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Thermal and Photochemical Fragmentation of α,α-Dialkoxybenzyl Radicals: A Comparison of the Thermal Reactions with Laser Induced Fragmentations by Using Laser Flash and Laser-Jet Photolyses

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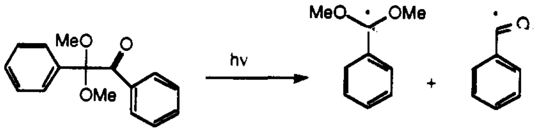
Abstract: The thermal and photochemical cleavage of α,α-dialkoxybenzyl radicals has been examined using a combination of techniques, including two-laser two-color laser flash photolysis and the laser-jet technique. For the parent α,α-dimethoxybenzyl radical photofragmentation occurs with a quantum yield of 0.80. The study of several unsymmetrically substituted radicals (e.g., methoxyisopropoxy) leads to the conclusion that the photoinduced fragmentation shows no selectivity. In contrast, the thermal decomposition of the radicals shows that fragmentation follows the expected radical stabilities, i.e., isopropyl > ethyl > methyl, the differences being almost exclusively due to changes in the activation energy. By comparing with literature data for methyl elimination it is possible to estimate the rate constants for fragmentation at 56 °C as 213, 1380, and 16 600 s^{-1} for methyl, ethyl, and isopropyl elimination.

Introduction

2,2-Dimethoxy-2-phenylacetophenone (I, commercially known as Irgacure-651 from Ciba-Geigy) is a very efficient and frequently used free radical photoinitiator. The primary photoprocess in this molecule involves Norrish type I photocleavage to yield α,α-dimethoxybenzyl (II) and benzoyl radicals (III), reaction 1.



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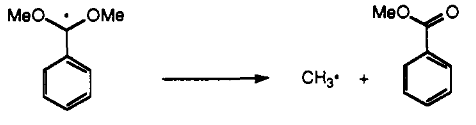
I II III

It has been known for many years that one of the forms of decay from II involves its fragmentation to give methyl and methyl benzoate, reaction 2.



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II

The mechanism and yield of this reaction has been the subject of considerable discrepancies and inconsistencies in the literature. In the last few years this fragmentation has been examined by Fischer et al.,[3,4] and their work has put to rest many of the problems with earlier reports.[5-8] Fischer's work clearly establishes that radical II is a highly photosensitive species and that reaction 2 can occur either thermally or photochemically. The relative importance of these two pathways is a function of the light intensity and excitation wavelength employed; notably, the photofragmentation pathway can contribute significantly even at moderately low light intensities.[4]

Reactions of this type are not unique for radical II. The fragmentation of α-alkoxybenzyl and dialkoxyethyl radicals are well-known. Huang et al.[9] compared the ratio of dimerization to fragmentation products for a number of α-alkoxybenzyl radicals (reactions 3 and 4) to determine the relative stabilities for a number of alkyl radicals. In a similar study, Huyser et al.[10] studied the fragmentation of 1-alkoxy-1-butoxyethyl radicals (reactions 5 and 6). In both studies it was found that the product ratios could be predicted on the basis of radical stabilities, that is, cleavage of the carbon–oxygen bond favors production of the more stable radical.

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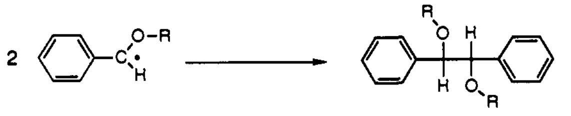

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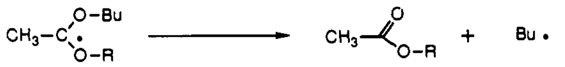

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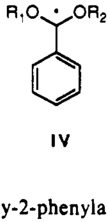
In the present investigation we have examined the thermal and photochemical fragmentation of a series of radicals of general structure IV, with emphasis on the unsymmetrical radicals (i.e., $R_1 \neq R_2$). The study of these reactions required the use of a variety of laser techniques and our report provides a rare direct comparison of photoreactions under conditions of (pulsed) laser flash photolysis and the (cw) laser-jet technique. In addition, we have verified that the photofragmentation of the dimethoxybenzyl radical is indeed an efficient process with a quantum yield approaching unity.



IV

Experimental Section

Materials. 2,2-Dimethoxy-2-phenylacetophenone (Aldrich) (I) was recrystallized twice from ethanol before use. Di-*tert*-butyl peroxide (Aldrich) was passed through a column of alumina to remove hydroperoxides before photolysis. Aberchrome-540 (Aberchromics Ltd.,

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(1) University of Ottawa.

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(3) Jent, F.; Paul, H.; Fischer, H. *Chem. Phys. Lett.* **1988**, *146*, 315.

(4) Fischer, H.; Baer, R.; Hany, R.; Verhoolen, I.; Walbiner, M. *J. Chem. Soc., Perkin Trans. 2* **1990**, 787.

(5) Allen, N. S.; Catalina, F.; Green, P. N.; Green, W. A. *Eur. Polym. J.* **1986**, *22*, 49.

(6) Fouassier, J.-P.; Merlin, A. *J. Photochem.* **1980**, *12*, 17.

(7) Jaegermann, P.; Lendzian, F.; Rist, G.; Möbius, K. *Chem. Phys. Lett.* **1987**, *140*, 615.

(8) Sandner, M. R.; Osborn, C. L. *Tetrahedron Lett.* **1974**, *5*, 415.

(9) Huang, R. L.; Lee, T.-W.; Ong, S. H. *J. Chem. Soc. (C)* **1969**, 40.

(10) Huyser, E. S.; Wang, D. T. *J. Org. Chem.* **1964**, *29*, 2720.

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Cardiff, U.K.), benzaldehyde dimethyl acetal (Aldrich), and all solvents (acetonitrile, benzene and toluene, BDH, Omnisolv) were used as received.

Methyl benzoate (*p*-toluenesulfonyl)hydrazone[11] was prepared from trimethyl orthobenzoate and *p*-toluenesulfonyl hydrazide. In a typical preparation, 10.0 g (55 mmol) of trimethyl orthobenzoate and 10.0 g (54 mmol) of *p*-toluenesulfonyl hydrazide were refluxed for 4 h in 60 mL of methanol. This solution was then placed in the freezer overnight, and the resulting amorphous powder was collected by filtration and washed with 10 mL of cold methanol to yield 14.2 g (86%) of white powder: mp 84–88 °C.

Ethyl benzoate (*p*-toluenesulfonyl)hydrazone[11] was prepared from triethyl orthobenzoate and *p*-toluenesulfonyl hydrazide as above. A solution of 12.0 g (54 mmol) of triethyl orthobenzoate and 10.0 g (54 mmol) of *p*-toluenesulfonyl hydrazide was refluxed in 60 mL of ethanol for 4 h. This solution was then placed in the freezer overnight, and the resulting crystals were collected by filtration and washed with 10 mL of cold ethanol to yield 13.7 g (80%) of white amorphous powder: mp 114–118 °C.

Benzaldehyde ethyl methyl acetal[11] was obtained by adding 10.0 g (32.7 mmol) of methyl benzoate (*p*-toluenesulfonyl)hydrazone to a solution of potassium (1.3 g, 33.2 mmol) in 100 mL of absolute ethanol and irradiated at room temperature. Initially, a yellow solid was formed and gas was evolved. After about 48 h, gas evolution had ceased, and a small amount of a yellow and white solid remained. The solid was removed by filtration, and the ethanol evaporated (rotary evaporator) to leave a white paste. The acetal was extracted with 20 mL of ether and washed with 30 mL of water. The aqueous phase was extracted with 2 × 10 mL of ether, and the combined organic phases were washed with 4 × 20 mL of distilled water. The ether extract was dried with $MgSO_4$, and the solvent was removed to give 4.2 g of a clear yellow liquid. Vacuum distillation of the residue yielded 3.3 g (61%) of benzaldehyde ethyl methyl acetal: bp 39–40 °C (0.20 mm): ^1H NMR ($CDCl_3$) δ (ppm) 1.2–1.3 (t, 3 H), 3.3 (s, 3 H), 3.5–3.7 (q, 2 H), 5.5 (s, 1 H), 7.3–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.2 (CH_3), 52.4 (CH_3), 61.2 (CH_2), 102.1 (CH), 126.7 (CH), 128.1 (CH), 128.2 (CH), 138.6 (C).

Benzaldehyde isopropyl methyl acetal[11] was prepared as above, except that 2-propanol was used in place of ethanol: yield 3.4 g (58%); bp 42–43 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ (ppm) 1.17–1.12 (d, 3 H), 1.23–1.26 (d, 3 H), 3.4 (s, 3 H), 3.8–4.0 (m, 1 H), 5.5 (s, 1 H), 7.3–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.2 (CH_3), 23.0 (CH_3), 51.9 (CH_3), 68.4 (CH), 101.1 (CH), 126.7 (CH), 128.1 (CH), 128.2 (CH), 138.6 (C).

Benzaldehyde ethyl isopropyl acetal[11] was prepared as above except that ethyl benzoate (*p*-toluenesulfonyl)hydrazone was used in place of methyl benzoate (*p*-toluenesulfonyl)hydrazone: yield 3.6 g (57%); bp 59–60 °C (0.20 mm); ^1H NMR ($CDCl_3$) δ (ppm) 1.15–1.25 (t, 3 H), 1.16–1.19 (d, 3 H), 1.22–1.25 (d, 3 H), 3.4–3.5 (q, 2 H), 3.8–4.0 (m, 1 H), 5.5 (s, 1 H), 7.3–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.2 (CH_3), 22.3 (CH_3), 23.1 (CH_3), 60.0 (CH_2), 68.5 (CH), 100.2 (CH), 126.7 (CH), 128.1 (CH), 128.2 (CH), 139.6 (C).

Di-*tert*-butyl hyponitrite[12] was prepared from *tert*-butyl bromide and sodium hyponitrite. Anhydrous zinc chloride was added to a mixture of *tert*-butyl bromide (5 mL) and ether (5 mL) followed by 0.6 g (5.7 mmol) of sodium nitrite, which was added slowly (5 min) with swirling and occasional cooling to insure that the temperature of the reaction mixture was kept below 45 °C. After allowing the reaction mixture to stand for 75 min, the inorganic salts were removed by filtration, and the organic phase was washed with 5 mL of water. The wash was extracted with 4 mL of ether and the organic phases combined, which was washed with 4 × 5 mL of water and dried over $MgSO_4$. The solvent was removed under reduced pressure to give 0.80 g (80%) of an off-white solid. Recrystallization from pentane gave 0.60 g of pure white needles.

Thermally Initiated Reactions. To examine the effects of temperature on the thermal fragmentation of α-ethoxy-α-methoxybenzyl radicals, *tert*-butoxy radicals were generated thermally from either di-*tert*-butyl hyponitrite (temperatures below 100 °C) or di-*tert*-butyl peroxide (temperatures above 100 °C). Stock solutions were made containing 10% di-*tert*-butyl hyponitrite in benzaldehyde ethyl methyl acetal or 10% di-*tert*-butyl peroxide in benzaldehyde ethyl methyl acetal. In a typical run, 200 μL of stock solution was placed in a glass ampule and degassed by 5 freeze–pump–thaw cycles. After degassing, the ampule was sealed and placed in a refluxing solvent to maintain constant temperature. The reaction was allowed to remain in the refluxing solvent for at least 5 half-lives of the *tert*-butoxy radical source.[13,14] The reaction was then stopped, and the ampule was broken and washed with 2 mL of ether. The ether solution was treated with 1 mL of concentrated HCl to convert the acetal to benzaldehyde. The acid was neutralized with sodium bicarbonate, and the organic layer was separated, which was washed with 3 × 2 mL of water. The organic layer was analyzed by GC, and the ratio of the benzoate products was determined from the integrated areas.

Laser-Jet Experiments. In order to ensure that the dialkoxybenzyl radicals underwent a significant degree of photofragmentation, it was necessary to use a method of irradiation capable of delivering a high photon flux. The technique of laser-jet photochemistry provides the photon flux necessary to photoexcite transient species and lead to sequential two photon processes.[15,16]

In our experiments, the beam from a continuous wave (cw) argon ion laser (excitation lines at 333, 351, and 364 nm) was focussed with a quartz lens (f = 80 mm) onto a thin microjet (~100 μm in diameter) of the photolysis solution. The flow rate was maintained at 0.60 mL/min with a Bischoff 2200 HPLC pump, and the microjet was generated by passing the solution through a 100 μm capillary. Under these conditions, the residence time of a molecule within the focal region of the laser is about 85 μs.

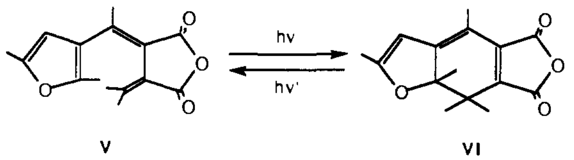
In a typical experiment, 5 mL of a 75 mM solution of acetal in di-*tert*-butyl peroxide was passed through the laser-jet and recycled until approximately 30% of the acetal had been depleted (ca. 3 h, 22 cycles). The samples were degassed by purging with a slow stream of dry argon for 20 min and the irradiation chamber was kept under a positive argon gas pressure. The ratio of the benzoate products were determined by GC.

Low-Intensity Photolysis. To make a direct comparison of the thermal and photochemical product yields, it was necessary that the temperatures of the reactions were also comparable. Since higher than ambient temperatures are required to produce *tert*-butoxy radicals from either di-*tert*-butyl peroxide or di-*tert*-butyl hyponitrite, it was decided to use low intensity irradiation as an alternative method, thus, the steady-state concentration of the dialkoxybenzyl radicals would be small, and we anticipated that only a minimal fraction of the radicals would fragment photochemically. In fact this fraction turned out to be somewhat higher than we had expected (vide infra).

In a typical experiment, 1.0 mL of a degassed solution of 75 mM acetal in di-*tert*-butyl peroxide was photolyzed by irradiation with 300 nm Rayonet lamps until all of the acetal had been depleted (approximately 30 min). The ratio of the benzoate products was then determined by gas chromatography.

Laser Flash Photolysis (LFP). Early experiments in this work were carried out at the National Research Council Laboratories in Ottawa (Canada) with the system described in earlier work.[17,18] A Lumonics TE-860 excimer laser filled with Xe/HCl/He mixture (~6 ns, ≤20 mJ/pulse) or a Molectron UV-24 nitrogen laser (~8 ns, ≤10 mJ/pulse) were used for sample excitation, while a Candela dye laser with stilbene-420 dye (~250 ns, ≤80 mJ/pulse) was employed to excite the radicals in the two-color, two-laser experiments. Recent experiments were carried out at the University of Ottawa on a laser system of similar design as the one described above, where instrument control was handled by Macintosh computers equipped with National Instruments control cards and LabVIEW-2 software. Static samples (usually 2 mL) were contained in cells made of 7 × 7 mm² square Suprasil tubing. Flow experiments employed a flow cell constructed of the same tubing. Unless otherwise indicated, the samples were deaerated by bubbling with oxygen-free nitrogen, and experiments were carried out at room temperature.

The quantum yield for the bleaching of the dimethoxybenzyl radical in benzene was measured with Aberchrome-540 (V) as a two-color actinometer.[19] Aberchrome-540 is the commercial name for the fulgide



V VI

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(11) Crawford, R. J.; Raap, R. *Can. J. Chem.* **1964**, *43*, 126.

(12) Mendenhall, G. D. *Tetrahedron Lett.* **1983**, *24*, 451.

(13) Loucks, L. F.; Liu, M. T. H.; Hooper, D. G. *Can. J. Chem.* **1979**, *57*, 2201.

(14) Kiefer, H.; Traylor, T. G. *Tetrahedron Lett.* **1966**, *49*, 6163.

(15) Wilson, R. M.; Hannemann, K.; Schnapp, K. A.; Memarian, H. R.; Azadnia, A. In *SPSE Proceedings: Summer Symposium on Photochemistry for Imaging*; SPSE—The Society for Imaging Science and Technology: White Bear Lake, Minnesota, 1988; p 167.

(16) Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta* **1990**, *46A*, 551.

(17) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(18) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(19) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511.

V.[20] which is isomerized to VI with a quantum yield of 0.20 in toluene and has been widely used as an actinometer for steady-state irradiations.[20,21] The Aberchrome-540 system has been shown to be photoreversible with a quantum yield that depends linearly upon the irradiation wavelength.[20] This reaction may be conveniently used as an actinometer for the measurement of transient extinction coefficients and for the determination of bleaching quantum yields for transients in two-laser experiments.[19] The latter requires the parallel generation of both the colored form **VI** of Aberchrome-540 and the transient to be bleached with the first laser pulse and the matching of the optical densities of these two at the wavelength and time of the second laser. Both the transient of interest and **VI** are then excited with the second laser. The quantum yield for bleaching (Φ_{bl}) of the transient can then be evaluated according to eq 7.

$$\Phi_{bl} = \frac{\epsilon_{VI}\Delta OD_R{}^0 \ln(\Delta OD_R{}^0/\Delta OD_R{}^d)}{\epsilon_R\,\Delta OD_{VI}{}^0 \ln(\Delta OD_{VI}{}^0/\Delta OD_{VI}{}^d)}\Phi_{VI} \tag{7}$$

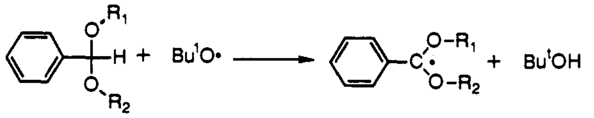
where ϵ_{VI} and ϵ_R are the extinction coefficients at the wavelengths for which they were monitored for **VI** and the dimethoxybenzyl radical. $\Delta OD_{VI}{}^0$ and $\Delta OD_{VI}{}^d$ are the changes in optical densities before and after the dye laser pulse for **VI** (monitored at 494 nm). $\Delta OD_R{}^0$ and $\Delta OD_R{}^d$ are the changes in optical densities before and after the dye laser pulse for the dimethoxybenzyl radical (monitored at 390 nm), and Φ_{VI} is the quantum yield for the photoconversion of **VI** to **V** at the wavelength of the dye laser (420 nm).

Results

Absorption Spectroscopy of Dialkoxybenzyl Radicals. α,α-Dimethoxybenzyl radicals may be generated by direct photolysis of **I** (reaction 1) or by hydrogen abstraction of the benzylic hydrogen of benzaldehyde dimethyl acetal (reaction 9) by *tert*-butoxy radicals produced upon photolysis of di-*tert*-butyl peroxide (reaction 8).

$$\mathrm{Bu^tOOBu^t} \xrightarrow{\Delta \text{ or } h\nu} 2\mathrm{Bu^tO}\bullet \tag{8}$$

Fischer et al.[4] reported that the transient spectra obtained upon photolysis of **I** may be contaminated by contributions from other species. Figure 1 shows the spectra obtained by laser flash



(9)

photolysis (1 μs after the laser pulse) of a 1.50 mM solution of **I** in benzene by employing for excitation the pulse from an excimer laser (308 nm). Figure 1A displays the spectrum obtained when the solution is allowed to flow through the photolysis cell, thus this ensures that a fresh sample of **I** is irradiated by each pulse from the laser. This spectrum agrees well with that obtained by Fischer, with λ_{max} at 420 nm. Figure 1B shows the spectrum from the same solution but where a static cell was used. It must be pointed out here that these spectra are obtained on a point by point basis; thus, the sample received six shots of the laser for each point as the spectrum is scanned from longer to shorter wavelengths. By the time the points below 520 nm are obtained, the sample had received 40 laser shots. The spectrum in Figure 1B has absorption maxima at 370 and 480 nm; this is similar to the triplet–triplet absorption spectrum for benzil, a product which may be formed by the recombination of benzoyl radicals and which will accumulate as the irradiation proceeds.

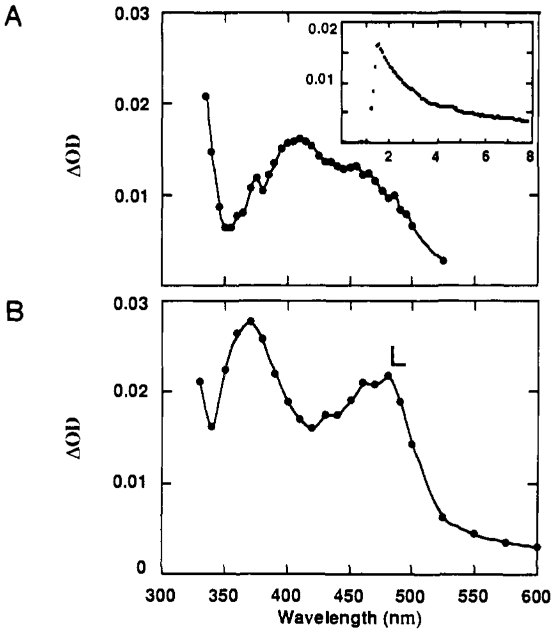


Figure 1. (A) Transient spectrum obtained 1 μs after 308-nm laser pulse for a 1.50 mM solution of **I** in benzene by using a flow cell. Inset shows decay trace monitored at 420 nm. (B) Transient spectrum obtained 1 μs after 308-nm laser pulse for a 1.50 mM solution of **I** benzene by using a static cell.

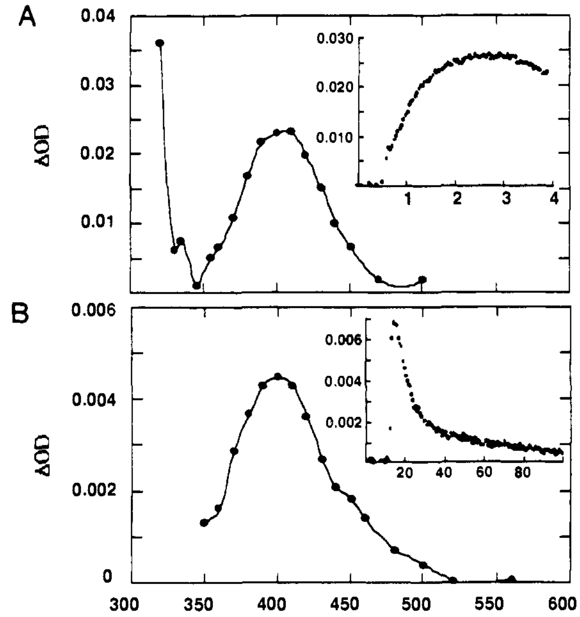


Figure 2. (A) Transient spectrum of the α,α-dimethoxybenzyl radical. (Corrected for acetal photolysis, see text). The radical was produced from a solution of 0.33 M benzaldehyde dimethyl acetal and 0.28 M di-*tert*-butyl peroxide in benzene with the pulse from an excimer laser (308 nm). Inset shows the growth of the radical monitored at 420 nm. (B) Transient spectrum of α-ethoxy-α-methoxybenzyl radical (also corrected for acetal photolysis), produced from a solution of 0.33 M benzaldehyde ethyl methyl acetal in a 1:2 (v/v) mixture of benzene/di-*tert*-butyl peroxide with the pulse from a nitrogen laser (337 nm). Inset shows decay of the radical monitored at 400 nm.

Figure 2A shows the transient spectrum obtained upon laser flash photolysis (308 nm, 1.2 μs after the laser pulse) of a benzene solution which was 0.28 M di-*tert*-butyl peroxide and 0.33 M benzaldehyde dimethyl acetal, this is similar to Figure 1A, except that the maximum is located at 400 nm. Figure 2B shows the transient spectrum obtained upon laser flash photolysis (337 nm, 1.7 μs after the laser pulse) of 0.33 M benzaldehyde ethyl methyl acetal in a 1:2 (v/v) mixture of benzene/di-*tert*-butyl peroxide and is attributed to the α-ethoxy-α-methoxybenzyl radical. In both spectra (Figure 2A and 2B), some spectral contamination was caused by the direct photolysis of the acetals; this was corrected for by subtracting the spectrum recorded at times less than 100 ns after the laser pulse from that obtained at times >1 μs. The two spectra are identical, with maxima at 400 nm. The decay traces for all the above spectra could not be fitted to first- or second-order kinetics. This is an indication that the radicals disappear by mixed first- (fragmentation of dialkoxybenzyl rad-

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(20) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. II* **1981**, 341.

(21) Heller, H. G. In *Electronic Materials: From Silicon to Organics*; Miller, L. S., Mullin, J. B., Eds.; Plenum Publ.: New York, 1991; p 471.

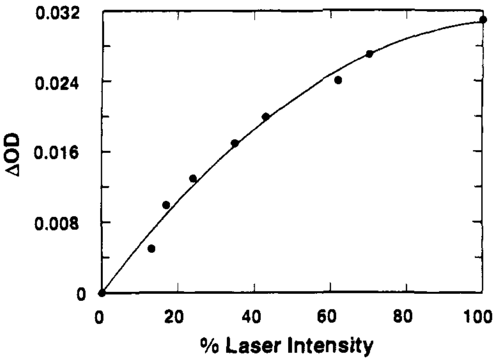


Figure 3. Absorption signal (ΔOD) as a function of laser intensity for laser flash photolysis (308 nm) of I (monitored at 420 nm).

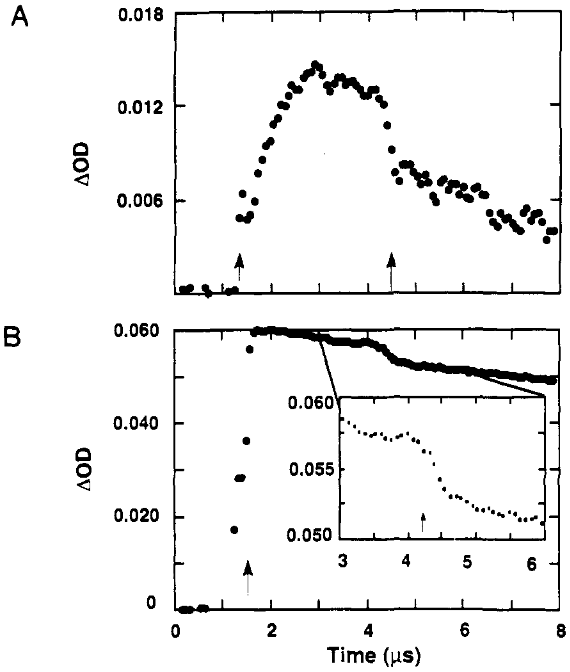


Figure 4. (A) Bleaching of dimethoxybenzyl radical upon excitation with a dye laser (420 nm). The dye laser was fired 3 μs after the synthesis laser (308 nm). The radical was produced from a solution of 0.33 M benzaldehyde dimethyl acetal and 0.28 M di-*tert*-butyl peroxide in benzene (monitored at 390 nm). (B) Bleaching of VI to form V upon excitation with a dye laser (420 nm). The dye laser was fired 3 μs after the synthesis laser (308 nm). VI was formed from a solution of V (OD = 0.55) in toluene (monitored at 494 nm). Inset shows expansion of the region in which the dye laser was fired.

icals) and second- (radical–radical reactions) order processes.

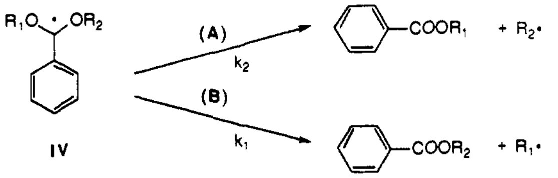
Bleaching of Dimethoxybenzyl Radicals. A preliminary experiment to investigate the possibility of the photofragmentation of the dimethoxybenzyl radical was performed by comparing the change in absorption signal (ΔOD) as a function of the laser intensity for the laser flash photolysis of **I**. A plot of ΔOD vs % laser power, in which the laser was attenuated by passing the beam through precalibrated neutral density filters, is shown in Figure 3. There is a definite downward curvature as the laser power is increased, which indicates secondary photolysis of the radical during the laser pulse. This is further evidence that a photofragmentation of the dimethoxybenzyl radical is responsible for the increased production of methyl benzoate upon increased laser intensity as reported by Fischer.[4]

Two-laser, two-color experiments were performed to provide further evidence for the photofragmentation and to measure its quantum yield. The dimethoxybenzyl radical was generated by reaction of *tert*-butoxy radicals and benzaldehyde dimethyl acetal in benzene by excimer laser excitation at 308 nm and then excited with the pulses from a dye laser at 420 nm. The dye laser pulse led to efficient and irreversible bleaching (Figure 4A) of the dimethoxybenzyl radical, which was monitored at 390 nm.

Transient bleaching quantum yields were determined by using Abercrome-540 actinometry as described in the Experimental Section and in earlier reports.[19] The extinction coefficient for **VI** is 8200 M^{-1} cm^{-1} at 494 nm, and the bleaching quantum yield at 420 nm is 0.0772.[20] The extinction coefficient for the dimethoxybenzyl radical at 390 nm was estimated to be 1000 M^{-1} cm^{-1} from the transient absorption spectrum (Figure 2A) and the extinction coefficient at 418 nm (800 M^{-1} cm^{-1}) reported by Fischer.[4] The changes in optical densities were the values obtained from the two-laser experiments. The bleaching of the dimethoxybenzyl radical and the fulgide **VI** are shown in Figure 4 (parts A and B respectively). The optical densities for the transient involved were matched at 420 nm, the wavelength of the dye laser. A value of 0.80 ± 0.16 was obtained for the bleaching quantum yield of the dimethoxybenzyl radical in benzene.

Errors in these experiments tend to be moderately large,[19] not only due to the complexity of the two-laser experiment but also because the errors in the extinction coefficients are incorporated in the quantum yields. The error limits given above (±20%) are slightly smaller than those estimated in earlier work, which reflects the availability[4] of an independent determination of the extinction coefficient for the dimethoxybenzyl radical.

Thermally Initiated Experiments on the Fragmentation of Unsymmetric Dialkoxybenzyl Radicals. The present study centers on a comparison of thermal and photoinduced fragmentations of unsymmetric dialkoxybenzyl radicals such as that produced in reaction 9 above. These fragmentations lead to two different alkyl benzoates as indicated in reaction 10.



(10)

Although in addition to reaction 9 other reactions may contribute as decay paths for the radicals, the ratio of the two benzoates is a direct measure of k_1/k_2, the relative rates of the two competing fragmentation processes.

In order to determine k_1/k_2 ratios, several acetals were allowed to react with either di-*tert*-butyl peroxide or di-*tert*-butyl hyponitrite as sources of *tert*-butoxy radicals, as indicated in the Experimental Section. We note that while reaction 9 may be accompanied by hydrogen abstraction processes at other positions, such reactions are not expected to yield the alkyl benzoates used to determine the k_1/k_2 values. These side reactions are expected to be more important when the substituents carry labile hydrogens, such as in the case of isopropyl derivatives. The methoxy ethoxy benzyl derivative was mostly free from any significant problems related to side reactions and allowed the determination of k_1/k_2 values over a range of temperatures. The corresponding Arrhenius plot is shown in Figure 5 and leads to a difference of −1.4 kcal/mol in the activation energies and a ratio of 0.77 for the preexponential factors (ethyl-to-methyl fragmentation).

The plot of Figure 5 gives a ratio of rate constants of 7.6 at room temperature and of 6.5 at 56 °C, the temperature at which other derivatives were examined (see Table I). For the methyl–isopropyl system, we were unable to detect isopropyl benzoate by gas chromatography. Given our analytical sensitivity, this places the corresponding k_1/k_2 ratio as greater than 40.

Low-Intensity Irradiations with Predominant Thermal Fragmentation of Unsymmetric Dialkoxybenzyl Radicals. In these experiments the radicals were generated by low-intensity lamp photolysis of di-*tert*-butyl peroxide. While the process is initiated photochemically, the fragmentation of the radicals is expected to be a predominant thermal process. The selectivities observed, as measured by the k_1/k_2 ratio, suggest a mixture of thermal and photoinduced radical decay (Table I). Clearly, even under conditions of very low-intensity illumination, close to one-half of

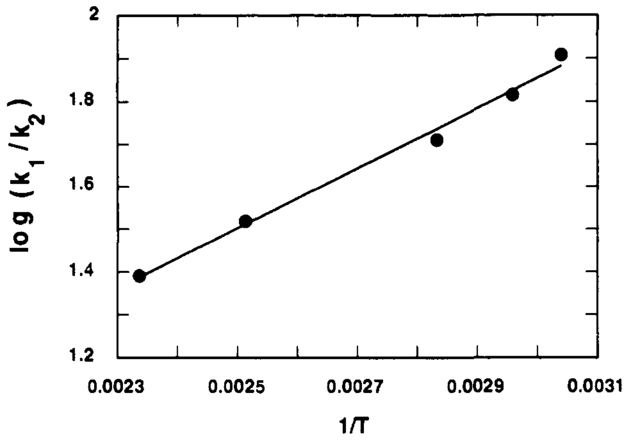


Figure 5. Arrhenius plot for the relative rates (k_1/k_2) of the two fragmentation pathways for the α-ethoxy-α-methoxybenzyl radical.

Table I. Fragmentation Ratios k_1/k_2 of the Radicals IV Obtained under Various Experimental Conditions

radicals IV		fragmentation ratios k_1/k_2[a]		
		thermolysis 56 °C	low-intensity photolysis 35 °C	laser-jet photolysis ≤40 °C
R_1	R_2			
CH_3	C_2H_5	6.5[b]	4.2	0.90
CH_3	i-C_3H_7	>40	25	1.25
C_2H_5	i-C_3H_7	12	6.4	1.10

[a] Error ca. ±10% of stated values. [b] Value derived from the plot in Figure 5.

the radicals undergo photolysis.

Laser-Jet Experiments. The technique employed in this work employs a high-velocity microjet (~100 μm in diameter) which is irradiated with the focussed output from an argon-ion laser.[15,16,22] The microjet intensifies the light by trapping it as a standing wave within the stream. Under these conditions photogenerated transients may undergo further photolysis. Further details of these experiments have been given in the Experimental Section.

The values of k_1/k_2 were determined by chromatographic analysis of the benzoate ratios and are given in Table I. Clearly the photoinduced radical fragmentation shows virtually no selectivity.

It is interesting to note that we originally considered the two-laser, two-color approach already described in the determination of quantum yields in order to study product ratios from the fragmentation of the excited radicals. However, we found that increased absorption at 308 nm (the laser wavelength) upon irradiation prevented high conversion experiments. Attempts to carry out similar experiments with the 337-nm pulses from a nitrogen laser (where product absorption was not a problem) were unsuccessful due to the low and insufficient power of this laser. This shows the value of the laser-jet technique as a complementary tool for the examination of two-photon processes.

Discussion

The work reported here on the fragmentation reactions of dialkoxybenzyl radicals illustrates the high sensitivity of these radicals to photodecomposition, a characteristic feature already observed in other laboratories.[3,4] Even low-intensity irradiation (see Table I) tends to cause extensive light-induced fragmentation. Extensive photodecomposition even under conditions of very low-intensity irradiation reflects a combination of various factors, e.g., lifetime and absorption characteristics of the radicals. The di-*tert*-butyl peroxide, used as a source for *tert*-butoxy radicals and as cosolvent, has a very low extinction coefficient in this wavelength region (~1 M^{-1} cm^{-1}) and thereby acts as an inefficient internal filter. On the other hand, the dialkoxybenzyl radicals exhibit a relatively strong absorption and compete efficiently for the incident photons. Effective absorption is assisted through their long lifetime, which is only limited by slow thermal fragmentation and even slower dimerization. Thus, nearly every absorbed photon induces cleavage, as indicated by the high quantum yields for fragmentation. Consequently, even under the conditions of the mild low-intensity irradiation the photolysis of the intermediates competes with that of the *tert*-butyl peroxide and a combination of photochemical and thermal fragmentation is observed.

In order to elucidate the structural influence on the fragmentation aptitudes, the thermal reactions under exclusion of light were examined. In these thermolyses the differences in reactivity arise almost exclusively from activation energy differences, as revealed by the results for the ethoxy–methoxy case in Figure 5. If one assumes that merely the stability of the resulting radical controls the fragmentation, independently of the structure of the second alkyl group in the molecule, then the expected k_1/k_2 ratio for the CH_3/i-C_3H_7 system would be ~78, which is well in line with the value >40 observed experimentally.[23] The same holds true for the intermediate case, the C_2H_5/i-C_3H_7 combination. Thus, as expected, the more stable the incipient radical species, the lower the activation energy and the more pronounced the fragmentation is. Comparison of our fragmentation ratios (Table I) with the rate constant reported by Fischer[4] for the fragmentation of the dimethoxybenzyl radical allows us to estimate the absolute rate constants for the fragmentation of the ethyl and isopropyl radicals. The rate constants for the methyl fragmentation is 260 s^{-1} at room temperature and with the help of Fischer's estimate of the Arrhenius parameters[4] one calculates a value of 426 s^{-1} at 56 °C, which corrected for the statistical factor (i.e., the presence of two methoxy groups) leads to 213 s^{-1} per methoxy group. Substitution of this value in the k_1/k_2 ratios (Table I) leads to the absolute rate constants of 1380 and 16600 s^{-1} for the thermal cleavage of ethyl and isopropyl at 56 °C. In view of the high rate constants for thermal isopropyl cleavage it is rather remarkable that for this case (last entry in Table I) considerable photolytic radical fragmentation takes place even under low-intensity irradiation.

Contrary results were obtained in the laser-jet photolyses (Table I). Under the high intensity of the laser-jet experiments the radicals undergo exclusively photoinduced fragmentation with low selectivity, i.e., k_1/k_2 ca. unity. The deviations from unity in these ratios are most probably within the experimental error. Thus, the excitation of the radicals IV provides enough energy (351 nm represents 81.5 kcal/mol) to overcome the ground-state activation barriers. The lack of selectivity is expected for photochemical fragmentations, but we provide herein one of the first examples for electronically excited radicals.

Finally the laser-jet and two-laser, two-color techniques provide complementary information on the photochemistry of transient species. Together they provide a quantitative description of the kinetics, quantum yields, and product characterization of two-photon processes.

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(22) Wilson, R. M.; Adam, W.; Schulte Oestrich, R. *The Spectrum* **1991**, *4*, 8.

(23) The estimate of 78 is based on the product of the methyl:ethyl (6.5) and ethyl:isopropyl (12) ratios of reactivities, see Table I.