Radical generation from photoinitiator (IC 2959) decomposition and radical addition to acrylate. A laser photolysis Fourier transform electron paramagnetic resonance study

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The decomposition of the photoinitiator 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methylpropan-1-one (trade name IC 2959) was studied using time-resolved laser photolysis Fourier transform electron paramagnetic resonance. The emissive CIDEP polarization of both benzoyl and 2-hydroxy-2-propyl radicals indicates the triplet state of IC 2959 as the radical precursor. By adding *n*-butyl acrylate it was shown that the addition of 2-hydroxy-2-propyl radicals to the acrylate double bond is two orders of magnitude faster than that of benzoyl radicals.

Introduction

The photoinitiator 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methylpropan-1-one with the trade name IC 2959 enjoys widespread application in aqueous and water-miscible photocurable systems. It is well documented[1] that α-cleavage from the excited triplet state is the main photochemical reaction. In a first step, photons are absorbed by the photoinitiator, generating its triplet state, which decomposes into a pair of radicals. *para*-substituted benzoyl and 2-hydroxy-2-propyl radicals are expected to be formed as primary products. This has been concluded from photolysis products studied using ^{1}H-NMR-CIDNP[2] and other analytical methods.[3]

The photodecomposition of 2,2-dimethoxy-2-phenylacetophenone (trade name IC 651),[4,5] 1-hydroxycyclohexyl phenyl ketone (trade name IC 184)[6] and pivalophenone[7] followed by time-resolved optical detection revealed the existence of benzoyl radicals. By means of electron pulse radiolysis with optical detection, benzoyl radicals have been observed after dissociative electron attachment to benzoyl chloride.[8] Benzoyl radicals display an unspecific optical absorption in the UV range and a shoulder at 370 nm. A rate constant of 5×10^5 dm^3 mol^{-1} s^{-1} has been determined[6] from the decrease in benzoyl radical (PhC$^\bullet$O) decay upon addition to *n*-butyl acrylate (reaction (1)).

$$\mathrm{PhC^{\bullet}O + CH_2{=}CH{-}COO(CH_2)_3CH_3 \longrightarrow PhCOCH_2{-}C^{\bullet}H{-}COO(CH_2)_3CH_3} \quad (1)$$

The addition of benzoyl radicals to methyl methacrylate occurs at a rate constant of 2×10^5 dm^3 mol^{-1} s^{-1}.[5]

The counterpart of the benzoyl radical in the pair formed after the decomposition of IC 2959, the 2-hydroxy-2-propyl radical absorbs at lower wavelengths and could not be observed by optical detection methods. It is widely assumed[1] that 2-hydroxy-2-propyl radicals are less reactive than benzoyl radicals and do not contribute to the initiation of the polymerization of acrylates. But, in this study we have shown that the addition of 2-hydroxy-2-propyl radicals to acrylates is faster by two orders of magnitude than that of benzoyl radicals.

Using laser photolysis with Fourier transform electron paramagnetic resonance (FT-EPR), well-resolved radical spectra can be obtained on a nanosecond time scale. In this respect, FT-EPR represents a valuable complementary detection method to optical spectroscopy. Benzoyl and 2-hydroxy-2-propyl radicals, generated from the decomposition of IC 2959, show well resolved and separated EPR spectra. The formation pathway and kinetics of both radicals can thus be studied simultaneously. The aim of this study was to directly characterize the structure of the primary radicals formed after the photodecomposition of IC 2959 and to follow the initiation of the acrylate polymerization.

Experimental

The laser photolysis experiments were performed using a 308 nm excimer laser produced by Lambda Physik (LPX 105ESC). An energy of 20–50 mJ per pulse and a pulse width of 10 ns were used. FT-EPR spectra were recorded with a home-made X-band spectrometer[9] with a Bruker split-ring module ER 4118 X-MS-5W. The microwave pulse was generated by a fast ECL-PIN diode (rise time 4 ns) and amplified by a 20 W travelling wave tube amplifier 8000H (Hughes Aircraft Comp.). The pulse width of the $\pi/2$ microwave pulse was 48 ns. The EPR data were extrapolated into the dead time (~100 ns) by the Linear Prediction Singular Value Decomposition method (LPSVD),[10] which yields spectra with a correct baseline and correct intensities.

IC 2959 (Ciba) and *n*-butyl acrylate $CH_2{=}CHCOOC_4H_9$ (UCB) were used without further treatment. 1,2-Dimethoxyethane (Merck-Schuchardt, purity > 99%) containing 10% distilled water was used as a solvent meeting the demands of FT-EPR. The concentration of IC 2959 was usually 10^{-3} mol dm^{-3}, corresponding to an optical density of 0.07 for a 2 mm optical path length at 308 nm. Oxygen was removed from the solution by bubbling with argon.

In order to avoid the accumulation of stable photolysis products, the degassed solutions flowed through the sample cell (quartz tube with an inner diameter of 2.0 mm) at a rate of approximately 1–2 ml min^{-1}. The number of repetitions per spectrum ranged from 100 to 500.

Results

The FT-EPR spectrum taken 96 ns after 308 nm laser photolysis of 10^{-3} mol dm^{-3} IC 2959 in 1,2-dimethoxyethane–water solution is presented in Fig. 1. The whole spectrum is emissive and consists of two parts. The first is a central triplet ($g = 2.0007$) with a binomial intensity ratio and a splitting of $a(2H_m) = 0.114$ mT. Each triplet line shows a poorly resolved

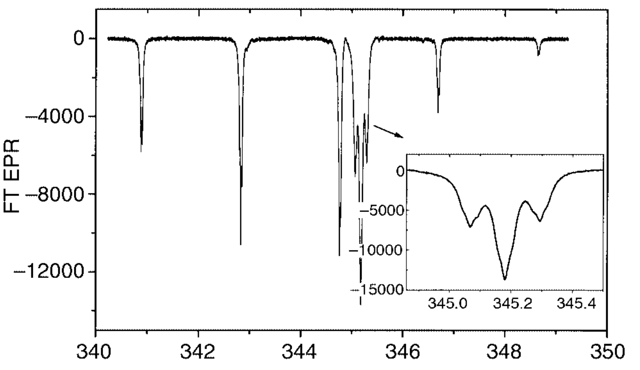

Fig. 1 FT-EPR spectra of *para*-substituted benzoyl and 2-hydroxy-2-propyl radicals produced in a 1,2-dimethoxyethane–water (90 : 10) mixture with 0.001 mol dm^{-3} 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methylpropan-1-one (IC 2959) as solute. Spectra were taken 96 ns after a 308 nm laser pulse. The insert shows an expanded spectrum of the *para*-substituted benzoyl radical.

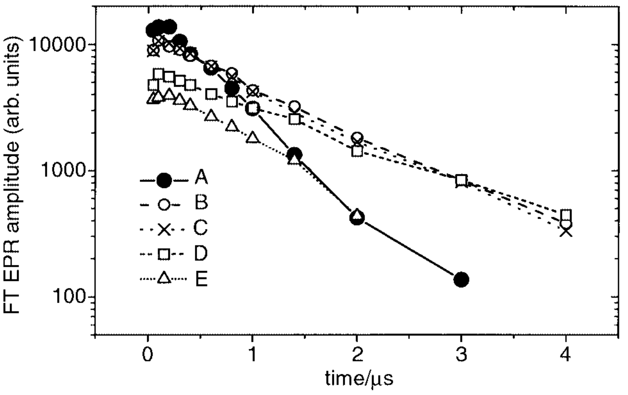

Fig. 2 FT-EPR amplitudes as a function of time: decay of benzoyl (A) and 2-hydroxy-2-propyl radicals (B = 4th, C = 3rd, D = 2nd, E = 5th line).

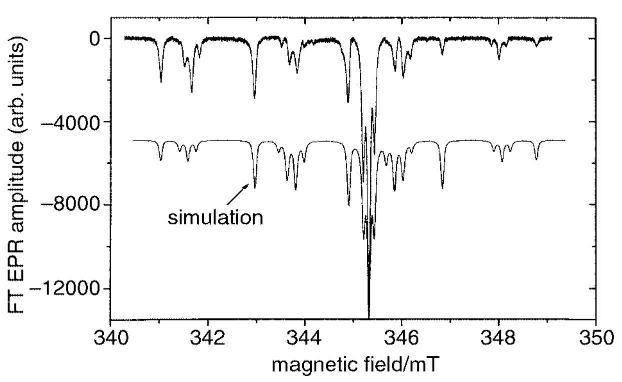

Fig. 3 Experimental and simulated FT-EPR spectra of benzoyl, 2-hydroxy-2-propyl and *n*-butyl acrylate radicals. Experimental spectra were taken 400 ns after a 308 nm laser flash in the system 1,2-dimethoxyethane–water (90 : 10) with 0.001 mol dm^{-3} IC 2959 and 0.08 mol dm^{-3} *n*-butyl acrylate added. The parameters of simulated spectra are given in the text.

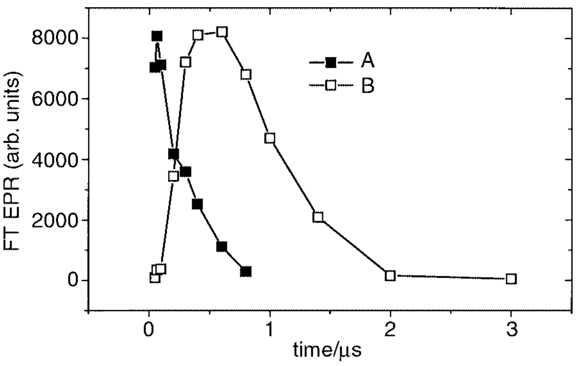

Fig. 4 Time profile of the 4th line of the 2-hydroxy-2-propyl radical (A) and the area under the power spectrum of the *n*-butyl acrylate radical line group (B).

triplet substructure with $a(2H_o) = 0.02$ mT. The benzoyl radical is responsible for this part of the spectrum and the splittings originate from the two *meta* (*m*) and two *ortho* (*o*) hydrogens. Hyperfine coupling constants and the *g*-factor tally closely with data given by Leopold and Fischer.[11]

The second part of the EPR spectrum shown in Fig. 1 consists of five equidistant narrow line groups with $a(6H, CH_3) = 1.94$ mT, each split into a doublet with $a(1H, OH) = 0.024$ mT and with second-order hfs splittings. The five line groups represent the central part of a septet belonging to the 2-hydroxy-2-propyl radical, the counterpart of the benzoyl radical. Both outer septet lines are located beyond the range of the magnetic field of the FT-EPR spectrometer. The six protons of two CH_3 groups and the proton of the OH group are responsible for septet and doublet splitting, whereas the additional splitting is caused by hfs second-order effects. The intensity ratio of five lines observed from the septet is not binomial because radical pair polarization (CIDEP) is observed.

At 96 ns after the laser flash, the areas beneath the spectra corresponding to the benzoyl radical and 2-hydroxy-2-propyl radical are in the ratio of 1 : 0.998. This is close to the theoretically expected value of 1 : 0.969 if the outer lines of the 2-hydroxy-2-propyl radical are omitted. Hence at this time the concentrations of both radicals are almost equal.

The decay of the EPR signal amplitude can be followed for both radicals between 64 ns and up to 3 μs when the signal disappears in noise. As illustrated in Fig. 2, the decay of both radical signals can be approximated by a simple exponential function. The first-order rate constants obtained are 1.5×10^6 s^{-1} and 0.9×10^6 s^{-1} for the benzoyl and the 2-hydroxy-2-propyl radical, respectively.

The addition of *n*-butyl acrylate (concentrations of 2, 4, 8 and 10×10^{-2} mol dm^{-3}) leads to the appearance of four new groups of lines (Fig. 3). Assuming radical addition to the double bond of butyl acrylate, the EPR spectrum was simulated for the radical with the structure of $R–CH_2–CH^{\bullet}COOCH_2CH_2CH_2CH_3$ and splittings of $a(CH_2) = 2.14$ mT, $a(CH) = 2.01$ mT and $a(RCOOCH_2C_3H_7) = 0.17$ mT. The good agreement between experimental and simulated spectra is illustrated in Fig. 3, where benzoyl, 2-hydroxy-2-propyl and acrylate radicals are shown. The line groups of the 2-hydroxy-2-propyl radical are broadened (*cf.* Fig. 1) and decrease in intensity. This indicates a decay mechanism with the acrylate.

Fig. 4 shows the area of the FT-EPR power spectrum of the central line of the 2-hydroxy-2-propyl radical (A) and that of the acrylate radical (B) as a function of time. The time profile of the acrylate radical shows the typical behaviour of a reactive intermediate: an initial increase, followed by a maximum and a subsequent decay. Fig. 5 reveals the effect of the *n*-butyl acrylate concentration on the decay kinetics of both primary radical species. Whereas the decay rate of the benzoyl radical remains almost constant and independent of acrylate concentration, the decay rate of the 2-hydroxy-2-propyl radical increases with growing acrylate concentration. The effect of the *n*-butyl acrylate concentration on the exponential decay of the 2-hydroxy-2-propyl radical signal indicates pseudo-first-order rate constants. Fig. 5 shows typical first-order plots for experimental time profiles of the 3rd, 4th and 5th 2-hydroxy-2-propyl radical lines taken at *n*-butyl acrylate concentrations from 0.02 to 0.1 mol dm^{-3}.

Discussion

The FT-EPR spectra of both primary radicals show that the CIDEP triplet mechanism dominates as the polarization

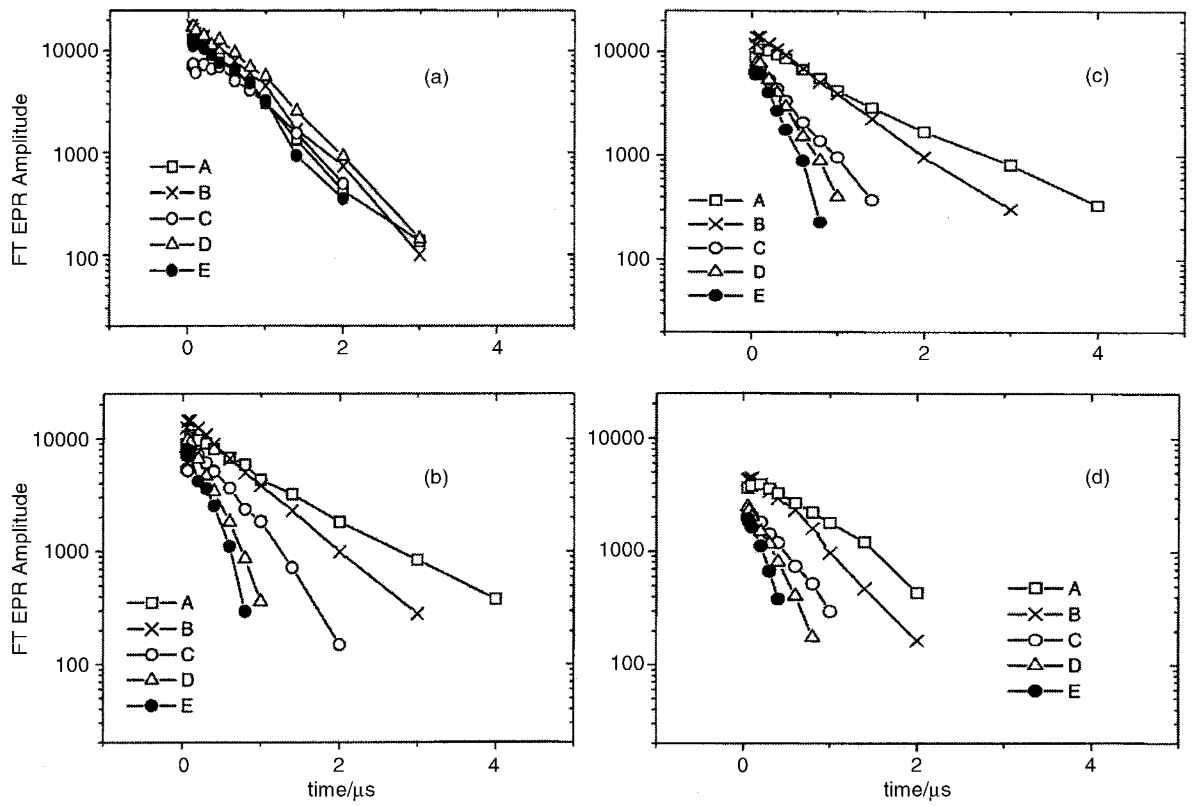

Fig. 5 Effect of the *n*-butyl acrylate concentration (A = 0.00, B = 0.02, C = 0.04, D = 0.08, E = 0.10 mol dm^{-3}) on the decay of the FT-EPR amplitude of the benzoyl radical (a) and of the 4th (b), 3rd (c) and 5th (d) line of the 2-hydroxy-2-propyl radical.

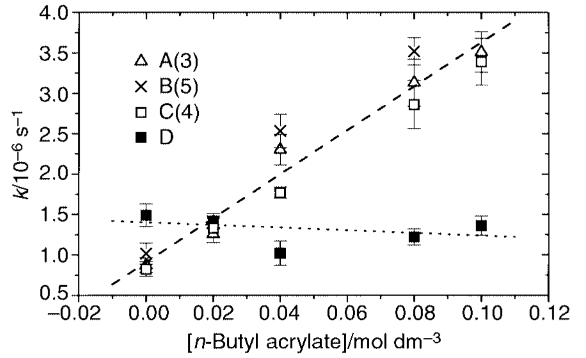

Fig. 6 Plot of the decay rate of the 2-hydroxy-2-propyl radical (A = 3rd, B = 5th, C = 4th line) and the benzoyl radical (D) against *n*-butyl acrylate concentration.

process with a small part of radical pair polarization generated by geminate primary. It is evident from the total emissive character of the spectra that the precursor of this radical pair is a triplet-excited state. It is known from laser photolysis studies[12] that in IC 2959 intersystem crossing $S_1 \rightarrow T_0$ occurs in less than 0.6 ns and the lifetime of the triplet state amounts to 11 ns. Decomposition of the IC 2959 triplet leads to the primary *para*-substituted benzoyl and 2-hydroxy-2-propyl radicals.

The decrease in the FT-EPR signal for both primary radicals may be chiefly explained by the T_1 relaxation process. The radical pair mechanism contributes to a small extent as can be seen from the nonbinomial intensity ratio of 2-hydroxy-2-propyl radical lines. The emissive nature of the whole acrylate radical spectrum also underlines that the triplet mechanism prevails in the polarization, and that polarization persists in addition to the double bond.

The decay rate of the benzoyl radical (1.5×10^6 s^{-1}) was not affected by acrylate concentrations up to 0.1 mol dm^{-3}. This behaviour is expected from the low rate constant of reaction (1). From the Stern–Volmer plot shown in Fig. 6, a rate constant of 2.9×10^7 dm^3 mol^{-1} s^{-1} is deduced for the reaction (2).

$$(CH_3)_2C^{\bullet}OH + CH_2{=}CH{-}COO(CH_2)_3CH_3 \longrightarrow (CH_3)_2COH\,CH_2{-}C^{\bullet}H{-}COO(CH_2)_3CH_3 \tag{2}$$

This closely corresponds to the rate constant value of 2.7×10^7 dm^3 mol^{-1} s^{-1} found by Batchelor and Fischer[13] for the addition of the 2-hydroxy-2-propyl radical to methyl acrylate. These rate constants are nearly two orders of magnitude higher than the rate constant for benzoyl radical addition to acrylates (reaction (1)). Therefore, the main initiating species in acrylate formulations containing IC 2959 as photoinitiator ought to be the 2-hydroxy-2-propyl radical rather than the benzoyl radical.

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