

102. Rate Constants for the Addition of 2-Hydroxy-2-propyl Radicals to Alkenes in Solution Studied by Laser Flash Photolysis

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Absolute rate constants for the addition of the highly nucleophilic 2-hydroxy-2-propyl radical to eight fast-reacting 1- and 1,1-disubstituted alkenes in MeOH at room temperature have been determined by laser flash photolysis. Also the absorption spectra of the 2-hydroxy-2-propyl and the benzylic and alkyl-type adduct radicals are presented. The rate constants were obtained using various methods for the analysis of the kinetic traces and support earlier findings.

1. Introduction. – The addition of C-centered radicals to alkenes is one of the most important free radical reaction in polymer chemistry and in organic synthesis, and the factors controlling the rate constants have been the subject of much experimental and theoretical work (for reviews, see [1]). They involve an interplay of polar, steric, and enthalpy effects of the radical and the alkene substituents which is difficult to disentangle.

Recently, we have published absolute rate constants for the addition of the 2-hydroxy-2-propyl radical to a large variety of alkenes measured by kinetic EPR [2] and time-resolved CIDNP spectroscopy [3]. It was shown that 2-hydroxy-2-propyl is a prototype nucleophilic radical with a reactivity dominated by polar effects, and its rate constants served as basis for the discussion of more complicated cases. In the meantime we became aware of earlier laser flash photolysis data of *Schnabel* and co-workers [4] for the addition of the same radical to styrene, methyl methacrylate, and acrylonitrile. These alkenes were also covered in our studies, and our rate constants partly disagree by up to 1–2 orders of magnitude with *Schnabel*'s findings. Since some of our earlier rate constants are at the upper limit covered by kinetic EPR, we decided to re-investigate the addition of 2-hydroxy-2-propyl to these and other highly reactive alkenes by laser flash photolysis (LFP).

LFP is a well established technique to study photochemically generated short-lived intermediates [5]. For the determination of radical addition rate constants from kinetic traces several methods are known [6]. Most frequently, one measures the desired rate constant somewhat indirectly in competition to that of a standard reaction [7] which gives a conveniently observable product with a large absorption coefficient, and neglects small contributions from fast self- and cross-termination reactions. In most of this work, we avoid this complication, and analyze traces which are only due to the primary 2-hydroxy-2-propyl and its adduct radicals to the alkenes, *i.e.*, do not add a 'probe' substance. The absorption spectra of the radicals are also obtained, in some cases both by direct kinetic and by auxiliary modulation spectroscopy. In addition, we also use the probe technique for analysis.

2. Experimental. – Fig. 1 shows a schematic representation of our experimental setup. It combines a laser flash photolysis with a modulation-spectroscopy arrangement. The LFP system in the upper part of Fig. 1 is an improved version of that described previously and similar to the apparatus used by others [8]. Radiation from a *Lambda Physik LPX 100* excimer laser (308 nm, maximum pulse energy 100 mJ) is collimated via spherical and cylindrical lenses, and then passed through calibrated glass filters (F) for intensity reduction and the shutter (S1) to a *Suprasil* cell of $3 \times 10 \times 50$ mm³ inner dimension. The front of the cell has an illuminated area of 9×11 mm², and on the backside a mirror is installed. The solns. flow through the cell with rates of $1.5\text{--}3$ cm³ min⁻¹ and are replaced in the photolysis region after 1–2 pulses to avoid educt depletion or the formation of absorbing products. The laser output is monitored by a *Gentec ED-500* joulemeter (JM) and was constant within 20% during one experiment.

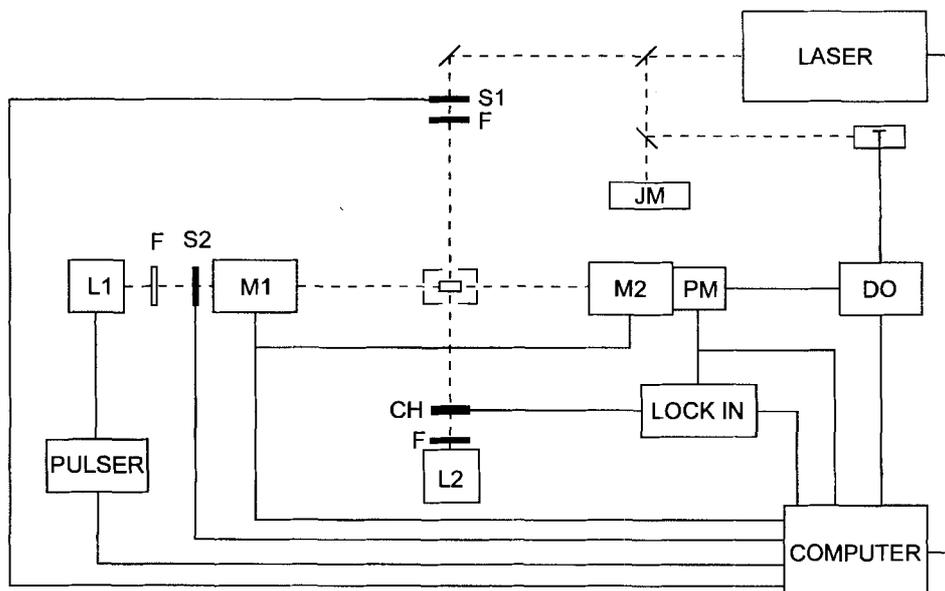


Fig. 1. Experimental arrangement. See text for symbols.

The modulation-spectroscopy part (MS) also follows an earlier design [9]. The light of a 1-kW Hg/Xe short-arc lamp *Hanovia 977-B-1* (L2) is limited to $225 \leq \lambda \leq 340$ nm by an aq. NiSO₄/CoSO₄ soln. filter [10] (F) and is transmitted by lenses to the same cell with the mirror in opposite position. Modulation is achieved by a *Ortec Brookdeal 9479* chopper (CH).

For monitoring the absorbance, we use a 450-W Xe short-arc lamp *Osram XBO 450 W/4* (L1) which, in the LFP experiments, is pulsed via a home-built high-current lamp pulser with 100–250 A for 2 ms. The two monochromators M1 (*Bausch & Lomb* high intensity, 1350 grooves/mm, bandwidth 10 nm) and M2 (home-built, 1200 grooves/mm, bandwidth 5 nm) operate synchronously, and the photomultiplier (PM) is a *Hamamatsu R 955*. In the LFP mode, it is charged with 1000 V across four dynodes only and is connected over a 50-Ω resistor to the digital oscilloscope (DO) which is triggered by the laser pulse via a photodiode (T). In the MS mode, five dynodes with 1000 V total operate, and the PM is connected over a 1-kΩ resistor to the computer and the lock-in amplifier (*Ithaco Dynatrac 391a*) which takes its reference from the chopper.

To obtain kinetic traces in LFP, the following procedure is applied. For each of the three shutter configurations $\overline{S1}S2$ (S1 closed, S2 open, background only), $S1\overline{S2}$ (fluorescence only), and $S1S2$ (background, fluorescence and kinetic signal), the digital oscilloscope takes one trace, and these are then transferred to the computer. Combination of the three traces corrects the kinetic trace for background and fluorescence. However, because of laser intensity fluctuations, the latter is not cancelled completely and disturbs the final trace in the first 100-ns post flash. Generally, the sequence is repeated 10–50 times to achieve a sufficient signal-to-noise ratio by averaging.

The computer also controls the operation of the laser, the lamp pulser, and a shutter control unit *via* an IEEE interface *MP488CT*.

In modulation spectroscopy, the light of the excitation lamp is modulated typically by 50–100 Hz, and the signal from the lock-in amplifier is recorded *via* an A/D converter (*Computer Boards CIO-DAS08-PGA*) into the computer. The first harmonic of the absorbance as function of the wavelength yields the absorption spectrum of the transient.

Most of the chemicals were from commercial sources and used in the purest available form. The alkenes were purified additionally by distillation. 2,4-Dihydroxy-2,4-dimethylpentan-3-one (DDP) was synthesized according to [11] and purified. Solns. were freed from oxygen by at least 30 min purging with Ar prior to use, and all experiments were carried out at r.t. ($22 \pm 2^\circ$).

3. Absorption Spectra. – An absorption spectrum recorded during photolysis of 0.05M DDP in MeOH and averaged over 1–4 μs after the laser flash is shown in *Fig. 2*. The structureless absorption band with a maximum below 250 nm and a weaker band with a maximum at 345 nm are in good agreement with literature spectra of the 2-hydroxy-2-propyl radical, and we have used the known decadic absorption coefficient, $\epsilon_{280} = 860 \text{ M}^{-1} \text{ cm}^{-1}$, for the conversion of the directly measured changes of absorbance which ranged typically from 0.02 to 0.2 [12] [13]. The insert in *Fig. 2* displays a kinetic trace obtained for 0.015M DDP at $\lambda = 300 \text{ nm}$ in MeOH. As expected from the well-characterized photochemistry of the ketone [12], there is a very fast (20 ns) initial rise in absorption which is obscured here by the fluorescence and is due to *Reactions 1* and *2*. It is followed by a much slower second-order decrease which reflects the radical self-termination

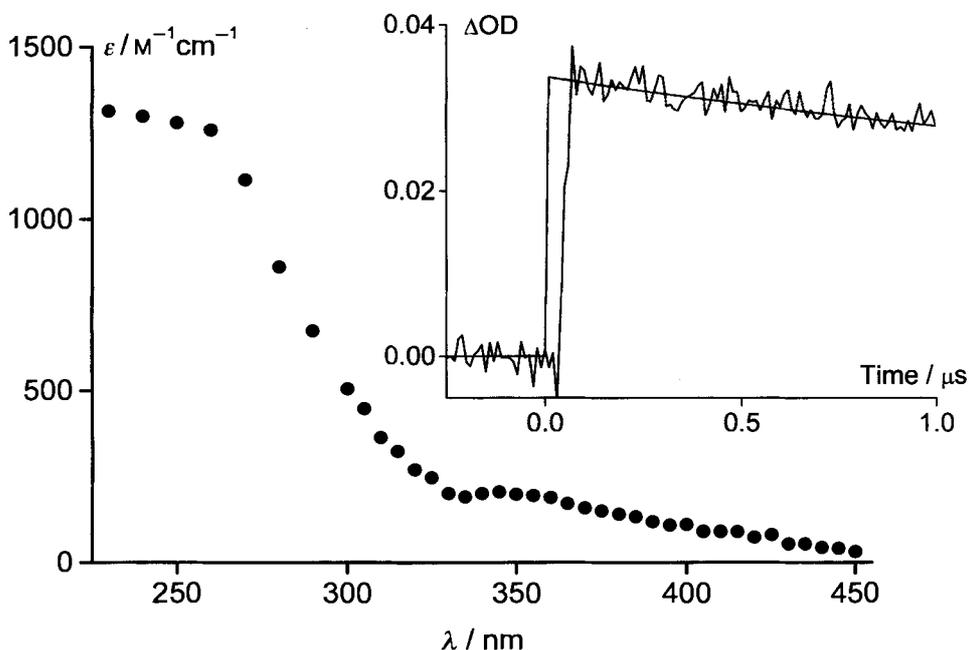
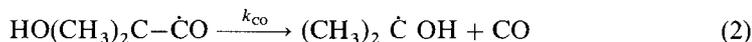
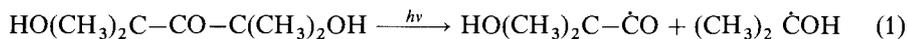


Fig. 2. Absorption spectra of the 2-hydroxy-2-propyl radical in MeOH. Insert: Average of 33 kinetic traces together with the best fit to a second-order decay ([DDP] = 0.015M, $\lambda = 300 \text{ nm}$).

reaction. In the first μs , this decrease is small which is important for the following determination of addition rate constants.



In presence of alkenes, new absorbing species appear. Their optical densities increase to plateau values which decrease with decreasing laser energy and were found independent of the alkene concentration within 10% at each laser energy, whereas the rates of formation of the new absorptions increased with increasing alkene concentration. Therefore, the build-up of the new absorptions reflects the formation of secondary radicals by the addition of the 2-hydroxy-2-propyl radical to the alkene M, and we know from the previous EPR experiments that the addition occurs to the unsubstituted C-atom only [2].



The absorption spectra of the radical adducts were taken for an averaged time-delay of 3–8 μs after the photolysis flash at which the addition is complete. For the conversion of optical densities to absorption coefficients, *Eqn. 4* was used

$$\frac{\epsilon_{\text{R}}}{\epsilon_{\text{RM}}} = \frac{A_0^{\text{R}}}{A_{\infty}^{\text{RM}}} \quad (4)$$

where the indices R and RM refer to the parent 2-hydroxy-2-propyl and the secondary adduct radicals. A_{∞}^{RM} is the plateau optical density reached with alkene present, and A_0^{R} is the initial value of the absorbance measured without alkene, but for otherwise the same conditions and ketone concentration. Because of error propagation, the absorption coefficients given in the *Figures* should only be accurate within a factor of two.

Absorption spectra of the secondary radicals formed from styrene, α -methylstyrene, and 1,1-diphenylethene taken point by point from kinetic traces and continuously by modulation spectroscopy are presented in *Fig. 3*. Within the wavelength inaccuracy of ± 2 nm, they coincide and show characteristic bands from 300 to 340 nm, typical for the benzyl radical [8a] [9] and substituted benzyl radicals [14]. For benzyl, the band starting at ca. 320 nm is due to the transitions from the ${}^2\text{B}_2$ electronic ground state to the ${}^2{}^2\text{A}_2$ excited state [15]. As also found in [14], the absorption maxima of the substituted benzyl radicals are red-shifted with respect to that of benzyl.

The spectra obtained from addition of 2-hydroxy-2-propyl to acrylonitrile (*Fig. 4,a*) and methacrylonitrile (*Fig. 4,b*) exhibit less structured absorptions, and the same holds for those found for methyl acrylate, methyl methacrylate, and acrolein (*Fig. 5*). As for other alkyl-type radicals, the absorption coefficients are rather low.

4. Addition Rate Constants. – In a first series of experiments, the addition rate constants were obtained directly from the initial pseudo-first-order growth of the absorption. In the selected observation time of 100–800 ns, the terminations of $\text{RM} \cdot$ and $\text{R} \cdot$ are negligible

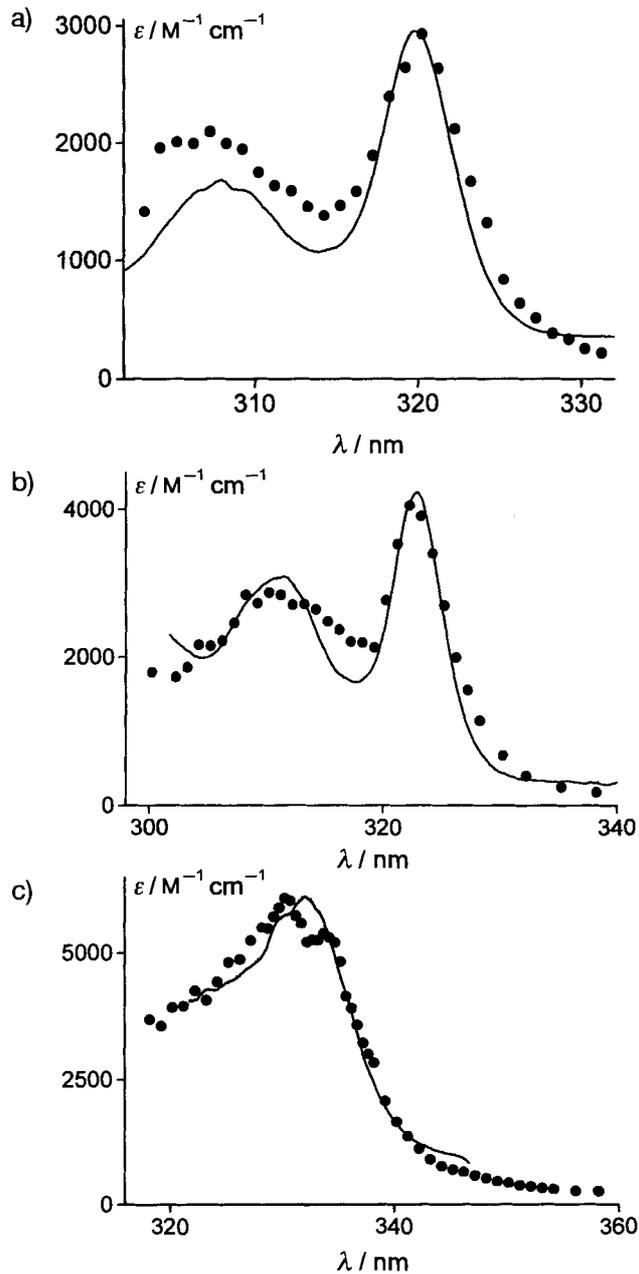


Fig. 3. Absorption spectra of radicals formed by the addition of 2-hydroxy-2-propyl radicals in MeOH to styrene (a, LFP: $[\text{M}] = 3.9\text{M}$, MS: $[\text{M}] = 0.05\text{M}$), α -methylstyrene (b, LFP: $[\text{M}] = 4.3\text{M}$, MS: $[\text{M}] = 0.05\text{M}$), and 1,1-diphenylethene (c, LFP: $[\text{M}] = 1.0\text{M}$, MS: $[\text{M}] = 0.05\text{M}$) ([DDP] = 0.015M)

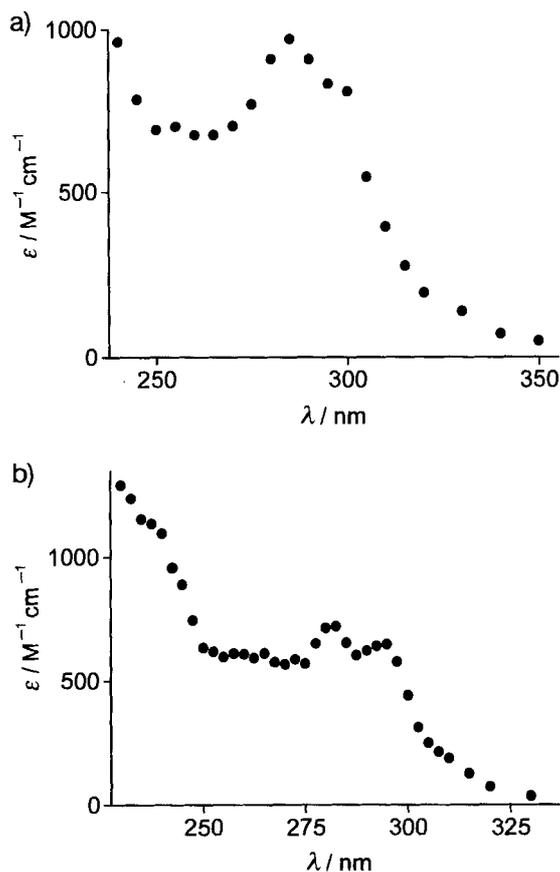


Fig. 4. Absorption spectra of radicals formed by the addition of 2-hydroxy-2-propyl in MeOH to acrylonitrile (a, 1.0M) and methacrylonitrile (b, 0.5M) ([DDP] = 0.015M)

(Fig. 2). Since the spectra of 2-hydroxy-2-propyl and the adduct radicals overlap, the kinetic trace is a superposition of the decay of the primary radical and the growth of the adduct radicals. For these conditions one has

$$\frac{d[\text{R}\cdot]}{dt} = \frac{d[\text{RM}\cdot]}{dt} = k[\text{M}][\text{R}\cdot] \quad (5)$$

$$[\text{R}\cdot]_0 = [\text{RM}\cdot]_\infty \quad (6)$$

$$A(t) = \varepsilon_{\text{R}}[\text{R}\cdot](t) + \varepsilon_{\text{RM}}[\text{RM}\cdot](t) = \varepsilon_{\text{RM}}[\text{RM}\cdot]_\infty \left[1 - \frac{\varepsilon_{\text{RM}} - \varepsilon_{\text{R}}}{\varepsilon_{\text{RM}}} \exp(-k[\text{M}]t) \right] \quad (7)$$

and

$$\ln \frac{A_\infty}{A_\infty - A_t} = \ln \frac{\varepsilon_{\text{RM}}}{\varepsilon_{\text{RM}} - \varepsilon_{\text{R}}} + k_{\text{exp}} t \quad \text{with } k_{\text{exp}} = k[\text{M}] \quad (8)$$

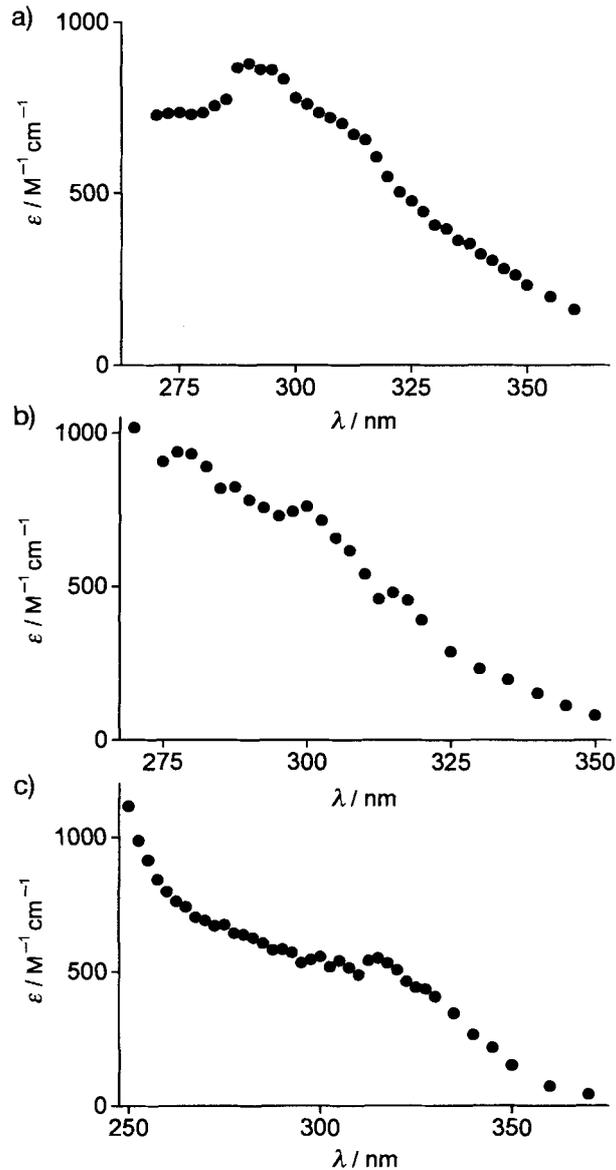


Fig. 5. Absorption spectra of radicals formed by the addition of 2-hydroxy-2-propyl in MeOH to methyl acrylate (a, 0.1M), methyl methacrylate (b, 0.1M), and acrolein (c, 0.05M) ([DDP] = 0.015M)

where the subscripts ∞ and t refer to the plateau value and time t , respectively. Of course, alkene depletion can be safely neglected, since $[M] \gg [R \cdot]_0$. The analysis method used here is a slightly modified version of one given by *Scaiano* and co-workers [7a], and it was checked that the results did not depend on the laser intensity.

Fig. 6 shows a typical transient absorption trace taken at $\lambda = 317$ nm for the addition to styrene in MeOH. Overlaid is the best fit to Eqn. 7 after the end of the fluorescence disturbance. The insert shows $\ln[A_\infty/(A_\infty - A_t)]$ vs. time. As expected, Eqn. 8 is obeyed, and the offset at zero time is due to the first term on the rhs of Eqn. 8. To determine the addition rate constant from the slopes of the linear dependencies, various styrene concentrations were employed, and k_{exp} was plotted vs. the styrene concentration (Fig. 7).

For the other alkenes, the same procedure was applied. However, for these the ratios $\epsilon_{\text{RM}}/\epsilon_{\text{R}}$ are closer to one. This complicates the analysis, because the initial absorbance is

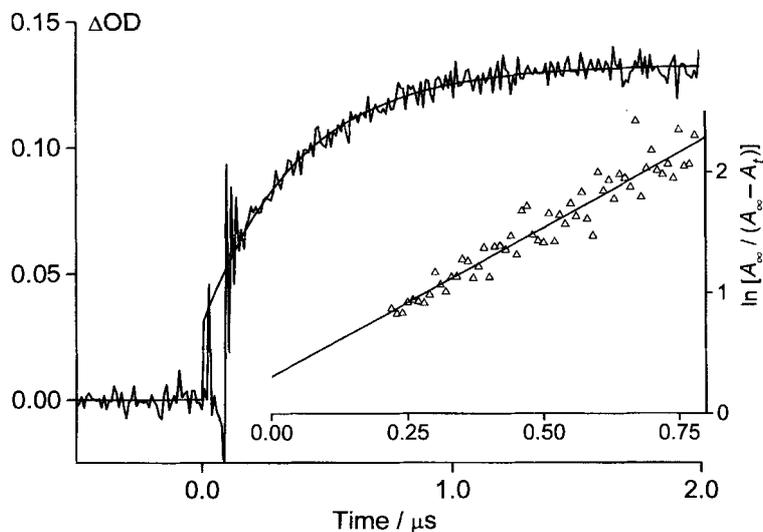


Fig. 6. Average of 10 kinetic traces for the addition of 2-hydroxy-2-propyl to styrene in MeOH ([DDP] = 0.015M, [M] = 3.55M, $\lambda = 317$ nm). Insert: $\ln[A_\infty/(A_\infty - A_t)]$ vs. time.

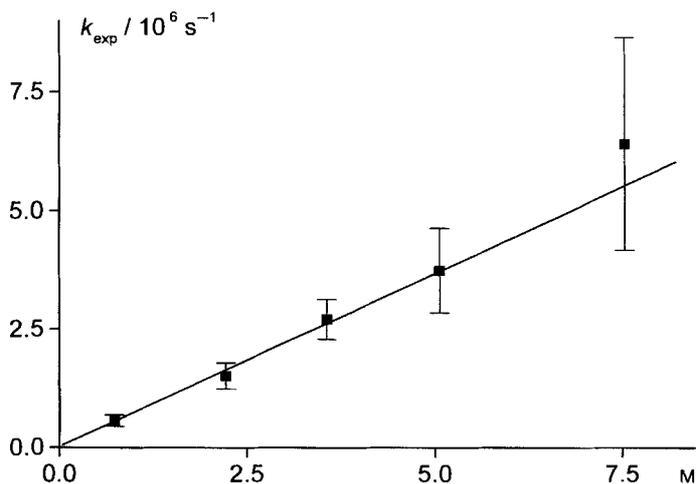


Fig. 7. k_{exp} vs. [M] for the addition of 2-hydroxy-2-propyl to styrene ([DDP] = 0.015M)

already close to the plateau value. The largest difficulties were encountered with methacrylonitrile. A transient trace taken at $\lambda = 295$ nm is shown in Fig. 8, and Fig. 9 demonstrates that even in this case the plot of k_{exp} vs. $[M]$ was satisfactory. The resulting rate constants are listed in the Table under Method A.

As an alternative analysis approach, we also evaluated kinetic traces obtained for the addition to styrene, α -methylstyrene, and 1,1-diphenylethene in more extended time regions where for the two styrenes the termination reactions cannot be neglected. One example is presented in Fig. 10. The monitoring wavelength was set to the absorption

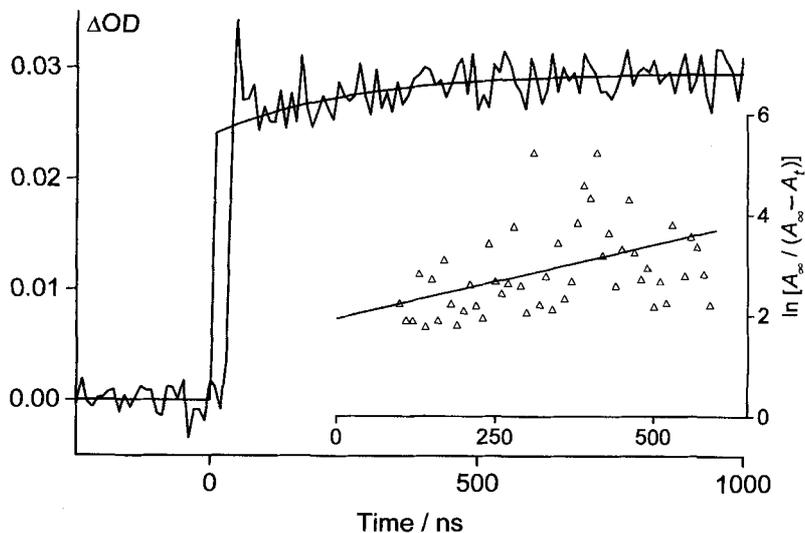


Fig. 8. Average of 33 kinetic traces for the addition of 2-hydroxy-2-propyl to methacrylonitrile in MeOH ([DDP] = 0.015M, $[M] = 0.057$ M, $\lambda = 295$ nm). Insert: $\ln[A_{\infty}/(A_{\infty} - A_t)]$ vs. time.

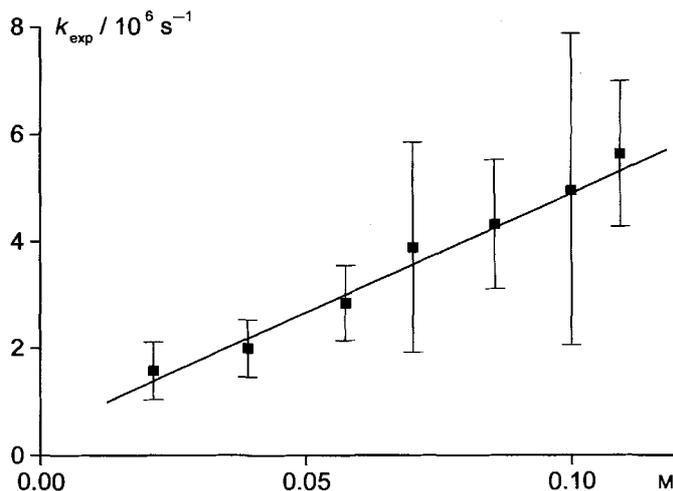


Fig. 9. k_{exp} vs. $[M]$ for the addition of 2-hydroxy-2-propyl to methacrylonitrile ([DDP] = 0.015M)

Table. Rate Constants for the Addition of the 2-Hydroxy-2-propyl Radical to Alkenes

Alkene	Method ^{a)}	Concentration [M]	k^c ($\times 10^{-5}$) [M ⁻¹ s ⁻¹]	$2k_i/\epsilon$ ($\times 10^{-4}$) [cm s ⁻¹]
Styrene	A	0.725–7.5	7.3	
	B	1.2	4.1	26
α -Methylstyrene	A	2.7–7.0	2.0	
	B	0.8	2.0	13
1,1-Diphenylethene	A	1.0–2.15	7.1	
	B	0.1	7.3	
	B ^{b)}	0.09	15	
Acrylonitrile	A	0.01–0.05	1500	
	C	8.95×10^{-4}	1100	5.1
Methacrylonitrile	A	0.02–0.11	450	
	C	$(3.04, 5.02) \times 10^{-3}$	310	12
Methyl acrylate	A	0.05–0.26	350	
	C	$(3.09, 7.73) \times 10^{-4}$	400	8.5
Methyl methacrylate	A	0.1–0.6	150	
	C	0.005, 0.010	160	11
Acrolein	A	0.0057–0.05	2700	
	C	$(0.41, 1.38) \times 10^{-3}$	2300	4.5

^{a)} See text.

^{b)} Solvent propan-2-ol.

^{c)} Statistical errors were below 15%.

maximum of the benzyl-type adduct radical (Fig. 3) so that the absorption by the primary 2-hydroxy-2-propyl radical could be neglected. With the assumption of equal self- and cross-termination constants of all transient species, the appropriate rate laws were numerically integrated and simultaneously fitted to the traces using the initial radical concentration, the addition rate constant, and the ratio of $2k_i/\epsilon_{RM}$ as free parameters. Fits are shown in Fig. 10, and data obtained in this way are listed in the Table under Method B.

Finally, the reaction of 2-hydroxy-2-propyl with the acrylates, acrylonitriles, and acrolein was also followed in competition to the reaction with α -methylstyrene, and the adduct radical of the latter alkene served as kinetic probe. Proceeding with the same assumptions as before and holding the rate constant for addition to α -methylstyrene fixed at $2.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, we arrived at the data given under Method C in the Table.

The addition rate constants derived by the various methods for analysis agree reasonably well with each other, and Method A is of course the most direct way. They also confirm the validity of our earlier data [2] [3], except for the values obtained by kinetic EPR for the styrenes which are found now considerably lower. Probably, the difference is due to alkene depletion in the earlier kinetic EPR experiments. The termination constants which can be derived from $2k_i/\epsilon_{RM}$ are close to diffusion control. They deserve no further discussion and may be subject to large errors caused by the simplifications of the rate laws.

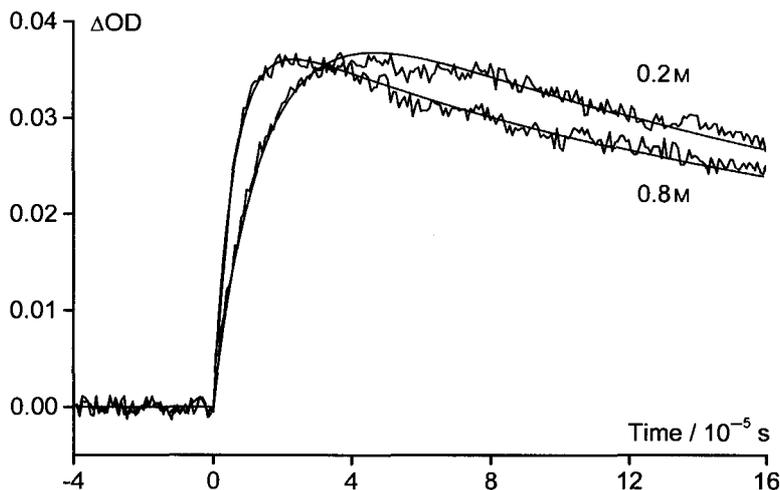


Fig. 10. Time-extended kinetic trace for the addition of 2-hydroxy-2-propyl to α -methylstyrene ([DDP] = 0.015M, $\lambda = 324$ nm), together with the best fits

For styrene, the addition rate constant $3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ given by *Schnabel* and coworkers [4] agrees fairly well with our results. However, for methyl methacrylate and acrylonitrile these authors reported values of 5.4×10^5 and $1.58 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, which are 1–2 orders of magnitude lower than found here and by CIDNP [3]. From the details given in [4], there is no clear reason for the discrepancy. One source of error may have been the use of a ketone precursor which leads to the formation of benzoyl radicals besides 2-hydroxy-2-propyl so that the kinetic traces are influenced by the addition of both radicals to the alkenes and difficult to analyze.

We have noted previously that 2-hydroxy-2-propyl is a strongly nucleophilic radical for which the rate constants of addition and their activation energies correlate well with the alkene electron affinities. This is exemplified in *Fig. 11* where $\log(k/\text{M}^{-1} \text{ s}^{-1})$ is plotted vs. the electron affinities, and where our new data are represented by open symbols. Except for the Ph-substituted alkenes for which the charge delocalization in the transition state lowers the polar effects [1c] there is an excellent linear correlation

$$\log(k/\text{M}^{-1} \text{ s}^{-1}) = 8.37 (\pm 0.16) + 2.86 (\pm 0.15) EA/\text{eV} \quad (9)$$

With the correlation coefficient, $r = 0.98$, and the standard error of the estimate, $\sigma = 0.46$, this correlation is even better than those given earlier.

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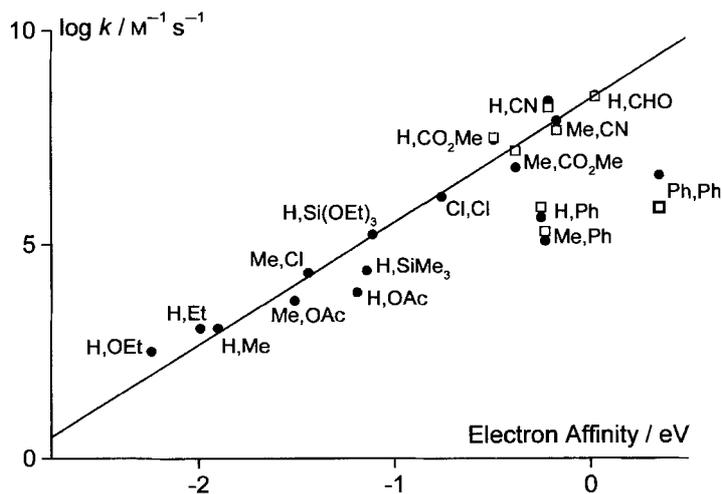


Fig. 11. Addition rate constants vs. electron affinity of the alkenes $\text{CH}_2 = \text{CXY}$, labeled with X, Y (solid symbols: data from [2] [3], open symbols: data from this work)

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