Structure−Reactivity Relationships in Radical Reactions: A Novel Method for the Simultaneous Determination of Absolute Rate Constants and Structural Features

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Abstract: Analysis of the ESR line width in time-resolved (TR-ESR) experiments is shown to be a suitable tool for the measurement of addition constants of phosphinoyl and substituted benzoyl radicals. Compared with kinetic investigations, which make use of the resonance intensity or integral, observation of the line width as a function of monomer concentration has the advantage that the experimental parameter is not affected by spin-polarization processes and, therefore, a lengthy determination of these polarization parameters is avoided. The resulting addition constants are discussed with respect to the experimental hyperfine coupling constants and the geometry of the radicals. TR-ESR experiments simultaneously provide rate constants and ESR parameters and allow structure−reactivity relationships to be established.

Introduction

Reactions of phosphorus- and carbon-centered radicals are key steps in organic synthesis, biological transformations, and polymer chemistry. A typical example is the addition of these reactive species to alkenes.

An efficient method for the controlled formation of radicals is to generate them by a photochemical reaction from a photoinitiator designed for this purpose. Upon irradiation these initiators undergo homolytic cleavage. The primary radicals then add to the double bond of an alkene and thereby initiate polymerization. Important for the efficiency of this reaction sequence is the quantum yield and equally important the rate of addition of the initiator radicals to monomers.

The most widely applied method to determine addition rate constants is time-resolved optical spectroscopy, which easily lends itself to measuring the rate constants, if an absorption band of the initiator radical is resolved. The power of this technique has recently been demonstrated on phosphinoyl radicals.[1,2] Time-resolved infrared spectroscopy is another technique, which may be applied as a selective tool for kinetic studies of radicals with well-resolved vibrational absorptions.[3]

A limitation of all optical methods is the fact that they can inherently not provide much information on the structure of the observed radicals and are applicable only in a limited range of optical densities. Hence, identification of the species responsible for an observed transient absorption is often not clear-cut. Recently the chemically induced dynamic nuclear polarization (CIDNP) effect has been used in a set of elegant experiments to establish the addition constant of 2-hydroxypropyl radicals

to a variety of alkenes.[4] Although CIDNP spectra allow the extraction of valuable structural information, only the products formed from radicals are observed by this technique, and information on the precursor radicals is obtained *indirectly*.

The most powerful method to follow the time development of radicals is electron spin resonance (ESR). This method allows the *direct* observation of the radicals and concomitantly provides unambiguous structural information on these species. However, the deduction of rate constants from intensity−time profiles in time-resolved ESR (TR-ESR) experiments is very tedious. These ESR intensities are strongly influenced by spin polarization processes. This impedes the direct determination of the kinetic parameters of radical reactions because a lengthy determination of polarization and relaxation parameters is needed.[5]

However, a parameter of the ESR line shape that is not influenced by the spin polarization process is the ESR line width.

In this contribution, we develop the basic background of the "line width method" for the determination of addition rate constants of radicals to monomers, and demonstrate its scope and effectiveness. To this end, we have chosen a number of acylphosphine oxide photoinitiators, **1**−**10**. Some addition rate constants of phosphinoyl radicals obtained by optical spectroscopy have been reported in the literature.[1,2] Since these values were measured in a different solvent, they cannot directly be compared with those obtained by the ESR method. The reactivities of some of the acylphosphine oxide photoinitiators were, therefore, also determined by optical spectroscopy in the solvent used for the ESR experiments. These data serve as a well-suited reference for the new technique. Moreover, it will be shown that the simultaneous determination of rate constants and ESR parameters allows structure−reactivity relationships to be established.

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Figure 1. α-Cleavage of mono-, bis-, and trisacylphosphine oxides.
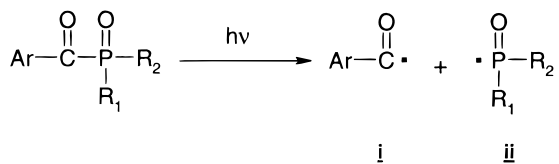
R_1, R_2= alkyl, aryl: **MAPO**

R_1 = acyl, R_2 = alkyl or aryl: **BAPO**

R_1, R_2 = acyl: **TAPO**

Chart 1. Monoacylphosphine Oxide (MAPO) Photoinitiators

Chart 2. Bisacylphosphine Oxide (BAPO) Photoinitiators

Chart 3. Trisacylphosphine Oxide (TAPO) Photoinitiators

Experimental Section

Experimental Techniques. TR-ESR experiments were performed without modulation of the static magnetic field on a Bruoker ESP 300E spectrometer equipped with a microwave amplifier. The response of the ESR spectrometer after a light pulse at a fixed value of the static magnetic field was stored in a Le Croy 9400 dual 125 MHz digital oscilloscope. The system is controlled by the CROYDOS software (Walter AG, Zurich, Switzerland). A Nd:Yag laser (Continuum Surelite II) with a fixed repetition frequency of 20 Hz (4−6 ns, pulse width, frequency-tripled, 350 nm) was used as the light source. The TR-ESR experiments were performed at room temperature using a home-built flow system, providing a fast, turbulent flow to obtain optimum mixing. The photoinitiators, synthesized and purified by Ciba Specialty Chemicals, were dissolved in toluene (0.005−0.01 M) and the solutions saturated with helium. *n*-Butyl acrylate (Fluka purum) was used in concentrations which varied between 0.3 and 3.0 M.

Laser flash photolysis experiments employed the pulses (351 nm, approximately 100 mJ per pulse, 25 ns) from a Compex 205 excimer laser. Solutions were degassed by 3 freeze−pump−thaw cycles. The concentrations of the photoinitiators were chosen to give an absorbance of 0.1−0.2 at the excitation wavelength, and quencher concentrations were varied in the range 30−150 mM. The signals were captured on a Tektronix TDS 540 transient recorder and analyzed by nonlinear least-squares fitting to a first-order rate law.

Phosphine Oxide Initiators Investigated. Acylphosphine oxides are a class of efficient photoinitiators which have recently been introduced for the curing of thick pigmented coatings and glass fiber reinforced materials.[6] Monoacylphosphine oxides (MAPO; **1**, **2**) were discovered several years ago,[7] while bisacylphosphine oxides (BAPO; **3**−**8**) were introduced as commercial products more recently.[8] Photochemical and photophysical characteristics of these compounds have been reported in a number of publications.[1,2,9] Very recently, polymerization experiments using trisacylphosphine oxides (TAPO; **9**, **10**) have also been described.[10]

After excitation by light, MAPO, BAPO, and TAPO derivatives undergo an efficient α-cleavage from the excited triplet state.[9,10] A substituted benzoyl radical (**i**) and a phosphinoyl radical (**ii**) are formed by this process. Both radicals induce the polymerization reaction, the phosphinoyl radical being much faster in the first addition step. This process is shown in Figure 1. The BAPOs and TAPOs can undergo further cleavages leading to the formation of additional benzoyl and phosphinoyl radicals.[9]

These photoinitiators are well suited for TR-ESR and line width studies thanks to the remarkably strong electron spin polarization, partly a consequence of the large hyperfine coupling constants of the P-centered radicals. These characteristics lead to intense TR-ESR signals and an unambiguous identification of the reactive species. The structures investigated in this study are collected in Charts 1−3.
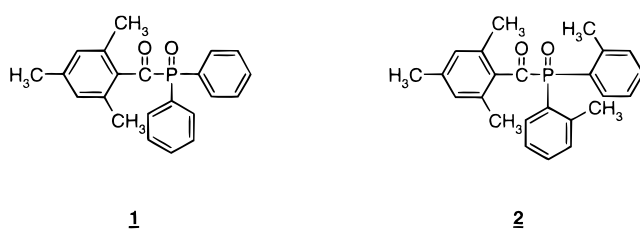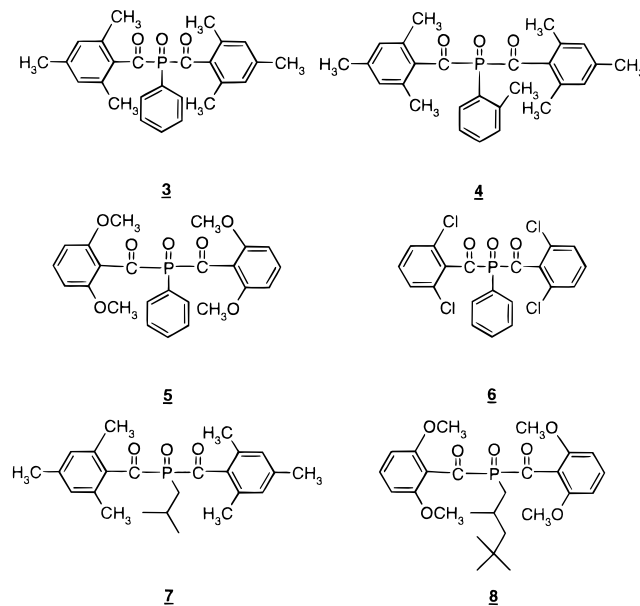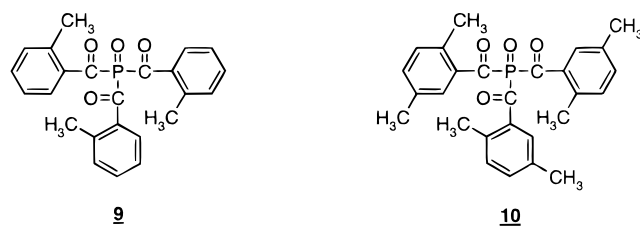
The photoinitiators were irradiated in the presence of *n*-butyl acrylate and studied by TR-ESR. The addition constants of the primary phosphinoyl radicals to the monomer were calculated from the ESR line width and compared with the values obtained by optical spectroscopy in the same solvent (toluene). Gaussian line shapes lead to a better fit of the experimental absorptions compared with Lorentzian line shapes. Direct comparison with the addition constants reported in the literature[1,2] is not possible, as they were measured in acetonitrile. This solvent is not suitable for the ESR line width experiments, because it reduces both the ESR-*Q* value and the sensitivity of the instrument.

Results and Discussion

Theory: Modeling of the Addition Reaction. The shape and the time profile of the TR-ESR lines are described by the Bloch equations.[11,12] The solution of these equations for the transverse magnetization is composed of line shape functions,

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their shapes being influenced by the time-dependent magnetic fields, relaxation and radical lifetimes, and amplitudes that depend on the polarization. In other words, careful analysis of these equations shows that the ESR line width is not influenced by the spin polarization processes, since the latter force the populations of the magnetic states to deviate from thermal equilibrium, but do not alter the transverse relaxation time T_2 (by faster relaxation or by broadening the energy levels).

Hence, the ESR line width increases with decreasing lifetime of the observed radicals and thus represents an essential experimental parameter for the determination of the radical-to-monomer addition rate constant k_{add}. Moreover, this method benefits from the much higher signal-to-noise ratio brought about by spin polarization processes (compared with thermal equilibrium).[13]

The rate constant k_{add} describes the addition of an initiator radical (I$^{\bullet}$) to a monomer (M):

$$I\cdot + M \xrightarrow{k_{add}} I-M\cdot$$
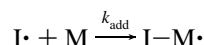
Typically the monomers are present at a much higher concentration than the photoinitiators (ca. 10^3-fold excess). Therefore, the adequate kinetic description for this reaction is a pseudo-first-order process. A single laser pulse induces an amount of polymerization that leaves the monomer concentration virtually constant; moreover, chain termination reactions stop the polymerization process before a significant amount of monomer is consumed.

First-order kinetics translates into a linear relationship between line broadening and monomer concentration.[11,12] Indeed, experiments performed at high monomer concentrations revealed this predicted linear behavior:

$$1/T_2 = k_0 + k_{add}[M] \tag{1}$$

where k_0 is the monomer independent line width, k_{add} is the rate constant of radical addition to the alkene, and $1/T_2$ is total line width (half width at half-height).

In the field-swept ESR experiment, the line broadening is measured in magnetic-field units ($1/T_2^*$). The ESR resonance condition, which connects microwave frequency and magnetic field, leads to the following conversion factor:

$$1/T_2 = 2\pi\nu(1/T_2^*)/B \tag{2}$$

where B is the magnetic field at the position of the observed resonance and ν is the microwave frequency (approximately 9 GHz).

The addition constant k_{add} is determined as the slope of the straight line defined by eq 3. In addition, eq 3 shows the lower limit of k_{add} which is accessible by TR-ESR:

$$(1/T_2^*) - (B/2\pi\nu)k_0 = (B/2\pi\nu)k_{add}[M] \tag{3}$$

where the left side of eq 3 is the experimental broadening by the addition reaction.

Assuming that 0.005 mT is the smallest detectable value of line broadening, and that this line broadening must be achieved at the upper limit of an approximately 3 M monomer concentration, the slowest rate constant detectable under the experimental conditions used here is estimated to be about 3×10^5 M^{-1} s^{-1}.

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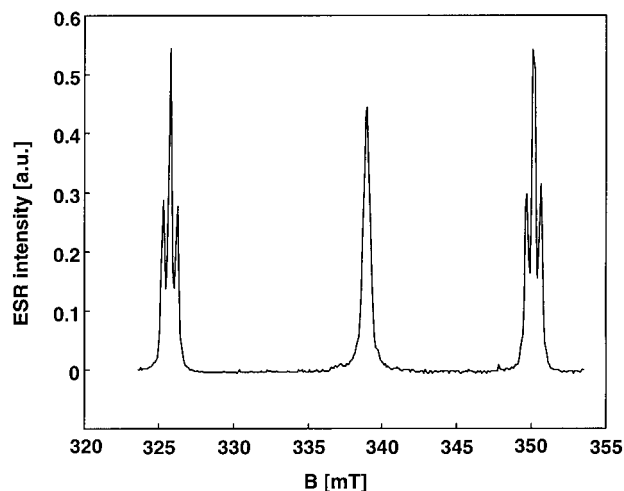

Figure 2. TR-ESR spectrum of initiator **7** observed between 200 and 400 ns after the laser flash.
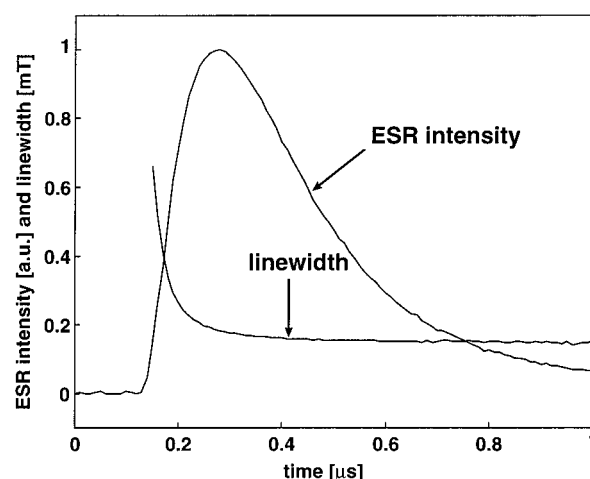

Figure 3. High-field resonance of initiator **3**: time response of ESR−intensity and line width.

Line Width Measurements. A typical TR-ESR spectrum (initiator **7**), obtained in toluene by irradiation at 355 nm in the absence of a monomer, is reproduced in Figure 2. The two outermost triplets represent the ESR spectrum of the phosphinoyl radical with a large phosphorus hyperfine coupling (hfc) and a much smaller hfc of the two β-protons. The resonance in the center is due to the benzoyl radical. The small hfc's of the aromatic protons are not resolved.

The time dependence of the ESR line width of initiator **3**, measured in the absence of the monomer after a laser pulse, is shown in Figure 3, together with the time profile of the ESR intensity. During the first 250 ns, line broadening due to the initial spread of microwave frequencies and build-up of magnetization is dominant.[11] After approximately 600 ns, the initially strongly polarized ESR signal has relaxed and it is increasingly difficult to measure the ESR line width accurately (poor signal-to-noise ratio, SNR).

Consequently, a time interval between approximately 300 and 500 ns was chosen for the determination of the rate constants. In this domain contributions of the initial broadening are negligible and the SNR allows an accurate measurement of the line width.

A three-dimensional view of the time development of the high-field phosphinoyl resonance of initiator **3** in the presence of excess *n*-butyl acrylate is reproduced in Figure 4. Figure 5
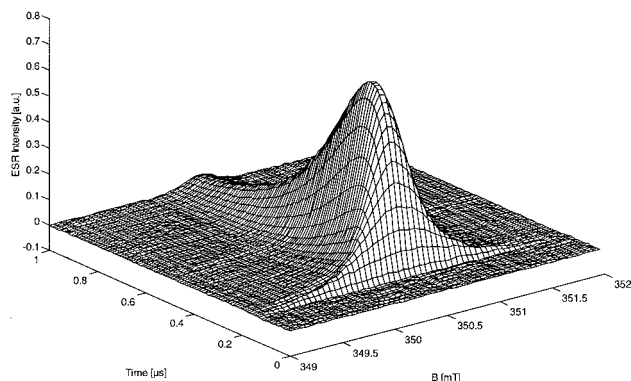
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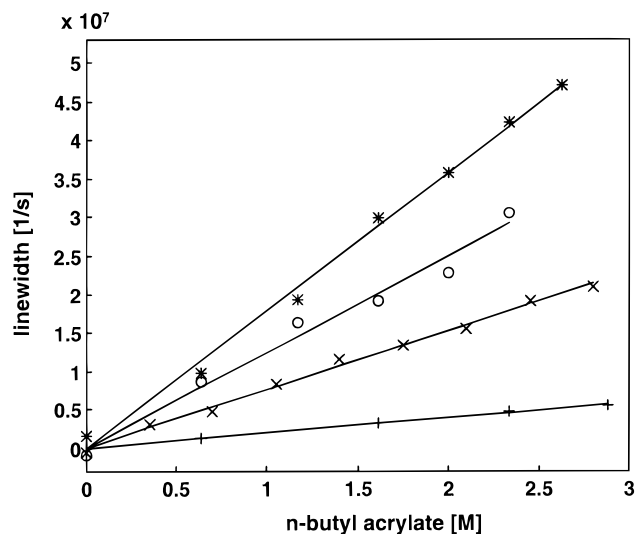**Figure 4.** High field resonance of initiator **3**: time response.

Figure 5. Line width as a function of monomer concentration: initiator **1** (*), initiator **3** (×), initiator **5** (○), and initiator **9** (+).

Table 1. ^{31}P hfc's and Addition Rate Constants k_{add} for the Addition of Phosphinoyl Radicals, Derived from Photoinitiators **1−10**, to *n*-Butyl Acrylate (Solvent:Toluene)

| | ^{31}P hfc [mT] | k_{add} 10^7 [M^{-1} s^{-1}] | |
		TR-ESR experiments	LFP experiments
1	36.3	1.79 ± 0.07	1.98 ± 0.06
2	35.8	0.123 ± 0.035	0.145 ± 0.003
3	25.8	0.765 ± 0.022	0.867 ± 0.019
4	25.4	0.080 ± 0.056	0.092 ± 0.009
5	28.3	1.25 ± 0.08	1.46 ± 0.03
6	27.9	0.88 ± 0.08	
7	24.6	0.23 ± 0.01	
8	27.3	1.14 ± 0.15	1.41 ± 0.12
9	22.2	0.219 ± 0.044	0.26 ± 0.08
10	21.9	0.373 ± 0.006	

displays the linear relationship between ESR line widths and monomer concentrations for various photoinitiators.

The simultaneously detected ^{31}P hfc's of the phosphinoyl radicals of initiators **1−10** and their addition rate constants k_{add} to *n*-butyl acrylate are collected in Table 1. The phosphinoyl radicals are denoted by the labels of the corresponding precursor molecules.

For phosphinoyl radicals derived from compounds **1−5, 8,** and **9**, the rate constants in the same solvent (toluene) were determined by laser flash photolysis (LFP). The two experimental techniques yield k_{add} values in good agreement with each other. The addition rate constants measured in toluene are

considerably smaller than those obtained earlier by optical spectroscopy in acetonitrile.[1,2]

Structural Considerations. It has been pointed out in a number of publications that a relationship exists between the hyperfine α-coupling of a phosphinoyl radical and its addition constant to a carbon−carbon double bond.[1,14] A decrease of the ^{31}P hfc should at least partly be related to a change of the phosphinoyl radical from a pyramidal to a more planar structure. A corresponding relationship is well documented for alkyl[15] and N-centered radicals.[16] The changes toward a more planar structure lead to an increasing p-character of the orbital containing the unpaired electron, and possibly to spin delocalization into the conjugated substituents of the phosphinoyl radical. Due to these changes, the more planar radicals are expected to be less reactive in addition reactions.

The relationship between rate and hyperfine coupling constants of the phosphinoyl radicals formed from initiators **1−10** is shown in Figure 6. A general trend is evident;[1,2] in most cases, and especially within the series of BAPO initiators without a methyl substituent in the phenyl ring linked directly to the phosphorus, an increase of the ^{31}P hfc correlates with a faster addition of *n*-butyl acrylate.

Electronegative substituents in the benzoyl ortho positions in the P-centered radicals lead to a simultaneous increase of the ^{31}P hfc and k_{add}. As the number of benzoyl substituents on the phosphorus is varied, the slope changes, indicating that the relationship between initiator structure and addition constant is more complicated, as might be expected. This becomes even more apparent for **2** and **10**, where the *o*-methyl group in the phenyl substituent leads to a pronounced decrease of the addition constant of the phosphinoyl radical to the particular monomer *n*-butyl acrylate. On the other hand, the ^{31}P hfc is hardly affected by the additional methyl groups.

The simultaneous detection of kinetic and structural parameters reveals the delicate interplay of steric and/or electronic factors. It is, e.g., very likely that steric hindrance overwhelms the electronic effects in the two initiators **2** and **10**. Calculations which should allow the influence of spin density distribution and s-character at the P radical and steric effects of the substituents to be distinguished are under way.

Scope and Limitations. For initiators **1**, **2**, **3**, **4**, and **7**, cleavage leads to a phosphinoyl and the 2,4,6-trimethylbenzoyl radical. The kinetics of the latter, in general, cannot be studied by optical spectroscopy in the presence of an acrylic ester quencher because of overlapping bands. The substituted benzoyl radical, however, can be easily observed by TR-ESR. It adds much more slowly to an acrylic double bond than the phosphinoyl radical. In TR-ESR experiments with initiator **4** and *n*-butyl acrylate, an addition constant of $(3.6 ± 1.3) × 10^5$ M^{-1} s^{-1} was deduced for the 2,4,6-trimethylbenzoyl radical, while the constants for sterically unhindered phosphinoyl radicals are of the order of 10^7 M^{-1} s^{-1}.

The addition rate has to be fast enough to lead to appreciable line broadening. An estimate has shown that rate constants $>3.0 × 10^5$ M^{-1} s^{-1} can be determined accurately. The high concentrations of the alkene, which were required to create sufficient line broadening, are much closer to the technological

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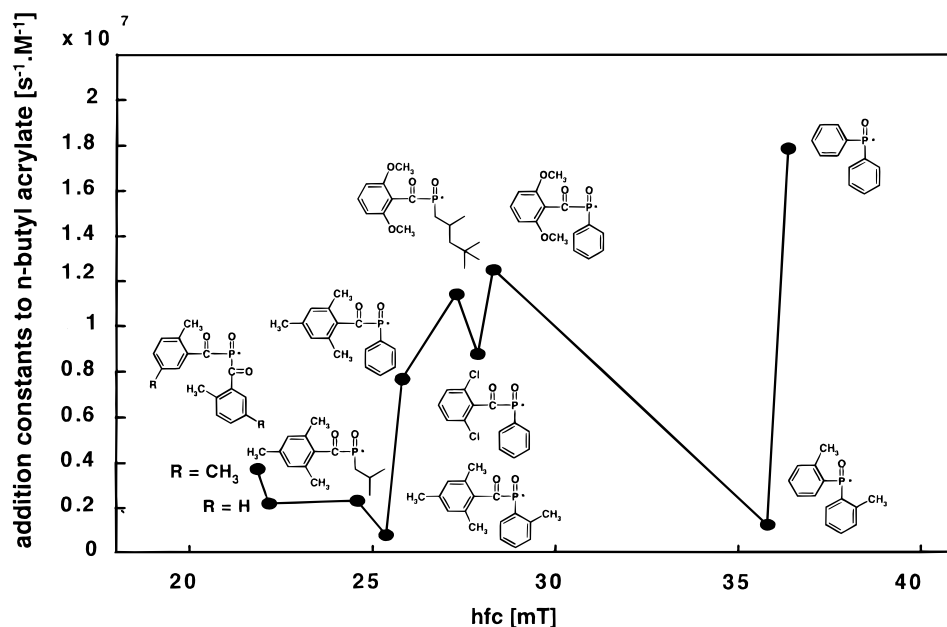
Figure 6. Addition constants to *n*-butyl acrylate as a function of the phosphorus hyperfine coupling constant.

reality than those used in optical experiments. In ESR experiments, the upper monomer concentration is limited by viscosity only, while the limiting parameter in optical spectroscopy is the optical density.

An inherent drawback of the ESR technique is the high signal-to-noise ratio needed to measure line shapes and line widths accurately. For some very unstable radicals this will not be easily accomplished.

Conclusions

The analysis of ESR line widths is a suitable tool for the measurement of addition constants and is certainly applicable to a variety of radical reactions. Rate constants determined by ESR line width analysis are in good agreement with the values obtained by optical spectroscopy for radicals which are detect-

able by both methods, which indicates that the new technique is reliable. Not only does this method allow the determination of addition constants in cases where optical experiments fail due to insufficient resolution, it also provides structural features of the reactive species. This opens the door for the determination of structure−reactivity relationships combining kinetic, structural, and steric factors.