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Decarboxylation Rates of Benzoyloxyl Radicals as Determined by Laser Flash Photolysis. Further Insight into the Mechanism for Photodecomposition of Dibenzoyl Peroxides

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Bis(4-methoxybenzoyl), bis(4-chlorobenzoyl), and dibenzoyl peroxide were photolyzed in various solvents by 308-nm laser pulses to determine the rate constants for decarboxylation of the corresponding benzoyloxyl radicals. The activation energies of this process were lower than those estimated by indirect methods.

Diaroyl peroxides are among the most important radical initiators; however, there have been long arguments about the kinetic behavior of the intermediate radicals including aroyloxyl radicals,[1-4] since none of such intermediates were observed. Recently, we succeeded, for the first time, in direct observation of benzoyloxyl radicals in photodecomposition of some dibenzoyl peroxides by means of time-resolved EPR spectroscopy (TREPR) and determined activation parameters for decarboxylation of $C_6H_5CO_2\cdot$.[5] The values were quite different from the often quoted ones.[1a] We also observed a phenoxymethyl-type radical, $\cdot CH_2OC_6H_4X$, in the photolysis of bis(4-methoxybenzoyl) peroxide (MeO-BPO) in CCl_4 and proposed, as its formation mechanism, abstraction of a hydrogen atom from the methoxy group of the peroxide by $4\text{-}MeOC_6H_4CO_2\cdot$ in competition with decarboxylation.[5] In order to confirm this mechanism we made steady irradiation experiments and laser flash photolysis (LFP) with optical detection. Before our work is completed, Ingold et al.[6] applied our system to LFP and reported absolute rate constants for the reactions of $4\text{-}MeOC_6H_4CO_2\cdot$. This prompted us to report our own results on the photolysis of MeO-BPO and other dibenzoyl peroxides, particularly on determination of the decarboxylation rate constants of the corresponding benzoyloxyl radicals in solution as well as a striking solvent effect of CH_3CN on their stability.

Steady irradiation was made on a solution of MeO-BPO (1.2×10^{-3} mol dm^{-3}) in CCl_4 with 313 nm light isolated from a high pressure mercury lamp through an appropriate filter system. Table 1 lists the products determined by GLPC and gravimetry (for CO_2).

Laser flash photolyses of MeO-BPO in CCl_4, $CHCl_3$, and CH_3CN with 308-nm laser pulses (Xe/HCl, 10-ns fwhm, 5-90 mJ/pulse) gave transient absorption spectra, which are shown in Fig. 1, a, b, and c, respectively. The spectrum observed in CCl_4 is in complete agreement with that reported by Ingold et al.[6] A broad, structureless absorption was observed in all the three solvents in the 550-800 nm region, and reasonably assigned to $4\text{-}MeOC_6H_4CO_2\cdot$.[6] Structured absorptions at shorter wavelengths depended upon the solvent used. For the absorptions observed at 320 and 380 nm in CCl_4, Ingold et al.[6] have described that these absorptions are derived from $4\text{-MeOC}_6\text{H}_4\text{CO}_2^{\bullet}$ since they grow-in after the laser pulse at the same rate at which the 720-nm absorption decays. However, careful inspection of our decay curve at 780 nm and rise curves at 320 and 380 nm shows that the rise rate constants are by a factor of ca. 2 higher than the decay rate constant. The faster rise might be associated with a contribution of simultaneous two-bond fission of the excited peroxide molecule ($\text{MeO-BPO}^{*} \rightarrow 4\text{-MeOC}_6\text{H}_4^{\bullet} + CO_2 + 4\text{-MeOC}_6\text{H}_4\text{CO}_2^{\bullet}$).[1,7-9] Furthermore, the decay and rise rates depended on the laser intensity; the more intense the laser pulse, the faster the decay and rises. This indicates that $4\text{-MeOC}_6\text{H}_4\text{CO}_2^{\bullet}$ absorbes 308-nm light to decarboxylate, leading to secondary radicals including $4\text{-MeOC}_6\text{H}_4^{\bullet}$.[10] In $CHCl_3$ and CH_3CN a strong absorption appeared around 300 nm and decayed at the same rate as the 780-nm absorption. These results show that $4\text{-MeOC}_6\text{H}_4\text{CO}_2^{\bullet}$ possesses also its absorption in the shorter wavelength region. (Our attempts to identify other shorter-wavelength absorptions were unsuccessful so far.)

Table 1. Products in Photolysis of Bis(4-methoxybenzoyl) Peroxide in CCl_4

Product	Yield (mol/mol MeO-BPO)
$CH_3OC_6H_4Cl$	0.51
$ClCH_2OC_6H_4Cl$	0.45
$CH_3OC_6H_4CO_2H$	0.62
CCl_3CCl_3	0.82
CO_2	0.98

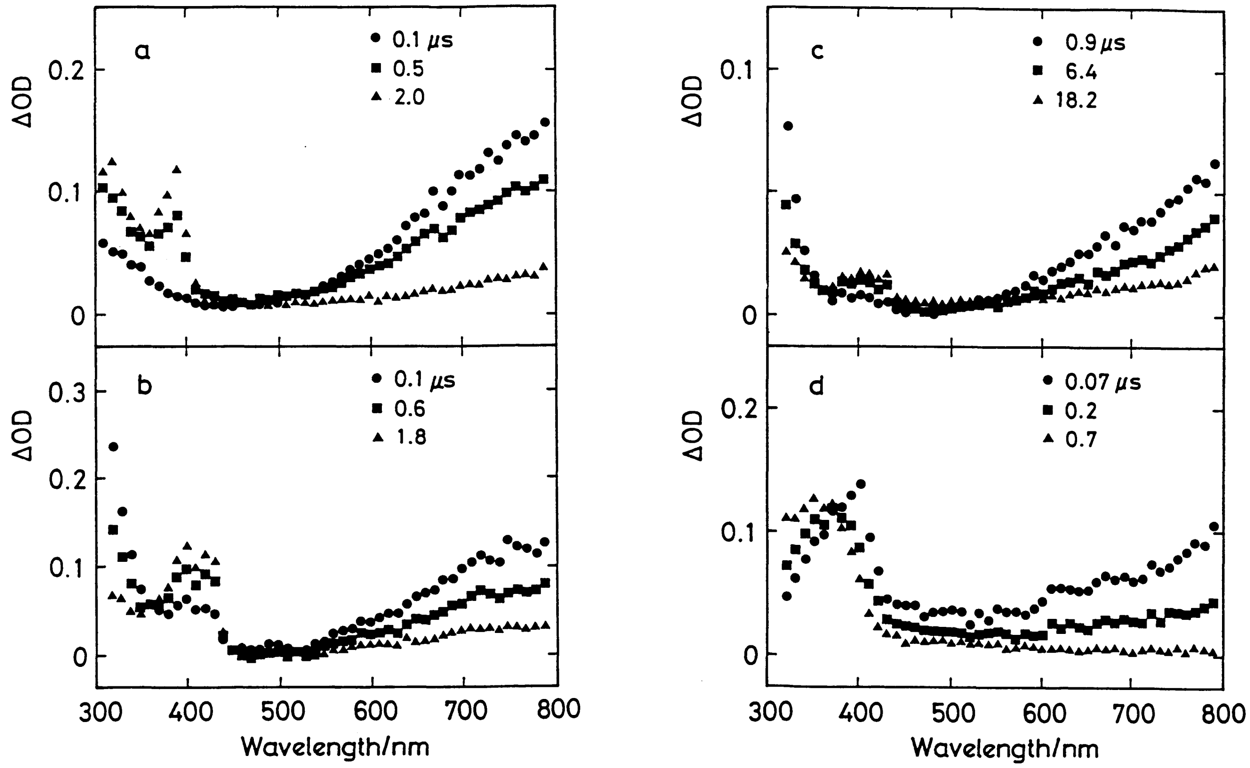

Fig. 1. Transient Absorption Spectra Obtained at Various Times after 308-nm Laser Pulse Irradiation of Dibenzoyl Peroxides; a) MeO-BPO in CCl_4, b) MeO-BPO in $CHCl_3$, c) MeO-BPO in CH_3CN, and d) BPO in CH_3CN.

The long-wavelength broad band absorption (as measured at 780 nm) decayed with a pseudo-first order rate constant (k_{obs}) of (6.9 ± 0.6) x 10^5 s^{-1} in a 1 x 10^{-2} mol dm^{-3} concetration of MeO-BPO at 25 °C. [Ingold et al.[6] reported (6.8 ± 0.2) x 10^5 s^{-1} at 24 °C, monitored at 720 nm.] However, k_{obs} increased linearly with increasing MeO-BPO concentration. This fact as well as the above product distribution, particularly the formation of $ClCH_2OC_6H_4Cl$, is in keeping with the above mechanism proposed on the basis of the TREPR results. The rate constants k_{obs}'s were determined in varying MeO-BPO concentration ($2x10^{-3}$ - $1x10^{-2}$ mol dm^{-3}) at various temperatures (10-50 °C). Plot of k_{obs} against [MeO-BPO] afforded a straight line at each temperature. Analysis of the results according to Eq. 1 gave the rate constants for the decarboxylation (k_D) and H-atom abstraction (k_H) from the peroxide. The Arrhenius plots (Fig. 2) of k_D and k_H afforded the activation energies (E_a) and preexponential factors (A) as listed in Table 2.

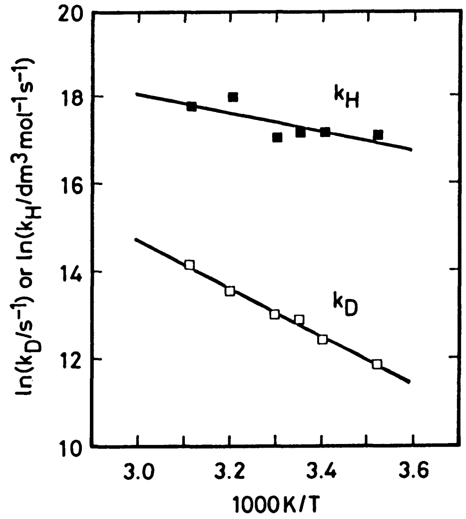

Fig. 2. Arrhenius Plots of Rate Constants for Decarboxylation and H-atom Abstraction of $4\text{-}MeOC_6H_4CO_2\cdot$.

$$k_{obs} = k_D + k_H[\text{MeO-BPO}] \qquad (1)$$

The k_H [(2.9 ± 1.1) x 10^7 dm^3 mol^{-1} s^{-1} at 25 °C] and E_a value (4.3 ± 1.7 kcal mol^{-1}) for H-atom abstraction by $4\text{-}MeOC_6H_4CO_2\cdot$ are higher than those for H-atom abstraction by triplet benzophenone from toluene [4.1 x 10^5 dm^3 mol^{-1} s^{-1}, 2.5 kcal mol^{-1}, and log(A/dm^3 mol^{-1} s^{-1}) = 7.6].[11] For decarboxylation, the A factor is more or less comparable with those measured in thermolyses of organic peroxides in solution,[1-4] and E_a is slightly lower than that estimated previously by indirect methods.[1-4]

A striking solvent effect of CH_3CN was found on the stability of aroyloxyl radicals. For example, $4\text{-}MeOC_6H_4CO_2\cdot$ possesses its lifetime of 9.5 μs in CH_3CN compared to 1.7 μs in CCl_4. This effect made it possible to determine the decarboxylation rates of $4\text{-}ClC_6H_4CO_2\cdot$ and $C_6H_5CO_2\cdot$ in CH_3CN. On LFP in CCl_4 dibenzoyl peroxide (BPO) and bis(4-chlorobenzoyl) peroxide (Cl-BPO) afforded transients with an intensity too weak to provide reliable kinetic data. However, in CH_3CN they afforded at 550-800 nm transients (Fig. 1, d) similar to that observed for MeO-BPO. These transients can be reasonably assigned to the corresponding benzoyloxyl radicals[6] and their first order decay rates were determined at various temperatures (10-55 °C). The activation parameters are summarized in Table 2 together with those of $C_6H_5CO_2\cdot$ determined previously by TREPR.[5]

The stabilizing effect of CH_3CN might be due to a charge-transfer interaction between the aroyloxyl radicals and the solvent. This is supported by the observation that the lifetime of $4\text{-}ClC_6H_4CO_2\cdot$ was not so much affected by this solvent.

Table 2. Rate Constants (at 25 °C) and Activation Parameters for Decarboxylation and H-atom Abstraction of Benzoyloxyl Radicals

H-atom abstraction	k_H/dm^3 mol^{-1} s^{-1}	E_a/kcal mol^{-1}	log(A/dm^3 mol^{-1} s^{-1})
$4\text{-MeOC}_6H_4CO_2{}^\bullet/CCl_4$	$2.9 \pm 1.1 \times 10^7$	4.3 ± 1.7	10.7 ± 1.3
Decarboxylation	k_D/s^{-1}	E_a/kcal mol^{-1}	log(A/s^{-1})
$4\text{-MeOC}_6H_4CO_2{}^\bullet/CCl_4$	$4.1 \pm 0.7 \times 10^5$	11.0 ± 0.5	13.6 ± 0.4
$4\text{-ClC}_6H_4CO_2{}^\bullet/CH_3CN$	$1.9 \pm 0.1 \times 10^6$	9.4 ± 0.4	13.2 ± 0.3
$C_6H_5CO_2{}^\bullet/CH_3CN$	$5.9 \pm 0.2 \times 10^6$	7.3 ± 0.6	12.1 ± 0.4
$C_6H_5CO_2{}^\bullet/CCl_4$[a]	4×10^6 [b]	5	10.3

a) Ref. 5. b) At 20 °C.

A specific solvation by CH_3CN may also be conceivable. Interestingly, the decay of $4\text{-MeOC}_6H_4CO_2{}^\bullet$ in CH_3CN obeys almost second order kinetics. The activation energy determined at 15-55 °C was 10.4 ± 1.0 kcal mol^{-1}. If the recombination of $4\text{-MeOC}_6H_4CO_2{}^\bullet$ leading to the starting MeO-BPO is the main pathway of its disappearance, this large activation energy might indicate that the slow rate of oxygen scrambling in diaroyl peroxides[12)] is due to a high activation energy barrier for recombination of the aroyloxyl radicals compared to their diffusion. However, we stay detailed discussion on the solvent effect until more information is obtained.

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