

Electron Spin Resonance and Laser Flash Photolysis Study of Radical Addition to Vinyl Acrylate and Related Alkenes[†]

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Addition of two radicals (diphenyl phosphinoyl and 2-hydroxy-2-propyl) to the bifunctional alkene, vinyl acrylate, was studied by both time-resolved (TR) and steady-state (SS) ESR and laser flash photolysis (LFP). The adduct radicals are predominately a result of tail addition (addition to the unsubstituted carbon atom) of the acrylate double bond. Chemical structures of the adducts were established by comparison of the observed ESR spectra with those of adducts of the same reactive radicals to structurally related alkenes, *tert*-butyl acrylate and vinyl pivalate, which have only one type of double bond. Adducts of bulky phosphinoyl radicals to the acrylates demonstrate hindered rotation and a *cis*–*trans* isomerization at room temperature. The structure of the adduct radicals and the reactivity of the two radicals are discussed. Absolute rate constants for the addition of the phosphinoyl radical to the alkenes were measured by LFP in ethyl acetate at 296 K. A rate constant of $k_{\text{add}} = (33 \pm 1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ was found for vinyl acrylate. The latter value is ~ 1.5 times higher than that for *tert*-butyl acrylate ($k_{\text{add}} = (22 \pm 1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) and ~ 17 times higher than that for vinyl pivalate ($k_{\text{add}} = (2.0 \pm 0.1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$). These rate constants are consistent with conclusions derived from the ESR data. The results provide some insights into free radical polymerization of vinyl acrylate and vinyl ethers.

1. Introduction

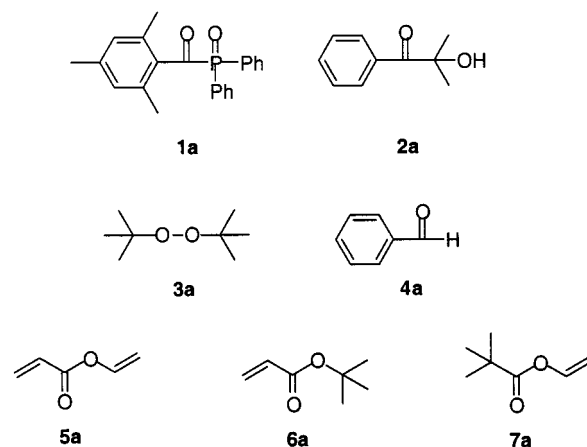
The addition of radicals to alkenes in order to initiate polymerization is one of the most important reactions in polymer chemistry and in organic synthesis, and has been reviewed in a number of articles^{1–7} and books.^{8–10} Radical addition reactions have been an important area for research in free radical chemistry and in chemical kinetics. The interplay of steric, polar, and substituent effects, as well as reaction enthalpy, affect the rate of addition of a radical to a double bond.^{11–15} Bifunctional alkenes have the potential to produce different kinds of polymers by copolymerization involving two double bonds. Of particular interest is the possibility of using bifunctional alkenes for generating polymers with active vinyl groups. Spectroscopic analysis [¹H NMR and infrared spectroscopy (IR)] of vinyl acrylate and the resulting polymers produced by nonradical polymerization^{16,17} and free radical polymerization^{16,18} showed unreacted vinyl ether groups attached to the polymer backbone. Time-resolved ESR offers a method for direct detection and characterization of radical structure and reactivity, but requires strong spin polarization of the radicals.^{19–25} Strong polarization of radical adducts is assured if the photoinitiators produce strong polarized radicals, which in turn, undergo fast addition to alkenes. Upon photolysis (2,4,6-trimethylbenzoyl)diphenylphosphine oxide^{26–28} and 2-hydroxy-2-methyl-1-phenyl-propan-1-one,^{29–33} which are widely used as photoinitiators for free radical polymerization, produce strongly polarized radicals that undergo fast addition to acrylate and, therefore, were chosen as photoinitiators for our studies. The time window for radical detection

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SCHEME 1: Structures of Compounds Used



is generally limited by the decay of spin polarization, not by the decay of radical concentration. On the other hand, steady-state ESR has the opportunity to study free radicals without the need for spin polarization, but on a time scale determined by the radical lifetimes (several hundred μs to ms ³⁴). The combination of TR–CW ESR and SS–CW ESR, which provides a means of tracking radicals over the time scale from hundreds of nanoseconds to milliseconds, was therefore employed in this investigation.

We report here a systematic study using standard photoinitiators (Scheme 1) of the addition of two well-studied radicals (phosphinoyl^{35–37} and 2-hydroxy-2-propyl^{38–40}) to the bifunctional monomer, vinyl acrylate. The radicals were photochemically generated from precursors that are known to give strong spin polarized radicals.^{37,41,42} TR- and SS-ESR techniques were used to identify and characterize the structure of the adduct

radicals for the initial stages of polymerization. The results of the ESR study were compared with the absolute rate constants for the addition of phosphinoyl radicals to alkenes measured by laser flash photolysis (LFP) experiments.

2. Experimental Section

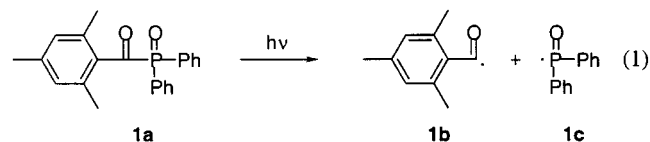
2.1. Materials. The structures of the photoinitiators, thermal initiators, and monomers employed in the production of radicals are shown in Scheme 1. (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (**1a**) obtained from BASF was recrystallized from diethyl ether (Aldrich). 2-Hydroxy-2-methyl-1-phenyl-propan-1-one (**2a**) from Ciba Specialty Chemicals, *tert*-butyl peroxide (**3a**) and benzaldehyde (**4a**) from Aldrich were used as received. HPLC grade ethyl acetate was obtained from Fisher and was used as solvent without further purification. Vinyl acrylate (**5a**), *tert*-butyl acrylate (**6a**), vinyl pivalate (**7a**) (all from Aldrich), were purified by treatment with inhibitor remover prior to use.

2.2. Techniques and Measurements. The time-resolved continuous wave (TR-CW) ESR equipment was described in detail earlier,^{43,44} and consists of a Bruker ER 100D X-band ESR spectrometer (Bruker ESP 300 console and a Bruker ER 100D X-band magnet), an EG&G PAR boxcar integrator model 4402 and signal processor model 4402. Typically, 1024–8192 points were recorded over a period of 10 min. Integration over different time windows was made after the laser pulse was performed. The steady-state (SS) ESR spectra were recorded with a Bruker EMX spectrometer (Bruker EMX 113 console and ER 070 6" magnet) over ca. 2 h. Prior excitation was performed with a Continuum Surelite I Nd:YAG laser ($\lambda = 355$ nm, 8 ns, 30 Hz, 9 mJ/pulse) for the time-resolved experiments or with a xenon lamp (400 W, $\lambda > 280$ nm) for the steady-state measurements. A quartz flow cell with a 0.3 mm path length was used in combination with a syringe pump for both TR and SS experiments. Solutions of the photoinitiators were prepared at concentrations such that the absorbance was ca. 0.3–0.5 at the excitation wavelength. Samples were prepared fresh and deoxygenated by bubbling with argon for at least 30 min. All experiments were carried out in ethyl acetate at (296 ± 2) K. Flow rates were measured between 1 and 15 mL/min. Hyperfine coupling (HFC) constants were determined by comparing simulated ESR spectra (WINEPR SimFonia, Version 1.25, Bruker Analytische Messtechnik GmbH) with the experimental spectra.

Laser flash photolysis experiments employed the pulse from a Nd:YAG laser (described above) and a computer-controlled system that has been described elsewhere.⁴⁵ The additional rate constants were measured by using argon-saturated static samples contained in 1×1 cm Suprasil cells, and detection of the absorbance of the phosphinoyl radicals was made at $\lambda = 330$ nm.³⁶

3. Results and Discussion

3.1. TR-ESR Experiments. Reactions of Phosphinoyl Radicals with Alkenes. Photolysis of acylphosphine oxide **1a** (25 mM) in ethyl acetate produce, after laser excitation, a pair of acyl (**1b**) and phosphinoyl radicals (**1c**) as shown in eq 1^{41,46}



The TR-ESR spectrum produced by photolysis of **1a** is presented in Figure 1a. Similar spectra were observed^{43,46–49}

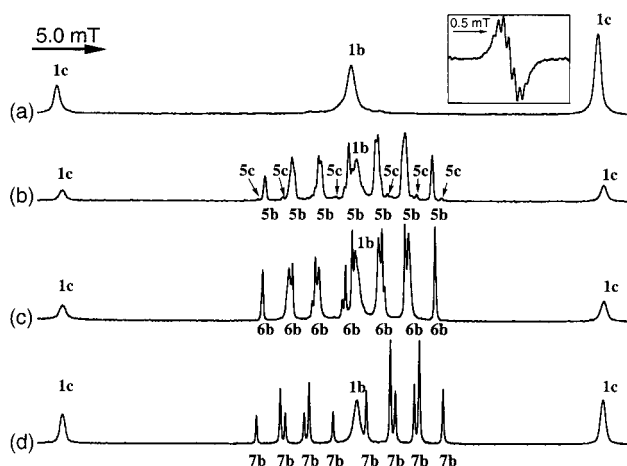


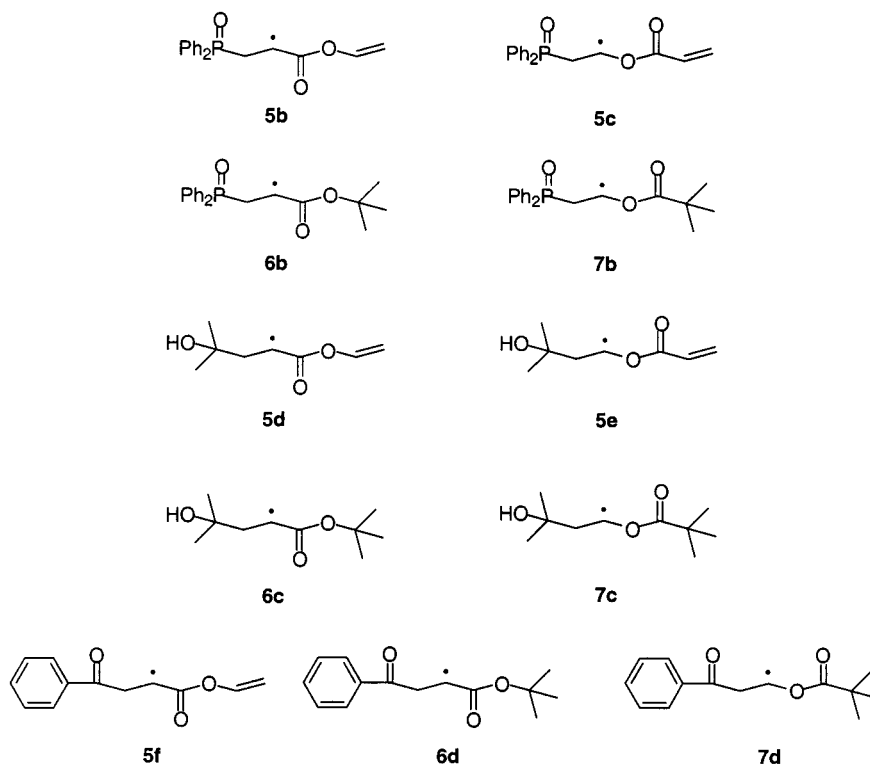
Figure 1. TR-ESR spectra recorded at 200–800 ns following laser excitation of **1a** (25 mM) in ethyl acetate solutions at 296 K in the presence of (a) 0 M alkene, (b) 0.48 M vinyl acrylate (**5a**), (c) 0.68 M *tert*-butyl acrylate (**6a**) and (d) 2.7 M vinyl pivalate (**7a**). The inset shows the SS-ESR spectrum of the high field line of the phosphinoyl radical during continuous photolysis of **1a** (25 mM) in ethyl acetate solution at 296 K.

and analyzed earlier.^{41,48} The spectrum is in polarized net absorption due to the triplet mechanism and shows a broad absorptive singlet near the centerfield assigned to benzoyl radicals **1b** and a doublet of multiplets (see inset in Figure 1) due to the phosphinoyl radical **1c** ($a(P_\alpha) = 36.26$ mT, $a(H_o) = 0.086$ mT, $a(H_m) = 0.072$ mT, $a(H_p) = 0.079$ mT). The observed phosphorus hyperfine coupling constant agrees with values from the literature ($a(P_\alpha) = 36.2$ mT,⁴¹ 36.3 mT⁴⁹). To the best of our knowledge, proton HFC constants for **1c** have not been previously reported.

The TR-ESR spectra recorded at $t \approx 500$ ns after a laser flash of a sample of **1a** in ethyl acetate containing the alkenes **5a**, **6a**, or **7a** are shown in Figure 1b–d. An important feature of the spectra is the presence of the complex absorptive multiplet of components in the center of the spectra. We assign these central components to adducts of photogenerated radicals to a double bond (cf. Scheme 2, structures **5b**, **5c**, **6b**, and **7b**). The absorptive polarization of the phosphinoyl radicals (**1c**) is transferred into the adduct radicals as was shown earlier for similar reactions reported elsewhere.^{35,37,41–43,50–52} At long detection times ($t > 2 \mu\text{s}$) the low field lines of the adduct radicals are in emission and the high field lines are in absorption caused by a late time contribution of the radical pair mechanism (RPM) to the early time triplet mechanism (TM).^{22,53–57} The absorptive doublet, due to unreacted **1c**, is still present in the TR-ESR spectra in the presence of alkenes, but it is weaker and broader than in the absence of alkenes, cf. Figure 1a. The line broadening is a result of the reduced spin–spin relaxation time caused by the addition of the radicals to the double bond.^{49,58–60} The singlet component near center field corresponds to the benzoyl radical **1b**. The intensity of **1b** was found to be practically the same in the presence and in the absence of alkenes. That observation allows the conclusion that adduct radicals (**5b**, **5c**, **6b**, and **7b**) are formed predominately by addition of the phosphinoyl radicals to the double bonds, and that benzoyl adducts are not found during this time period. This conclusion is in agreement with earlier observations.^{37,41}

Photolysis of **1a** in the presence of vinyl acrylate (**5a**) resulted in the formation of two different adduct radicals in a ratio of 20:1, determined from relative intensities of ESR signals, cf. Figure 1b. It follows from the observed ESR spectra that phosphinoyl radicals add to **5a** to produce two structurally

SCHEME 2: Structures of Adduct Radicals



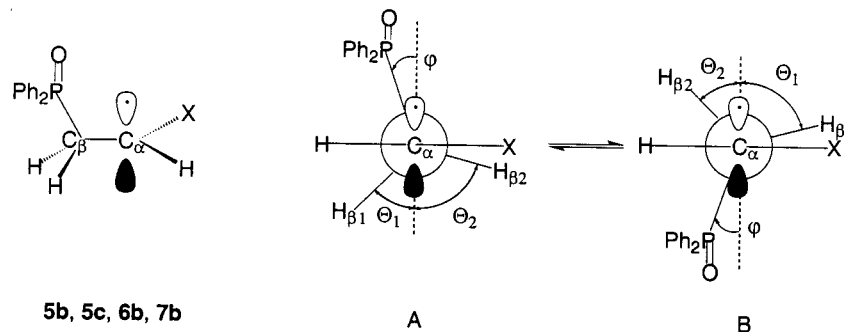
distinct adducts, but that one of the two radical additions is highly preferred. To identify the structures of the two adduct radicals, we obtained ESR spectra of radical adducts for *tert*-butyl acrylate (**6b**) and vinyl pivalate (**7b**) under similar conditions (Figure 1c and 1d). Alkenes **6a** and **7a** can be considered to be derivatives of **5a** formed by replacing one or the other double bond in **5a** by a *tert*-butyl group. The *tert*-butyl group was chosen to avoid hydrogens in the δ -position in the adduct radicals which can have HFC constants in the range of 0.10–0.20 mT⁶¹ and would yield to additional lines and, therefore, lower signal intensities. Because they have only one type of vinyl group, **6a** and **7a** can be used for an unequivocal mode of addition and determination of the HFC constants for the major mode of addition to the acrylate double bond and to the vinyl double bond in **5a**. The ESR spectrum of **6b** is very similar to the adduct spectra with a relatively strong signal intensity in the spectra of adducts of **5a**, indicating that the phosphinoyl radicals **1c** add preferably to the unsubstituted carbon atom of the acrylate group of **5a**. For vinyl pivalate (**7a**), well-resolved ESR spectra were observed for which the ESR lines are observed at essentially the same magnetic field positions as the minor adduct radical in Figure 1b. Therefore, these weak lines are assigned to the adduct radical, **5c**, formed by addition of the phosphinoyl to the unsubstituted carbon atom of the enol ether vinyl group in **5a**. Comparison of the simulated spectra with the experimental spectra provides the HFC constants for **5c**, and are presented in Table 1. The HFC constants obtained in this work are in the expected range for radicals of similar structure to **5c**, cf. ref 61

Upon close inspection of Figure 1c, it is noticed that some components in the ESR spectrum of the acrylate adduct **6b** are broadened. Line broadening effects in the ESR spectra of free radicals have been studied intensively by both experiment and theory.^{62–67} In acrylate adduct radicals, line broadening is usually observed at low temperatures⁶⁶ and interpreted as a dynamic phenomenon responsible for the (line width) alterna-

tions⁶⁷ in the ESR signals. This behavior is a feature of a dynamic two-site exchange process, and the ESR spectra can be described under the assumption of a two-site jump model.⁶⁷ On the basis of this literature precedent, we propose that the most probable reason for the observed broadening is the following: In the adduct radical, **6b**, the phosphorus moiety interacts with the carbonyl bond of the acrylate when these two groups find themselves in proximity of each other. This proximity results in a steric interaction which, in turn, leads to two preferred possible geometric configurations or “two sites” of phosphinoyl vs acrylate group which are presented in Scheme 3. Jumps between these sites are responsible for the broadened lines in the EPR spectrum of **6b**.

Inspection of the models suggests that the two lowest energy conformations of the adduct (**5b**, **5c**, **6b**, **7b**) are those depicted in Scheme 3 (A and B). Presumably, the phosphinoyl group is closer to the hydrogen atom (weaker steric repulsion) rather than to the ester group (stronger steric repulsion) in both conformers. The energies of the two conformers are very similar but there is a high energy barrier in the transition state by going from one conformer to the other resulting from the repulsion of the phosphinoyl group with the substitutions at the α -carbon. The nonzero angle between the phosphinoyl group and the axis of the single occupied orbital (φ , Scheme 3) leads to two different angles Θ , i.e., Θ_1 and Θ_2 , for the hydrogens in the adduct radicals and, therefore, to nonequivalent coupling constants.⁶⁸ In addition, this steric interaction yields to a hindered rotation of the $C_\beta H_2$ -group around the $C_\alpha-C_\beta$ -bond (Scheme 3) and results in broadened lines for the center line of the triplet resulting from the two β -protons.⁶⁷ The existence of the hindered rotation is expressed in the HFC constants for the β -protons. They are in the range 1.60–1.81 mT (Table 1) and they are much smaller than the value of 2.43 mT,⁶⁹ which is expected for hydrogens in the β -position of a free rotating group.

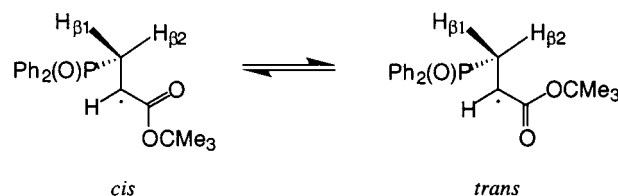
In addition to the existence of two interconverting conformers, the TR-ESR spectra of the *tert*-butyl acrylate adduct radicals

SCHEME 3: Structure and Newman Projection of Two Conformations (A and B) of the Adduct Radicals (X = C(O)OCH=CH₂, OC(O)CH=CH₂, OC(O)CMe₃ and C(O)OCMe₃)**TABLE 1: HFC Constants (± 0.005 mT) of the Identified Adduct Radicals**

Radical	Method	Conformer	HFC constants / mT			
			$a(P_\beta)$	$a(1H_\alpha)$	$a(2H_\beta)$	$a(3H_\beta)$
	TR-ESR		5.609	1.969	1.811	0.06
	SS-ESR		5.584	1.971	1.814	0.06
	TR-ESR	<i>cis</i>	6.003	2.015	1.765	
		<i>trans</i>	6.280	1.986	1.705	
	SS-ESR	<i>cis</i>	5.961	2.011	1.763	
		<i>trans</i>	6.260	1.987	1.694	
	TR-ESR		7.014	1.943	1.663	
	TR-ESR		7.389	1.939	1.603	
	SS-ESR		7.321	1.928	1.600	
	TR-ESR			2.038	2.151	0.055 ^a
	SS-ESR			2.04	2.16	
	TR-ESR			2.028	2.143	
	SS-ESR			2.030	2.134	
						Not detectable
	TR-ESR		1.971	1.741		
	SS-ESR		1.970	1.741		
	TR-ESR		1.976	2.342	0.06 ^a	
	SS-ESR		1.971	2.338		
	TR-ESR		2.07	2.28		
	SS-ESR		2.061	2.267		
			2.067	2.265		
	SS-ESR					
	TR-ESR		1.95	1.88		
	SS-ESR		1.93	1.90		
	SS-ESR		1.917	1.906		

^a Not resolved. ^b Benzoyl radicals were generated by photolysis of **2a** (eq 2). ^c Benzoyl radicals were generated according to eq 3–4.

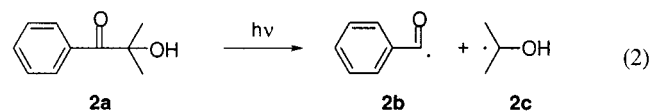
are consistent with the appearance of *cis*–*trans* isomers, Scheme 4, (*cis* refers to structures in which the carbonyl group of the ester moiety is oriented toward the CH₂-group). Analysis of the spectra show that the ratio of *cis*- to *trans*-isomer is ca. 4:1 at room temperature. It has been reported that α -(alkoxycarbonyl)-alkyl radicals have a planar structure and exist as two isomers^{66,70,71} at low temperatures (cf. Scheme 4). This assignment was proven later by computations of methacrylate adduct radicals⁷² and is also known for α -carbonyl radicals.^{73–75} The two isomers manifest small differences in their α - and β -

SCHEME 4: *Cis*- and *trans*-Isomers of Acrylate Adduct Radicals

hydrogen coupling constants and *g*-factors,^{66,70} but these differences are usually smaller than the line width, so it is usually difficult or impossible to distinguish the two isomers based on their ESR spectra. However, the occurrence of a phosphorus atom which possesses a large HFC constant in the β position to the radical center allows the ESR spectra of the two isomers to be distinguished, because they show changes in the phosphorus coupling constants which are higher than the line width. Table 1 shows the coupling constants of the isomers which were assigned by comparison with values from the literature.^{66,72}

The hindered rotation and the *cis*–*trans* isomers of acrylate adduct radicals will be discussed elsewhere in more detail.⁷⁶

Reactions of 2-Hydroxy-2-propyl Radicals with Alkenes. Upon irradiation, **2a** undergoes classical type I cleavage to produce a benzoyl-ketyl radical pair **2b** and **2c** (eq 2).^{77,78} Figure 2 presents TR-ESR spectra of **2a** (240 mM) in ethyl acetate after laser flash photolysis in the absence (Figure 2a) and presence of the alkenes **5a**–**7a** (Figure 2b–d). 2-Hydroxy-2-propyl (ketyl) radicals **2c** are emissively



polarized by the triplet mechanism (Figure 2a) as has been reported earlier.⁴² The emissive polarization is transferred to the adduct radicals by addition of **2c** to the alkenes (**5a**, **6a**, **7a**);⁴² the adducts produced also demonstrate net E-pattern of polarization, cf. Figure 2. The adduct radical **7c** produced only a very weak signal, probably because the addition of the ketyl radical **2c** to vinyl pivalate (**7a**) is relatively slow. For example, it is known that for a compound of similar structure, vinyl acetate, a rate constant of addition of ketyl radicals $k_{\text{add}} = 7500 \text{ M}^{-1}\text{s}^{-1}$ has been found in 2-propanol at 296 K.³⁸ Thus, the rate of addition of 2-hydroxy-2-propyl radicals to **7a** is probably slower than the spin–lattice relaxation of reactive radicals, and spin polarization disappears before addition occurs.

The ESR spectra produced by the photolysis of **2a** in the presence of vinyl acrylate **5a** show the formation of an adduct radical with broad components, cf. Figure 2b. The positions of

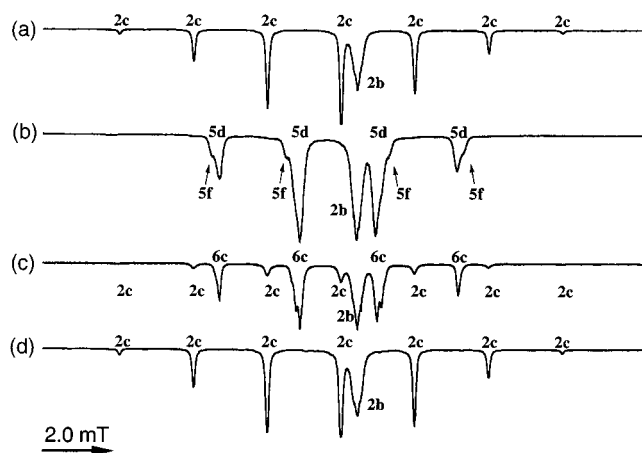


Figure 2. TR-ESR spectra recorded at 200–800 ns following laser excitation of **2a** (240 mM) in ethyl acetate solutions at 296 K in the presence of (a) 0 M alkene, (b) 0.48 M vinyl acrylate (**5a**), (c) 0.68 M *tert*-butyl acrylate (**6a**) and (d) 2.7 M vinyl pivalate (**7a**).

these components are comparable to those observed for spectra of radical adducts **6c** obtained for the photolysis of **2a** in the presence of *tert*-butyl acrylate **6a**. No adduct radical related to the addition of **2c** to the enol ether vinyl bond (**5e**) in vinyl acrylate was observed. Therefore, it is concluded that the 2-hydroxy-2-propyl radicals react preferentially with the unsubstituted carbon atom of the acrylate double bond of vinyl acrylate to form **5d** because (a) the ESR spectra and the coupling constants of **5d** are very similar to those of **6c**; (b) no TR-ESR spectrum was detectable for vinyl pivalate; and (c) the known addition rate constant to methyl acrylate ($k_{\text{add}} = 35 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ in methanol at 295 K⁴⁰) is 5000 times higher than that for addition to vinyl acetate ($k_{\text{add}} = 7500 \text{ M}^{-1}\text{s}^{-1}$ ³⁸). The ESR spectrum of **6c** (Figure 2c) shows the presence of ketyl radicals, which are not present in Figure 2b, even though nearly the same alkene concentrations were used in these experiments. This indicates that the addition of ketyl radicals to vinyl acrylate (**5a**) is much faster than addition of ketyl radicals to *tert*-butyl acrylate (**8**). In addition to the lines assigned above, some additional lines were found in the TR ESR spectra of the adduct radicals **5d** and **6c** and are assigned to signals from **5f** and **6d** which are generated by addition of the benzoyl radical (**2b**) to vinyl acrylate and *tert*-butyl acrylate.

3.2. Steady-State ESR Experiments. The steady-state (SS) ESR technique can detect the radicals over a longer time period (longest times, hundreds of μs to ms) than the TR-ESR (longest times, several μs) because of the field modulation with lock-in detection and, therefore, there is a high sensitivity in terms of concentration of paramagnetic species. Although the TR-ESR technique provides high time resolution (ns to μs), it requires spin polarized radicals to provide sufficient sensitivity for detection of radicals because it employs a direct detection mode (no field modulation). Another difference between TR-EPR and SS-ESR methods is that the latter allows the observation of spectra of radicals at the Boltzmann population; such species are generally invisible in TR-ESR experiments that require a certain degree of spin polarization, i.e., non-Boltzmann populations of spins.⁷⁹ Figure 3 shows SS-ESR spectra (recorded as the first derivative, which is traditional for signal detection by field modulation in steady-state ESR experiments) obtained by the photolysis of **2a** in the presence of alkenes **5a–7a** (only five of the seven lines of **2c** are shown). The spectra result from the addition of ketyl radicals to the alkenes. The lines are assigned the adduct radicals shown in Scheme 2. Table 1 presents the HFC constants extracted from the spectra, which

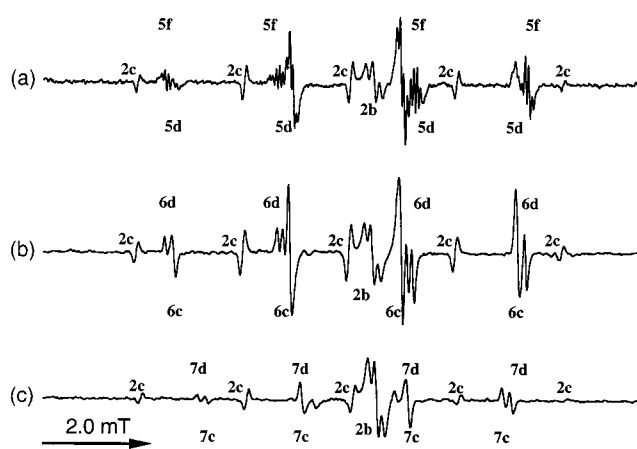


Figure 3. SS-ESR spectra recorded during photolysis of **2a** (240 mM) in ethyl acetate solutions at 296 K in the presence of (a) 0.024 M vinyl acrylate (**5a**), (b) 0.020 M *tert*-butyl acrylate (**6a**) and (c) 0.338 M vinyl pivalate (**7a**).

are in complete agreement with the relevant HFC constants obtained in TR-ESR experiments. Interestingly, the SS-ESR signal of the ketyl radicals appears in emission, not in absorption as expected, if the spins conformed to the Boltzmann population. This observation can be explained as follows: The ketyl radicals **2c** are produced at the moment of α -cleavage (eq 2) with an overpopulation of the corresponding upper Zeeman levels (Triplet mechanism)⁴² resulting in emissive signals (Figure 2a). In the presence of alkenes, they add to the double bond and can have a radical lifetime in the range of the spin polarization relaxation times. In this situation, the emissive polarization does not relax to a Boltzmann distribution and leads to the observed emissive ESR signals of **2c** in the spectra. The resulting adduct radicals do not show up in emission in the SS-ESR spectra because their lifetime is much longer and, therefore, the transferred polarization has time to equilibrate to the Boltzmann distribution. The steady-state vinyl acrylate adduct spectrum (Figure 3a) manifests a coupling of the electron spin with the protons of the vinyl double bond ($a(\text{H}_\delta) = 0.06 \text{ mT}$), which are higher than expected for δ -protons and were also observed for other α -(alkoxycarbonyl)alkyl radicals in solution.⁶¹ Therefore, there must be a significant spin delocalization through the ester group, which should be most efficient for a planar structure of the radical, and confirms the structure in Scheme 4.^{66,70–72}

The SS-ESR spectra of the adduct radicals (Figure 3) manifest additional components in addition to those corresponding to addition of ketyl radicals **2c** to alkenes **5a**, **6a**, and **7a**. These additional lines can be assigned to adduct radicals by addition of benzoyl radicals **2b** to the alkenes or “head adducts” of the ketyl radicals.

Of these two possibilities, we are able to demonstrate that the additional components correspond to benzoyl adducts to the unsubstituted carbon atom of the vinyl groups of the alkenes. This was established by determining the HFC constants of the benzoyl adduct radicals produced by an independent experimental method for producing the adduct radicals. Benzoyl radicals were generated independently of ketyl radicals as follows: Photolysis of 1.1 M di-*tert*-butyl peroxide **3a** (20% v/v) with UV-light generates *tert*-butoxyl radicals **3b** (eq 3), and these radicals abstract hydrogens from benzaldehyde **4a** (0.1 M) to produce benzoyl radicals **4b** and *tert*-butyl alcohol **3c** (eq 4).

The known photoreduction reaction of excited benzaldehyde with ground-state benzaldehyde^{80,81} plays a minor role in non-hydrogen donor solvents.⁸² Therefore, we used a low concentra-

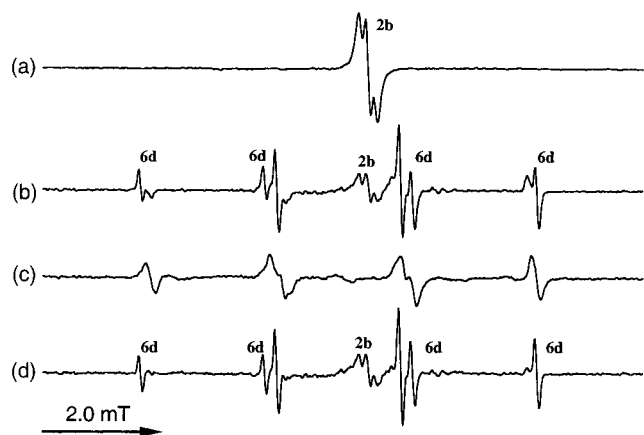
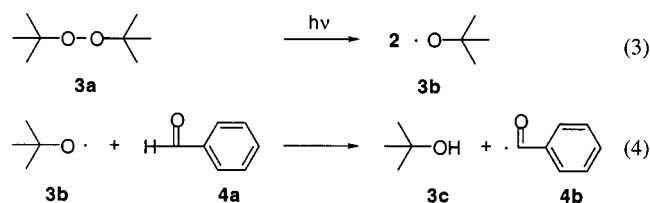


Figure 4. SS-ESR spectra recorded during photolysis of 1.1 M *tert*-butyl peroxide (**5**) in ethyl acetate solutions at 296 K in the presence of (a) 0.1 M benzaldehyde (**3a**), (b) 0.1 M benzaldehyde (**3a**) and 0.068 M *tert*-butyl acrylate (**6a**) and (c) 0.068 M *tert*-butyl acrylate (**6a**). Spectrum (d) shows the difference of spectra (b) and (c).

tion of benzaldehyde in ethyl acetate to minimize such side reactions. Photolysis of **3a** and **4a** in ethyl acetate generate the benzoyl radical **4b**, and the resulting SS-ESR spectrum is shown



in Figure 4a. In the presence of alkenes, benzoyl radicals add to the unsubstituted carbon atom of the vinyl group. We have determined the spectra without benzaldehyde to identify the radicals produced by side reactions (oligomeric radicals and radicals by addition of *tert*-butoxyl to the alkenes). Figure 4 shows an example for *tert*-butyl acrylate as an alkene. The coupling constants of the adduct of benzoyl radicals to the alkenes (**5a**–**7a**) are summarized in Table 1. The HFC constants for the benzoyl adducts determined by this method agree with the values measured by SS-ESR and TR-ESR (Figures 2 and 3) and, therefore, confirm the assumption that the weak components in SS-ESR spectra are, in fact, due to benzoyl adducts produced during the photolysis of **2a** in the presence of alkenes.

3.3. Laser Flash Photolysis (LFP). The ESR results indicate different reactivity of the radicals **1c** and **2c** to the double bonds of the alkenes. The absolute rate constants for radical addition to alkenes can be directly measured by LFP and provide a quantitative validation of the above conclusions. Laser flash photolysis of **1a** results in the appearance of transient absorption in the spectral range $\lambda = 300\text{--}350$ nm with $\lambda_{\text{max}} = 325$ nm.³⁶ The transient absorption decayed in the microsecond time scale.³⁷ This transient absorption was assigned to the phosphinoyl radical **1c**.³⁶ Addition of alkenes (A, e.g., **5a**, **6a**, and **7a**) reduce the lifetime of **1c**. At relatively high concentrations of alkenes, the decay of **1c** follows pseudo first-order kinetics. The bimolecular rate constants k_{add} for addition of **1c** were obtained from plots of the pseudo first-order rate constant k_{decay} vs [A], cf. eq 5:

$$k_{\text{decay}} = k_0 + k_{\text{add}}[\text{A}] \quad (5)$$

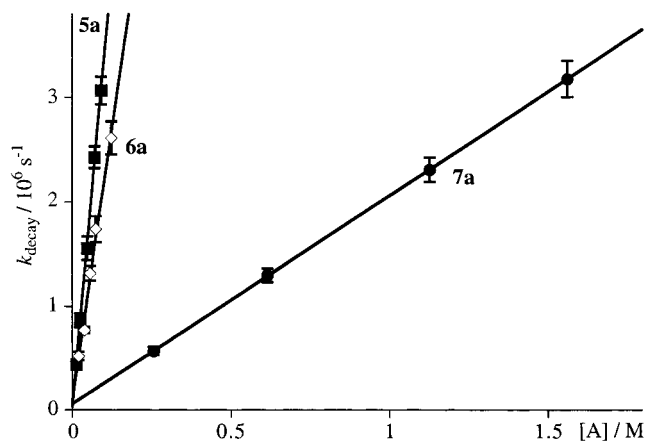


Figure 5. Pseudo-first-order decay rate constant k_{decay} of the radical **1c** vs alkene concentration. Alkenes are vinyl acrylate (**5a**), *tert*-butyl acrylate (**6a**) and vinyl pivalate (**7a**).

TABLE 2: Bimolecular Rate Constants^a (k_{add}) for Quenching of **1c in Ethyl Acetate Solutions at 296 K to a Series of Alkenes**

alkenes	$k_{\text{add}}/10^6 \text{ s}^{-1}$
$\text{H}_2\text{C}=\text{CHCO}_2\text{CH}=\text{CH}_2$ (5a)	33 (1)
$\text{H}_2\text{C}=\text{CHCO}_2\text{CMe}_3$ (6a)	22 (1)
$\text{Me}_3\text{CCO}_2\text{CH}=\text{CH}_2$ (7a)	2.0 (1)

^a Standard deviations are given in brackets in units of the last quoted digit.

where k_0 is the intercept of a linear plot. Figure 5 shows the resulting linear plots of k_{decay} vs [A] for the addition of **1c** to vinyl acrylate (**5a**), *tert*-butyl acrylate (**6a**) and vinyl pivalate (**7a**). The rate constants determined from the slopes of the linear plots in Figure 5 are listed in Table 2. They agree generally with previous data:⁴⁹ $k_{\text{add}} = (17.9 \pm 0.7) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $k_{\text{add}} = (19.8 \pm 0.6) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for *n*-butyl acrylate in toluene at room temperature.

We⁷⁶ have reported absolute values for *tert*-butyl acrylate of $k_{\text{add}} = (20.9 \pm 0.2) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and methyl acrylate $k_{\text{add}} = (20.4 \pm 1.0) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ in toluene at 296 K, whereas we find a value of $k_{\text{add}} = (22 \pm 1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for *tert*-butyl acrylate. The reported addition constant $k_{\text{add}} = (33 \pm 2) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for methyl acrylate³⁷ in hexane (Table 2) is slightly higher. Addition of rate constants to vinyl pivalate ($k_{\text{add}} = (2.03 \pm 0.11) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) in toluene⁷⁶ and $k_{\text{add}} = (2.5 \pm 0.1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ in benzene³⁵) and to vinyl acetate ($k_{\text{add}} = (2.7 \pm 0.1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ in benzene³⁵) are very similar to our value ($k_{\text{add}} = (2.0 \pm 0.1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) for vinyl pivalate.

Thus, k_{add} for an addition of **1c** radical to **5a** is only ~ 1.5 times higher than the value for **6a**, but by a factor of ~ 17 higher than k_{add} from the addition to **7a**. The obtained kinetic data from the laser flash photolysis are in agreement with our TR-ESR observation that a preferable addition of **1c** to the acrylate double bond of **5a** occurs, cf. Section 3.1, above.

Our observations provide some insight into the different behavior of acrylates and vinyl ethers (alkenes containing the $-\text{O}-\text{CH}=\text{CH}_2$ unit) in free-radical polymerization (FRP). It is known that acrylates readily participate in FRP with formation of polyacrylates, whereas vinyl ethers have very modest activity in FRP homopolymerization; on the other hand, vinyl ethers usually participate in cationic polymerization.⁸³ On the basis of our experiments with vinyl acrylate, we can assume that the reason for slow or inefficient FRP of vinyl ethers lies in the low rate of addition of free radicals to vinyl groups.

Our data also explain reported infrared (IR) data on vinyl

acrylate (**5a**) and poly(vinyl acrylate) obtained by FRP.^{16,18} IR spectra demonstrate that the vinyl ether groups in poly(vinyl acrylate) remain practically unaltered.^{16,18} The low value of k_{add} of the free radicals to the vinyl ether group in **5a** is a reason for preservation of the vinyl ether group during FRP of **5a**.

4. Conclusions

We have shown by two independent methods (TR-ESR and LFP) that the two radicals **1c** and **2c** add preferentially to the unsubstituted carbon atom of the acrylate double bond in vinyl acrylate (**5a**), because (a) k_{add} are rather close to known k_{add} for acrylates, and (b) the ESR spectra show adduct radicals with coupling constants very similar to those obtained for adducts to other acrylates. A hindered rotation and a cis-trans isomerization were found for acrylate adduct radicals. Furthermore, two different adducts of phosphinoyl radicals to vinyl acrylate **5a** can be observed by their ESR spectra, e.g., adducts formed by the addition to the unsubstituted carbon atom of the acrylate double bond and to the vinyl ether bond with relative intensity of ESR signals ca. 20:1, respectively. This ratio is in good agreement with a ratio of rate constants k_{add} for addition of **1c** to **5a** and vinyl pivalate **7a**, which is 17:1. Therefore, the vinyl ether group in **5a** stays practically intact during FRP of **5a**. In addition, the acrylate group in the vinyl acrylate shows an enhanced reactivity because the addition of radicals to **5a** is higher than that to alkyl acrylates, and the ratio of the signal intensities in the ESR spectra for acrylate and the vinyl adduct radicals is similar to the ratio of the absolute rate constants for the addition of phosphinoyl radicals to vinyl acrylate and vinyl pivalate. On the other hand, a slightly enhanced reactivity of the vinyl ether group in **5a** has been reported.¹⁶ Acrylate **5a**, which has a vinyl substituent, is characterized by a high rate constant.

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Supporting Information Available: Three figures (A, B, C) showing computer-simulated TR-ESR spectra of the radicals **1b**, **1c**, **2b**, and **2c** and the resulting adduct radicals and computer-simulated SS-ESR spectra of the radicals **2b** and **2c** and the resulting adduct radicals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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