Radical Intermediates in the Photochemical Decomposition of Benzoin and Related Compounds

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The radical scavenging technique used in conjunction with e.s.r. spectroscopy has been employed to characterise radicals produced by photolysis of benzoin, benzoin methyl ether, and benzil with reference to their relative efficiencies as photoactivators for radical polymerization. Radicals trapped by *N*-oxides and nitroso-compounds indicate that while benzoin and its methyl ether are photochemically cleaved in a similar manner, the latter produces radicals more efficiently. Possible mechanisms are presented.

BENZOIN, PhCO·CH(OH)Ph, its methyl ether, and benzil, PhCO·COPh, are well known and extensively used photoinitiators of free radical polymerization.[1] Benzoin derivatives in particular have found appreciable use as photoactivators for a wide range of image recording processes based on vinyl polymerization.[2] Typically, quantum yield measurements indicate that 1250 molecules of methyl methacrylate are polymerized per quantum of 366 nm radiation in the presence of benzoin,[3] and benzoin methyl ether appears to be an even more efficient photosensitizer.[4] Reports of the use of these materials as sensitizers are mainly to be found in the patent literature; however, early work by Melville and his collaborators has shown that benzil is less efficient than benzoin in sensitizing the polymerization of both vinyl acetate [5] and methyl methacrylate.[6]

Whilst the polymerizations are clearly radical in

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[1] Examples include (*a*) W. Cooper, G. Vaughan, S. Miller, and M. Fielden, *J. Polym. Sci.*, 1959, **34**, 651; (*b*) C. T. Chen and W.-D. Huang, *J. Chinese Chem. Soc.* (*Taipei*), 1969, **16**, 46; (*c*) S. R. Rafikov and G. P. Gladyshev, *Vysokomolekul. Soedinenii*, 1962, **4**, 1345 (*Chem. Abs.*, 1962, **58**, 14097f); (*d*) H. G. Heine, K. Fuhr, H. Rudolph, and H. Schnell, S. African P. 6904,724 (*Chem. Abs.*, 1970, **73**, 46220); (*e*) S. Okamuru and T. Motoyama, *Kobunshi Kagaku*, 1958, **15**, 487 (*Chem. Abs.*, 1960, **54**, 11552a); (*f*) Sun Chemical Corp., B.P. 1,198,259 (*Chem. Abs.*, 1970, **73**, 57311).

[2] J. Kosar 'Light-Sensitive Systems,' Wiley, New York, 1965, ch. 5.

[3] W. E. Mochel, J. L. Crandall, and J. H. Peterson, *J. Amer. Chem. Soc.*, 1955, **77**, 494.

[4] A. Ledwith, unpublished results.

[5] R. B. Whyte and H. W. Melville, *J. Soc. Dyers and Colourists*, 1949, 703.

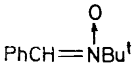
[6] R. B. Chinmayanandam and H. W. Melville, *Trans. Faraday Soc.*, 1954, **50**, 73.

nature, the precise mechanism of initiation by these carbonyl compounds is not clearly established, and there is evidence, based on tracer studies, for incorporation of these sensitizers into the resulting polymer.[3] It has been suggested that initiation proceeds from the radicals produced by Norrish Type I cleavage, with the rate of initiation controlled by the relative reactivities of the intermediate radicals towards particular monomers. Recently, CIDNP experiments[7] have demonstrated Type I cleavage of benzoin; the radical pair obtained [Ph$\dot{\mathrm{C}}$H(OH)O$\dot{\mathrm{C}}$Ph] being identical with that observed in irradiated benzaldehyde.

It appeared likely that the radical trapping technique[8] (spin trapping) could provide useful information on the mechanism of these photoinitiations, particularly by allowing identification of any intermediate radicals involved. The present paper reports the results of such a study, and illustrates further the scope of *N*-oxides and nitroso-compounds as radical probes.

RESULTS

Benzoin, benzoin methyl ether, and benzil were photolysed in benzene and methanol in the presence of one of the diamagnetic radical scavengers (I)—(III). Addition of intermediate radicals to the double bond of *N*-oxides (I) and (III) and 2-methyl-2-nitrosopropane (II) produces stable nitroxide radicals, examination of which by e.s.r. spectroscopy, permits identification of the scavenged intermediate radical. With the *N*-oxide (III), abstraction of the phenolic hydrogen may also occur producing the corresponding (stable) phenoxyl radical; this is easily identified by its characteristic e.s.r. signal.[9] Oxygen-centred radicals, as well as carbonyl triplet states prefer to abstract the phenolic hydrogen, whereas carbon-centred radicals generally add to the double bond. Thus each of the three diamagnetic scavengers has a different characteristic and conclusions are drawn from a combination of all the results.

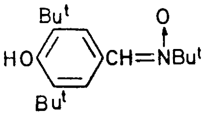


$\mathrm{PhCH{=}\overset{O}{\overset{\uparrow}{N}}Bu^t}$

(I)

$\mathrm{Bu^tN{=}O}$

(II)



(III)

Table 1

Nitroxides formed by the addition to nitroso-compound (II) of radicals produced by photolysis of sensitizers in benzene

Sensitizer	Typical concentration[a] (M)	Radical trapped	Nitroxide radical splittings (mT) a_N	a_H
Benzoin methyl ether	5×10^{-2}	Ph$\dot{\mathrm{C}}$=O	0·805	
		Ph$\dot{\mathrm{C}}$H–OMe	1·377	0·205
Benzoin	5×10^{-2}	Ph$\dot{\mathrm{C}}$=O	0·806	
		Ph$\dot{\mathrm{C}}$H–OH	1·38	0·22
Benzil	5×10^{-2}	No radicals trapped		

[a] Other concentrations of sensitizer gave similar results.

Table 2

Nitroxides formed by the addition to nitroso-compound (II) of radicals produced by photolysis of sensitizers in methanol

Sensitizer	Typical concentration (M)	Radical trapped	Nitroxide radical splittings (mT) a_N	a_H
Benzoin methyl ether	1×10^{-1}	Ph$\dot{\mathrm{C}}$=O	0·813	
		Ph$\dot{\mathrm{C}}$H–OMe	1·449	0·290
Benzoin	1×10^{-1}	Ph$\dot{\mathrm{C}}$=O	0·810	
		Ph$\dot{\mathrm{C}}$H–OH	1·48	0·25
Benzil[a]	1×10^{-1}	$\dot{\mathrm{C}}\mathrm{H_2OH}$	1·48	0·51

[a] A 366 nm u.v. filter was used to minimize production of $\mathrm{Bu^t{}_2N{-}O\cdot}$ which was otherwise produced in large amounts by (possibly sensitized) decomposition of nitrosobutane

Table 3

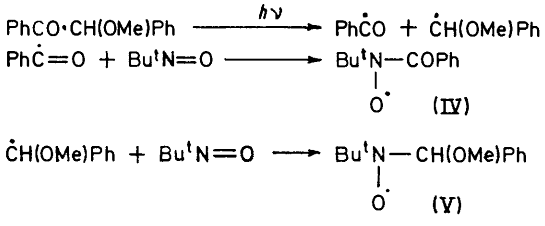
Generation of nitroxides (from nitrosobutane) listed in Tables 1 and 2 by independent routes

Source	Radical trapped	Nitroxide radical splittings (mT) a_N	a_H
t-Butoxyl radicals[a] in neat benzyl methyl ether	Ph$\dot{\mathrm{C}}$H–OMe	1·378	0·207
t-Butoxyl radicals[a] in neat benzyl alcohol	Ph$\dot{\mathrm{C}}$H–OH	1·493	0·288
	(H·)	1·39	1·23
t-Butoxyl radicals[a] in methanol	$\cdot\mathrm{CH_2OH}$	1·48	0·51
Photolysis of $\mathrm{PhCOCPh_3}$ in benzene[b]	Ph$\dot{\mathrm{C}}$=O	0·805	

[a] t-Butoxyl radicals were generated photochemically from $\mathrm{Bu^tOOBu^t}$, and thermally from $\mathrm{Bu^tON{=}NOBu^t}$. [b] Similar results were obtained by hydrogen abstraction from benzaldehyde.

It is pertinent to point out that *N*-oxide (I) and nitroso-compound (II) contain reactive double bonds similar to those found in many polymerisable monomers.

Photolysis in the Presence of Compound (II).—Although nitrosobutane is not photochemically stable it was found during the course of this work, in agreement with observations of other workers,[8,10] that it provides the most direct information as to the type of radical being scavenged. Accordingly this radical scavenger was used under carefully controlled conditions. Tables 1 and 2 summarize the results obtained. Both Ph$\dot{\mathrm{C}}$H–OMe and Ph$\dot{\mathrm{C}}$=O are trapped, apparently in high yield, upon short (<5 s) photolysis ($\lambda >$ 330 nm) of a benzene solution of benzoin methyl ether (Scheme 1).



$$\mathrm{PhCO{\cdot}CH(OMe)Ph} \xrightarrow{h\nu} \mathrm{Ph\dot{C}O} + \mathrm{\dot{C}H(OMe)Ph}$$

$$\mathrm{Ph\dot{C}{=}O} + \mathrm{Bu^tN{=}O} \longrightarrow \mathrm{Bu^t\underset{\overset{|}{O^{\cdot}}}{N}{-}COPh} \quad \text{(IV)}$$

$$\mathrm{\dot{C}H(OMe)Ph} + \mathrm{Bu^tN{=}O} \longrightarrow \mathrm{Bu^t\underset{\overset{|}{O^{\cdot}}}{N}{-}CH(OMe)Ph} \quad \text{(V)}$$

Scheme 1

The observed nitroxides (IV) and (V) are both stable and readily characterized by control experiments (Table 3) and from literature data. Similar photolysis of benzoin (Table 1) indicated that any radical intermediates were not so readily trapped. Although both Ph$\dot{\mathrm{C}}$=O and Ph$\dot{\mathrm{C}}$H(OH)

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[7] G. L. Closs and D. R. Paulson, *J. Amer. Chem. Soc.*, 1970, **92**, 7229.

[8] For reviews see E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; M. J. Perkins, *Chem. Soc. Special Publ.*, No. 24, 1970, ch. 5; C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466.

[9] J. G. Pacifici and H. L. Browning, *J. Amer. Chem. Soc.*, 1970, **92**, 5231.

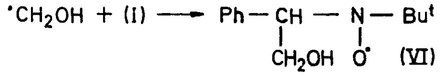
[10] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 395.

radicals are trapped, the resulting nitroxides (particularly the latter) are only stable enough to be detected on continuous irradiation.

Photolysis of benzil in a benzene solution of nitrosobutane gave only extremely weak signals of radical (IV) on prolonged irradiation. No radicals are trapped when photolysis times comparable with those used for benzoin derivatives are employed.

Results of similar experiments carried out for methanol solutions are summarized in Table 2. It was of interest to see if any differences occur when abstractable hydrogen atoms are available to the photoexcited carbonyl sensitizers, hydroxymethyl radicals are very readily scavenged by *N*-oxides and nitroso-compounds.[10,11] However, benzoin methyl ether again cleaved immediately to give high yields of nitroxides (IV) and (V), and both $Ph\dot{C}=O$ and $Ph\dot{C}H(OH)$ radicals are trapped during photolysis of benzoin in methanol. No hydroxymethyl adducts were detected, although they were trapped when benzil was irradiated in methanol solutions of nitrosobutane (Table 2).

Photolysis in the Presence of the N-*Oxide* (I). The *N*-oxide (I), whilst giving less information than the nitroso-compound is photochemically ($\lambda > 330$ nm) more stable, and thus longer photolysis times can be used. It was subsequently found to be of less value than nitrosobutane, due to a much lower efficiency for trapping radicals of the type $Ph\dot{C}H{-}OR$ where $R = Me$, and especially when $R = H$. Benzoyl radicals ($Ph\dot{C}=O$) were, however, immediately and efficiently trapped on photolysis of benzoin and its methyl ether in benzene, but no signals were observed on photolysis of benzil under similar conditions. Results for photolysis of the benzoin derivatives in methanol solution were similar; no hydroxymethyl radicals were detected but, in agreement with results obtained with the nitroso-scavenger these latter radicals are trapped readily when benzil is photolysed in methanol (Scheme 2). Identification of the nitroxide adduct (VI) was established from previous work.[11]



$$\dot{C}H_2OH + (I) \longrightarrow \underset{\displaystyle CH_2OH}{Ph{-}\underset{|}{CH}}{-}\underset{\displaystyle O^{\bullet}}{\underset{|}{N}}{-}Bu^t \quad (VI)$$

SCHEME 2

Photolysis in the Presence of the N-*Oxide* (III).—As mentioned above this bifunctional trap serves as a probe for differentiating between oxygen and carbon radicals.[9] The triplet state of benzophenone also acts as an oxygen radical in that it abstracts the phenolic hydrogen from (III) to form the corresponding phenoxyl radical. It was of interest therefore to employ this phenoxynitrone during photolysis of the carbonyl compounds under study.

Brief u.v. irradiation (several s at $\lambda > 330$ nm) of benzoin methyl ether, benzoin, and benzil in benzene solutions of (III) gave in each case an immediate intense e.s.r. signal due to the phenoxyl radical.* Using the same conditions of concentration, u.v. photolysis time, *etc.*, the results were compared with those for the phenoxyl radical produced on photolysis of a benzene solution of benzophenone and it was noted that: (*a*) the signal intensity obtained from benzil photolysis was exactly twice that from benzophenone; (*b*) the signal appears more readily from benzoin methyl ether than from benzoin, but both are similar in intensity to the signal from benzophenone; (*c*) together with the phenoxyl radical formation, nitroxide formation is also observed on photolysis of benzoin and its methyl ether. This indicates trapping of carbon-centred radicals and again these are more readily produced with the methyl ether than with benzoin itself.

The differences in intensity of signals due to phenoxyl radical almost certainly result from differing light absorption characteristics ($\lambda > 330$ nm) of the various sensitizers, since use of a 366 nm interference filter gave rise to signals of essentially the same intensity for all the carbonyl compounds.

DISCUSSION

The results allow a number of conclusions to be drawn for each of the photoinitiators.

Benzoin methyl ether is the simplest case and, from the radical trapping studies, particularly with the nitroso-compound (II) and the *N*-oxide (III) it is now shown that the molecule splits into two radicals after initial $n \longrightarrow \pi^*$ photoactivation of the carbonyl function. Fragmentation into radicals [$Ph\dot{C}H(OMe)$ and $Ph\dot{C}O$] occurs efficiently after photoexcitation and much more rapidly than hydrogen abstraction from methanol and even competing with the ready phenolic hydrogen abstraction from (III). Addition of each of the two radicals to nitrosobutane occurs readily and suggests that analogous rapid addition to polymerisable monomers explains the high efficiency of benzoin methyl ether as a photoinitiator of radical polymerization.

Results with benzoin itself are more complex. From studies with all three radical traps it is apparent that benzoin does not produce radicals as readily as its methyl ether derivative although both appear to have the same mode of photodecomposition. Photoexcited benzoin can abstract reactive hydrogens, as shown by reaction with (III), but also cleaves into the radical fragments $Ph\dot{C}O$ and $Ph\dot{C}H(OH)$.

It is reasonable to assume that benzoin and its methyl ether have rather similar photophysical characteristics in respect of intersystem crossing ($n \longrightarrow \pi^*$ singlet to $n \longrightarrow \pi^*$ triplet) and non-radiative decay processes for the $n \longrightarrow \pi^*$ triplets. Accordingly, the rather obvious differences in efficiency for production of ' out-of-cage ' radicals must reflect either differences in photochemical reactivity of the corresponding $n \longrightarrow \pi^*$ triplets or, differences in the degree, and possibly the nature, of ' in-cage ' primary radicals. Two possibilities are immediately apparent: (*a*) photoenolisation as a reaction competing with cleavage of excited $n \longrightarrow \pi^*$ triplets, and occurring to a larger extent for benzoin than benzoin methyl ether, *e.g.* Scheme 3; (*b*) ' in-cage ' reaction of the primary radicals from benzoin yielding benzaldehyde, a process not possible for primary radicals from benzoin methyl ether (Scheme 4).

Evidence in favour of alternative (*b*) may be adduced from the CIDNP experiments of Closs as noted in the introduction, and from observations in the present work, of strong signals due to $Bu^tNH{-}O^{\bullet}$ following production of $Ph\dot{C}H{-}OH$ radicals in the presence of $Bu^tN{=}O$. The

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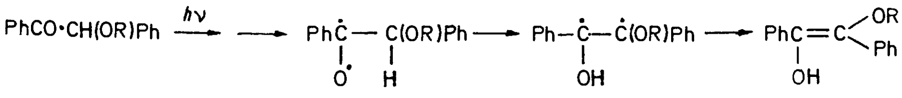
* Concentrations of sensitizer and *N*-oxide (III) were 5×10^{-2}M; coupling constants of the phenoxyl radical were similar to those reported in ref. 9.

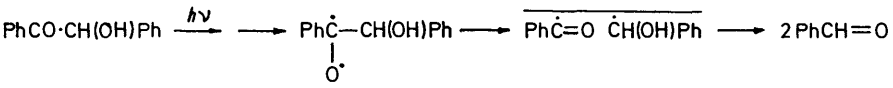
[11] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *Chem. Comm.*, 1971, 964.

latter radicals are generated by photolysis of Bu^tOOBu^t and thermolysis of $Bu^tON{=}NOBu^t$ in benzyl alcohol, and also by photolysis of dilute solutions of benzaldehyde in benzyl alcohol.

Similar behaviour has been noted previously with $Me_2\dot{C}OH$ radicals,[10,12] and can be explained by either a direct hydrogen-atom transfer or an electron-transfer process of the type: $Ph\dot{C}HOH + Bu^tN{=}O \longrightarrow [Ph\overset{+}{C}HOH, Bu^tN\dot{O}^{-}] \longrightarrow PhCHO + Bu^tNHO\cdot$.

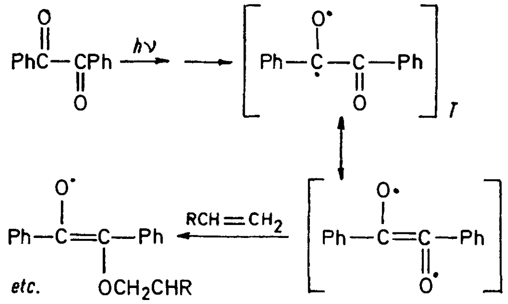


SCHEME 3



SCHEME 4

This hydrogen transfer reaction of $Ph\dot{C}H{-}OH$ radicals is analogous to the 'in-cage' reaction suggested and, whatever the mechanism, these observations have implications in initiation of polymerization by $Ph\dot{C}H(OH)$ radicals since similar possibilities exist for reactions with monomer molecules. In fact, the related semipinacol radicals $Ph_2\dot{C}{-}OH$ (which also transfer a hydrogen atom to nitrosobutane[12]) have been shown[13] to initiate polymerization by hydrogen transfer to monomer.



SCHEME 5

Unlike benzoin and its methyl ether, benzil apparently does not fragment upon irradiation ($\lambda > 330$ nm). No radicals are trapped upon photolysis of benzil in benzene solutions of either the *N*-oxide (I) or nitroso-compound (II). This supports the findings of some other workers,[14] but cleavage into benzoyl radicals has been assumed to be a major pathway in a number of cases.[6,15]

Although generally not as efficient as the benzoin derivatives,[5] benzil is nevertheless a good photoinitiator of polymerization, but our results suggest that, contrary to previous suggestions,[6] its mode of sensitization is completely different from that of the benzoin derivatives. The latter initiate polymerization by radicals liberated by rapid fragmentation after carbonyl excitation whereas benzil appears to operate in a manner similar to that of benzophenone and other aromatic carbonyl compounds which are known to initiate polymerization by hydrogen abstraction processes.[16] Alternatively it is at least a possibility that photoexcited benzil could initiate radical polymerization by direct addition to monomers (Scheme 5).

EXPERIMENTAL

Benzoin, benzoin methyl ether, benzil, and benzophenone were obtained commercially and recrystallized from suitable solvents to give the correct m.p.s. 3-Phenyl-2-t-butyloxaziridine was synthesized by peroxybenzoic acid[17] oxidation of α-t-butyliminotoluene.[18] Reflux of the oxaziridine in dry acetonitrile for 3 days gave benzylidene-t-butylamine *N*-oxide (I),[19] m.p. 76°. 2-Methyl-2-nitrosopropane (II) was prepared by a modification of Emmons procedure,[20] although small amounts have also been obtained by the simple process outlined by Holman and Perkins.[21] *N*-(4-hydroxy-3,5-di-t-butylbenzylidene)-t-butyl *N*-oxide (III) was obtained by a modified literature method.[9]

E.s.r. spectra were recorded on a Varian V4500 spectrometer with 100 kHz modulation and an *X*-band klystron. The field sweep was calibrated with alkaline aqueous solutions of potassium nitrosodisulphonate (Fremy's salt) having $a_N = 1{\cdot}309$ mT. Other details have been described previously.[22] Photolysis was by a 250 W medium pressure mercury lamp, radiation of less than 330 nm being cut off by suitable glass filters. All solutions were nitrogen purged ($\frac{1}{2}$ h) before irradiation in the cavity of the spectrometer. Photolyses were carried out at room temperature.

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[15] D. L. Bunbury and C. T. Wang, *Canad. J. Chem.*, 1968, **46**, 1473.

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[19] W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739; see also E. G. Janzen and B. J. Blackburn, *ibid.*, 1969, **91**, 4481.

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[22] R. A. W. Johnstone, A. F. Neville, and P. J. Russell, *J. Chem. Soc.* (*B*), 1971, 1183.