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Photolysis and Photopolymerization of Novel Organic Peroxides Having a Benzophenone Chromophore

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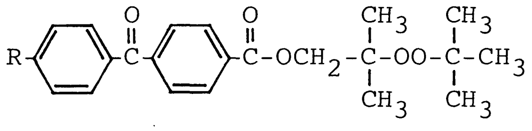
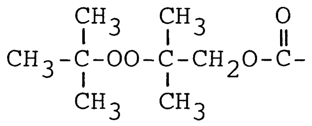
Dialkyl peroxides having a benzophenone chromophore have been successfully synthesized from the reaction of 2-t-butyldioxy-2-methyl-1-propanol and corresponding benzoyl chloride. These peroxides had UV absorption above 300nm. The free radicals produced during the photolysis of these compounds initiated the radical polymerization of methyl methacrylate at room temperature.

Organic peroxides having a chromophore have attracted much attention because of their potential ability for photoinitiator. The compounds frequently referred, however, are limited to several molecular structures, such as diacyl peroxides,[1] peroxyesters,[2-4] and dialkyl peroxides.[5,6] During the course of study of various dioxy derivatives, we found a new type of photoreactive peroxides having a benzophenone chromophore, 4-(2-t-butyldioxy-2-methylpropoxycarbonyl)benzophenone (**1**) and 4,4'-bis(2-t-butyldioxy-2-methylpropoxycarbonyl)benzophenone (**2**), which initiate the polymerization of methyl methacrylate (MMA) under UV light.



1: R = H

2: R = 

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OO-\overset{CH_3}{\underset{CH_3}{C}}-CH_2O-\overset{O}{\overset{\|}{C}}-$$

Compounds **1** and **2** were prepared by the reaction of 2-t-butyldioxy-2-methyl-1-propanol (**3**)[7] and corresponding benzophenone carbonyl chloride derivatives, respectively. The structure of **1** and **2** were fully characterized by NMR, IR, mass spectra, and elemental analyses.[8]

The UV absorption spectra of **1**, **2**, and benzophenone are shown in

Fig. 1. Both compounds behaved like benzophenone with respect to the absorption, that is, the maxima in the range 300-380 nm and the typical n-π^* extinction coefficients of 173 and 192 dm^3 mol^{-1} cm^{-1}, respectively.

Photodecomposition studies of **1** was carried out in a Pyrex tube at 25 °C by irradiating with 365 nm light. The quantum yield of photolysis of **1** in carbon tetrachloride was observed to be 0.52. The value of the benzophenone-sensitized decomposition of 2-t-butyldioxy-2-methylpropanol which is the starting material of compound **1**, was 0.20. This result indicated the efficiency of the intramolecular energy transfer in **1** in contrast to the intermolecular process.

Decomposition of compound **1** gave a linear Stern-Volmer plot when naphthalene was used as a triplet quencher (Fig. 2). The resulting value of $k_q\tau$ was 1.8 x 10^3 dm^3 mol^{-1}. If the rate constant k_q was assumed to be equal to the diffusion-controlled rate constant (k_q = 10^{10} dm^3 mol^{-1} s^{-1}), the lifetime of the excited triplet state, τ, of **1** was estimated to be 2 x 10^{-7} s. The lifetime of the benzophenone triplet in carbon tetrachloride was reported to be 1.1 x 10^{-4} s,[9)] and τ of **1** was 550 times shorter than

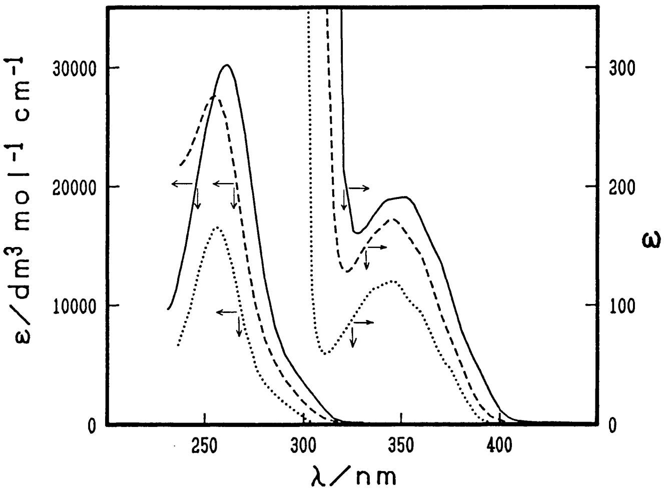


Fig. 1. UV absorption spectra of the peroxides and benzophenone in 1,4-dioxane. --------- :**1**, ———— :**2**, ·············· :benzophenone.

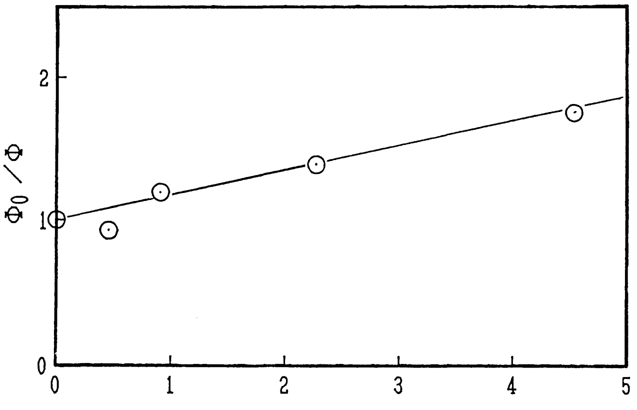


Fig. 2. Stern-Volmer plots for quenching of decomposition of **1** by naphthalene in carbon tetrachloride.

that of benzophenone. The values of τ for other peroxides have been estimated by Leffler, Neckers, and Kumura to be 0.87×10^{-9} s, 4×10^{-9} s, and 0.5×10^{-9} s for bis(p-benzoyl benzoyl) peroxide,[1] t-butyl p-benzoyl perbenzoate,[2] and 2,5-bis(o-benzoyldioxy)-2,5-dimethyl-3-hexyne,[3] respectively. It was shown that the rate of energy transfer from the excited triplet state of benzophenone to a dioxy bond were affected by the chain length between a chromophore and a dioxy bond.

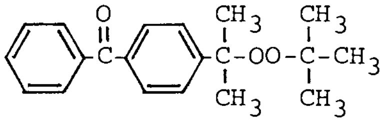
Photopolymerization of MMA was carried out at room temperature using the newly developed peroxides and compared with the polymerization using 4-(1-t-butyldioxy-1-methylethyl)benzophenone (**4**) which was developed by us.[5,6] The results are given in Table 1.[10] It is interesting that two dialkyl peroxides (**1** and **2**) initiated the photopolymerization of MMA. The polymerization rates (Rp) using **1** and **2** were higher than that with the benzophenone-sensitized **3**. While the Rp using **1** and **2** were lower than that using **4**.

In conclusion, the initiation of the photopolymerization with **1** or **2** mainly occurred via the intramolecular energy transfer from the n-π^* excited state of a benzophenone group to a dioxy bond and the Rp of MMA was influenced by the distance between a benzophenone group and a dioxy bond.

Table 1. Photopolymerization of MMA with 365 nm Light

Peroxide	Concn.	$Rp \times 10^4$	Molecular weight		
	mol dm^{-3}	mol dm^{-3} s^{-1}	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
Blank	-	0.2	91.5	205	2.2
1	0.01	2.4	5.9	20.2	3.4
2	0.005	3.4	5.3	17.3	3.3
2	0.01	2.6	4.7	15.3	3.2
4[a)]	0.01	8.5	1.7	3.2	1.9
Benzophenone / **3**	0.01 /0.01	1.2	15.7	31.6	2.0

a)



References

1) J. E. Leffler and J. W. Miley, J. Am. Chem. Soc., **93**, 7005 (1971).

2) L. Thijs, N. Gupta, and D. C. Neckers, J. Org. Chem., **44**, 4123 (1979);

S. N. Gupta and D. C. Neckers, J. Polym. Sci., Polym. Chem. Ed., **19**, 103 (1981); I. I. Abu-Abdoun, L. Thijs, and D. C. Neckers, ibid., **21**, 3129 (1983).

3) H. Kumura, T. Nakamura, Y. Higuchi, and S. Suyama, Bull. Chem. Soc. Jpn., **64**, 3538 (1991).

4) Nippon Oil & Fats Co., Japan patent 59-197401 (1984).

5) Y. Higuchi, S. Suyama, H. Misawa, H. Sakuragi, and K. Tokumaru, 59th National Meeting of the Chemical Society of Japan, Yokohama, April 1990, Abstr., No.2E430.

6) Y. Higuchi and S. Suyama, "Radtech Asia '91 Conference Proceedings," Osaka, April 1991, p.417.

7) Y. Higuchi, K. Matsuyama, and T.Komai, Bull. Chem. Soc. Jpn., **61**, 1821, (1988).

8) **1:** Mp 71-73 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23 (s, 9H, $C(CH_3)_3$), 1.33 (s, 6H, CH_3), 4.39 (s, 2H, CH_2), 7.48-8.19 (m, 9H, ArH); ^{13}C NMR (68 MHz, $(CD_3)_2CO$) δ 22.4, 26.7, 68.9, 79.3, 79.7, 129.4, 130.2, 130.5, 130.7, 133.7, 134.2, 137.9, 42.3, 165.8, 195.9; IR ($CHCl_3$) 1730, 1670, 880 cm^{-1}; MS m/z 314 $[M - C(CH_3)_3]^+$, 281 $[M - OOC(CH_3)_3]^+$, 209 $[M - OCH_2C(CH_3)_2OOC(CH_3)_3]^+$. Anal. Found: C,71.6; H, 7.3%. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07%. **2:** Mp 99-102 °C; ^{1}H NMR (270 MHz, $(CD_3)_2CO$) δ 1.23 (s, 18H, $C(CH_3)_3$), 1.33 (s, 12H, CH_3), 4.40 (s, 4H, CH_2), 7.95 (d, 4H, ArH), 8.24 (d, 4H, ArH); ^{13}C NMR (68 MHz, $(CD_3)_2CO$) δ 22.5, 26.8, 68.9, 79.3, 79.7, 130.3, 130.8, 134.7, 141.6, 165.8, 195.5; IR ($CHCl_3$) 1725, 1670, 880 cm^{-1}; MS m/z 558 (M^+), 209 $[M - (OCH_2C(CH_3)_2OOC(CH_3)_3) \times 2]^+$. Anal. Found: C, 66.5; H, 7.9%. Calcd for $C_{31}H_{42}O_9$: C, 66.65; H, 7.58%.

9) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, J. Am. Chem. Soc., **92**, 410 (1970).

10) The measurement of Rp was carried out using merry-go-round equipped with a 400 W high pressure mercury arc lamp. A solution of peroxide and MMA was added in Pyrex tubes, purged with nitrogen, and then irradiated with 365 nm light for the appropriate time at 25 °C (below 20% conversion). After the irradiation, the polymers were precipitated in methanol and analyzed gravimetrically. The average molecular weight ($\overline{M}_w$ and $\overline{M}_n$) were measured by GPC.

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