ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 112 (1998) 87–93

Journal of Photochemistry and Photobiology A:Chemistry

Photoinitiators and photoinitiation Part 13. The photodecomposition of sulphonic esters of α-hydroxymethylbenzoin ethers

Hardew Angad Gaur, Hendrik J. Hageman [1]*, Pieter Oosterhoff, Ton Overeem, Jan Verbeek, Sake van der Werf

Akzo Nobel Central Research, Arnhem, The Netherlands

Accepted 15 August 1997

Abstract

The photodecomposition of some sulphonic esters of α-hydroxymethylbenzoin ethers is examined using ESR and radical trapping techniques. Photoinduced α-cleavage into benzoyl and α-alkoxy-α-sulphonyloxymethylbenzyl radicals from a short-lived triplet excited state is observed. The α,α-disubstituted benzyl radicals undergo subsequent fragmentation, generating benzoylmethylradicals and sulphonic acids at a rate $k_{el} < 10^7$ s^{-1}. The fate of the alkyl ether part of the α,α-disubstituted benzyl radicals after elimination of sulphonic acid is unknown at present.

Keywords: α-Hydroxymethylbenzoin ethers; Sulphonic esters; Photodecomposition; α-Alkoxy-α-sulphonyloxymethylbenzyl radicals

1. Introduction

Sulphonic esters of α-hydroxymethylbenzoin have been shown to undergo photoinduced α-cleavage into benzoyl and α-hydroxy-α-sulphonyloxymethylbenzyl radicals through a short-lived triplet excited state [1]. The α,α-disubstituted benzyl radicals were found to undergo an extremely rapid heterolytic elimination of sulphonic acid to give benzoylmethyl radicals.

The benzoyl and benzoylmethyl radicals were shown to be equally reactive towards the carbon–carbon double bond of 1,1-diphenylethylene (DPE) used as a nonpolymerizing model substrate for vinyl monomers.

This photoinduced fragmentation makes these sulphonic esters particularly suitable both as acid-releasing photocatalysts for acid-hardening systems [2,3], and as photoinitiators for free radical polymerization processes [4,5].

Sulphonic esters of α-hydroxymethylbenzoin ethers have also been claimed as sulphonic acid-releasing photocatalysts [2,3], and as photoinitiators for free radical polymerization processes [4,5]. It seems justified to assume that these compounds also undergo a photoinduced α-cleavage into benzoyl and α-alkoxy-α-sulphonyloxymethylbenzyl radicals through a short-lived triplet excited state.

From the performance of 1-dodecanesulphonic esters of some α-hydroxymethylbenzoin ethers in the photocuring of particular acrylate formulations[2], it must be concluded that 1-dodecanesulphonic acid is released. The 1-dodecanesulphonic acid must stem from the α-alkoxy-α-sulphonyloxymethylbenzyl radicals, the elimination mode, however, being somewhat obscure.

We now report on a study of some sulphonic esters of several α-hydroxymethylbenzoin ethers by ESR spectroscopy and by radical trapping experiments.

2. Experimental details

2.1. General

The ^{1}H NMR spectra were recorded on a Bruker WH-270 spectrometer using tetramethylsilane ($\delta = 0$ ppm) as internal standard. The mass spectra were recorded on a Finnegan MAT 212 (EI) and MAT 112 (CI), respectively. Melting points were determined on a melting point microscope (Zeiss,

---

* Corresponding author.

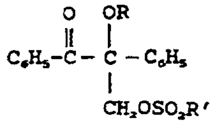
[1] Present address. The Chemical Laboratory, The University of Kent, Canterbury, Kent CT2 7NH.

[2] Cf. Ref. [5], figure 1, curves b and c.

1010-6030/98/$19.00
PII S1010-6030(97)00255-4

Table 1

Sulphonic esters of α-hydroxymethylbenzoin ethers



$$C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_2OSO_2R'}{|}}{\overset{\overset{OR}{|}}{C}}-C_6H_5$$

R		*a* R' = $-CH_3$	*b* R' = $-(CH_2)_{11}CH_3$	*c* R' = $-C_6H_4-CH_3$
$-H$[a]	**1**	108.9–109.5	47.8–48.3	133.0–133.6
$-CH_3$	**2**	117.8–118.4	52.6–53.9	115.1–115.5
$-CH_2CH_3$	**3**	95.0–95.7	–	89.0–90.0
$-CH(CH_3)_2$	**4**	131.0–131.8	45.2–45.8	117.5–118.5
$-(CH_2)_3CH_3$	**5**	67.5–68.3	–	131.0–131.9
$-CH_2CH(CH_3)_2$	**6**	81.5–83.5	–	123.4–124.1

[a] Included for comparison.

equipped with a Mettler Hot Stage and FP-80 Processor) and are corrected. The UV spectra were recorded on a Hitachi 110-80 A spectrophotometer. The ESR spin trapping experiments using 2-methyl-2-nitrosopropane (MNP) were carried out in the cavity of a Varian E-4 spectrometer with a Philips SO 100 W Hg-lamp with a glass filter. The irradiation time was 10–30 s. The *g*-values of the radicals observed were determined relative to the benzoyl radical ($g = 2.0008$ [6]).

2.2. Materials

Benzoin, the methyl, ethyl, isopropyl, and isobutyl ethers of benzoin (from Aldrich) were used without purification. Methanesulphonyl chloride (Aldrich) and *p*-toluenesulphonyl chloride (Merck) were also used without purification. 1-Dodecanesulphonyl chloride was available from a previous study [1]. The sulphonic esters, **1b–1d** of α-hydroxymethylbenzoin, included for comparison, were also available from previous studies [1,5]. MNP, and 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) (Aldrich) were used as received. 1,1-Diphenylethylene[3] (Merck) was fractionated b.p. 79–80°C at 0.3 mbar. Trimethylolpropane triacrylate (TMPTA) was obtained from Akzo Nobel Resins.

2.3. Syntheses

2.3.1. Benzoin n-butyl ether

This was synthesized from benzoin and *n*-butanol using thionyl chloride following a standard procedure [8].

2.3.2. α-Hydroxymethylbenzoin methyl ether (2a)

This was synthesized from benzoin methyl ether and paraformaldehyde as described [9], m.p. 72.5–73.5°C (reported 72–73°C [10]).

2.3.3. α-Hydroxymethylbenzoin ethers (3a–6a)

These compounds, similarly synthesized from the respective benzoin ethers, were syrupy substances.

2.3.4. Sulphonic esters (2–6)

These were synthesized from the respective α-hydroxymethylbenzoin ethers by treatment with the appropriate sulphonyl chlorides in THF or chloroform in the presence of triethylamine or pyridine followed by conventional work-up [9]. The structures of the new esters were confirmed by ^1H NMR and MS. They all showed a UV absorption maximum at $\lambda = 320 \pm 2$ nm ($\log \epsilon = 2.30 \pm 0.02$). The sulphonic esters synthesized are collected in Table 1.

2.4. Irradiation procedures

2.4.1. Photodecomposition in the presence of TMPO

Solutions of the various esters (10^{-2} mol l^{-1}) in benzene in the presence of TMPO (3×10^{-2} mol l^{-1}) were irradiated in a Rayonet photoreactor (model RPR-208) equipped with 350 nm lamps. The Pyrex reaction vessels were equipped with a magnetic stirrer, a gas dispersion tube, and a reflux condenser. The solutions were flushed with nitrogen before and during the irradiation. The reactions were monitored by TLC of samples withdrawn at regular intervals.

2.4.2. Photoinduced crosslinking of TMPTA in solution

Solutions of TMPTA (10 g l^{-1}) in 2-propanol containing the various esters (10^{-2} mol l^{-1}) were irradiated in cuvettes (polystyrene; 4 ml; from Witeg) with a high-pressure Hg-lamp (90 W; Ealing Optics No. 26-2865) at a distance of 10 cm. The crosslinking (insolubilization) of TMPTA was monitored by laser nephelometry as described by Decker and Fizet [11]. Induction periods (T_{ind}) were determined as the irradiation time (in seconds) until the onset of the crosslinking. Relative rates of crosslinking were determined from the slope of the curves ($tg\alpha$) using a calibration curve obtained by plotting the amount of polymer formed (by gravimetry) vs.

---

[3] Although we abandoned the use of DPE as a model substrate in favour of 1,1-di(*p*-tolyl)ethylene (DTE) on very good grounds [7], we used DPE in this study to facilitate the comparison with the sulphonic esters of α-hydroxymethylbenzoin [1].

time (in seconds), benzoin isopropyl ether (BIPE) being the standard [12].

2.4.3. Photoinduced acid generation

Solutions of the various esters (10^{-2} mol l^{-1}) in CH_3CN/H_2O (1:1) were irradiated in a Rayonet photoreactor as described. The pH was determined of samples withdrawn at regular intervals.

2.4.4. Photocuring of a melamine resin

The equipment consisted of a high-pressure Hg-lamp (Philips HOK-6, 80 W cm^{-1}) mounted (15 cm in distance) over a conveyor belt. The belt had a variable speed and had been calibrated so that speed (in m min^{-1}) and the irradiation time (in seconds) could be determined.

The formulation used consisted of:

37.5 g of diesterdiol [13,14] + 10^{-3} mol of sulphonic ester

10 g of Cymel-303, and

10 g of ethyleneglycol monoacetate

The formulations were applied onto Bonder steel plates using Erichsen rods resulting in thin films of 30 and 80 μm thickness, respectively. The plates were then passed under the light source at 2 m min^{-1} (irradiation time of 4 s) and baked for 30 min at 100°C in an oven. The pendulum hardness of the films was determined after 24 h (Erichsen 299 and 300).

2.4.5. Photodecomposition in a model substrate (DPE)

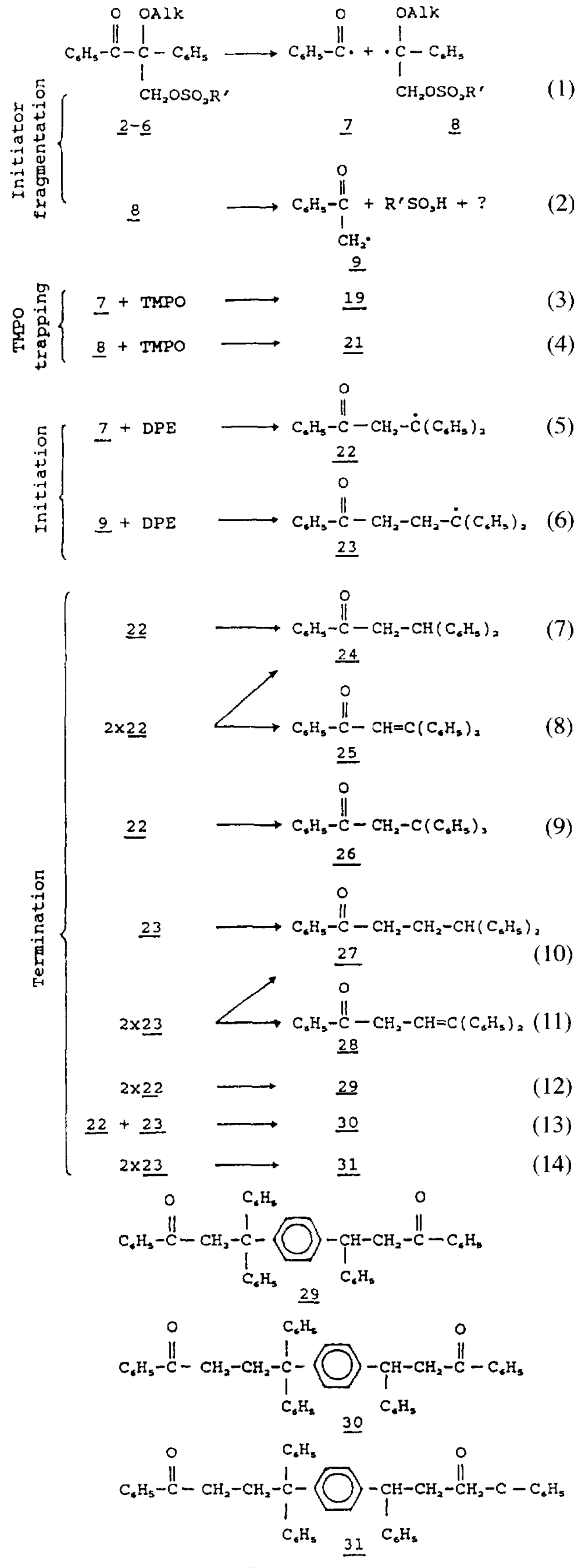
Solutions of sulphonic esters **2b** and **2d** (10^{-2} mol l^{-1}) in benzene in the presence of DPE (10^{-2} mol l^{-1}) were irradiated in a Rayonet photoreactor as described. The work-up procedure on a preparative scale and the isolated reaction products 24–31 (cf. Scheme 1) have been described in detail before [1]. The quantitative irradiations were also carried out as described in Ref. [1].

3. Results

3.1. Results from ESR spectroscopy

At room temperature the ESR spectra of all esters showed the presence of the benzoyl radical **7**. In the presence of MNP the ESR spectra clearly showed the trapped benzoyl radical **14**. In addition the various trapped α,α-disubstituted benzyl radicals **15** were observed as concluded from a comparison with the trapped benzyl radicals **16** and **17** obtained from benzoin methyl ether and α-methylbenzoin methyl ether respectively (cf. Table 2).

It should be emphasized here that we failed to detect the trapped benzoylmethyl radical ($g = 2.0062$, $a_N = 1.44$ mT, and $a_H = 0.77$ (2 H) [17,18]).

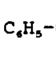


Scheme 1.

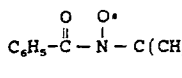
Table 2
Radicals observed by ESR from **2a**, esters **2d**–**6d**, BME and α-MeBME at 20°C

Compound	7	14[a]		15		16/17		
	$a_{H(m)}$	g	a_N	g	a_N	g	a_N	a_H
2a	0.11	2.0073	0.8	2.0066	1.43			
2d	0.11	2.0074	0.8	2.0067	1.39			
4d	0.11	2.0074	0.8	2.0067	1.39			
5d	0.11	2.0073	0.8	2.0066	1.38			
6d	0.11	2.0074	0.8	2.0067	1.39			
BME	0.11	2.0074	0.8			2.0068	1.47	0.2[a]
α-MeBME[b]	0.11	2.0073	0.8			2.0068	1.40	

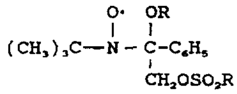
[a] Cf. Ref. [15].
[b] Available from a previous study [16].


$\mathrm{C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\cdot}$

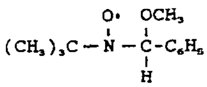
7


$\mathrm{C_6H_5\text{-}\overset{O}{\overset{\|}{C}}-\overset{O\cdot}{\overset{|}{N}}-C(CH_3)_3}$

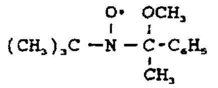
14


$\mathrm{(CH_3)_3C-\overset{O\cdot}{\overset{|}{N}}-\underset{CH_2OSO_2R'}{\underset{|}{\overset{OR}{\overset{|}{C}}}}-C_6H_5}$

15


$\mathrm{(CH_3)_3C-\overset{O\cdot}{\overset{|}{N}}-\underset{H}{\underset{|}{\overset{OCH_3}{\overset{|}{C}}}}-C_6H_5}$

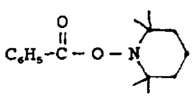
16

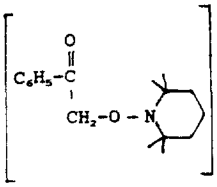

$\mathrm{(CH_3)_3C-\overset{O\cdot}{\overset{|}{N}}-\underset{CH_3}{\underset{|}{\overset{OCH_3}{\overset{|}{C}}}}-C_6H_5}$

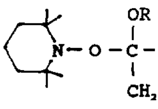
17

3.2. Results from TMPO trapping

TLC analyses of the irradiation mixtures of esters **2**–**6** clearly showed the well known trapped benzoyl radical **19** (cf. Refs. [1,19]). An additional product was observed in each case which proved to be different from the trapped benzoylmethyl radical **20** as concluded from a parallel experiment run with ester **1b** (cf. Ref. [1]), and was considering also the ESR results, tentatively assigned to the trapped α,α-disubstituted benzyl radical **21**.


19


20


21

3.3. Results from crosslinking of TMPTA

All sulphonic esters induced crosslinking of TMPTA on irradiation. Esters **2**–**6** showed similar induction periods T_{ind} and relative polymerization rates R_p within the limits of accuracy suggesting that varying the ether group from methyl to isobutyl does not really affect the performance as photoinitiator for free radical polymerizations (see Table 3). Comparing sulphonic esters **2**–**6** with sulphonic esters **1b**–**1d** of α-hydroxymethylbenzoin, however, shows the former to have shorter T_{ind} (average of 15.1 vs. 25.1 s) but lower relative rates of polymerization (average of 3.76 vs. 4.99).

3.4. Results from pH measurements

All the different sulphonic esters on irradiation apparently produced approximately equal amounts of sulphonic acid, implying that this method, although suitable to indicate acid generation, is not able on this time scale (a few minutes) to distinguish between the different esters (see Table 4).

3.5. Results from melamine curing

The various sulphonic esters on irradiation (4 s) apparently produce approximately equal amounts of sulphonic acid, which after baking for 30 min at 100°C leads to a comparable pendulum hardness (Table 5), in excellent agreement with the results of Section 3.4.

3.6. Photodecomposition in a model substrate (DPE)

Esters **2b** and **2d** were photolyzed in benzene solution in the presence of DPE.

The products formed fall into two categories, as enumerated below.

(i) Products not containing the DPE moiety, i.e., products of ‘wastage’ from the viewpoint of initiation, such as benzaldehyde **10**, benzil **11**, benzophenone **12**, and acetophenone

Table 3
Crosslinking of TMPTA in solution

Compound	T_{ind} (s)	$tg\alpha$	$10^{-3} R_p$ (mol l^{-1} s^{-1})
1b	25.3	11.2	5.0
1c	24.9	11.0	4.90
1d	25.2	11.4	5.08
2b	14.5	8.5	3.79
2c	14.8	8.2	3.66
2d	14.4	8.5	3.79
3b	16.2	8.3	3.71
4b	18.4	8.1	3.62
4c	14.0	8.6	3.84
4d	13.1	8.6	3.84
5b	14.5	9.1	4.06
6b	16.0	8.0	3.57
BIPE[a]	35.5	7.8	3.38

[a] Benzoin isopropyl ether, the calibrated standard applied [12].

Table 4
Photoinduced generation of sulphonic acids from some sulphonic esters

Ester	Irradiation time			
	1 min		5 min	
	pH	[H$^+$]	pH	[H$^+$]
1b	3.25	5.6×10^{-4}	2.81	1.6×10^{-3}
2b	3.34	4.6×10^{-4}	2.80	1.6×10^{-3}
3b	3.78	1.7×10^{-4}	2.85	1.4×10^{-3}
4b	3.48	3.3×10^{-4}	2.76	1.7×10^{-3}

Table 5
Melamine curing by photoinduced generated sulphonic acids from some sulphonic esters

Ester	Pendulum hardness (s)			
	Film thickness 30 μm		Film thickness 80 μm	
	Δ^{a}	$h\nu/\Delta^{b}$	Δ^{a}	$h\nu/\Delta^{b}$
1b	wet film	356	wet film	312
1c	wet film	346		
1d	wet film	358		
2b			wet film	316
2c	wet film	334		
3b			wet film	320
4b	wet film	340	wet film	311
4c	wet film	324		

[a] Baking for 30 min at 100°C without prior irradiation.
[b] Irradiation (4 s) followed by baking for 30 min at 100°C.

13. Some methyl benzoate was also formed, presumably originating from radical **8**.

(ii) Products resulting from the addition of radicals **7** and **9**, respectively to the carbon–carbon double bond of DPE. Both primary adduct-radicals **22** and **23** undergo the usual termination reactions, such as hydrogen-abstraction, disproportionation, coupling and cross-coupling as indicated in Scheme 1.

A satisfactory material balance was obtained for both the benzoyl (90 and 93%) and the benzoylmethyl (97 and 95%) fragments generated from **2b** and **2d**, respectively (cf. Tables 6 and 7). The initiating efficiencies f_{p} defined as the fraction of the generated radicals that initiate the polymerization could be calculated from the products.

Thus for radical $\mathbf{7}\, f_{\mathrm{p7}}=\Sigma(\mathbf{24},\mathbf{25},\mathbf{26},\mathbf{29},\mathbf{30})/2_{\mathrm{convd.}}=0.60$ and 0.63 for **2b** and **2d**, respectively, which is in excellent agreement with previous results obtained with esters **1b** and **1d** (0.61 and 0.57, respectively [1]).

Likewise for radical $\mathbf{9}\ f_{\mathrm{p9}}=\Sigma(\mathbf{27},\ \mathbf{28},\ \mathbf{30},\ \mathbf{31})/2_{\mathrm{convd.}}=0.49$ and 0.52 for **2b** and **2d**, respectively, compared with 0.59 and 0.53 for esters **1b** and **1d**, respectively [1]. From these values the ratio of contributions to the initiation of radicals **7** and **9** can be calculated to be $f_{\mathrm{p7}}/f_{\mathrm{p9}}=1.22$ and 1.21 for **2b** and **2d**, respectively.

4. Discussion

The ESR spectra showed that the sulphonic esters **2–6** undergo photoinduced α-cleavage into benzoyl radicals **7** and α-alkoxy-α-sulphonyloxymethylbenzyl radicals **8** like the sulphonic esters **1** [1]. The fate of the α,α-disubstituted benzyl radicals **8** now is particularly interesting in comparison with the corresponding α-hydroxy-α-sulphonyloxy-methylbenzyl radicals **8′** derived from the sulphonic esters **1** (cf. Scheme 2).

Table 6
The photodecomposition of **2b** in the presence of DPE[a]

Product	Amount of product (mmol)	Corresponding amount of **7** (mmol)	Corresponding amount of **9** (mmol)	Corresponding amount of DPE (mmol)
2b	19.7	19.7	19.7	
10	trace	trace		
11	0.1	0.2		
12	0.8	0.8		
13	3.5		3.5	
Me benzoate	0.8		0.8	
DPE	8.4			8.4
24	1.5	1.5		1.5
25	1.1	1.1		1.1
26	0.4	0.4		0.4
27	0.6		0.6	0.6
28	2.0		2.0	2.0
29	0.8	1.6		1.6
30	1.6	1.6	1.6	3.2
31	0.4		0.8	0.8

[a] The starting solution contained 30 mmol of both **2b** and DPE. The irradiation time was 4 h.

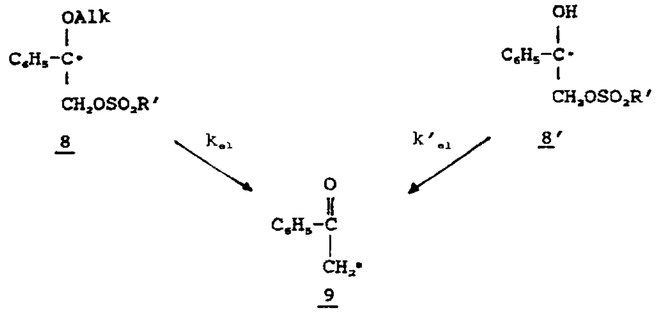
Table 7
The photodecomposition of **2d** in the presence of DPE[a]

Product	Amount of product (mmol)	Corresponding amount of **7** (mmol)	Corresponding amount of **9** (mmol)	Corresponding amount of DPE (mmol)
2d	20.7	20.7	20.7	
10	trace	trace		
11	0.2	0.4		
12	0.8	0.8		
13	2.4		2.4	
Me benzoate	0.6		0.6	
DPE	9.8			9.8
24	1.3	1.3		1.3
25	1.0	1.0		1.0
26	0.4	0.4		0.4
27	0.7		0.7	0.7
28	1.7		1.7	1.7
29	0.8	1.6		1.6
30	1.6	1.6	1.6	3.2
31	0.4		0.8	0.8

[a] The starting solution contained 30 mmol of both **2d** and DPE. The irradiation time was 4 h.

The ESR spectra showed, in addition to the well-known MNP-trapped benzoyl radical **14**, the presence of radicals assigned to the MNP-trapped α,α-disubstituted benzyl radicals **15** upon a comparison with the corresponding MNP-trapped α,α-disubstituted benzyl radicals obtained from α-hydroxymethylbenzoin methyl ether **2a**, benzoin methyl ether (BME), and α-methylbenzoin methyl ether (α-MeBME), respectively.

The TMPO-trapping experiments showed, in addition to the known trapped benzoyl radical **19**, one other product,



	Method	
8 trapped by MNP, trapped 9 not observed	ESR spin-trapping	8′ not trapped by MNP, but 9 is trapped
8 trapped by TMPO, and trapped 9 not observed	TMPO trapping	no redox reaction of 8′ with TMPO, but trapped 9 observed
pH decrease with time, generation of acid	pH vs time	pH decrease with time, generation of acid
curing of Melamine i.e. generation of acid	Melamine-curing	curing of Melamine, generation of acid
7 and 9 "initiate" $f_{p7}/f_{p9}=1.22$, i.e. 9 generated slower than 7.	DPE trapping	7 and 9 "initiate" $f_{p7}/f_{p9}=1$, 7 and 9 equally reactive and generated equally fast

Scheme 2.

different (on TLC) from the previously observed 2,2,6,6-tetramethyl-1-piperidyloxymethyl phenyl ketone **20** (the trapped benzoylmethyl radical [1]), which is tentatively assigned to the trapped α,α-disubstituted benzyl radical **21**. Coupling with TMPO is the expected reaction of the α,α-disubstituted benzyl radicals **8** considering previous results with some benzoin ethers [19]. The results of both the pH measurements vs. irradiation time, and the acid-catalyzed melamine curing indicate, however, that at some time elimination of sulphonic acid from radicals **8** must have occurred.

The coupling of carbon-centred radicals with TMPO (reaction 4) has been reported to proceed at a rate of $k_c = 10^8$–10^9 l mol^{-1} s^{-1} [20,21]. From the ratio of rates of the coupling and the elimination reaction (estimated lower limit of 10), applying an average value of 5×10^8 for k_c and a TMPO concentration of 3×10^{-2} mol l^{-1} we arrive at

$$\text{Rate}_c/\text{Rate}_{e1} = k_c x[8]x[\text{TMPO}]/k_{e1}x[8] \geqslant 10$$

$$10xk_{e1} \leqslant k_c x[\text{TMPO}]$$

$$k_{e1} \leqslant 1.5x10^6 s^{-1}$$

which is clearly lower than was previously estimated for the corresponding radicals **8′** from esters **1** ($k_{e1}' = 1.5\times10^8$ s^{-1} [1]).

Supporting evidence is provided by the results of the TMPTA crosslinking. The induction period T_{ind}, due to scavenging of the first radicals by the oxygen present (both dissolved and from the surrounding air) before the onset of the crosslinking, is considered to represent the rate of radical formation. The rate of crosslinking R_p is considered to represent the sum of the initiation-reactivities of the radicals formed.

Esters **2** now show a shorter T_{ind} than esters **1** as expected since benzoin ethers show a shorter T_{ind} than benzoin (H.J. Hageman, unpublished observations). Esters **2** show a lower R_p than esters **1** also as expected on account of the lower rate at which the reactive radicals **9** are being generated from the distinctly less reactive α,α-disubstituted benzyl radicals **8** (cf. Ref. [16]).

The DPE trapping experiments provide additional evidence. Radicals **7** and **9** apparently initiate the 'polymerization' as observed before [1]. When comparing the partial contributions of radicals **7** and **9**, respectively to the initiation it is noteworthy that the f_{p7}/f_{p9} ratio is 1.22 in the case of esters **2**, i.e., radical **7** showing the greater contribution. Since it has been established that radicals **7** and **9** are equally reactive towards the olefinic double bond of DPE [1], the ratio of 1.22 can only be explained by a slower generation of radicals **9**.

The formation of products **29–31** resulting from coupling and cross-coupling respectively of primary adduct-radicals **22** and **23** has been commented upon previously [1]. The complications associated with the formation of these 'anomalous' termination products was in fact the reason to the use of 1,1-di-(*p*-tolyl)-ethylene (DTE) as a more suitable model substrate [7]. However, we still feel that DPE served a purpose, i.e., the products **29–31** are actually formed only in the absence of radicals that have a pronounced tendency to terminate the polymerization, such as α-alkoxybenzyl radicals [16,22], α-alkoxy-α-methylbenzyl radicals [16], and to a lesser extent α,α-dialkoxybenzyl radicals [16].

Finally it must be mentioned that up till now we failed to detect any product that would reveal the fate of the alkyl ether part of radicals **8** during or after the elimination of the sulphonic acid.

References

[1] H.A. Gaur, C.J. Groenenboom, H.J. Hageman, G.T.M. Hakvoort, P. Oosterhoff, T. Overeem, R.J. Polman, S. v.d. Werf, Makromol. Chem. 185 (1984) 1795.

[2] H.G. Heine, H. Rudolph, H.J. Kreuder, Ger. Offen. 1.919.678, 1970.

[3] H. Rudolph, H.J. Rosenkranz, H.G. Heine, Appl. Polym. Symp. 26 (1975) 157.

[4] H.J. Hageman, W.J. de Klein, E.A. Giezen, EP 37.152, 1981.

[5] H.J. Hageman, L.G.J. Jansen, Makromol. Chem. 189 (1988) 2781.

[6] S. Adam, dissertation, Univ. of Karlsruhe, 1973.

[7] J.E. Baxter, R.S. Davidson, H.J. Hageman, T. Overeem, Makromol. Chem. 189 (1988) 2769.

[8] H. Muller, H.J. Traencker, H. Habetz, H. Pelster, Ger. Offen. 2.420.474, 1975.

[9] H.J. Hageman, Makromol. Chem., Rapid Commun. 2 (1981) 517.

[10] H. Hoffmann, H. Hartmann, C.H. Krauch, O. Volkert, US 3.689.565, 1972.

[11] C. Decker, M. Fizet, Makromol. Chem., Rapid Commun. 1 (1980) 637.

[12] J.E. Baxter, R.S. Davidson, H.J. Hageman, Polymer 29 (1988) 1569.

[13] J.B. Reesink, H.J. Hageman, U.E. Wiersum, EP 44.115, 1982.

[14] W.J. Mijs, W.J. Muizebelt, J.B. Reesink, J. Coat. Technol. 55 (697) (1983) 45.

[15] A. Ledwith, P.J. Russell, L.H. Sutcliffe, J. Chem. Soc., Perkin Trans. 2 (1972) 1925.

[16] C.J. Groenenboom, H.J. Hageman, T. Overeem, A.J.M. Weber, Makromol. Chem. 183 (1982) 281.

[17] C.J. Groenenboom, H.J. Hageman, P. Oosterhoff, T. Overeem, J. Verbeek, J. Photochem. Photobiol. A: Chem., in press.

[18] I. Rosenthal, M.M. Mossaba, P. Riesz, Can. J. Chem. 60 (1982) 1486.

[19] H.J. Hageman, T. Overeem, Makromol. Chem., Rapid Commun. 2 (1981) 719.

[20] K.D. Asmus, S. Nigam, R.L. Willson, Int. J. Radiat. Biol. Rel. Stud. Phys. Chem. Med. 29 (1976) 211.

[21] S. Nigam, K.D. Asmus, R.L. Willson, J. Chem. Soc., Faraday Trans. 1 (1976) 2324.

[22] H.J. Hageman, F.P.B. v.d. Maeden, P.C.G.M. Janssen, Makromol. Chem. 180 (1979) 2531.