

LASER FLASH PHOTOLYSIS INVESTIGATION OF PRIMARY PROCESSES IN THE SENSITIZED POLYMERIZATION OF VINYL MONOMERS IV: EXPERIMENTS WITH HYDROXY ALKYLPHENONES

J. EICHLER and C. P. HERZ

E. Merck, Zentrallaboratorium für Industriechemikalien, Abt. Forschung, Frankfurter Strasse 250, D-6100 Darmstadt (F.R.G.)

I. NAITO and W. SCHNABEL

Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, Glienicker Strasse 100, D-1000 Berlin 39 (F.R.G.)

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Summary

1-phenyl-2-hydroxy-2-methyl-propanone-1 (compound I) and 1-[4-(2-propyl)-phenyl]-2-hydroxy-2-methyl-propanone-1 (compound II) were irradiated at room temperature with 25 ns laser flashes ($\lambda = 347$ nm) and with 15 ns flashes ($\lambda = 265$ nm) in deaerated solutions of various solvents. Triplet excited ketone molecules were formed ($\phi(T) \approx 0.25$) which decomposed essentially by α cleavage in the absence of an effective hydrogen donor. The triplet lifetimes were found to be 30 - 50 ns. In the absence of unsaturated compounds or oxygen the radicals formed during or immediately after the flash decayed predominantly by mutual deactivation. Two modes of radical absorption decay were detected with first half-lifetimes of about 4 μ s and 0.8 ms. In the presence of oxygen a strongly absorbing species was formed after the flash, due to the reaction of O₂ with fragment radicals of the ketones.

The results can be used to explain why compounds I and II are capable of acting very effectively as polymerization initiators in many cases.

1. Introduction

Recently UV-induced processes for the curing of coatings and printing inks have become quite important [1]. Current research programs are aimed at developing procedures which provide economic and ecological advantages over the procedures utilized at present. Of paramount significance appears to be the discovery and selection of compounds capable of acting as photoinitiators. It has been reported [2] that hydroxy alkylphenones having the structure shown in Fig. 1 can be used successfully for curing systems con-

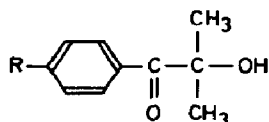


Fig. 1. The structure of compound I (R = H; 1-phenyl-2-hydroxy-2-methyl-propanone-1) and compound II (R = 2-propyl; 1-[4-(2-propyl)-phenyl]-2-hydroxy-2-methyl-propanone-1).

taining acrylic ester derivatives. In this work we extend earlier [3,4] investigations on benzophenone and benzoin compounds, and we report on flash photolysis experiments which were carried out to elucidate the mechanism of the photoreactions of compounds I and II.

We also compare the present data with those obtained recently with pivalophenone (phenyl-*t*-butyl ketone) [5]. On irradiating pivalophenone in benzene solution a transient absorption was detected which was ascribed to the triplet state (lifetime about 370 ns). It was inferred from the transient spectrum recorded a long time after the triplet decay (assigned to the benzoyl radical) that α cleavage is the major photochemical event occurring during the irradiation in benzene solution. However, it was concluded analogously that α cleavage is strongly suppressed in 2-propanol. In this case the transient spectrum recorded a long time after the flash indicated the formation of ketyl radicals (see Fig. 2).

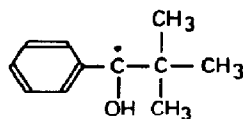


Fig. 2. The structure of the ketyl radical formed from pivalophenone in 2-propanol.

2. Experimental

2.1. Materials

Compounds I and II were synthesized in the Merck* laboratories. The organic solvents were of the highest purity available. They were distilled prior to use via a 1 m splitting tube column (Fischer, Bonn). Benzene (Merck, 99.5%) was shaken several times with concentrated H_2SO_4 , was washed with distilled water and was dried over $CaCl_2$ and CaH_2 . Acetonitrile (Merck, 99.6%) was refluxed over P_2O_5 and was distilled from K_2CO_3 using a Vigreux column. Water was triply distilled on a special apparatus.

2.2. Irradiation of samples

The samples were irradiated at the Hahn-Meitner-Institut in rectangular quartz cells, either with 25 ns flashes from a ruby laser ($\lambda =$

*Compounds I and II correspond to commercial products of E. Merck, Darmstadt: I, Darocur[®] 1173 (Art. Nr. 7005); II, Darocur[®] 1116 (Art. Nr. 13710).

347.1 nm after frequency doubling) or with 15 ns flashes from a neodymium-YAG laser ($\lambda = 265$ nm after frequency quadrupling). Transient optical absorption spectra were recorded as functions of the time after the flash. Details of the optical absorption set-up have been reported previously [6].

Deaeration of the samples was achieved by bubbling with purified argon or by connecting the samples to a high vacuum line and repeating the cycle freeze-pump-thaw several times.

The absorbed dose per flash was determined for the ruby laser irradiations by irradiating argon-saturated cyclohexane solutions of anthracene (5.6×10^{-6} mol l $^{-1}$) and monitoring the T-T absorption of anthracene at 420 nm ($\epsilon = 5.7 \times 10^4$ l mol $^{-1}$ cm $^{-1}$, $\phi(T) = 0.72$). For the neodymium laser irradiations ($\lambda = 265$ nm) the decomposition of tetraphenylcyclobutane was measured [7] at 300 nm, *i.e.* where the product (*trans*-stilbene) absorbs strongly ($\epsilon = 2.8 \times 10^4$ l mol $^{-1}$ cm $^{-1}$, $\phi(\textit{trans-stilbene}) = 0.2$).

An S-5 vacuum photodiode (ITT) was used as an intensity reference. For this purpose a small fraction of the light emitted by the laser was guided by a beam splitter to the photodiode after doubling and before reaching the sample cell. In all cases a linear relationship between the optical absorption and the digital read-out of the reference photodiode was observed, indicating that non-linear effects (biphotonic photodissociation etc.) did not occur.

3. Results

3.1. Ground state spectra

The ground state absorption spectra and the decadic molar extinction coefficients at 265 and 347 nm of compounds I and II recorded in various solvents are shown in Fig. 3 and Table 1. Compound I absorbs intensely below 300 nm with a strong maximum at 240 - 250 nm and a pronounced

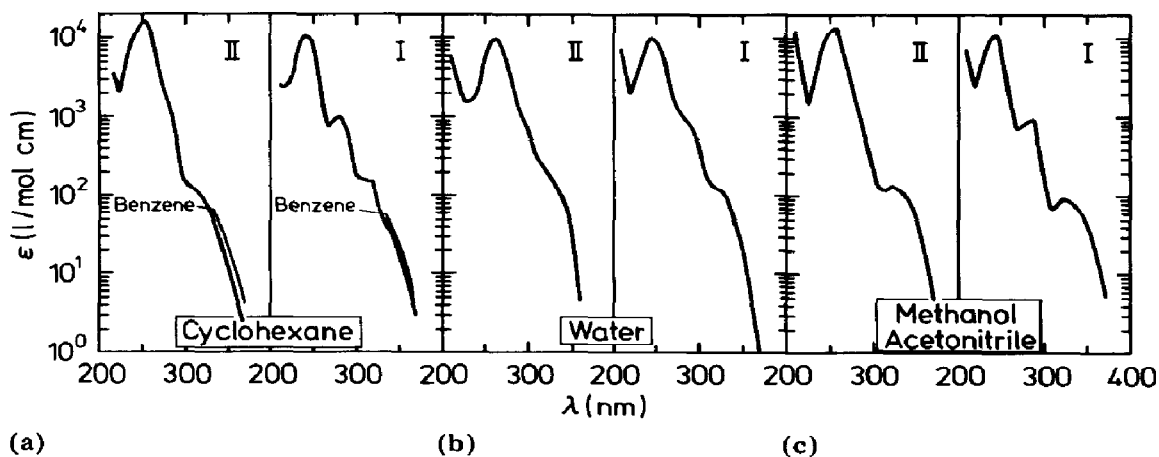


Fig. 3. The ground state spectra of compounds I and II recorded at room temperature in air-saturated solutions of (a) cyclohexane, benzene; (b) water; (c) methanol, acetonitrile. Appropriate concentrations were chosen and were between 6×10^{-5} and 3×10^{-2} mol l $^{-1}$.

TABLE 1

Decadic molar extinction coefficients of the ground state absorption of compounds I and II at 265 and 347 nm

Solvent	Compound I		Compound II	
	ϵ_{265} ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	ϵ_{347} ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	ϵ_{265} ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	ϵ_{347} ($l \text{ mol}^{-1} \text{ cm}^{-1}$)
Benzene		29		31
Cyclohexane	8.2×10^2	22	9.8×10^3	20
Acetonitrile	1.0×10^3	50	1.0×10^4	60
Methanol	1.0×10^3	50	1.0×10^4	60
Water	3.5×10^3	29	1.0×10^4	42

shoulder at about 280 nm. A minor peak is situated at about 325 nm. It is the absorption band at approximately 325 nm which is excited by irradiations with 347 nm laser light. With 265 nm light the band with the strongest maximum is excited. Similar spectra were obtained for compound II. Figure 3 shows that the strongest maximum is located between 250 and 260 nm. The shoulder between the first absorption band at about 320 nm and the main maximum at about 255 nm is not as distinct as that for compound I. For compound II the wavelength of the light produced by the neodymium laser (265 nm) is close to the position of the strong maximum.

3.2. Transient spectra

Compounds I and II were irradiated with 25 ns flashes of 347 nm light in the absence of oxygen. Optical absorption spectra observed immediately after the flash and 8 μs later are presented in Figs. 4 and 5.

For compound I it can be seen from Fig. 4 that the initial spectra obtained in methanol, water and cyclohexane are very similar. They possess maxima at about 410 nm, 345 nm and probably at 290 - 300 nm. The position of the maximum at approximately 295 nm could not be located with certainty because of the strong ground state absorption of compound I at wavelengths below 300 nm. These spectra are essentially assigned to the benzoyl radical which is generated simultaneously with the 2-hydroxypropyl-2 radical by α scission (see Fig. 6). The initial spectrum observed in benzene solutions (Fig. 4(a)) differs remarkably from the spectra obtained in the other solvents; the peak at about 310 nm does not occur for the spectra recorded in the other solvents. It is assumed that this spectrum contains a strongly absorbing component. This component is attributed to a radical precursor which is believed to be an excited triplet state (see Section 3.3). The spectrum observed 8 μs after the flash no longer possesses a pronounced maximum above 300 nm. There are two minor maxima at about 350 and 400 nm. However, contrary to the spectra given in Figs. 4(b) - 4(d), the maximum at 400 nm is more intense than that at 350 nm. This is probably due to the coexistence of benzoyl and ketyl radicals. Ketyl radicals can be

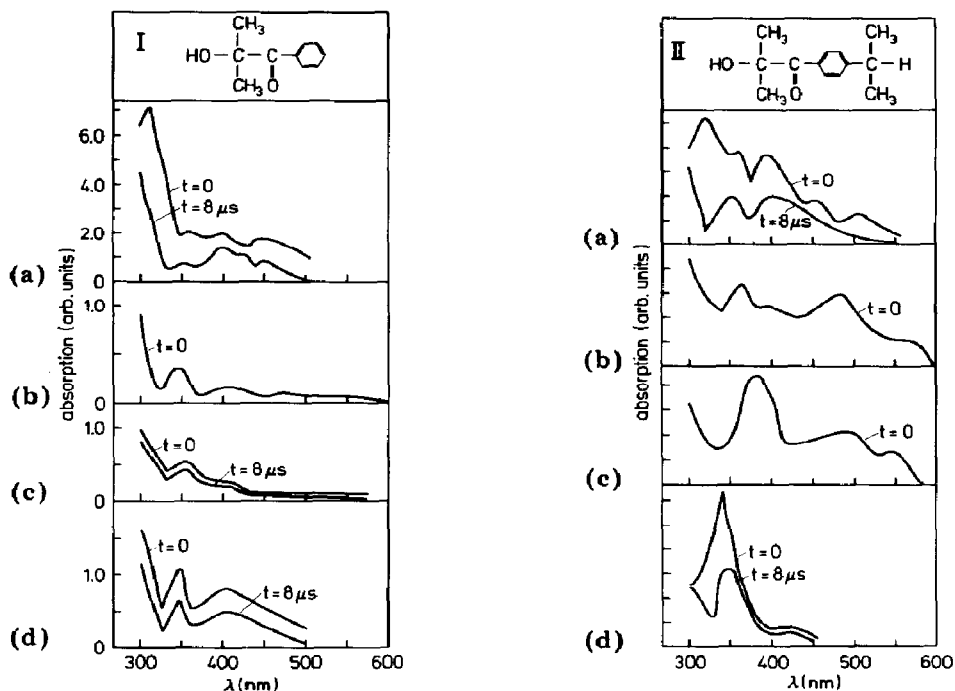


Fig. 4. Transient spectra obtained for compound I in the absence of oxygen in various solvents: (a) benzene; (b) methanol; (c) water; (d) cyclohexane. The concentration of compound I was $(2-4) \times 10^{-3} \text{ mol l}^{-1}$, corresponding to an absorption at 347 nm of about 20%. The absorbed dose per flash was about $3.8 \times 10^{-5} \text{ einstein l}^{-1}$.

Fig. 5. Transient spectra obtained for compound II in the absence of oxygen in various solvents: (a) benzene; (b) acetonitrile; (c) methanol; (d) cyclohexane. The concentration of compound II was $(2-4) \times 10^{-3} \text{ mol l}^{-1}$, corresponding to an absorption at 347 nm of about 20%. The absorbed dose per flash was about $3.8 \times 10^{-5} \text{ einstein l}^{-1}$.

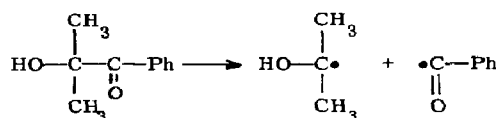


Fig. 6. The α scission reaction for compound I.

formed either via hydrogen abstraction from the solvent (a reaction which is unlikely to occur in benzene) or via the reaction of excited with unexcited molecules of compound I (Fig. 7). The occurrence of the reaction shown in Fig. 7 (to a significant extent) becomes feasible if its rate constant exceeds $10^7 \text{ l mol}^{-1} \text{ s}^{-1}$.

For compound II, the initial spectra shown in Figs. 5(a) - 5(d) are not as easy to interpret as the spectra obtained with compound I. In cyclohexane solution there is a pronounced peak at about 340 nm which decays very rapidly (see Section 3.3). The absorption spectrum remaining after $8 \mu\text{s}$ strongly resembles the spectrum of compound I recorded in cyclohexane solution and might be attributed (to its major part) to the benzoyl radical.

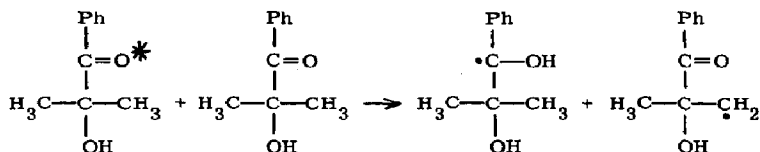


Fig. 7. The reaction between excited and unexcited molecules of compound I.

The initial spectrum is assigned to a radical precursor, presumably the triplet state of compound II. Thus, it is concluded that the triplet lifetime of compound II is longer than that of compound I. It follows that chemical deactivation routes other than α scission should be more probable for compound II. This assumption is in agreement with the observation that the initial spectrum obtained with methanol solutions shows a broad peak at about 375 nm with a strong shoulder at about 400 nm. In this case evidence for a rapidly decaying radical precursor was not obtained. Therefore, we believe that ketyl radical formation (via the reaction of triplet excited molecules of compound II with methanol) competes with α scission. In benzene solutions compound II behaves in a manner similar to compound I. This can be seen from the spectra obtained immediately after the flash and 8 μs later (see Fig. 5(a)). When compounds I and II were irradiated with 15 ns flashes of 265 nm light in argon-saturated cyclohexane solution, the transient spectra obtained were identical to the spectra shown in Figs. 4(d) and 5(d). The quantum yields for transient formation at both wavelengths of the incident light are of the same order of magnitude. A more exact estimate cannot be made at the present time because of uncertainties in the determination of the absorbed dose per flash.

3.3 Search for radical precursors

We have shown in Section 3.2 that the existence of a short-lived radical precursor can be inferred from the initial transient spectra recorded in benzene and cyclohexane solutions. Difference spectra obtained with benzene solutions are shown in Fig. 8. They are very similar to the difference spectrum observed previously [4] for benzoin acetate. These difference spectra are attributed to the triplet state, *i.e.* they are caused by triplet-triplet absorption.

Evidence for the formation of triplet states was obtained from quenching experiments with naphthalene. The T-T absorption of naphthalene was formed by irradiating benzene solutions containing ketone and naphthalene with 347 nm light during the flash. Since naphthalene does not absorb light at 347 nm it is concluded that ketone triplets are generated beforehand. Obviously the lifetime of the ketone triplets is long enough to permit energy transfer to the naphthalene. It follows also that the triplet energy E_T of the two ketone compounds is higher than E_T of naphthalene (approximately 61 kcal [8]). The triplet lifetime was estimated from quenching experiments at various naphthalene concentrations [6]. Plots of the reciprocal absorbance (O.D.) versus the reciprocal naphthalene concentration $[Q]$ were linear according to the following equation:

$$\frac{1}{\text{O.D.}} = \frac{1}{\text{O.D.}_L} + \frac{k_T}{\text{O.D.}_L k_Q [Q]}$$

where O.D. is the absorbance at a quencher concentration $[Q]$ and O.D._L is the limiting absorbance value obtained by extrapolating the straight lines to $[Q]^{-1} = 0$.

By assuming that $k_Q = 5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ the following values for the triplet lifetimes were obtained: $\tau = 30 \text{ ns}$ for compound I and $\tau = 50 \text{ ns}$ for compound II.

Estimates of the triplet lifetimes were also derived from the fact that relatively long lasting emission signals were detected when compounds I and II in cyclohexane solution were irradiated with 15 ns flashes of 265 nm light. These emission signals could be clearly distinguished from a more rapidly decaying luminescence. A typical example is presented in Fig. 9. The luminescence observed at 290 nm is shown in Fig. 9(a). It can be seen that a strong luminescence signal is formed simultaneously with the development of the flash. The rapidly decaying portion is assigned to fluorescence and the longer-lived portion to phosphorescence. In Fig. 9(b) a first order plot of the phosphorescence decay of compound I is shown. It yields a lifetime τ of 36 ns. Analogously a triplet lifetime τ of 48 ns was determined for compound II.

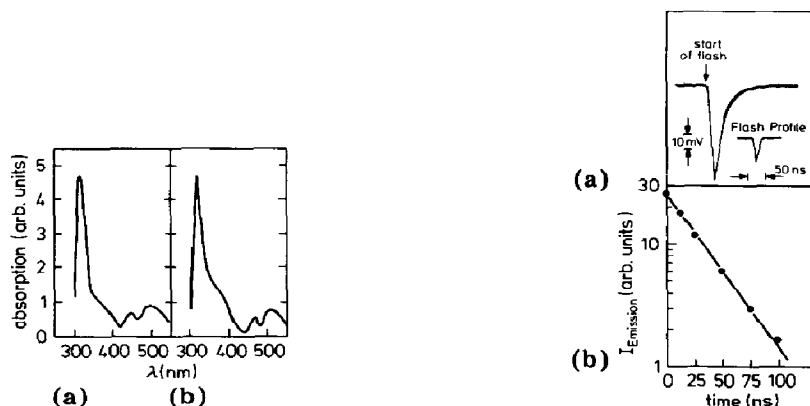


Fig. 8. Difference spectra obtained by subtraction of the spectra (in deaerated benzene solution) recorded $8 \mu\text{s}$ after the flash from those recorded immediately after the flash: (a) compound I; (b) compound II.

Fig. 9. The decay of the emission at 290 nm when a cyclohexane solution of compound I ($1.2 \times 10^{-4} \text{ mol l}^{-1}$) was irradiated with a 15 ns flash of 265 nm light (absorbed dose per flash = $1.5 \times 10^{-5} \text{ einstein l}^{-1}$): (a) an oscilloscope trace (the flash profile is the fluorescence at 320 nm of an oxygen-saturated solution); (b) a first order plot of the slow mode of emission decay shown in Fig. 9(a).

Further evidence for the short lifetime of the radical precursor was obtained by irradiating cyclohexane solutions of compound II with 25 ns flashes of 347 nm light or with 15 ns flashes of 265 nm light. In this case the triplet absorption could be clearly distinguished from the absorption of radicals (see Fig. 10). Comparison with the flash profile obtained by record-

ing fluorescence shows that the short-lived absorption is formed with the start of the flash. The absorption spectrum for the short-lived species shown in curve a of Fig. 10 is given in Fig. 5(d).

3.4. Decay of the long-lived species

The decay of the long-lived absorption was studied in cyclohexane, water and benzene solutions. In all cases two modes of decay could be clearly distinguished. This is demonstrated in Fig. 11(a) for compound II dissolved in cyclohexane. (This result was selected as a typical example out of a large number of recorded oscillograph traces.) The initial rapid decrease is not correlated with the decay of the triplet-triplet absorption. On the time scale chosen for recording the trace in Fig. 11(a) ($200 \mu\text{s}$ division⁻¹) the rapidly decaying T-T absorption would not be observed. The two decay modes are attributed to two radical reactions and analysis of the decay curves yielded the following results. It was assumed that the initial absorption, detected by monitoring absorption changes at long times after the flash (Fig. 11(a)), is caused by radicals and that these radicals react to generate radicals which absorb negligibly in the wavelength range under investigation. Based on these assumptions the long-lived absorption was subtracted from the total absorption. The difference absorption decayed according to first order kinetics with a lifetime of about $4 \mu\text{s}$ in benzene and somewhat longer lifetimes in cyclohexane and water. The long-lived absorption decayed according to a second order process as is demonstrated in Fig. 11(b). The first half-lifetime was about 0.8 ms in cyclohexane and aqueous solutions. Similar decay rates were observed in other solvents.

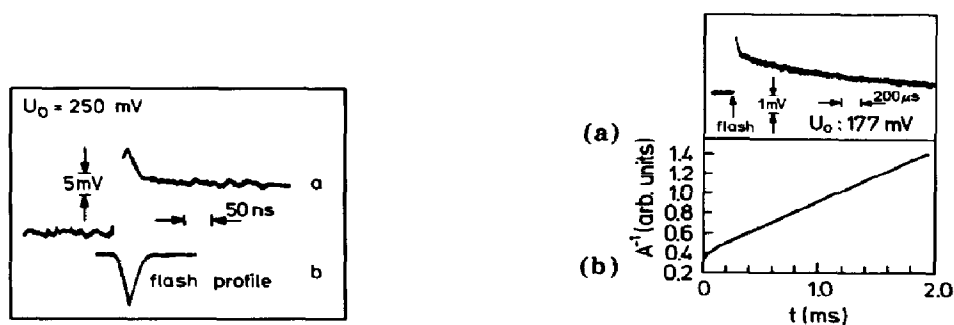


Fig. 10. Irradiation of compound II in cyclohexane solution ($4.5 \times 10^{-3} \text{ mol l}^{-1}$) in the absence of oxygen with a 25 ns flash of 347.1 nm light (absorbed dose per flash = $5.8 \times 10^{-5} \text{ einstein l}^{-1}$): curve a, an oscilloscope trace showing the change of the optical absorption at 340 nm during and after the flash; curve b, a profile of the laser flash obtained by recording the fluorescence at 360 nm of compound II in a benzene solution.

Fig. 11. Irradiation of compound II in argon-saturated cyclohexane solution ($4.5 \times 10^{-3} \text{ mol l}^{-1}$) (absorbed dose per flash = $6.6 \times 10^{-5} \text{ einstein l}^{-1}$): (a) an oscilloscope trace demonstrating the change of the optical absorption at 360 nm after irradiation with a 347.1 nm flash; (b) a second order plot relating to Fig. 11(a).

3.5. Experiments in the presence of oxygen

The formation of a relatively strongly absorbing species was detected in oxygen-saturated solutions. Typical build-up curves observed with aqueous solutions of compound I are shown in Fig. 12(a). Because of the strong absorptivity of the newly formed species, traces of oxygen in not thoroughly deaerated solutions could be detected easily as shown in Fig. 12(b). A more comprehensive description of the influence of oxygen will be given in a forthcoming publication.

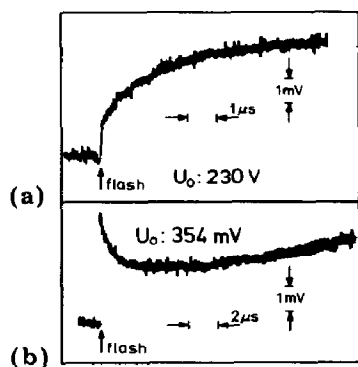


Fig. 12. The influence of oxygen on changes of the optical absorption at 320 nm after irradiation with a 347.1 nm flash: (a) compound I in air-saturated aqueous solution ($3.3 \times 10^{-3} \text{ mol l}^{-1}$) (absorbed dose per flash = $2.9 \times 10^{-5} \text{ einstein l}^{-1}$); (b) compound I in argon-saturated cyclohexane solution ($5.3 \times 10^{-3} \text{ mol l}^{-1}$) containing traces of oxygen (absorbed dose per flash = $4.3 \times 10^{-5} \text{ einstein l}^{-1}$).

4. Discussion

The important results of this work are as follows.

(1) Triplets are formed when compounds I and II are irradiated with UV light and a significant number are chemically deactivated predominantly by α cleavage. From the limiting value of the T-T absorbance of naphthalene obtained from quenching experiments the quantum yield $\phi(T)$ for ketone triplet formation was estimated to be about 0.2 - 0.3 for both compounds (with $\epsilon_{T-T} = 2.2 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the T-T absorption of naphthalene at 413 nm). This estimate was based on a comparison with the limiting T-T absorbance of naphthalene measured with acetophenone, where $\phi(T) = 1.0$.

(2) The triplet lifetime is relatively short (30 - 50 ns) for both compounds (*i.e.* about 10 times shorter than the triplet lifetime of pivalophenone). It is inferred from these values that triplet quenching by molecular oxygen can be neglected at the oxygen concentrations normally found in practice ($[\text{O}_2] \leq 2 \times 10^{-3} \text{ mol l}^{-1}$ in aerated systems). This holds if the rate constant for the reaction between oxygen and the triplet is less than about $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. However, certain unsaturated polymerizable compounds, such as styrene, with relatively low triplet energies might be capable of quenching the triplets of compounds I and II.

(3) The chemical routes for triplet deactivation of compounds I and II involve predominantly α cleavage in the absence of an effective hydrogen donor. Thus, benzoyl and 2-hydroxy-2-propyl radicals are formed which are quite effective in reacting with any unsaturated polymerizable substances present in the system.

However, in this work the systems did not contain unsaturated compounds, and the radicals formed during the decomposition of excited molecules decayed essentially by mutual deactivation processes.

5. Conclusions

The two hydroxy alkylphenones investigated in this work have been reported to be very successful as initiators for the photopolymerization of various monomers [2]. We have shown that their effectiveness as initiators derives mainly from the fact that short-lived triplet states with relatively high quantum yields are formed and that α cleavage is an important route for triplet deactivation.

Acknowledgment

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