photoproduct. The feature of the spectrum changes is independent of the amount of the dissolved oxygen. From these observations, the S_1 states of R-ODP are involved in the photochemical reactions. Unfortunately, the final photoproducts were not able to identify from the corresponding absorption spectra.

Photochemical reactions upon single and two-color laser photolysis of Ph-OBP

Figure S3 shows transient absorption spectra at 1.3 μs upon 308-nm laser photolysis of an Ac(0.6 mol dm^{-3})/Me-OBP(1.7 × 10^{-3} mol dm^{-3}) system in the absence and the presence of the second 355 nm laser pulsing at 1.3 μs after the first laser pulsing.

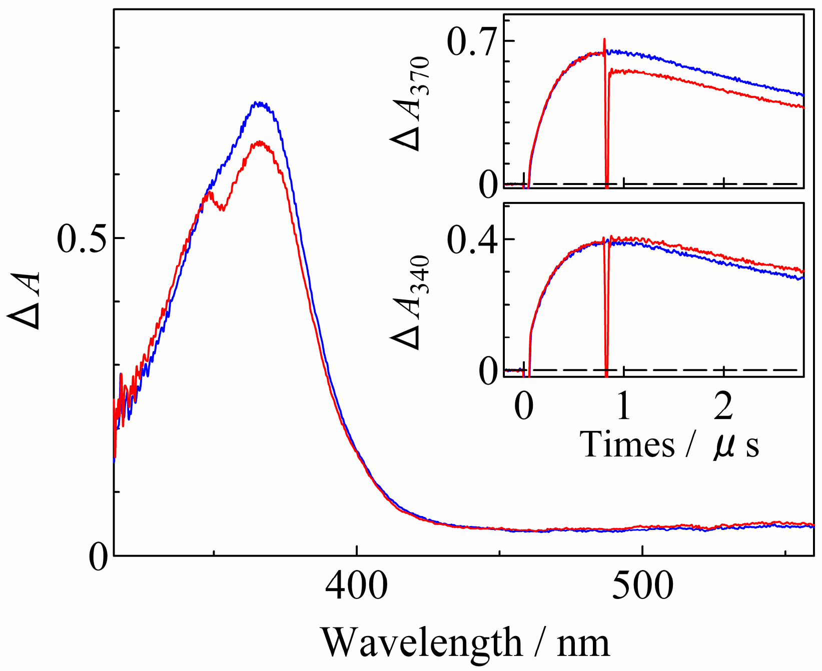

Figure S3 Transient absorption spectra obtained at 1.3 μs upon 308-nm laser pulsing an Ac (0.6 mol dm^{-3})/Ph-OBP (1.7 × 10^{-3} mol dm^{-3}) system in ACN in the absence (blue color) and the presence (red color) of the second 355 nm laser pulsing at 1.3 μs. A dimple at 355 nm in the transient absorption spectrum in red color is due to scattering of the second 355 nm laser pulse. Insets; time profiles at 370 nm (upper) and at 340 nm (lower) in the absence (blue color) and the presence (red color) of the second 355-nm laser pulsing. The spike at 1.3 μs is due to scattering of the second 355-nm laser pulse.

The transient absorption spectrum in the absence of the second laser pulse is due to triplet Ph-OBP. In the presence of the second 355-nm laser pulse, the intensity of the absorption of the triplet at 370 nm was found to decrease without showing the recovery to the initial intensity obtained upon 308-nm laser photolysis (see upper inset in Figure S3) while an increase of the intensity of absorbance at 340 nm can be recognized in the transient absorption in Figure S3 and in the time profile of the absorbance at 340 nm (lower inset in Figure S3). These changes in absorbance upon photolysis of triplet Ph-OBP show the formation of PPR due to C-O bond dissociation in a T_n state as well as the case for Me-OBP shown in the text.

Electronic character of the T_R state of R-OBP

In our previous study of β C-O bond cleavage in highly excited triplet states of biphenyl derivatives, we found that the dissociation rate is proportional to the energy difference, ΔE (= E_{TR} - BDE) between the corresponding bond dissociation energy, BDE and the energy level, E_{TR} of the dissociative triplet state, T_R.[1] That is,

$k_{dis(TR)} = \alpha \, \Delta E \qquad \text{(S1)}$

Here, α is a constant. The quantum yield, $\Phi_{dis}(T_R)$ for the cleavage can be expressed by eqn (S2) using the rates of dissociation and internal conversion in the dissociative triplet state.

$\Phi_{dis}(T_R) = k_{dis(TR)}(k_{dis(TR)} + k_{ic(TR)})^{-1} \qquad \text{(S2)}$

Eqn (S2) can be transformed by using eqn (S1) and a constant, β (= $\alpha \, k_{ic(TR)}^{-1}$).

$\Phi_{dis}(T_R)\ (= \Phi_{dec}) = \beta \, \Delta E\ (1 + \beta \, \Delta E)^{-1} \qquad \text{(S3)}$

We have reported that in the case of β C-O bond dissociation in highly excited triplet states of biphenyloxy derivatives, BPO-R, the E_{TR} and the β values are, respectively, 70 kcal mol^{-1} and 6.3×10^{-3} mol kcal^{-1}.[1]

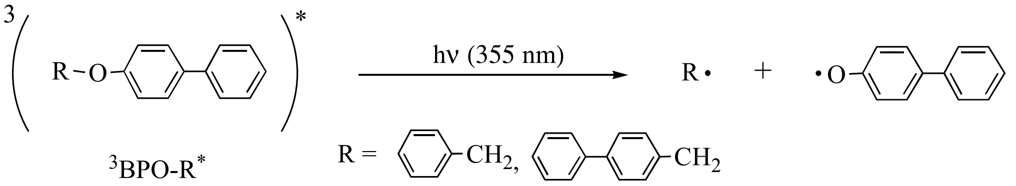

Figure S4 shows plots of Φ_{dec} obtained for R-OBP in the present work as a function of BDE(C-O) along with the calculated Φ_{dec} for BPO-R using eqn (S3).

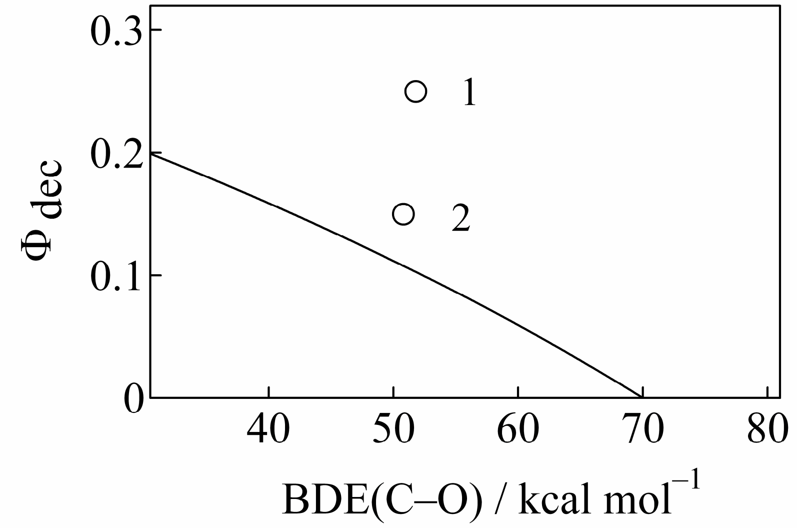

Figure S4 Plots of the quantum yields, Φ_{dec} for photodecomposition of triplet Me-OBP (1) and Ph-OBP (2), and calculated Φ_{dec} (solid curve) for triplet BPO-R using eqn (S3) as a function of the corresponding BDE(C-O).

The plots for R-OBP obtained in the present work do not follow the calculated curve. This disagreement may be explained in terms of the difference in electronic character of the T_R states as follows. The photochemical properties of the $T_1(\pi,\pi^*)$ state of R-OBP, such as triplet energies and the shape of the triplet-state absorption, are very similar to those of the $T_1(\pi,\pi^*)$ state of BPO-R.[1] These similarities indicate that triplet energy is localized on the biphenyloxy moiety of both R-OBP and BPO-R. Undoubtedly, the electronic character of the T_R state of BPO-R is of π,π^*. Considering the ruled-out plots of Φ_{dec} for R-OBP from the calculated one for cleavage in the $T_R(\pi,\pi^*)$ state of BPO-R, we suggest that the electronic structure of the T_R state of R-OBP may be not of π,π^*, but of n,π^* due to the carbonyl group incorporated in R-OBP. That is, in the $T_R(n,\pi^*)$ state of R-OBP, a π-electron derived from the excited acyl group is allowed to electronically conjugate with the π-electron system of the biphenyloxy moiety of R-OBP.

Reference

1. M. Yamaji, A. Kojima and S. Tobita, Stepwise laser photolysis studies of β-bond cleavage in highly excited triplet states of biphenyl derivatives having C-O bonds, *J. Phys. Chem. A*, 2007, **111**, 770-776.