Novel Dependence of the Bond Cleavage Pattern of Bis(2-phenylbenzoyl) Peroxide on the Irradiation Wavelength

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Bis(2-phenylbenzoyl) peroxide (2-PhBPO) photodecomposed by 100% O-O bond cleavage to give mainly biphenyl-2, 2'-carbolactone on 313 nm irradiation, however, on 254 nm, the photodecomposition proceeded through 60% two bonds cleavage (simultaneous C-C and O-O bonds cleavage).

Photodecomposition mechanism of diaroyl peroxides has been investigated from product analysis and the observation of transient species.[1] Especially, the observation of the transient absorption spectra of aroyloxyl radicals by laser flash photolysis, which is reported to have one of the absorption band at >600 nm with a few micro second lifetime in acetonitrile (MeCN),[1-3] is useful method to clarify the reaction mechanism. Now we applied these methods to reveal the decomposition mechanism of bis(2-phenylbenzoyl) peroxide (**2-PhBPO**) in comparison with that of bis(4-phenylbenzoyl) peroxide (**4-PhBPO**), and found that the bond cleavage pattern in **2-PhBPO** is dependent on the wavelength of irradiation (313 or 254 nm). Namely, yields of biphenyl and biphenyl-2, 2'-carbolactone (**BPCL**), an unique product from **2-PhBPO** were strongly dependent on the wavelength of irradiation. In addition to this, we first succeeded to observe the transient spectra of supposed to be 4-phenylbenzoyloxyl radical.

4-PhBPO (2.8×10^{-4} mol dm^{-3}, Abs$_{308}$=2.0) and **2-PhBPO** (1.0×10^{-3} mol dm^{-3}, Abs$_{308}$=2.0) were photolized by pulsed laser light at 308 nm from a XeCl excimer laser (Lambda Physik COMPex 102, 100 mJ/pulse, 10ns fwhm) in deaerated MeCN. Figures 1a and 1b depict the transient absorption spectra for **4-PhBPO** and **2-PhBPO**, respectively. As shown in Figure 1a, we can see the absorption of 4-phenylbenzoyloxyl radical at 600-800 nm, which decayed with the lifetime of 600 ns. Failure of this observation in earlier reports[2] was supposedly due to the difficulty in the preparation of **4-PhBPO**. Since **4-PhBPO** has very low solubility in common solvents, its purification is difficult. We succeeded to purify the sample by reprecipitation (addition of methanol to the chloroform solution) with examining purity by iodometry (>98%). In case of **2-PhBPO** (Figure 1b), a typical absorption due to an aroyloxyl radical in the range of wavelength longer than 600 nm was not appeared and only an intense absorption band at 350-400 nm was observed. This absorption was increased in intensity in the time range of 1 μs and then decreased. No observation of 2-phenylbenzoyloxyl radical is possibly explained by the following two reasons. One reason for the too short lifetime to be observed for the radical is the rapid decarboxylation of the radical. However, this is unlikely because the rate constant of decarboxylation of the typical aroyloxyl radicals is as small as around 2×10^{6} s^{-1}.[2-6] In addition, only trace amount of biphenyl is obtained by the 313 nm photolysis of **2-PhBPO** in MeCN (Table 1). The second reason is that very fast intramolecular radical attack occurs to give cyclohexadienyl type radical, which is finally oxidized to **BPCL**.

For stationary irradiation, a 15-W low-pressure mercury arc lamp and a 1 k-W high-pressure mercury arc lamp with NiSO$_4$ solution filter were used for the 254 nm and 313 nm light excitation, respectively, and the reaction was stopped at low conversions (lower than 45%) to prevent following reactions. The reaction was followed by HPLC, and product distribution and the conversion yields are listed in Table 1.

Products are listed in Table 1. The material balances are over 70% and these are higher than those of previous works.[1] For the decomposition of **4-PhBPO**, major products are originated from biphenylyl radical which is produced from decarboxylation of the 4-phenylbenzoyloxyl radical (Scheme 1a). The fate of the 4-phenylbenzoyloxyl radical is mainly decarboxylation, and the rate constant is determined to be 1.7×10^{6} s^{-1} in MeCN by transient absorption. Therefore, most of the 4-biphenylyl 4-phenylbenzoate must be a coupling product in a solvent cage, and it also indicates existence of two bonds cleavage. In PhH, the oxyl radicals gave cyclohexadienyl type radicals which is not easily oxidized. The addition to PhH is reported to be 7.8×10^{7} mol^{-1} dm^{3} s^{-1},[2] therefore, oxyl radical was not observed by transient absorption. The formation of cyclohexadienyl type radical is reversible, and during this reversible process most of the oxyl radicals lose the CO$_2$.

The mechanism to produce **BPCL** and 2-phenylbenzoic acid for **2-PhBPO** is proposed by disproportionation of the cyclized intermediate of 2-phenylbenzoyloxyl radicals (Scheme 1b). The ratio of yields of **BPCL** and 2-phenylbenzoic acid is not 1 might

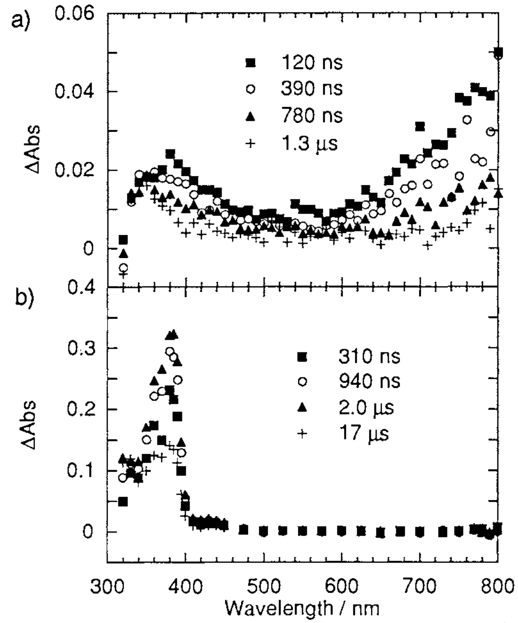
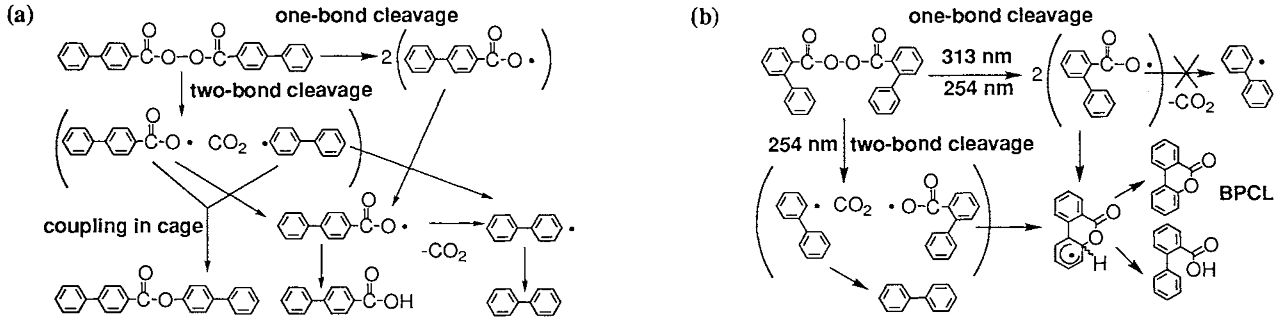
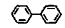
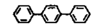
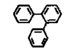
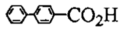
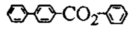
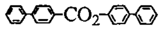
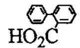
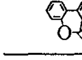


Figure 1. Transient absorption spectra of **4-PhBPO** (a) and **2-PhBPO** (b) in MeCN.



Scheme 1. Bond cleavage pattern of **4-PhBPO** (a) and **2-PhBPO** (b) in MeCN.

Table 1. Product yields in photolyses of **4-PhBPO** and **2-PhBPO** under argon (mol/mol peroxide)

	4-PhBPO			**2-PhBPO**			
Solvent	MeCN		PhH	MeCN			PhH
λ_{ex} / nm	313	254	313	313	313[a]	254	313
	1.43	1.50	trace	trace	trace	0.36	trace
	none	none	0.72	—	—	—	—
	—	—	—	none	none	none	0.05
	0.06	0.03	0.33	—	—	—	—
	none	none	0.10	—	—	—	—
	0.05	0.05	0.07	—	—	—	—
	—	—	—	0.60	0.28	0.22	0.41
	—	—	—	1.05	1.19	0.61	1.00
Total yield	1.59	1.63	1.29	1.65	1.47	1.17	1.41
Conversion	45%	30%	45%	15%	18%	12%	27%

[a] Irradiation under oxygen.

be explained by the partial contribution of oxidation by oxygen to give **BPCL**. In the photolysis under oxygen, the yield of **BPCL** is higher, and that of 2-phenylbenzoic acid is lower than those under argon, respectively. This means most of **BPCL** is obtained by the hydrogen abstraction from cyclized radicals to give 2-phenylbenzoic acid and/or by oxygen to give hydroperoxy radical. Formation of hydroperoxy radical may make the reaction complex and the material balance low.

Interestingly, the product distribution was dependent upon irradiation wavelengths for **2-PhBPO**. In the 254 nm irradiation, biphenyl was obtained over 30%. It is apparent that biphenyl is not produced from decarboxylation of 2-phenylbenzoyloxyl radical but from simultaneous two bonds cleavage in **2-PhBPO** to give 2-phenylphenyl radical. The separate control experiments showed that **BPCL** and 2-phenylbenzoic acid were not decomposed at all by the irradiation; biphenyl was not produced from **BPCL** and 2-phenylbenzoic acid in this experimental condition.

It has been discussed the pattern of bond cleavage of dibenzoyl peroxide (**BPO**) in its decomposition.[1,7-10] In the thermolysis it is proposed that decomposition initiates by the O-O bond cleavage, but in the photolysis the C-C (=O) bond cleavage occurred in addition to the O-O bond cleavage. It means that the former generates two benzoyloxyl radicals and the latter generates a phenyl radical, a benzoyloxyl radical, and a carbon dioxide from one **BPO** molecule. In the case of **2-PhBPO**, it is clear that only one bond is cloven by 313 nm photolysis because biphenyl is yielded in only trace amount in MeCN and PhH.

In the 313 nm irradiation, the decomposition must proceed through the O-O bond cleavage. However, by the 254 nm irradiation to explain a formation of biphenyl, two bonds cleavage (O-O bond and C-C (=O) bond, where a biphenyl radical, a 2-phenylbenzoyloxyl radical, and a carbon dioxide are generated from one **2-PhBPO** molecule) must occur in addition to the normal one bond cleavage. We estimate that one bond cleavage (α) and two bond cleavage (β) ratio is α:β=2:3 from the comparison of the product yields, those are the sum of the yield of **BPCL** and 2-phenylbenzoic acid (0.61+0.22=2α+β) and the yield of biphenyl (0.36=β).

The reason for the difference of the bond cleavage pattern is uncertain. However, one possibility is that n-σ^* excitation of O-O bond initiates O-O bond cleavage by 313 nm irradiation and the excitation of biphenyl carbonyl moiety of 2-PhBPO (may be n-π^* excitation) initiates C-C bond cleavage by 254 nm irradiation. This difference of the excitation may reflect on the difference of the bond cleavage pattern. The difference of **2-PhBPO** and **4-PhBPO** must be caused by the steric effect. For **2-PhBPO**, carbonyl group cannot take coplanarity with the aromatic moiety.

Here, we succeeded to clarify the bond cleavage pattern and its dependence on irradiation wavelength of **2-PhBPO** which undergoes characteristic cyclization reaction through the 2-phenylbenzoyloxyl radical. On the base of these results, the extended studies of diaroyl peroxides decomposition mechanism are undergoing.

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