Flash photolysis investigation on primary processes of the sensitized polymerization of vinyl monomers: 2. Experiments with benzoin and benzoin derivatives

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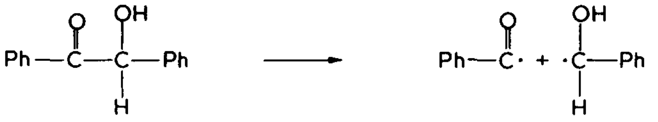
Benzene solutions of benzoin (B), benzoin acetate (BA), benzoinmethyl ether (BME) and benzoinisopropyl ether (BIPE) were irradiated with 0.1 or 25 nsec flashes of 347.1 nm light at room temperature. With B and BA optical absorptions due to radical precursors were detected. The first order decay constants of these absorptions are 1.1×10^8 sec^{-1} (B) and 5.3×10^7 sec^{-1} (BA). The radical spectra decayed according to second order laws. In the case of B only one mode of decay was observed which accounts for the major part of the reaction (benzaldehyde formation by disproportionation of unlike radicals). During the experiments with BA, BME and BIPE two modes of radical–radical reactions were detected. Styrene was found to react with the rapidly decaying species with $k_M = (1.3 \pm 0.2) \times 10^5$ M^{-1} sec^{-1}, but did not react with the slowly decaying species. By considering the end product analyses of other authors it was concluded that the rapidly decaying mode of the absorption decay is due to the combination of benzoyl radicals forming benzil. The slowly decaying mode was assigned to the combination of alkoxybenzyl radicals (in the case of BME and BIPE) or of acetonbenzyl radicals (in the case of BA) forming pinacol derivatives. The rate constants of the reaction of naphthalene with triplet excited benzoin $(7.7 \pm 0.8) \times 10^9$ M^{-1} sec^{-1} and benzoin acetate $(5.0 \pm 0.5) \times 10^9$ M^{-1} sec^{-1} were determined.

INTRODUCTION

Benzoin and benzoin derivatives are very efficient photosensitizers for the free radical polymerization of unsaturated compounds. They are used for various u.v.-polymerizable systems, e.g. protective coating, photoresists and adhesives[1–7].

Mechanistic studies reported by various researchers[8–13] were essentially based on product analysis obtained in the absence and presence of quenchers. The results led to the following conclusions: benzoin, benzoin ethers and benzoin esters undergo photochemical α-cleavage, e.g.



$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\overset{OH}{C}}{-}Ph} \longrightarrow \mathrm{Ph{-}\overset{O}{\overset{\|}{C}}\cdot + \cdot\underset{H}{\overset{OH}{C}}{-}Ph} \qquad (1)$$

In the case of benzoin and benzoin acetate, α-cleavage is a relatively slow triplet state reaction. On the other hand, α-cleavage of benzoin ethers appeared to be a relatively rapid process, which occurs either via a singlet state or a very short-lived triplet state[8,9,13].

From radical trapping experiments using *N*-oxides and nitroso compounds as trapping agents it was inferred that benzoin cleaves into the radicals $Ph\dot{C}O$ and $Ph\dot{C}H(OH)$, and benzoinmethyl ether cleaves into the radicals $Ph\dot{C}O$ and $Ph\dot{C}H(OMe)$[12]. In the present work the flash photolysis method was applied: (a) in order to measure the rate of the formation of radicals and to follow their decay and (b) in order to elucidate the kinetics of the reaction of the radicals (produced during α-cleavage) with styrene.

Flash photolysis studies (part 1 of this series[14]) and stationary state polymerizations[15] concerning benzophenone and benzophenone derivatives were carried out recently. Another recent report was devoted to the role of CT-complexes as intermediates during the deactivation of triplet excited benzophenone derivatives[16].

EXPERIMENTAL

Materials

Benzoin (B) (C. Roth, Karlsruhe) was twice recrystallized from methanol, m.p. 137°C. Benzoinmethyl ether (BME) (Aldrich), m.p. 49°C, benzoinisopropyl ether (BIPE) (Bayer AG), m.p. 79°C, and benzoin acetate (BA) (Eastman–Kodak), m.p. 82°C, were twice recrystallized from hexane solution. Benzene (Merck, 99.5%) and styrene (Merck) were purified as described in part I[14].

Irradiation of samples

Benzene solutions were used throughout these investigations. The solutions were deaerated by bubbling with purified Ar (O_2 content less than 3 ppm). Samples were irradiated in rectangular cells with 347.1 nm flashes of a frequency doubled ruby laser (half-width of flash 25 nsec) (Korad model

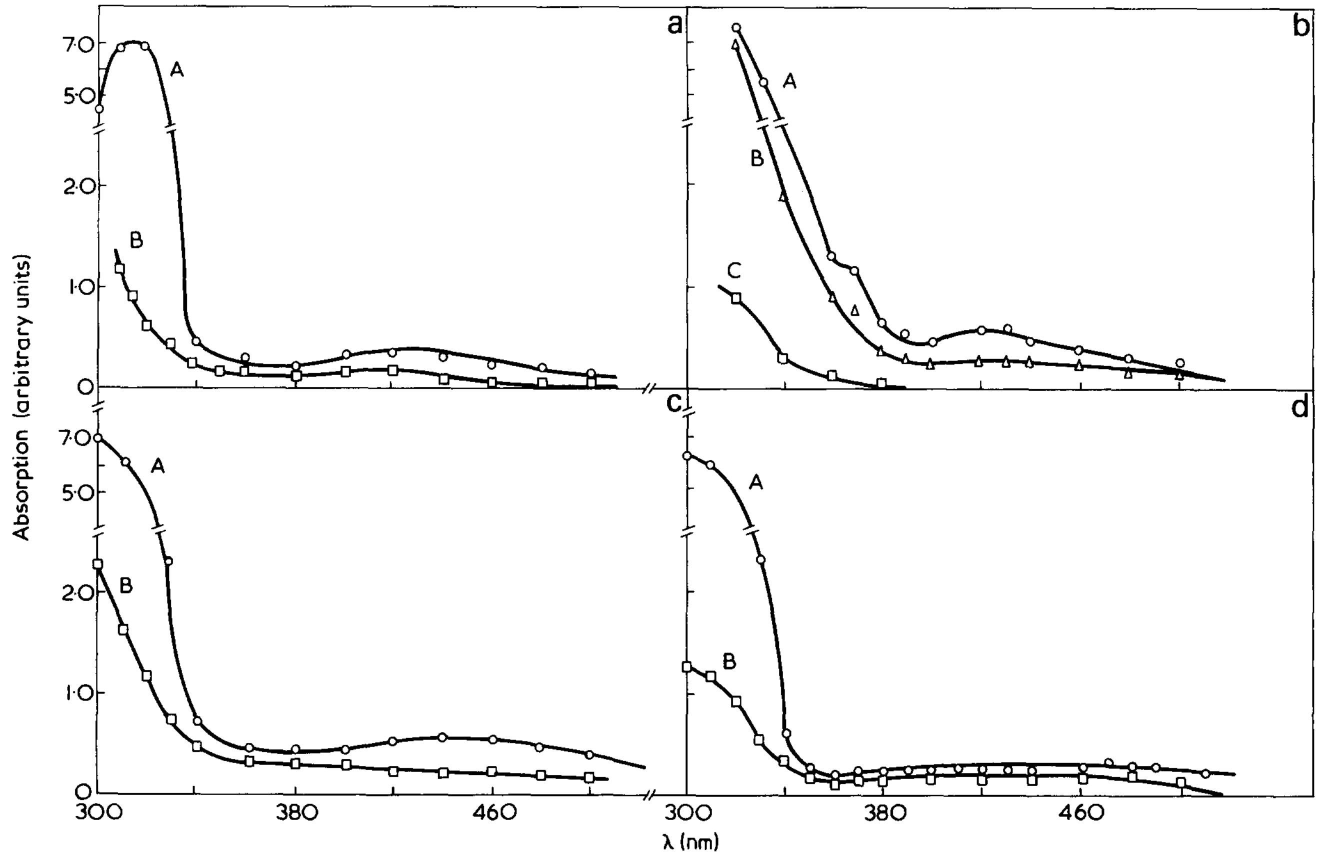


Figure 1 Absorption spectra obtained at room temperature in benzene solution; duration of flash, 25 nsec. Ketone concentrations: (a) [B] : 1.78×10^{-3}M: A, immediately after flash; B, 70 μsec after flash. (b) [BA] : 7.87×10^{-4}M: A, immediately after flash; B, 100 nsec after flash; C, 70 μsec after flash. (c) [BME] : 4.73×10^{-4}M: A, immediately after flash; B, 110 μsec after flash. (d) [BIPE] : 4.5×10^{-4}M: A, immediately after flash; B, 110 μsec after flash. Absorbed dose per flash: 4.6×10^{-5} Einstein/l

K1QS2) or with a mode locked ruby laser (half-width of flash ~0.1 nsec) (Korad model K1300).

The optical absorption detection method was used throughout. The signal rise time (10 to 90%) was 3 nsec (work with K1QS2) and 0.7 nsec (work with K1300).

RESULTS

Radical formation

Figure 1 shows the optical absorption spectra observed immediately after the irradiation of benzene solutions of B, BA, BME and BIPE with 25 nsec flashes. According to Lewis *et al.*[9] the life-time for the formation of radicals should be shorter than 10^{-10} sec for BME and BIPE. Therefore, the spectra observed at the end of the flash shown in *Figures 1c* and *1d* were assumed to be due to radicals formed via α-cleavage of the ethers during the flash. The relatively long decay time of these spectra (*vide infra*) supports this view. The rate for α-cleavage of excited B and BA molecules should be slower than for excited BME and BIPE molecules[9]. Thus, the observation of the formation of radicals using our techniques appeared to be feasible with B and BA. By irradiating benzene solutions of benzoin with 0.1 nsec flashes of 347 nm light evidence for the radical precursor could be obtained. In *Figures 2a* and *b* it is seen that during the 0.1 nsec flash an absorption was formed at 325 nm and 480 nm which decayed rapidly with a lifetime of about 9 nsec and simultaneously gave rise to the formation of a new absorption. A similar behaviour was observed in the wavelength range in between 325 nm and 480 nm. However, for the stronger absorption of the radicals the decay of the

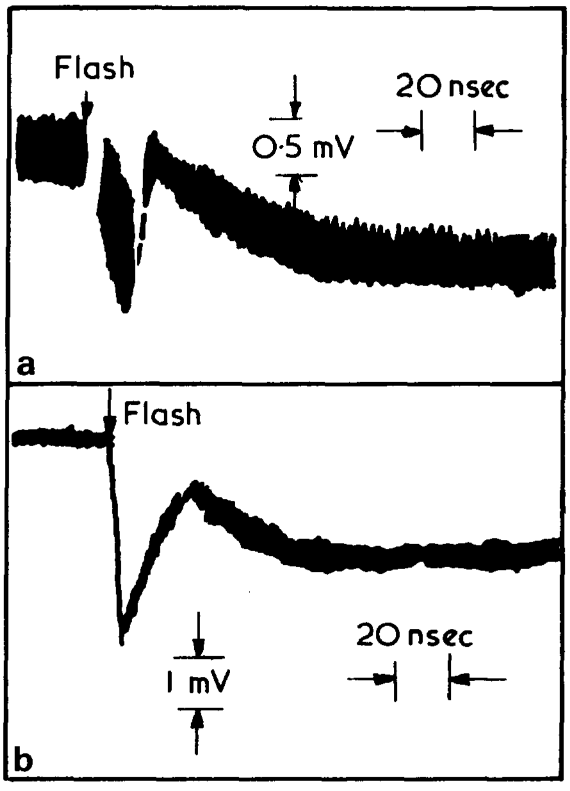


Figure 2 Oscilloscope traces observed with a benzene solution of benzoin (1.78×10^{-3}M) at room temperature. Duration of flash: ~0.1 nsec. Variations of absorption after the flash at 325 nm (a) and at 480 nm (b) as a function of time

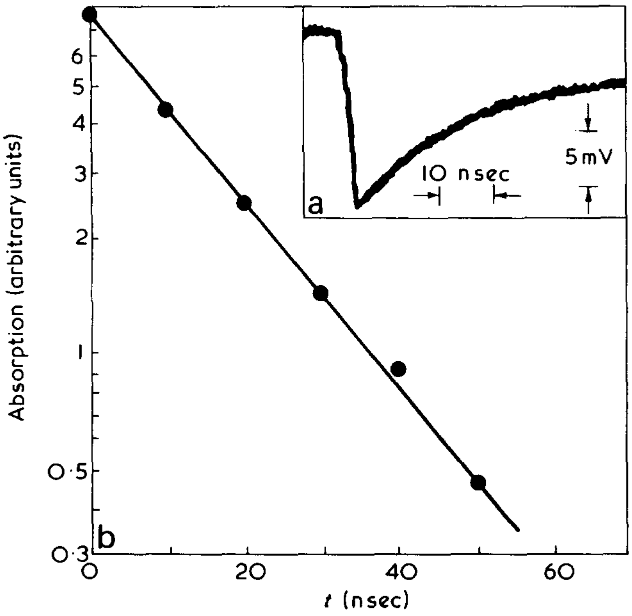


Figure 3 Oscilloscope trace (a) and first order plot (b) demonstrating the decay of the optical absorption at λ = 420 nm of a benzene solution of benzoin acetate (~7.8 X 10^{-4}M) at room temperature. Duration of flash: ~0.1 nsec. The first order plot in (b) was obtained from (a) by accounting for the formation of the radical absorption

shortlived absorption could not be followed quantitatively at most wavelengths. The observed lifetime of 9 nsec ($k = 1.1 \times 10^8$ sec^{-1}) is about one order of magnitude longer than the lifetime (0.8 nsec) found by Lewis *et al.*[9] from a linear Stern–Volmer plot for quenching of benzaldehyde formation by naphthalene in the presence of dodecanethiol. The authors[9] did not quote the naphthalene concentration used. Thus, it cannot be seen whether their quenching experiments pertain to singlet quenching. As shown in *Figure 1b* the spectrum observed with BA immediately after 25 nsec flashes decays at first rapidly indicating a radical precursor. Using 0.1 nsec flashes we could measure the rate of this rapid decay. As shown in *Figure 3* the absorption decays according to a first order law with a rate constant $k = (5.3 \pm 0.3) \times 10^7$ sec^{-1}, which agrees very well with the value obtained from end product quenching with naphthalene by Lewis *et al.*[9]. The difference spectrum obtained from *Figure 1b* is shown in *Figure 4* and is assigned to the triplet state.

Radical decay

The decay of the radical spectra shown in *Figure 1* occurs in the μsec range. Typical oscilloscope traces and corresponding second order plots are presented in *Figure 5*. In the case of benzoin (*Figure 5a*) the decay follows a second order law almost down to zero absorption. Only a very small fraction of the initial absorption decays with a slower rate than the major part. For the benzoin derivatives both the oscilloscope traces and the second order plots clearly indicate the existence of several different modes of radical–radical reactions. k/ϵ values obtained from the initial slopes of the curves in *Figure 5* are given in *Table 1*. In obtaining these values it was accounted for the fact that the initial absorption is composed of the absorption of benzoyl and alkoxybenzyl radicals or acetoxybenzyl radicals, respectively. It may be noted that no indication for an initial first order decay of the radical absorption could be observed which would be expected if radical pairs generated by α-cleavage undergo cage recombination.

Naphthalene quenching

In order to determine the rate constant k_q of the reaction of naphthalene with triplet excited benzoin and benzoin acetate, benzene solutions containing 0.1 M naphthalene were irradiated with 0.1 nsec flashes. The formation of the naphthalene triplet–triplet absorption was followed at 420 nm (see *Figure 6b*). From the first order plot in *Figure 6a* k_q was evaluated according to equation (2):

$$\ln \frac{[\mathrm{T}]_\infty - [\mathrm{T}]_t}{[\mathrm{T}]_\infty} = -k_q[\mathrm{Naph}]\,t \qquad (2)$$

$[\mathrm{T}]_t$ and $[\mathrm{T}]_\infty$ designate the concentrations of triplet naphthalene at time t and a long time after the flash. The rate constants determined at room temperature are $k_q = (7.7 \pm 0.8) \times 10^9$ M^{-1} sec^{-1} for benzoin and $k_q = (5.0 \pm 0.5) \times 10^9$ M^{-1} sec^{-1} for benzoin acetate.

Reaction of styrene with radicals and triplets

Figure 7 shows results obtained with benzene solutions containing 4.73×10^{-4} M BME and varying concentrations of styrene. As already described above the absorption at 310 nm decays in the absence of monomer according to a second order law. With increasing monomer concentration the order changes and at relatively high styrene concentrations the decay follows first order kinetics. Another important result of these experiments is the fact that only the rapid second order decay of the absorption is influenced. The slowly decaying portion of the absorption (see *Figure 5*) is not influenced. Thus, it may be concluded that only one radical species is reacting with styrene and it seems to be feasible to treat the observed effect of styrene by assuming a competition of the combination of the rapidly decaying radical R_i:

$$R_i + R_i \longrightarrow \text{products} \qquad (3)$$

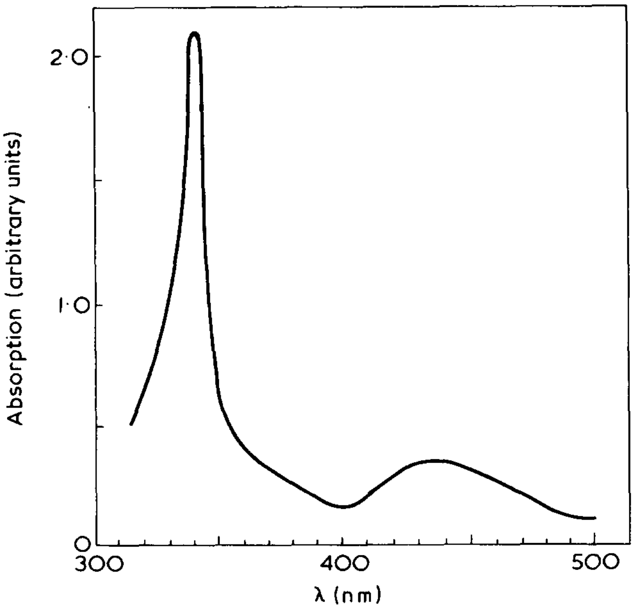


Figure 4 Spectrum of the radical precursor in the case of BA, obtained as the difference of spectra A and B in *Figure 1*

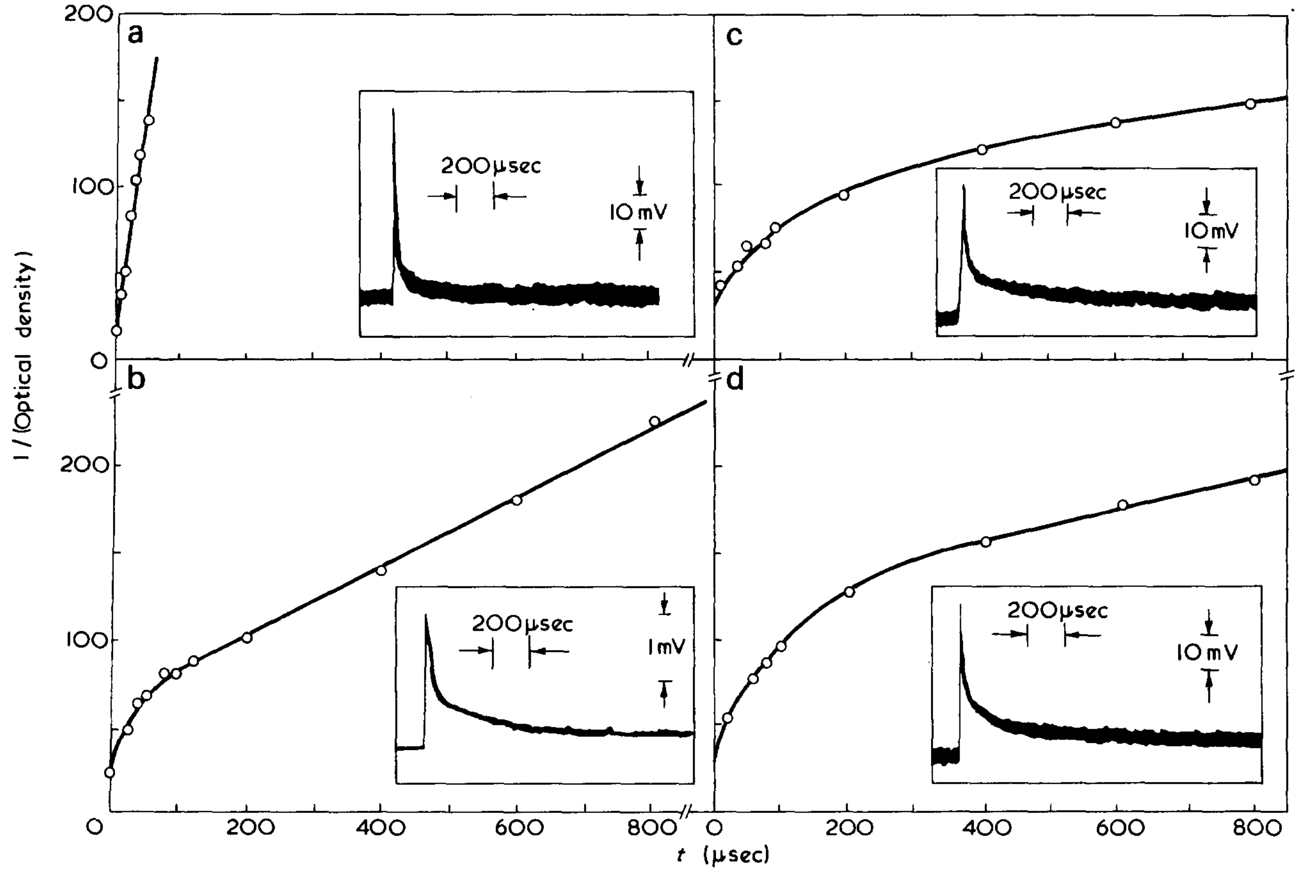


Figure 5 Second order plots of the reciprocal optical density *versus* time demonstrating the decay of radicals produced by α-cleavage. For experimental conditions see *Figure 1* (a) Benzoin, λ = 320 nm; (b) benzoin acetate, λ = 325 nm; (c) benzoinmethyl ether, λ = 320 nm; (d) benzoinisopropyl ether, λ = 320 nm

Table 1 $k/\epsilon d$ values obtained from the initial slopes of the curves in *Figure 5*. d = 1 cm

Carbonyl compound	$k/\epsilon d$ (sec^{-1})
Benzoin	$(2.1 \pm 0.2) \times 10^6$
Benzoinisopropyl ether	$(2.2 \pm 0.2) \times 10^6$
Benzoinmethyl ether	$(2.8 \pm 0.3) \times 10^6$
Benzoin acetate	$(2.5 \pm 0.2) \times 10^6$

with the reaction of $R_1^{\cdot}$ with styrene:

$$R_1^{\cdot} + M \longrightarrow R_1{-}M^{\cdot} \quad (4)$$

A reaction of the second radical according to equation (5):

$$R_2^{\cdot} + M \longrightarrow R_2{-}M^{\cdot} \quad (5)$$

was not detectable. The rate of decay of the radical $R_1^{\cdot}$ is:

$$-\frac{d[R_1^{\cdot}]}{dt} = k_R[R_1^{\cdot}]^2 + k_M[R_1^{\cdot}][M] \quad (6)$$

At sufficiently high concentrations of the monomer [M]: $k_R[R_1^{\cdot}]^2 \ll k_M[R_1^{\cdot}][M]$. Thus the observed first order decay of the radical absorption yields the rate constant k_M according to equation (7):

$$\ln\frac{[R_1^{\cdot}]_t}{[R_1^{\cdot}]_0} = -k_M[M]t \quad (7)$$

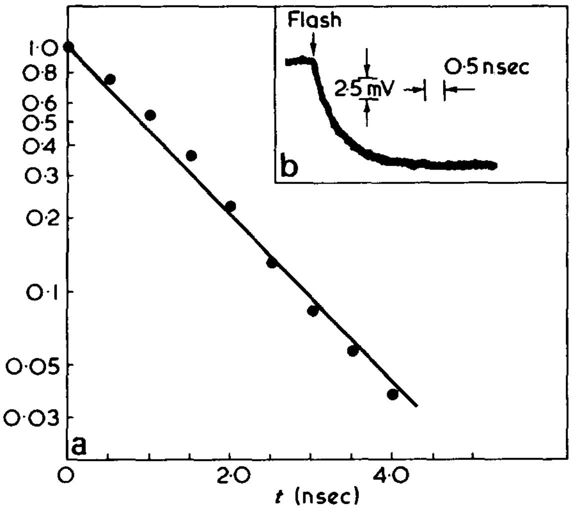


Figure 6 Formation of napthalene T—T absorption at λ = 420 nm due to the reaction of naphthalene with triplet excited benzoin. (a) First order plot according to equation (2) of data obtained from the oscilloscope trace in (b). [B] : 1.73×10^{-3}M; [Naph] : 10^{-1}M. Solvent: benzene. Duration of flash: ~0.1 nsec

The rate constant k_M obtained by plotting the experimental first order rate constants *versus* the styrene concentration is $k_M = (1.3 \pm 0.2) \times 10^5$ M^{-1}sec^{-1}.

It is also seen in *Figure 7* that the absorption observed immediately after the flash decreases with increasing styrene concentration, which indicates that the precursor of the radicals (probably triplet excited BME) is quenched by styrene. The Stern–Volmer treatment yielded $k_q\tau = 0.77$ M^{-1}.

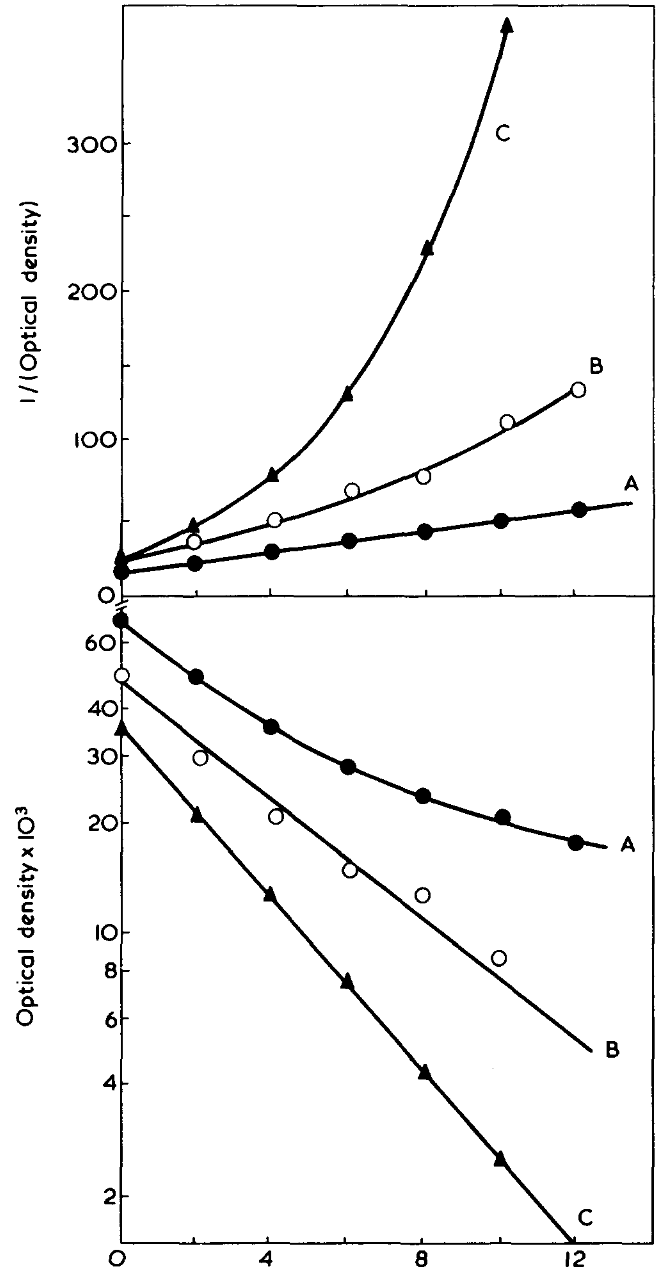


Figure 7 Influence of styrene on the time dependence of the decrease of the optical density: A, without styrene; B, 1M styrene; C, 2M styrene. BME (4.73 × 10^{-4}M) in benzene at room temperature. Solutions were irradiated with 25 nsec flashes of 347.1 nm light. Absorbed dose per flash: 9.0 × 10^{-5} Einstein/l

DISCUSSION

As described above evidence for radical precursors by their optical absorption could be obtained for benzoin and benzoin acetate. The optical absorption spectra of radicals generated by α-cleavage were obtained for the four benzoin compounds investigated.

In the following, several aspects concerning the reactions of the radicals are discussed with respect to analyses and yields of end products reported in the literature.

Benzoin

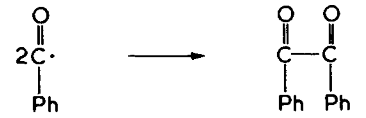
The decay of the optical absorption follows a second order law for the major portion of the absorption. This is in accord with the finding[9,17] that the major final product of the photolysis of benzoin in benzene solution is benzaldehyde formed by reaction (8):

$$\mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}\cdot} + \mathrm{Ph{-}\overset{\displaystyle OH}{\overset{|}{C}}H\cdot} \longrightarrow 2\,\mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H} \qquad (8)$$

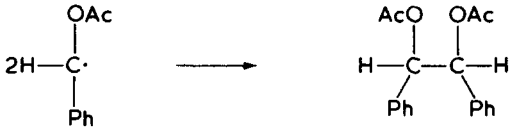
Evidence for a cage reaction could not be obtained. The first order decay of the absorption at λ > 400 nm cannot be considered as an indication for a cage reaction because of the difference between the slowly decaying spectrum (radicals) and the rapidly decaying spectrum. This conclusion is based on the assumption that radicals in a cage and radicals homogeneously distributed in the system have the same absorption spectrum. It may be emphasized, furthermore, that the rate of decay of the initial absorption is equal to the rate of formation of the radical absorption. This finding strongly indicates that the initial absorption is due to the radical precursor.

Benzoin acetate

The photolysis of BA yields benzil, pinacol acetate and 2-phenylbenzofuran (10–20%)[18,19]. Clearly, radicals of either sort prefer to combine with each other. Therefore, it appears to be feasible that the two branches of the second order plot shown in *Figure 5* can be attributed to the combination of benzoyl radicals and acetobenzyl radicals, respectively, according to reactions (9) and (10):



$$2\,\mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}\cdot} \longrightarrow \mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Ph} \qquad (9)$$

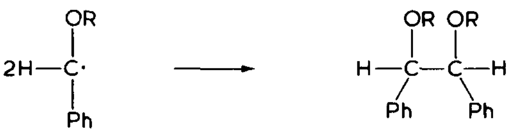


$$2\,\mathrm{H{-}\overset{\displaystyle OAc}{\overset{|}{\underset{\displaystyle Ph}{\underset{|}{C}}}}\cdot} \longrightarrow \mathrm{H{-}\overset{\displaystyle AcO}{\overset{|}{\underset{\displaystyle Ph}{\underset{|}{C}}}}{-}\overset{\displaystyle OAc}{\overset{|}{\underset{\displaystyle Ph}{\underset{|}{C}}}}{-}H} \qquad (10)$$

Benzoin ethers

The decay behaviour of radicals produced by irradiation of BME and BIPE is very similar. The curved second order plots indicate different modes of radical–radical reactions. As in the case of BA combination of like radicals plays an important role during the radical decay. Stationary irradiations in benzene[20,21] yielded benzaldehyde, benzil and pinacol ethers. BIPE irradiated in acetonitrile yielded benzil and α,α-di-isopropyloxydibenzyl in approximately equal amounts (quantum yield 0.20 to 0.35)[13].

An assignment of the two modes of absorption decay in the cases of BA, BME and BIPE appears possible by considering the fact that styrene does not influence the slowly decaying mode but only the fast one (see *Figure 7*). It has been reported by Lewis *et al.*[9] that styrene (1 M) reduces the yields of benzaldehyde and benzil but does not affect the pinacol ether formation. Therefore, it can be assumed that styrene reacts with benzoyl radicals and that the rapidly decaying mode is due to the formation of benzil via reaction (9). The slowly decaying mode, then, is assigned to the combination of alkoxybenzil radicals:



$$2\,\mathrm{H{-}\overset{\displaystyle OR}{\overset{|}{\underset{\displaystyle Ph}{\underset{|}{C}}}}\cdot} \longrightarrow \mathrm{H{-}\overset{\displaystyle OR}{\overset{|}{\underset{\displaystyle Ph}{\underset{|}{C}}}}{-}\overset{\displaystyle OR}{\overset{|}{\underset{\displaystyle Ph}{\underset{|}{C}}}}{-}H} \qquad (11)$$

In the case of BA the slow mode corresponds to reaction (10).

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