

# A comparative time-resolved CW EPR and FT EPR investigation of the addition of 2-hydroxy-2-propyl radicals to acrylate and methacrylate monomers†

Matthias Weber,<sup>a</sup> Nicholas J. Turro\*<sup>a</sup> and Dieter Beckert<sup>b</sup>

<sup>a</sup> Columbia University, Department of Chemistry, 3000 Broadway, New York, NY 10027, USA

<sup>b</sup> Faculty of Chemistry and Mineralogy, University of Leipzig, Permoserstr. 15, D-04318 Leipzig, Germany

Received 15th August 2001, Accepted 26th October 2001

First published as an Advance Article on the web 3rd January 2002

The addition of 2-hydroxy-2-propyl radicals to n-butyl acrylate and n-butyl methacrylate has been investigated by time-resolved continuous wave electron paramagnetic resonance (TR CW EPR) and time-resolved Fourier transform electron paramagnetic resonance (TR FT EPR). The 2-hydroxy-2-propyl radicals were generated by the photolysis of acetone in propan-2-ol (through hydrogen abstraction) and by the photolysis of a ketone **5** (through  $\alpha$ -cleavage). The TR CW and TR FT spectra were experimentally equivalent for the addition of 2-hydroxy-2-propyl radicals to n-butyl acrylate to produce **3a**. However, there are distinct differences between the TR CW and TR FT spectra for the addition of 2-hydroxy-2-propyl radicals to n-butyl methacrylate which produces the radical adduct **4a**. In particular, a number of hyperfine lines clearly present in the TR CW spectra are much weaker in, or are absent from, the TR FT spectra. The differences in the TR CW and TR FT spectra are attributed to hindered rotation, which is important in the spectrum of the adduct of 2-hydroxy-2-propyl radicals to n-butyl methacrylate (**4a**), but not in the spectrum of the adduct of 2-hydroxy-2-propyl radicals to n-butyl acrylate (**3a**). The hindered rotation is shown to selectively shorten the spin–spin relaxation time,  $T_2$ , for certain hyperfine lines in the spectrum of **4a**, resulting in broadening or disappearance of these lines and explaining the differences between the TR CW and TR FT spectra.

## Introduction

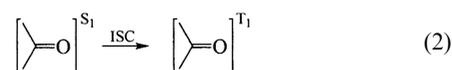
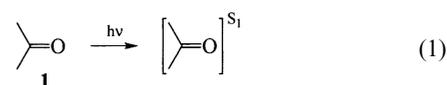
TR EPR has proven to be a valuable and powerful technique for the characterization of the structure and dynamics of radicals produced in photochemical reactions of organic molecules. In addition, the technique provides information on the interactions of radical pairs, spin polarization mechanisms, spin relaxation, molecular motion and the selectivity of triplet sublevel populations.<sup>1</sup> The TR EPR methods may be classified in terms of the methods of detection as continuous wave (CW) and Fourier transform (FT) methods.<sup>2,3</sup> The FT methods may be classified in terms of the process of analyzing the signal as a free induction decay (FID) or as an electron spin echo (ESE). The CW and FT methods are expected to differ somewhat in terms of sensitivity and resolution due to differences in the technical aspects of data acquisition and analysis. However, one might expect that experimentally equivalent spectra would be observed after taking into account technical differences in the technique.

However, since the CW method depends mainly on the spin–lattice relaxation time  $T_1$ , and the FT method depends mainly on the phase memory time  $T_M$  (which is a function of all processes that lead to the relaxation of the spin system, such as the spin–lattice relaxation time  $T_1$ , spin–spin relaxation times  $T_2$  and chemical reactions), there is a fundamental difference between the two methods that could result in significant differences in the experimental spectra under certain circumstances.<sup>4</sup> There have been relatively few examples of a comparison of systems that are analyzed by both the TR CW

and the TR FT methods. We report here the examination of the addition of the 2-hydroxy-2-propyl radical (**2a**) to n-butyl acrylate and n-butyl methacrylate by both TR CW and TR FT EPR, and demonstrate that substantial differences result in the spectra observed by the two techniques when one set of hyperfine lines are subject to a shortening of  $T_2$  as a result of hindered rotation in the vicinity of the radical center. In the extreme case, certain hyperfine lines are nearly completely absent in the TR FT spectrum, but the same lines are clearly visible in the TR CW spectrum. In this case a comparison of TR CW and TR FT methods allows an unambiguous assignment of radical structure to the observed spectra.

## TR EPR of the 2-hydroxy-2-propyl radical produced by the photolysis of acetone in propan-2-ol

The paradigm for the photochemical reaction of acetone with propan-2-ol is generally agreed to be the following.<sup>5</sup> UV excitation promotes acetone to its excited singlet state (reaction (1)). The latter undergoes intersystem crossing to the triplet state (reaction (2)). *A priori*, either singlet or triplet acetone, or both, could react with propan-2-ol to produce two 2-hydroxy-2-propyl radicals (reaction (3)):



† Dedicated to Professor Frank Wilkinson on the occasion of his retirement.

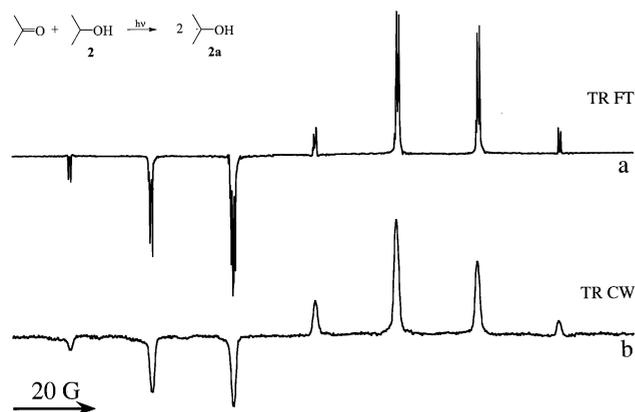


From a quantitative analysis of relevant rate constants (the quenching constants for propan-2-ol are  $^1k_q = 9.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $^3k_q = 1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ <sup>6</sup> and the rate of intersystem crossing is  $4.0 \times 10^8 \text{ s}^{-1}$  in solution<sup>5</sup>), it is concluded that hydrogen abstraction occurs mainly from the acetone triplet. The slow rate of hydrogen abstraction by triplet acetone results in a nearly complete loss of any spin polarization that might result initially from sublevel selective intersystem crossing. As a result, the main mechanism of production of CIDEP is due to the radical pair mechanism (RPM) of interacting **2a** radicals to produce a characteristic E/A CIDEP pattern. Published results employing both TR CW<sup>7</sup> and TR FT<sup>8</sup> methods are in full agreement with the RPM mechanism of CIDEP for the acetone propan-2-ol photochemical system at room temperature.

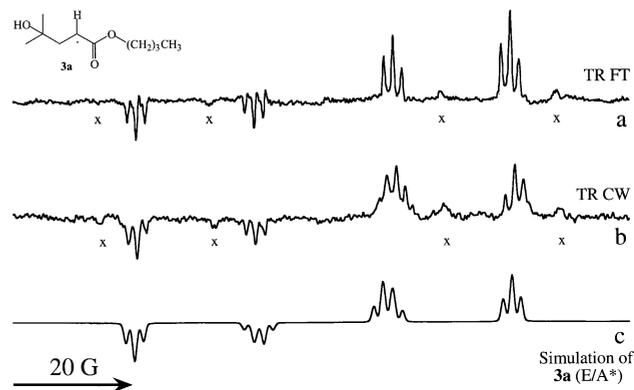
## Results

We have examined the photolysis of acetone propan-2-ol solutions by TR CW and TR FT methods (Fig. 1). In this report ESE, rather than FID, was employed for the FT experiments for several reasons. First, the FID signal in the dead time must be reconstructed (*e.g.*, by the linear prediction singular value decomposition (LPSVD) method) before performing the FT transformation.<sup>9</sup> This is not required in the ESE experiments, because the signal is shifted outside the dead time of the instrument. ESE signals are time-reversed FIDs followed by a normal FID and, therefore, no parts of the signals are lost. Second, no additional assumptions are necessary to analyze the ESE signal, whereas the LPVSD method that is required to reconstruct the FID assumes a Lorentzian lineshape and a given number of resonance lines. Finally, for weak spectral signals, it is difficult to reconstruct the signal by the LPVSD method.

Consistent with literature results,<sup>3,7,8</sup> the observed EPR lines of the 2-hydroxy-2-propyl radicals produced by photolysis of acetone in propan-2-ol show an E/A-spin polarized pattern as is expected for the RPM. Both the TR FT and TR CW gave nearly identical spectra (Fig. 1a and b), differing only in signal to noise and resolution of the main hyperfine lines. This result establishes that in “uncomplicated” cases the TR CW and TR FT EPR techniques lead to essentially experimentally equivalent results.



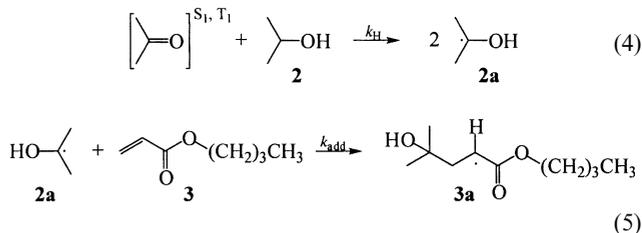
**Fig. 1** (a) TR FT EPR spectrum recorded 400 ns, and (b) TR CW EPR spectrum recorded 300–600 ns following laser excitation (308 nm) of 1.4 M acetone in argon-saturated propan-2-ol solution at 297 K.



**Fig. 2** (a) TR FT EPR spectrum recorded 1000 ns, and (b) TR CW EPR spectrum recorded 1000–1300 ns following laser excitation (308 nm) of 1.4 M acetone and 50 mM n-butyl acrylate in argon-saturated propan-2-ol solution at 297 K. (c) Simulation of the EPR spectrum of **3a** (E/A\*) with the parameters given in Table 1. (x) are assigned to the unreacted 2-hydroxy-2-propyl radical **2a**.

The 2-hydroxy-2-propyl radicals produced from the photolysis of acetone in propan-2-ol react rapidly with alkenes<sup>10†</sup> and transfer spin polarization<sup>11</sup> to the primary adduct radical (*e.g.*, reactions (4) and (5)). The TR CW and TR FT EPR spectra resulting from photolysis of acetone propan-2-ol in n-butyl acrylate are shown in Fig. 2. In comparison to Fig. 1, it is clear that at the time of signal acquisition (1000–1300 ns following laser excitation), the signal intensities of the 2-hydroxy-2-propyl radical have essentially disappeared and have been almost entirely replaced by a new signal of the radical adduct **3a** resulting from the addition of 2-hydroxy-2-propyl radicals to n-butyl acrylate (reaction (4)). The structure **3a** is assigned to the radical adduct through simulation of the observed spectrum with that expected for **3a** from literature coupling constants (Table 1). As for the case of Fig. 1, there is good correspondence between the TR CW and TR FT spectra in Fig. 2.

Fig. 3 shows the TR CW and TR FT EPR spectra resulting from photolysis of acetone propan-2-ol in n-butyl methacrylate. In contrast to the results shown in Fig. 1 and 2 where the TR CW and TR FT EPR spectra are experimentally very similar, there are substantial differences between the TR CW and TR FT EPR spectra. In particular, a number of hyperfine lines that are clearly present in the TR CW spectrum are either missing or strongly diminished in intensity in the TR FT spectrum. The species produced in the TR CW spectrum is readily assigned to the expected structure **4a** (reaction (5)) by simulation (Fig. 3c) employing literature coupling constants (Table 1). However, since the TR CW and TR FT spectra are clearly different, it is not possible to straightforwardly assign the structure **4a** to both the spectra shown in Fig. 3. From the photochemical standpoint, it seems apparent that **4a** is the most reasonable species produced by the photolysis of acetone in propan-2-ol containing sufficiently high concentrations of n-butyl methacrylate.

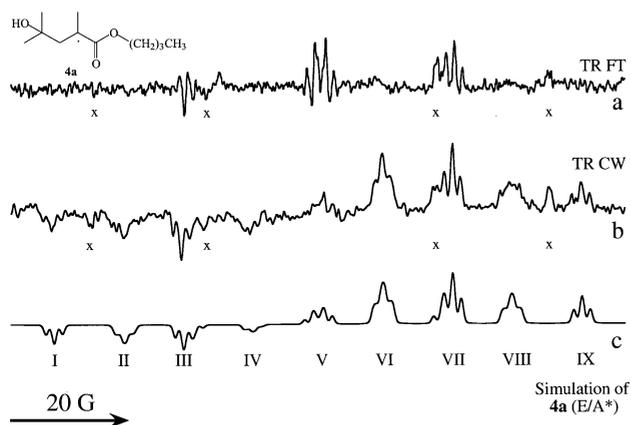


† For other systems see, for example, ref. 10g, h.

**Table 1** Hyperfine coupling constants (mT) of the acrylate adduct radicals

Acrylate	Initiator	Method <sup>a</sup>	$a(1H_\alpha)/a(3H_\beta)$	$a(2H_\beta)$	$a(2H_\delta)$	Ref.
n-Butyl acrylate	<b>5</b>	TR FT	1.997	2.175	0.157	
n-Butyl acrylate	<b>5</b>	TR CW	2.016	2.192	0.155	
n-Butyl acrylate	Acetone propan-2-ol	TR FT	2.010	2.185	0.155	
n-Butyl acrylate	Acetone propan-2-ol	TR CW	2.01	2.20	0.15	
n-Butyl acrylate	IC2959 <sup>b</sup>	TR FT	2.01	2.14	0.17	10b
Methyl acrylate	OC(CMe <sub>2</sub> OH) <sub>2</sub>	SS CW	2.003	2.178	0.155 <sup>b</sup>	13
n-Butyl methacrylate	<b>5</b>	TR FT	2.187	1.18	0.144	
n-Butyl methacrylate	<b>5</b>	TR CW	2.201	1.20	0.136	
n-Butyl methacrylate	Acetone propan-2-ol	TR FT	2.20	?	0.139	
n-Butyl methacrylate	Acetone propan-2-ol	TR CW	2.20	1.20	0.14	
Methyl methacrylate	<b>5</b>	TR CW	2.25	1.26	1.116 <sup>b</sup>	15
Methyl methacrylate	OC(CMe <sub>2</sub> OH) <sub>2</sub>	SS CW	2.209	1.193	0.135 <sup>b</sup>	20

<sup>a</sup> TR FT = time-resolved Fourier transform, TR CW = time-resolved continuous wave, SS CW = steady-state continuous wave. <sup>b</sup> IC2959 is HOCH<sub>2</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>C(O)CMe<sub>2</sub>OH. <sup>c</sup>  $a(3H_\delta)$ .

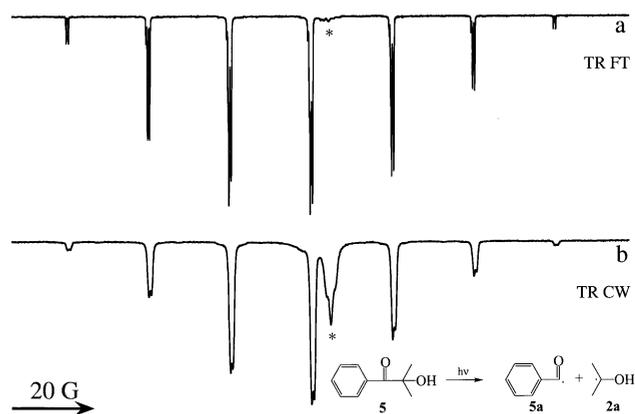
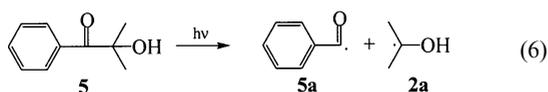


**Fig. 3** (a) TR FT EPR spectrum recorded 2000 ns, and (b) TR CW EPR spectrum recorded 2000–2300 ns following laser excitation (308 nm) of 1.4 M acetone and 100 mM n-butyl methacrylate in an argon-saturated propan-2-ol solution at 297 K. (c) Simulation of the EPR spectrum of **4a** (E/A\*) with the parameters given in Table 1. (x) are assigned to the unreacted 2-hydroxy-2-propyl radical **2a**.

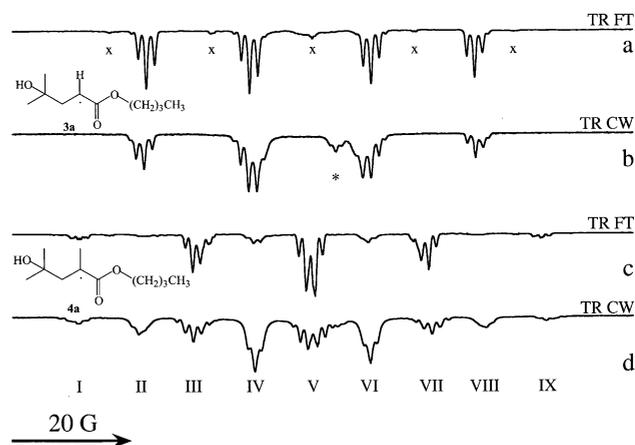
We noticed that at higher concentrations of n-butyl acrylate and n-butyl methacrylate (around 1 M) no EPR signals were detectable at the delay times used in this work. Alkenes at sufficiently high concentrations may serve as energy transfer quenchers of excited acetone triplets.<sup>12</sup> Such a quenching will compete with the hydrogen abstraction to produce 2-hydroxy-2-propyl radicals and accordingly decrease the intensity of the observed EPR signals.

Polarized 2-hydroxy-2-propyl radicals can also be produced by a method that is completely independent of the acetone propan-2-ol system, namely by the photolysis of the ketone **5** in propan-2-ol (reaction (6)). Upon photolysis **5** produces the benzoyl radical (**5a**) and the 2-hydroxy-2-propyl radical (**2a**) with nearly pure CIDEP emission (Fig. 4a and b). Photolysis of **5** in the presence of n-butyl acrylate or n-butyl methacrylate results in the spectra shown in Fig. 5a–d. The n-butyl acrylate system produces essentially the same results by both TR CW and TR FT methods (cf. Fig. 2)

For the n-butyl methacrylate system (Fig. 5c and d), the radical adduct is formed with very much better signal to noise, and the distinction between the TR CW and TR FT spectra, “alternating lines” of diminished intensity, is quite clear.



**Fig. 4** (a) TR FT EPR spectrum recorded 400 ns, and (b) TR CW EPR spectrum recorded 300–600 ns following laser excitation (308 nm) of 2.4 M of **5** in an argon-saturated propan-2-ol solution at 297 K. The asterisk signifies the benzoyl radical **5a**.



**Fig. 5** TR FT EPR spectra recorded (a) 1000 ns, or (c) 2000 ns, TR CW EPR spectra recorded (b) 1000–1300 ns, (d) 2000–2300 ns following laser excitation (308 nm) of 0.24 M of **5** and 50 mM n-butyl acrylate (a) and (b) or 100 mM n-butyl methacrylate (c) and (d) in an argon saturated propan-2-ol solution at 297 K. (x) are assigned to the unreacted 2-hydroxy-2-propyl radical **2a** and \* signifies the benzoyl radical **5a**.

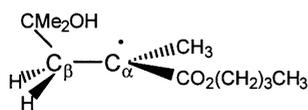
## Discussion

We seek to explain the basis for the experimental equivalence of the TR CW and TR FT EPR spectra for the addition of 2-hydroxy-2-propyl radicals to n-butyl acrylate (reaction (4))

and the difference in the TR CW and TR FT EPR spectra for the addition of 2-hydroxy-2-propyl radicals to n-butyl methacrylate (reaction (5)).

The hyperfine line groups in the radical adduct spectrum assigned to **4a** may be classified as I–IX (Fig. 3, simulation of **4a**), in going from low field to high field. The TR FT spectra involving addition of 2-hydroxy-2-propyl radicals to n-butyl methacrylate (Fig. 3a and 5c) appear to possess fewer lines than does the TR CW spectrum (Fig. 3b and 5d). A comparison of the TR FT and TR CW spectra to the simulated spectrum (Fig. 3c) reveals that it is mainly the “alternating lines” corresponding to  $M_{I, C\beta H_2} = 0$  (line groups II, IV, VI and VIII) that appear to be either missing, or of diminished intensity in the TR FT spectra of **4a**. The same lines display a significant line broadening in the TR CW spectrum (Fig. 3b and 5d).

The specific broadening of hyperfine lines in the methacrylate adduct **4a** can be explained in terms of the known hindered rotation<sup>13</sup> of the  $C\beta H_2$  group in the adduct radicals around the  $C\alpha$ – $C\beta$  bond (see Scheme 1).



**Scheme 1** Schematic representation of the geometry of the adduct radical **4a**.

Hindered rotation about the  $C\alpha$ – $C\beta$  bond leads to non-equivalent protons of the  $C\beta H_2$  group which are manifest in the EPR spectrum (Fig. 3b) by broadening of the line groups with the quantum number  $M_{I, C\beta H_2} = 0$  (line groups II, IV, VI and VIII), precisely the lines which are absent or which show considerably diminished intensity in the TR FT spectrum (Fig. 3a). This diminished intensity is explained as follows. FT detection involves the application of a microwave pulse. Typically, a dead time,  $T_{\text{dead}}$  (*ca.* 100 ns) after application of the microwave pulse is required before a FID or ESE can be acquired. Broad lines are associated with shorter phase memory times  $T_M$  compared to sharp lines.<sup>14</sup> For broad lines,  $T_M < T_{\text{dead}}$ , the FID or ESE signal will be more difficult to detect by TR FT caused by the detector dead time problem of the FT method. In other words, in the time domain, data acquisition signal contributions from the broad peaks may decay to a significant extent during the dead time of the instrument; this, in turn, leads to an attenuation of the associated peaks in the frequency domain. In severe cases, such as those shown in Fig. 3a and Fig. 5c, the broadened lines that are clearly apparent in the TR CW spectrum may be difficult to discern in the TR FT spectrum.

In the presence of acrylates the spin polarized 2-hydroxy-2-propyl radicals produced by the photolysis of **5** add to the unsubstituted double bond of the **3** and **4** (reactions (4) and (5)) with spin conservation during the reaction.<sup>11</sup> In the case of **5**, it has been established<sup>15</sup> that the polarization observed in TR CW EPR results mainly from addition of the polarized 2-hydroxy-2-propyl radicals **2a** to the acrylates. The addition of the benzoyl radical, **5a**, to acrylates, is typically a factor of 10 slower than the addition of 2-hydroxy-2-propyl radicals to acrylates<sup>16</sup> so that the adduct produced by addition of **5a** is either very weak in intensity or is not observed in the TR EPR spectra. Fig. 4b shows the TR CW EPR spectra of **5** in propan-2-ol. The resulting TR FT and TR CW EPR spectra in the presence of n-butyl acrylate and n-butyl methacrylate are shown in Fig. 5. The spectra produced with **5** as a precursor to the 2-hydroxy-2-propyl radicals show superior signal to noise relative to the spectra in which the 2-hydroxy-2-propyl radicals are produced from the acetone propan-2-ol system, thereby allowing an unambiguous determination of the differences between TR CW and TR FT spectra. Again, there are only

minor differences (Fig. 5a and b) in the adduct EPR spectra for the addition of 2-hydroxy-2-propyl radicals to n-butyl acrylate detected by either TR FT or TR CW. On the other hand, the TR FT adduct spectrum (Fig. 5c) for n-butyl methacrylate shows “missing” lines compared with the TR CW (line groups II, IV, VI, VIII) similar to the observations for acetone propan-2-ol system (Fig. 3a and b). The line groups IV and VI, which are the strongest in the TR CW Fig. 5d, are observed with very weak intensities in the TR FT spectra if one is using **5** as radical source. Therefore, the “missing lines” in the TR FT spectra are proposed to result from the shorter phase memory time of these line groups, and the shorter phase memory time is attributed to line broadening resulting from hindered rotation.<sup>14a,17</sup>

The coupling constants of the adduct radicals are independent of the method of radical generation (Table 1). Therefore, the radicals generated by addition of 2-hydroxy-2-propyl radicals to the acrylates can be unambiguously characterized during the photolysis of acetone in propan-2-ol in the presence of acrylates and methacrylates. However, an interpretation of the results of the acetone propan-2-ol system by TR FT EPR spectroscopy has complications in the detection of “broad signals” for both adduct radicals **3a** and **4a**:

The signal intensities of the four line groups of the adduct radical **3a** are equal in the TR FT using **5** as the radical source, but not in the TR CW with **5** as the radical source (Fig. 5a and b) and in the simulation (not shown).

Broad lines of the methacrylate adduct radical **4a** are either missing (or difficult to detect) in the TR FT spectrum using **5** as the radical source, but they appear clearly in the TR CW with **5** as the radical source.

## Conclusions

Although TR CW and TR FT EPR spectra of radicals produced by laser flash photolysis are typically experimentally equivalent except for signal to noise and resolution of the EPR signals, there are cases in which specific effects can influence  $T_2$  for certain lines in the TR FT spectrum and thereby complicate the identification of the radicals responsible for the experimental spectrum. In this report it is shown that certain lines can be reduced in intensity in the TR FT spectra as a result of the shortening of  $T_2$  due to hindered rotation. Although the “missing or diminished signals” in a TR FT spectra caused by a short  $T_M$  complicates the interpretation of TR FT EPR spectra,<sup>10b</sup> a combination of TR CW and TR FT and multiple methods of generation of radicals provides a means of resolving the complications and also leads to insights into the radical structure being investigated.

## Experimental

Acetone (**1**, Fisher), n-butyl acrylate (**3**), n-butyl methacrylate (**4**) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (**5**) from Ciba Specialty Chemicals were used as received. HPLC grade propan-2-ol (**2**) was obtained from Acros.

The time-resolved EPR equipment was described earlier<sup>18</sup> and consists of a Bruker ER 100D-X band EPR spectrometer (Bruker ESP 300 console and a Bruker ER 100D-X magnet), an EG&G PAR boxcar integrator model 4402 and signal processor model 4402. Between 1024 and 2048 points were recorded. Integration over different time windows after the laser pulse was performed. Excitation was performed with a Lambda Physik Lextra 50 excimer laser (308 nm, 20 ns, 30–100 mJ pulse<sup>-1</sup>). A quartz flowcell with a 0.3 mm path-length was used in combination with a syringe pump. Solutions of the photoinitiators were prepared at concentrations such that the absorbance was *ca.* 0.3–0.5 at the excitation

wavelength. Samples were made fresh and were deoxygenated by bubbling with argon for at least 30 min. Flow rates were between 2.0 and 4.0 ml min<sup>-1</sup>.

Two-pulse electron spin echo experiments were performed on TR-FT EPR equipment which was described earlier,<sup>19</sup> consisting of a Bruker ESP 300/380 pulsed FT EPR spectrometer. Excitation was performed with a Lambda Physik OPTex excimer laser ( $\lambda = 308$  nm, 8 ns, 5 Hz, ca. 10 mJ pulse<sup>-1</sup>). A coaxial quartz flow cell with a diameter of 3 mm was used in combination with a syringe pump (flow rate 1.5 ml min<sup>-1</sup>). Solutions were prepared fresh and were deoxygenated by bubbling with argon for at least 30 min. Experiments were carried out at room temperature. The spectra were recorded by a laser pulse- $t-90^\circ-\tau-180^\circ-\tau$ -echo sequence with different delay times  $t$  and  $\tau = 96$  ns in combination with an eight-phase cycling in order to suppress unwanted signals. Microwave pulses with lengths of 16 and 24 ns were used. The excitation range of the microwave field was around  $\Delta B = \pm 0.5$  mT under our experimental conditions and exceed the spectral range of the ketyl radical (14 mT). Therefore, it was necessary to record the spectra at different field positions (8 or 16 positions with a distance of 2.0 or 1.0 mT were used). Hyperfine coupling constants were determined by comparing simulated EPR spectra (WINEPR SimFonia, Version 1.25, Bruker Analytische Messtechnik GmbH) with the experimental spectra.

## Acknowledgments

The authors at Columbia University thank the National Science Foundation (CHE98-12676) for generous support of this research. This work was supported in part by the MRSEC Program of the National Science Foundation under Award Number DMR-9809687. The authors thank Professor Hans van Willigen and Professor David Doetschman for informative discussion of the line broadening effect on the signal intensity of FT spectra. They also thank Professor van Willigen for a preprint of relevant research<sup>4b</sup> from his laboratory.

## References

- (a) P. J. Hore, C. G. Joslin and K. A. McLauchlan, *Chem. Soc. Rev.*, 1979, **8**, 29; (b) N. Hirota and S. Yamauchi, in *Studies in Physical and Theoretical Chemistry* ed. K. Kuchitsu, Elsevier, Amsterdam, 1994, vol. 82, p. 513; (c) M. D. E. Forbes, *Photochem. Photobiol.*, 1997, **65**, 73.
- (a) K. A. McLauchlan and D. G. Steven, *Acc. Chem. Res.*, 1988, **21**, 54; (b) K. A. McLauchlan, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2465.
- H. van Willigen, H. P. R. Levstein and M. H. Ebersole, *Chem. Rev.*, 1993, **93**, 173.
- (a) K. A. McLauchlan and M. T. Yeung, *Electron Spin Resonance*, Specialist Periodical Report, The Royal Society of Chemistry, Cambridge, 1994, vol. 14, p. 32; (b) A. Bussandri and H. van Willigen, *J. Phys. Chem. A*, 2001, **105**, 4669.
- J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, 1970, **21**, 499.
- (a) W. M. Nau, F. L. Cozens and J. C. Scaiano, *J. Am. Chem. Soc.*, 1996, **118**, 2275; (b) M. J. MacDonald and J. M. Roscoe, *J. Photochem. Photobiol. A*, 1991, **57**, 441.
- (a) M. D. E. Forbes, *J. Phys. Chem.*, 1992, **96**, 7836; (b) K. Tominaga, S. Yamauchi and N. Hirota, *J. Chem. Phys.*, 1987, **88**, 553 and references therein.
- (a) P. R. Levstein and H. van Willigen, *Z. Phys. Chem.*, 1993, **190**, 33; (b) P. R. Levstein, P. Doering and H. van Willigen, *Chem. Phys. Lett.*, 1992, **197**, 265; (c) P. R. Levstein and H. van Willigen, *J. Chem. Phys.*, 1991, **95**, 900.
- (a) A. Schweiger, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 265; (b) L. Kevan and M. K. Bowman, *Modern Pulsed and Continuous-Wave Electron Spin Resonance*, Wiley, New York, 1990; (c) D. S. Stephenson, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1988, **20**, 515.
- (a) H. Fischer and L. Radom, *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 1340; (b) A. Beckert, S. Naumov, R. Mehnert and D. Beckert, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1075; (c) K. Vacek, J. Geimer, D. Beckert and R. Mehnert, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2469; (d) R. Martschke, R. D. Farley and H. Fischer, *Helv. Chim. Acta*, 1997, **80**, 1363; (e) S. N. Batchelor and H. Fischer, *J. Phys. Chem.*, 1996, **100**, 9794; (f) K. Héberger and H. Fischer, *Int. J. Chem. Kinet.*, 1993, **25**, 913; (g) J. Q. Wu and H. Fischer, *Int. J. Chem. Kinet.*, 1995, **27**, 167; (h) B. C. Gilbert, J. R. Smith, B. C. Milne and A. C. Whitwood, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1759.
- (a) K. A. McLauchlan and N. J. K. Simpson, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1371; (b) K. A. McLauchlan, R. C. Saley and J. M. Wittman, *Mol. Phys.*, 1978, **35**, 51; (c) K. A. McLauchlan, in *Chemically Induced Magnetic Polarization* ed. L. T. Muus, P. W. Atkins, K. A. McLauchlan and J. B. Pedersen, Reidel, Dordrecht, 1977.
- (a) J. B. Guillet, A. N. Ainscough, T. Kilp, S. Poos and N. J. Turro, *Can. Polym. Photochem.*, 1986, **7**, 439; (b) K. Otsuka and A. Morikawa, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3025; (c) G. Porter, S. K. Dogra, R. O. Loufty, S. E. Sugamori and R. W. Yip, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 1462.
- P. D. Sullivan and J. R. Bolton, *Adv. Magn. Reson.*, 1970, **4**, 39.
- (a) I. Gatlik, P. Rzedek, G. Gescheidt, G. Rist, B. Hellrung, J. Wirz, K. Dietliker, G. Hug, M. Kunz and J.-P. Wolf, *J. Am. Chem. Soc.*, 1999, **121**, 8332; (b) J. A. Weil, J. R. Bolton and J. E. Wertz, *Electron Paramagnetic Resonance*, Wiley, New York, 1994; (c) P. B. Ayscough, *Electron Spin Resonance in Chemistry*, Methuen, London, 1967.
- (a) M. Weber, I. V. Khudyakov and N. J. Turro, *J. Phys. Chem. B*, 2001, **105**, in press; (b) E. Karatekin, B. O'Shaughnessy and N. J. Turro, *Macromolecules*, 1998, **31**, 7992.
- W. Schnabel in *Lasers in Polymer Science and Technology: Applications*, ed. J.-P. Fouassier and J. F. Rabek, CRC Press, New York, 1991, vol. 2, pp. 95-144.
- (a) M. Spichty, B. Giese, A. Matsumoto, H. Fischer and G. Gescheidt, *Macromolecules*, 2001, **34**, 723; (b) W. Lung-min and H. Fischer, *Helv. Chim. Acta*, 1983, **66**, 138; (c) G. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 139; (d) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 326.
- I. V. Koptuyug, N. D. Ghatlia, P. F. McGarry, G. W. Sluggett, N. J. Turro and D. M. Watkins, *J. Am. Chem. Soc.*, 1995, **117**, 9486.
- I. V. Koptuyug, S. H. Bossmann and N. J. Turro, *J. Am. Chem. Soc.*, 1996, **118**, 1435.
- Matthias Weber, Ph.D. Thesis, University of Zurich, 2000.