Transient Spectra and Photoreaction of 4-Methoxybenzoyloxyl Radical

Shigero Oishi, Hirotaka Tsubaki, and Hideyo Matsuzawa
Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara 228-8555

(Received May 14, 1999; CL-990382)

An absorption maximum and a molar extinction coefficient of a transient in the laser flash photolysis of bis(4-methoxybenzoyl) peroxide were determined as 900 nm and 750 $M^{-1}cm^{-1}$, respectively. The comparison of products for the photolysis at 266 nm with and without 1064-nm pulse gave a solid evidence of 4-methoxybenzoyloxyl radical being responsible for the absorption.

On the laser flash photolysis of bis(4-methoxybenzoyl) peroxide, a peculiar absorption is observed, which begins to appear at around 500 nm and rises as it approaches to the longer wavelength end of visible region. Though 4-methoxybenzoyloxyl radical was reported to be responsible for this rise, total spectral features, namely, the absorption maximum, an extinction coefficient, and a type of transition have not been cleared.[1-3] It is reported also that the second laser pulse caused the abrupt depletion of this absorption.[2] Careful product analysis is necessary to conclude that the depletion is due to decarboxylation reaction. We describe here complete spectral features and the detailed analysis of products containing compounds not documented so far.

Acetonitrile solutions of bis(4-methoxybenzoly) peroxide (0.13 mM) were deaerated by bubbling argon for 20 min and then subjected to pulsed laser photolysis at 266 nm (4 mJ/pulse, the forth harmonic of a Q-switched Nd:YAG laser; Quanta-Ray DCR-11) with using a photomultiplier detector sensitive to near-infrared light (R5509-42, Hamamatsu) and a photodiode-array detector (IRY-1024G/RB, Princeton). As the peroxide was consumed by the photolysis, the sample solutions were renewed for every laser pulse. Figure 1 shows transient spectra at 1 μs after the laser pulse, in which the absorption maximum appears at around 900 nm and the absorption continues over 1250 nm.

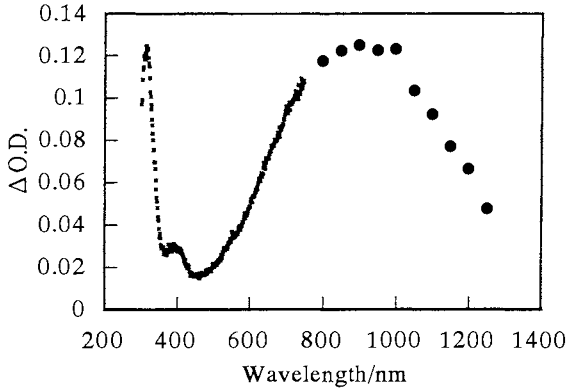


Figure 1. UV/VIS-NIR time-resolved spectra obtained 1 μs after 266-nm excitation of acetonitrile solutions of bis(4-methoxybenzoyl) peroxide (0.13 mM). A photodiode-array (▪) and a photomultiplier (●) detector were used for the measurement.

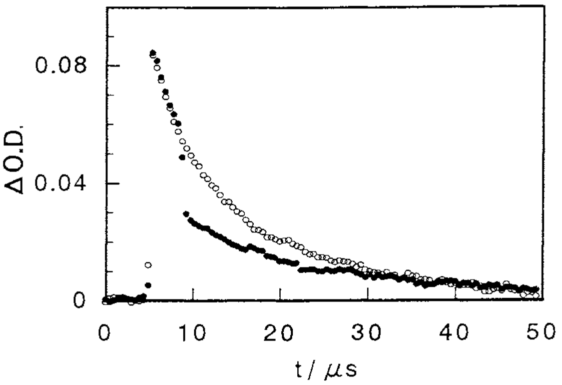
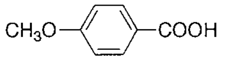
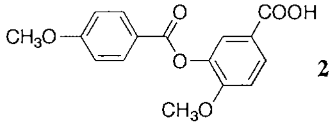
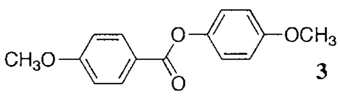
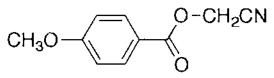
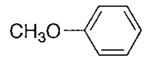


Figure 2. Decay traces monitored at 700 nm for the 266-nm pulse photolysis of acetonitrile solutions of bis(4-methoxybenzoyl) peroxide (0.13 mM) without (○) and with (•) a 1064-nm pulse.

Figure 2 shows the decay traces monitored at 700 nm in the photolysis with and without the second laser pulse (1064 nm, 200 mJ/pulse) delayed by 3 μs after the first one.[4] In order to clarify what reaction corresponds to this abrupt depletion of absorption caused by the second pulse, distributions of products were determined by means of HPLC. Typical results were shown in Table 1. Compound **2** and **4** have not been reported so far.[5] Considering low yields of **2** and **4** in the photolysis with using stationary light from a low-pressure mercury lamp (254 nm),[6] these products are specific in the pulsed laser photolysis, where local concentrations of radicals are high. In case of prolonged irradiation to complete the decomposition of the peroxide, **2** disappeared by photo-degradation and the ortho-isomer of **3** (2-methoxyphenyl 4-methoxybenzoate) appeared, which was given by the reaction of 4-methoxybenzoyloxyl radical to methoxybenzene **5**. For avoiding the repeated reactions of the products, distributions of products in the photolysis at 266 nm with and without the second pulse were compared at about 20% of decomposition of the peroxide in Table 1. Total yields of 4-methoxybenzoyloxyl moiety amount to 113.6 and 84.8% for the cases without and with the second pulse, respectively. This means that a 1064-nm pulse absorbed by the transient cleaved the bond between phenyl and carboxyl groups. Consistently, 4-methoxyphenyl moiety, the products of decarboxylation, increased to 61.8% from 27.2% by applying the second pulse. Thus, the second pulse induced decarboxylation in 4-methoxybenzoyloxyl moiety to decrease by ca. 30% in the yield. Therefore, it is rational to deduce 4-methoxybenzoyloxyl radical being responsible for the absorption (λ_{max} = 900 nm).

Figure 3 shows the dependence of absorption (at 700 nm) for the transient upon the intensity of exciting laser pulse (λ = 266 nm). The absorption reached a plateau at around 4 mJ/pulse and did not alter up to 12 mJ/pulse corresponding to 6.7 photons per one peroxide molecule. As the peroxide has a short excited-state lifetime, this experiment would satisfy the

Table 1. The distribution of photolysis products [a]

Product		Yield / %[b]	
		266 nm	266 nm +1064 nm
	**1**	61.2	38.8
	**2**	19.7	16.2
	**3**	5.6	4.8
	**4**	7.4	8.8
	**5**	21.6	57.2

[a] Acetonitrile solutions of bis(4-methoxybenzoyl) peroxide (1.4 mM) were irradiated under Ar by 266-nm pulse with and without 1064-nm pulse. [b] mol × 100/(mol of consumed peroxide). Average of triplicate runs.

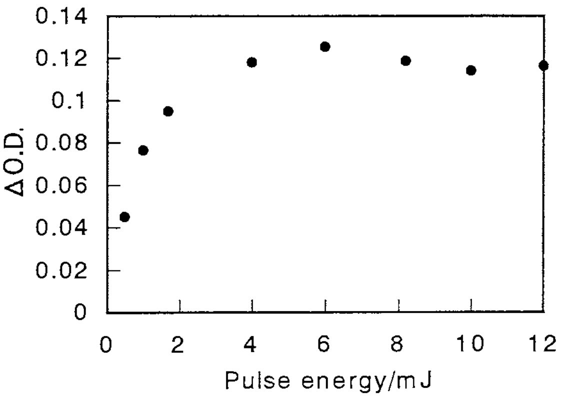


Figure 3. Dependence of absorption at 700 nm upon the excitation pulse energy for the 266-nm pulse photolysis of acetonitrile solutions of bis(4-methoxybenzoyl) peroxide (0.13 mM).

criteria for the total depletion method.[7] Therefore, the molar extinction coefficient for 4-methoxybenzoyloxyl radical at the maximum (900 nm) could be estimated as 750 $M^{-1}cm^{-1}$. Even if O-O and C(phenyl)-C(carboxyl) bonds break simultaneously,[8] the value would become only twice, considering that the yield of 4-methoxybenzoyloxyl moiety amounts to 113.6%. This suggests that the absorption should be a forbidden band.

Tentative MO calculations based on the spin non-polarized discrete variation $X\alpha$ (DV-$X\alpha$) method[9] for a benzoyloxyl radical[10] indicated that the low energy absorption band (λ_{max} = 900 nm, 1.38 eV) corresponded to the transition from $2a_2(\pi)$ (the second HOMO) to $16a_1(\sigma)$ (SOMO) as shown in Figure 4. The SOMO is a non-bonding orbital localized on oxygen atoms of carboxyl group and its energy is strongly dependent on the bond angle of O-C-O (θ). The observed excitation energy (1.38 eV) can be reproduced only when θ is equal to 160°. This widening may correlate to the ease of decarboxylation.

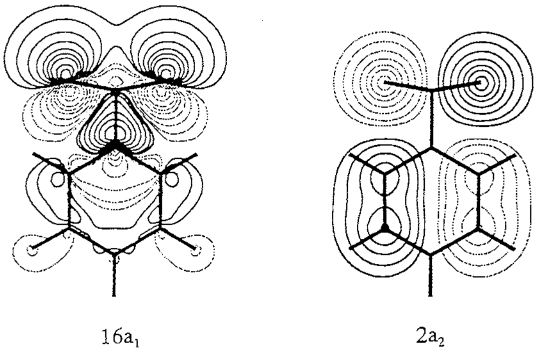


Figure 4. $16a_1(\sigma)$ (SOMO) and $2a_2(\pi)$ (the second HOMO).

We now intend to determine the absorption maxima for benzoyloxyl radical itself and substituted one.

References and Notes

1 S. Yamauchi, N. Hirota, S. Takahara, H. Sakuragi, and K. Tokumaru, *J. Am. Chem. Soc.*, **107**, 5021 (1985).
2 J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.*, **110**, 2877 (1988).
3 H. Misawa, K. Sawabe, S. Takahara, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1988**, 357.
4 The peroxide and its reaction products listed in Table 1 were not decomposed by a 1064 nm pulse alone.
5 **2** and **4** were isolated from the reaction mixture by a preparative HPLC and confirmed to be identical with independently synthesized authentic samples. **2**: ^{1}H NMR (400 MHz, acetone-d_6) δ 3.91 (3H, s), 3.94 (3H, s), 7.12 (2H, d, J_o=8.6 Hz), 7.27 (1H, d, J_o=8.8 Hz), 7.83 (1H, d, J_p=2 Hz), 7.99 (1H, d of d, J_o=8.6 Hz, J_m=2 Hz), 8.15 (2H, d, J_o=8.8 Hz). **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (3H, s), 4.93 (2H, s), 6.94 (2H, d, J_o=11.9 Hz), 8.00 (2H, d, J_o=11.9 Hz).
6 Yields of **2** and **4** were 7.4 and 0.8%, respectively, at the same consumption of the peroxide as in Table 1, in the photolysis using a low-pressure mercury lamp
7 I. Carmichael and G. L. Hag, *J. Phys. Chem.*, **89**, 4036 (1985).
8 A. Kitamura, H. Sakuragi, M. Yosida, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **53**, 1393 (1980).
9 H. Adachi, M. Tukada, and C. Satoko, *J. Phys. Soc. Jpn.*, **45**, 875 (1978).
10 The molecular geometry of benzoyloxyl radical is assumed to be the same as benzoic acid in crystal (C_{2v} symmetry).[11] The sample points were taken up to 6000 points. Self-consistency within 0.001*e* was obtained for orbital populations. The excitation energies are calculated by use of the transition state method[12] in which a half-electron is promoted from the ground state configuration to the excited state configuration.
11 C. C. Wilson, N. Shankland, and A. J. Florence, *J. Chem. Soc., Faraday Trans.*, **92**, 5051(1996).
12 J. C. Slater, J. B. Mann, T. M. Wilson, and J. H. Wood, *Phys. Rev.*, **184**, 672 (1969). J. C. Slater, "Advances in Quantum Chemistry;" Academic Press, New York (1972), Vol. 1, p. 1.