

## LASER INVESTIGATION OF NORRISH TYPE I PHOTOSCSSION IN THE PHOTOINITIATOR IRGACURE (2,2-DIMETHOXY 2-PHENYL-ACETOPHENONE)

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### Summary

Irgacure is one of the most efficient photoinitiators for vinyl polymerization. The nanosecond spectroscopy technique gave accurate information about the evolution of the radicals produced after laser excitation. The photophysical processes in the excited states were determined, the absorption spectra were recorded and the lifetimes and the quenching rate constants were calculated. Some conclusions can be drawn about the photoinitiation process of the polymerization.

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### 1. Introduction

Benzoin derivatives are used extensively as photoinitiators for ultraviolet curable coatings and printing inks [1]. Of these molecules, 2,2-dimethoxy 2-phenylacetophenone (DMPA), which is used commercially for the photopolymerization of vinyl monomers under the name Irgacure, is one of the most efficient photoinitiators. Surprisingly, this molecule has not been investigated by laser spectroscopy; however, such a study may provide further information to help elucidate some aspects of the mechanism of the photoinitiation of vinyl polymerization. In this work laser experiments are reported and the results are discussed in terms of the primary processes involved in the excited states.

It has been postulated [2 - 5] that benzoin derivatives undergo photochemical  $\alpha$  cleavage (Norrish type I photoscission) to form a benzoyl-substituted benzyl radical pair (see Fig. 1). The  $\alpha$  cleavage has been shown to proceed through triplet states whose lifetimes are drastically dependent on the substituent R (240 ns for R = H [6]; 20 ns for R = OCOCH<sub>3</sub> [3]; 800 ps for R = OH [7]). In the case of benzoin ethers no quenching could be observed with standard triplet quenchers [4]. It has been concluded that the

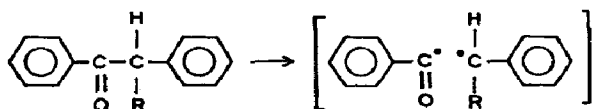


Fig. 1.

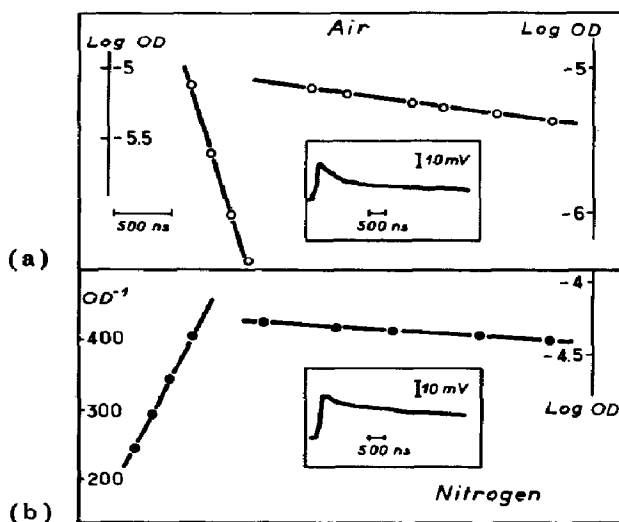


Fig. 2. Oscilloscope traces of the transient absorptions observed for DMPA in benzene after laser excitation: (a), first order plots of the absorption of the two transients in an aerated solution; (b), second order and first order plots in degassed solutions.

$\alpha$  cleavage must be either an exceptionally rapid triplet process ( $k$  greater than  $10^{10} \text{ s}^{-1}$ ) or a singlet process which competes efficiently with intersystem crossing.

## 2. Results

Picosecond laser excitation of a solution of DMPA in benzene leads to transients in the near-UV and visible regions (Fig. 2). Under a nitrogen atmosphere the long-lived transient (LLT) obeys first order kinetics (its lifetime is greater than  $10 \mu\text{s}$ ). The fast decaying portion of the absorption, the short-lived transient (SLT), may be calculated either with first order kinetics or with second order kinetics within experimental error ( $k = 750 \text{ ns}$  or  $k/rl = 33 \times 10^7 \text{ s}^{-1}$ ). In an aerated solution the relaxation of the two transients is faster and the kinetics may be interpreted in terms of two first order plots corresponding to quenching of the transients by oxygen. Values of  $350 \text{ ns}$  and  $6 \mu\text{s}$  are obtained for the SLT and the LLT respectively; the rate constants of the oxygen quenching are estimated to be  $1.4 \times 10^9 \text{ s}^{-1}$  (or  $0.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  if we take into account a relaxation of the transient under a nitrogen atmosphere with first order kinetics) and  $8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for the SLT and the LLT respectively (a value of  $[\text{O}_2]$  of  $2 \times 10^{-3} \text{ M}$  is assumed).

TABLE 1

Lifetimes and quenching rate constants of the two radicals as a function of the solvent

Solvent	Short-lived transient (SLT)		Long-lived transient (LLT)				$\rho$	
	$\tau^0$ (ns)	$\tau$ (ns)	$k_q^{O_2} \times 10^{-9}$ ( $M^{-1} s^{-1}$ )	$\tau^0$ ( $\mu s$ )	$\tau$ ( $\mu s$ )	$k_q^{O_2} \times 10^{-9}$ ( $M^{-1} s^{-1}$ )		$k_q^{THF} \times 10^{-5}$ ( $M^{-1} s^{-1}$ )
Benzene	750	350	0.8	17	6	0.08	-	0.65
Isopropanol	450	240	1	5.8	1.4	0.25	1.3	0.55
THF	-	200	-	4.7	2	0.15	1.7	0.60

$\tau^0$  and  $\tau$  are the lifetimes in degassed and aerated solutions respectively;  $k_q^{O_2}$  and  $k_q^{THF}$  are the rate constants for quenching by  $O_2$  and THF;  $\rho$  is the corrected ratio of the absorbances in aerated solution and is proportional to the concentration of radicals formed on laser excitation, i.e.  $\rho = SLT/LLT$ . (It is assumed that the extinction coefficients vary only slightly with the solvent.)

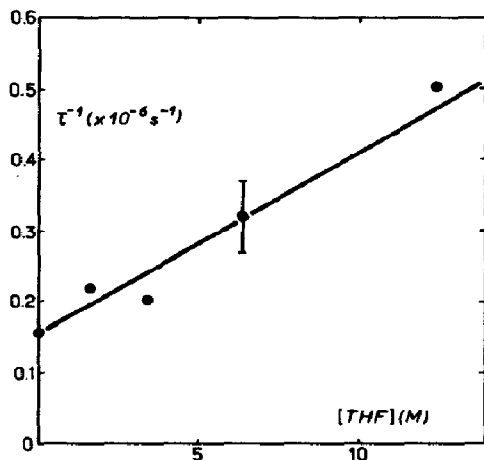


Fig. 3. A Stern-Volmer plot of the reciprocal value of the LLT lifetime in an aerated solution as a function of the THF concentration. ( $\lambda = 430$  nm.)

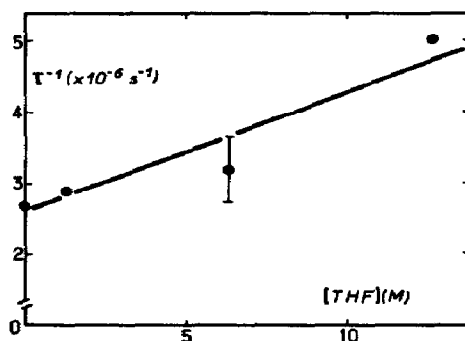


Fig. 4. A Stern-Volmer plot of the reciprocal value of the SLT lifetime in a degassed solution as a function of the THF concentration. ( $\lambda = 430$  nm.)

The same kind of relaxation for the two transients is still observed in hydrogen-donating solvents (Table 1), especially in tetrahydrofuran (THF) which is a solvent commonly used in polymerization experiments in solution. Furthermore, it may be emphasized that the rates of decay of the transients are increased. The quenching rate constant of the LLT transient can be determined from a Stern-Volmer plot of the reciprocal value of the LLT lifetime as a function of the THF concentration (Fig. 3). A value of  $k_q$  of  $2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  is calculated. A Stern-Volmer plot for the SLT is also available (Fig. 4). The quenching rate constant is estimated to be  $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , which shows that the SLT is strongly quenched by THF compared with the LLT. Similar behaviour is observed with isopropanol.

The relative absorbances of the two radicals were determined at time  $t = 100$  ns from the oscilloscope traces. They were corrected to take into account the increase of the population between the moment when the  $i$ th pulse struck the sample and  $t = 100$  ns, according to a formula developed in ref. 8. Thus the ratio of the absorbances can easily be calculated (Table 1). Within experimental error it may be concluded that the ratio remains constant, which means that the two radicals are simultaneously formed in the excited states through the same process.

The absorption spectra of the two transients are reported in Fig. 5 in the wavelength range 380–500 nm. The concentrations of the two radicals are equal; from the relative values of the optical density of the transients it is deduced that the LLT radical exhibits higher extinction coefficients.

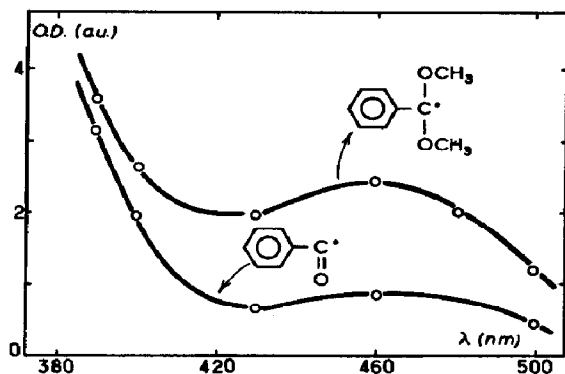
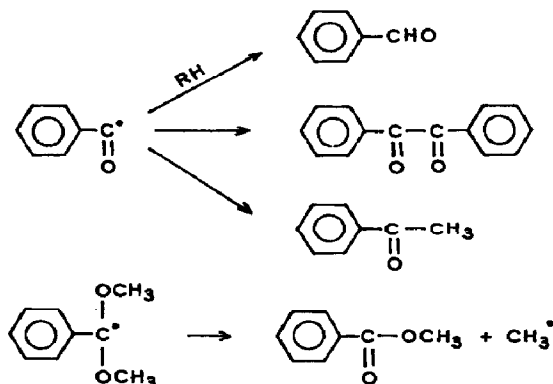


Fig. 5. Absorption spectra of the two radicals in benzene.

Fig. 6.



### 3. Discussion

From a general consideration of the results obtained under steady state conditions [5], it appears that the two transients can be assigned to the radicals produced by the  $\alpha$  cleavage. In deoxybenzoin [6] a similar fast absorption has been demonstrated as being caused by the benzoyl radical. Therefore the SLT and the LLT are identified as the benzoyl radical and the substituted benzyl radical respectively and all the results may be explained on this basis. Since stationary irradiation of DMPA in benzene has yielded benzaldehyde and benzil with very similar quantum yields and acetophenone [5] (see Fig. 6), it is quite reasonable to expect rather complicated kinetics for the relaxation of the benzoyl radical (superposition of the first and second order kinetics). The first order kinetics for the disappearance of the LLT is in agreement with the highly efficient conversion of the benzyl radical to methyl benzoate [5].

Moreover, the benzoyl radical interacts strongly with oxygen, in agreement with the easy generation of peroxide radicals, whereas the benzyl derivative radical appears to be substantially less reactive. Indeed, oxidation of the benzoyl radical has led to an increase of the amount of methyl benzoate during the photolysis of DMPA in a polymer matrix [9]. Subsequent reactions (see Fig. 7) have also been observed with the polymer  $\textcircled{P}$  and yield an increase of the efficiency of the photocrosslinking reactions [10] by an increase of the amount of the macroradical  $\textcircled{P}^{\bullet}$ .

However, no clear evidence was found for the generation of a ketyl radical through a hydrogen abstraction reaction. Previous experiments in our laboratory seemed to show qualitatively that the ratio of the concentration of the two radicals varied slightly with the solvent in DMPA; the more accurate results of the present work performed under better conditions allow

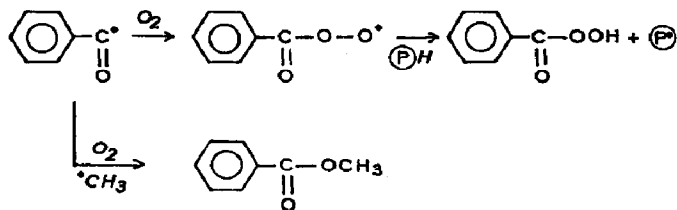
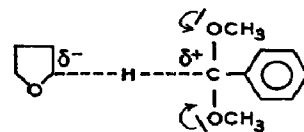


Fig. 7.

Fig. 8.



us to postulate that the photoreduction, if it really exists, is not an important deactivation route. It is concluded that hydrogen abstraction does not compete efficiently with the  $\alpha$  cleavage, in contrast with the behaviour of deoxybenzoin [6].

Hydrogen-donating systems enhance the yield of benzaldehyde, as has been observed in steady state experiments [2]. Moreover, it is shown that both the benzoyl and the substituted benzyl radicals are quenched by THF. This is in contrast with deoxybenzoin where the benzyl radical does not show any significant quenching (the quenching rate constant  $k_q$  is assumed to be less than  $5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ). This may be explained by the fact that, because of the electron donor ability of the methoxy group, polar contributions to the transition state are expected (see Fig. 8).

The energy level diagram given in Fig. 9 shows the evolution of the different transients after laser excitation as a function of the environment. In the case of reactions with THF, THF radicals are obtained which are capable of initiating the polymerization, similar to the photoinitiation by benzophenone systems [11]. This explains the increase of the rate of polymerization occurring in a benzene-THF mixture compared with pure benzene [12]. Moreover, quenching of the two radicals by methyl methacrylate (MMA) is observed, yielding quenching rate constants  $k_q$  of  $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and  $2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for the benzoyl and the substituted benzyl radicals respectively. These values suggest that the two radicals are almost equally efficient in initiation (in a recent paper [13], an equivalent incorporation of these two radicals was found in a DMPA polymer by using  $^{14}\text{C}$ -labelled benzoin methyl ether (2-methoxy 2-phenylacetophenone) as the photoinitiator; but the authors could not conclude whether the radicals were incorporated during the initiation or were introduced through primary radical chain termination). It has also been suggested that the substituted benzyl radical is strongly quenched by MMA compared with the benzyl radical [6]; this was postulated to explain the grafting of the substituted radical onto the polymer backbone [13] as shown in Fig. 10.

A discussion of the mechanisms for the photopolymerizations with DMPA and deoxybenzoin in solution will be reported elsewhere.

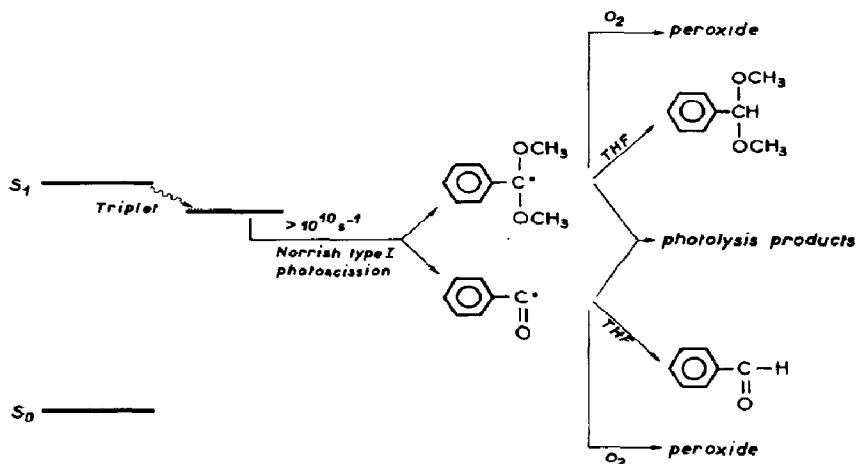


Fig. 9. A diagram showing the evolution of the excited states.

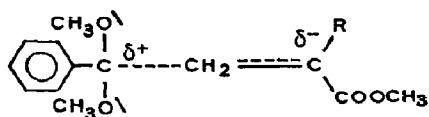


Fig. 10.

#### 4. Experimental

The DMPA was purchased from Ciba-Geigy Co. All the solvents were purified before use. The laser excitation consisted of a train of 6 pulses (200 ps full width at half maximum). The incident energy density was  $50 \text{ mJ cm}^{-2}$  at 347 nm. Full details of the laser and the analysing system have been given in ref. 8.

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