Rate coefficient for the H atom reaction with acrylate monomers in aqueous solution

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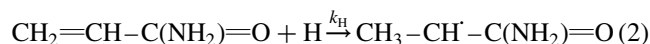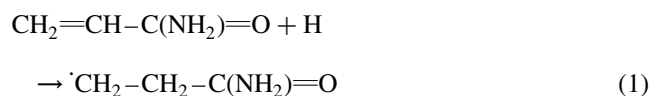
Abstract—The rate coefficients of H atom addition to 20 acrylate type monomers were measured in dilute aqueous solutions by pulse radiolysis technique. All the measured values were in a relatively narrow range (2×10^9–1×10^{10} mol^{-1} dm^3 s^{-1}). The rate coefficients changed in the following order: crotonates≈maleates<fumarates<acrylic acid esters≈acrylamides<methacrylic acid esters. Some correlation between the H and OH addition rate coefficients was found.
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1. Introduction

Numerous data are published on the rate coefficients of the reaction of hydrated electron (e_{aq}^-, radiation chemical yield G=2.7 species/100 eV energy absorbed) and hydroxyl radical (OH, G=2.7) intermediates of water radiolysis with acrylate type olefins.[1] Less data are available on rate coefficients of hydrogen atom (in acidic pH 1–2 solutions G=3.3) reactions with these olefins and the results are not consistent:[2–10] for compounds, which were measured by several groups values differing sometimes by an order of magnitude were published. The k_H-values are reported in the 5.6×10^8–3.1×10^{10} mol^{-1} dm^3 s^{-1} range. Most of the very high and very low values were determined in the early period of radiation chemical investigations when the technical possibilities and also the level of knowledge about the selection of proper experimental conditions were more limited than nowadays.[2,3,9,10]

In principle the H atoms may add to the α- or to the β-carbon atom with respect to the C=O group, forming alkyl (Reaction (1)), or α-carboxyalkyl radicals (Reaction (2)), respectively. However, the H-atoms and also the OH radicals were shown react in the β-position of acrylic and methacrylic acid esters and acrylamides producing α-carboxyalkyl radicals. As an example we show H atom addition to acrylamide:[6]

$$CH_2{=}CH{-}C(NH_2){=}O + H$$

$$\rightarrow \ ^{\cdot}CH_2{-}CH_2{-}C(NH_2){=}O \quad (1)$$

$$CH_2{=}CH{-}C(NH_2){=}O + H \xrightarrow{k_H} CH_3{-}CH^{\cdot}{-}C(NH_2){=}O \quad (2)$$

The H or OH adduct radicals of acrylic acid esters have characteristic transient UV absorption bands with λ_{max} between 280 and 330 nm, ε_{max}=300–600 mol^{-1} dm^3 cm^{-1}. For acrylamide type compounds λ_{max}=360–480 nm, ε_{max}=600–1000 mol^{-1} dm^3 cm^{-1}. Although these molar absorptivities are low, they allow optically monitoring of the build-up and decay of the adduct radicals in pulse radiolysis experiments.[3–6,10] When the H-atom reactions are studied, the solutions usually contain 0.2–1 mol dm^{-3} *tert*-butanol in order to convert the OH radicals, to less reactive $^{\cdot}CH_2C(CH_3)_2OH$ radicals:

$$OH + (CH_3)_3COH \rightarrow H_2O + \ ^{\cdot}CH_2C(CH_3)_2OH$$
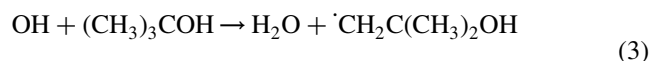
$$k_{OH} = 6 \times 10^8 \ \text{mol}^{-1} \ \text{dm}^3 \ \text{s}^{-1} \quad (3)$$

The $^{\cdot}CH_2C(CH_3)_2OH$ radicals may also add to the double bond of acrylates, however, the rate coefficients are ca. two orders of magnitude smaller than the rate coefficients of the H-atom reactions.[11] The H atoms also react with *tert*-butanol, the rate coefficient reported recently based on direct measurement of the $^{\cdot}CH_2C(CH_3)_2OH$ radical absorbance is $k_{H,t\text{-BuOH}}$=$(1.0 \pm 0.2) \times 10^6$ mol^{-1} dm^3 s^{-1}.[12]

$$H + (CH_3)_3COH \xrightarrow{k_{H,t\text{-BuOH}}} H_2 + \ ^{\cdot}CH_2C(CH_3)_2OH \quad (4)$$
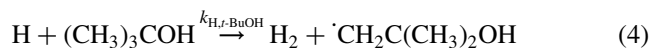
In this work we re-evaluate some of these inconsistent data and present a substantial set of new rate coefficients aiming to discuss the factors that influence H-atom reactions with

Table 1. Acrylic type monomers discussed

Acrylates, methacrylates	Name	Abbrev.	R	R^1	
	n-Butyl acrylate	NBA	H	CH$_2$CH$_2$CH$_2$CH$_3$	
	Hydroxyethyl acrylate	HEA	H	CH$_2$CH$_2$OH	
	Hydroxypropyl acrylate	HPA	H	CH$_2$CH(OH)CH$_3$	
CH$_2$=C–C=O	Hydroxyethyl methacrylate	HEMA	CH$_3$	CH$_2$CH$_2$OH	
	Hydroxypropyl methacrylate	HPMA	CH$_3$	CH$_2$CH(OH)CH$_3$	
OR^1	Cyclohexyl methacrylate	CHMA	CH$_3$	*c*-C$_6$H$_{11}$	

Crotonates	Name	Abbrev.	R^1	R^2	R^3
R^3	Methyl crotonate	MC	CH$_3$	H	CH$_3$
C=CH–C=O	Ethyl crotonate	EC	CH$_2$CH$_3$	H	CH$_3$
R^2 OR^1	3,3-Dimethyl methylacrylate	3,3DMMA	CH$_3$	CH$_3$	CH$_3$

Fumarates, Maleates	Name	Abbrev.	Conformation	R
OR	Fumaric acid	FA	*trans*	H
	Dimethyl fumarate	DMF	*trans*	CH$_3$
O=C–CH=CH–C=O	Diethyl fumarate	DEF	*trans*	CH$_2$CH$_3$
	Maleic acid	MA	*cis*	H
OR	Dimethyl maleate	DMM	*cis*	CH$_3$
	Diethyl maleate	DEM	*cis*	CH$_2$CH$_3$

Acrylamides	Name	Abbrev.	R	X
R	Acrylamide	AA	H	NH$_2$
	N-Hydroxymethyl acrylamide	NOHMAA	H	NHCH$_2$OH
CH$_2$=C–C=O	*N,N*-Dimethyl acrylamide	NNDMAA	H	N(CH$_3$)$_2$
	N-Isopropyl acrylamide	NIPAA	H	NHCH(CH$_3$)$_2$
X	Methacryloyl-L-prolin methyl-ester	MA-ProOMe	CH$_3$	NCHCH$_2$CH$_2$CH$_2$ / COOCH$_3$
	Methacrylamide	MAA	CH$_3$	NH$_2$

Others	Name	Abbrev.	Formula
	Cinnamic acid	CA	C$_6$H$_5$–CH=CH–COOH
	Acrylonitrile	AN	CH$_2$=CH–CN
	Allyl alcohol	Aal	CH$_2$=CH–CH$_2$OH
	Vinyl acetate	VA	CH$_2$=CH–O–C(O)CH$_3$

acrylates (Table 1). For this purpose, we apply well-designed reaction conditions by using nanosecond pulse radiolysis technique with optical detection.[13]

2. Results and discussion

2.1. H-atom reaction with acrylate type olefins

Two typical absorbance build-up curves showing the radical formation in acrylamide solutions are shown in the inset of Figure 1. The curves were taken at 380 nm where the ˙CH$_2$C(CH$_3$)$_2$OH radicals do not absorb the light and the absorbance is completely due to CH$_3$–CH˙–C(NH$_2$)=O radicals. The build-up curves always showed good first-order behaviour:

$$A = A^{\text{inf}}(1 - \exp(-k_{\text{obsd}}t)) \tag{5}$$

The extrapolated absorbances, A^{inf} $(=A_{\max}^{\text{inf}}k_{\text{H}}[\text{Olefin}]/(k_{\text{H}}[\text{Olefin}]+k_{\text{H},t\text{-BuOH}}[t\text{-BuOH}]))$ determined from the kinetic analyses, showed concentration dependence, par-

ticularly at low solute concentration. This dependence could be fitted by a Stern–Volmer type equation (Fig. 1):

$$\frac{1}{A^{\text{inf}}}\frac{[\text{Olefin}]}{[t\text{-BuOH}]} = \frac{1}{A_{\max}^{\text{inf}}}\frac{[\text{Olefin}]}{[t\text{-BuOH}]} + \frac{1}{A_{\max}^{\text{inf}}}\frac{k_{\text{H},t\text{-BuOH}}}{k_{\text{H}}} \tag{6}$$

As shown in Figure 1 for acrylamide, the plots of the observed rate coefficients k_{obsd} $(=k_{\text{H},t\text{-BuOH}}[t\text{-BuOH}]+k_{\text{H}}[\text{Olefin}])$ as a function of the acrylate concentration show a positive intercept with the ordinate $(k_{\text{H},t\text{-BuOH}}[t\text{-BuOH}])$. Both A^{inf} and k_{obsd} suggest a rate coefficient of $k_{\text{H},t\text{-BuOH}}=(1.3\pm0.3)\times10^6$ mol^{-1} dm^3 s^{-1} for Reaction (4). This value is in good agreement with the rate coefficient determined in direct measurements.[12]

Our k_{H}-values in Table 2 calculated using both k_{obsd} and A^{inf} have an estimated accuracy of ca. $\pm15\%$. This estimate is based on a large number of k_{H} values measured independently for acrylamide. In the table, in addition to our measurements, we also show some rate coefficient data for similar compounds taken from the literature.
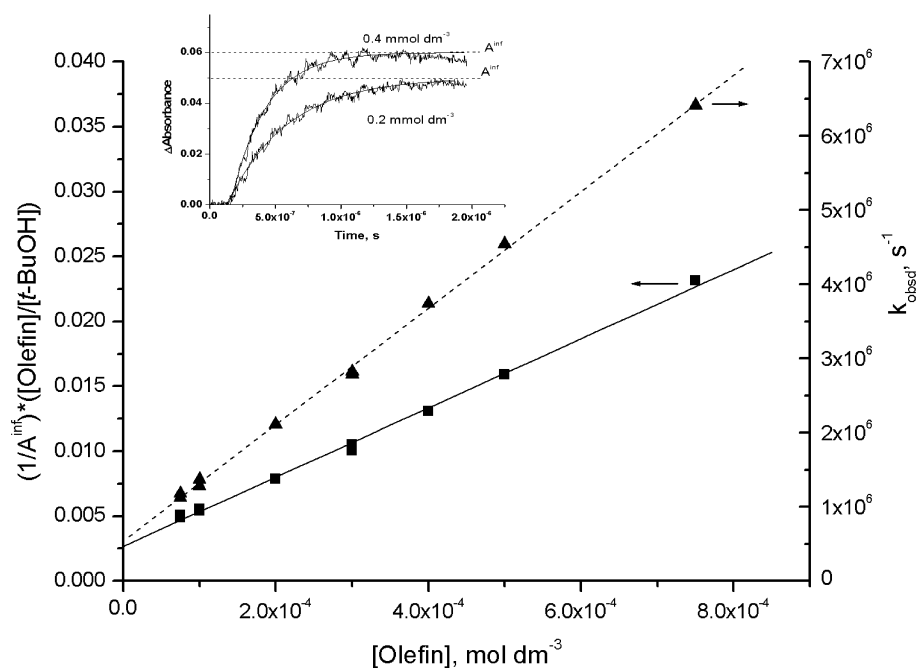
Figure 1. Concentration dependence of the extrapolated maximum absorbances at $\lambda = 380$ nm, A^{inf}, and those of the observed pseudo-first-order rate coefficients, k_{obsd} in acrylamide solutions, $[t\text{-BuOH}] = 0.5$ mol dm^{-3}. Inset shows two typical build-up curves at 0.2 and 0.4 mmol dm^{-3} acrylamide concentrations.

We made all of our measurements at wavelengths $\lambda \geq 300$ nm, above 300 nm the alkyl radicals absorb weakly, therefore we observe the formation and decay of the α-carboxyalkyl radicals. As was mentioned in Section 1, the reaction of H atoms with acrylic acid and methacrylic acid esters and acrylamides yields α-carboxyalkyl radicals (Reaction (2)). Since in the reaction of crotonates the $A^{\text{inf}}_{\text{max}}$ values were just slightly lower than found in the reaction of acrylic acid esters, we suppose that β-addition predominates also there. This is in agreement with the work of Gilbert et al.,[22] they suggested that the radicals add to crotonates at the β-position, and only the larger, sterically hindered radicals, like t-butyl add to the α carbon atom. The hydrogen atoms instead of addition to the double bond may also abstract H atoms from some of the molecules investigated. The rate coefficients of H atom abstraction are ca. two orders of magnitude smaller than those of H addition.

2.2. Correlation with the reaction enthalpies

The H atom addition rate coefficients measured fall in a relatively narrow range, they are between 1.9×10^9 and 1.1×10^{10} mol^{-1} dm^3 s^{-1}. The largest values approach the diffusion limited rate coefficient. The rate coefficients are the smallest for the crotonate group (methyl-, ethyl-crotonate, 3,3-dimethyl methylacrylate), $k_{\text{H}} \approx 2.4 \times 10^9$ mol^{-1} dm^3 s^{-1}. Similar rate coefficients were determined for the maleates, while the k_{H}s' for the fumarates are considerably higher. The alkyl acrylates and acrylamides have k_{H}-values around 7×10^9 mol^{-1} dm^3 s^{-1}. We measured the largest values for the methacrylates: $k_{\text{H}} \approx 9 \times 10^9$ mol^{-1} dm^3 s^{-1}. Methyl substitution in the α position (methacrylates) increases the reactivity, while when the substitution is in the β position (crotonates) the reactivity greatly decreases. The low

reactivity of crotonates was also noted in reaction with methyl or hydroxymethyl radicals and it was interpreted in terms of extra steric hindrance introduced at the non-carboxyl-substituted end of the double bond.[22] However, we think that in H atom addition reactions steric effects play minor role in determining the rate coefficients.

We suppose that the variation in the rate coefficients is basically due to reaction enthalpy effects (ΔH_{add}, Fig. 2). The enthalpy has a general and often dominating influence on the activation energy (E_a): this relation is often described by the linear Evans–Polanyi–Semenov equation, $E_a = 50 + 0.22\Delta H_{\text{add}}$ (kJ mol^{-1}).[23] The reaction enthalpy values mentioned here were taken from the papers of Denisov,[24–26] or they were estimated using thermochemical data collected from the references mentioned in this paper or in other publications.[27,28] The ΔH_{add}-values are subject to large uncertainties, however, the relative values are more accurate. The H atom addition to methacrylates is more exothermic by ca. 30 kJ mol^{-1} than to crotonates ($\Delta H_{\text{add}} \approx -190$ and ~ -160 kJ mol^{-1}), which can explain the large difference in the rate coefficients measured for α and β methyl substituted acrylates. Due to the higher stability of the tertiary type radical in H adducts of methacrylates than the secondary type radical in adducts of acrylates the reaction is somewhat less exothermic (by ~ 10 kJ mol^{-1}) in acrylates than in methacrylates in agreement with the somewhat higher rate coefficients for the latter. The exothermicities of the H reactions with allyl alcohol and vinyl acetate are estimated to be relatively low ($\Delta H_{\text{add}} \approx -(160-170$ kJ mol$^{-1})$) and the rate coefficients of H addition to these compounds belong to the lowest ones determined. Simple reaction enthalpy considerations cannot be used to explain the higher rate coefficients measured for the fumarates as compared to maleates. In H atom addition

Table 2. Rate coefficients of H-atom and OH radical addition to monomers ($mol^{-1} dm^3 s^{-1}$)

| Acrylate	k_H	k_{OH}
n-Butyl acrylate	5.7×10^9	5.5×10^{9a}
Hydroxyethyl acrylate	7.8×10^9	1.1×10^{10b}
Hydroxypropyl acrylate	8.5×10^9	8.7×10^{9b}
Hydroxyethyl methacrylate	1.1×10^{10}	1×10^{10}
Hydroxypropyl methacrylate	8.3×10^9	6.2×10^9
Cyclohexyl methacrylate	8.7×10^9	1×10^{10c}
Methyl crotonate	2.2×10^9	2.9×10^{9b}
Ethyl crotonate	2.7×10^9	3.2×10^{9b}
3,3-Dimethyl methylacrylate	2.1×10^9	3.4×10^{9b}
Fumaric acid	3.3×10^9	6×10^{9d}
Dimethyl fumarate	3.2×10^9	3.5×10^{9b}
Diethyl fumarate	6.5×10^9	5.9×10^{9b}
Maleic acid	1.9×10^9	6×10^{9d}
Dimethyl maleate	1.9×10^9	3.5×10^{9b}
Diethyl maleate	2.8×10^9	5.9×10^{9b}
Acrylamide	7.5×10^9	5.9×10^{9e}
N-Hydroxy methyl acrylamide	3.5×10^{9f}	3.4×10^{9f}
N,N-Dimethyl acrylamide	8×10^9	7.3×10^{9e}
N-Isopropyl acrylamide	6.6×10^{9g}	6.9×10^{9g}
Methacryloyl-L-prolin methyl-ester	5×10^{9h}	4.8×10^{9h}
Methacrylamide	7.6×10^9	1.1×10^{10}
Cinnamic acid	$\sim 8.4 \times 10^9$	
Acrylonitrile	4.0×10^{9i}	5.3×10^{9j}
Allyl alcohol	3.4×10^{9k}	5.9×10^{9l}
Vinyl acetate	3.1×10^9	4.5×10^9

a Ref. 15.
b Ref. 1.
c Ref. 14.
d Ref. 17.
e Ref. 6.
f Ref. 21.
g Ref. 5.
h Ref. 4.
i Ref. 16.
j Ref. 18.
k Ref. 19.
l Ref. 20.

to compounds of both groups the same radical type, $ROOC-CH_2-{}^\bullet CH-COOR$, forms. Since the heat of formation of the fumarate molecules (*trans* olefin) is smaller (by $\sim 20 kJ mol^{-1}$) than of the maleate molecules (*cis* olefin), ΔH_{add} is less exothermic for the fumarate group ($\sim 155 kJ mol^{-1}$) than for maleates. This is in contrast to the reversed order of rate coefficients. The small rate coefficients for the maleate group may be due to an unfavourable (*cis*-like) conformation of the H adduct intermediate at the moment of its formation. After the addition the intermediate with an unfavourable conformation may relax to the same more favourable (*trans*-like) conformation as forms in H addition to the *trans* olefin (fumarates).

2.3. Comparison of the reactivates of H atoms and OH radicals in addition reactions

H atoms are assumed to be less reactive in both radical addition and radical abstraction reactions than the OH radicals.[29] Apparently this may not be true for the olefins shown in Table 2 since for the same compound practically the same H and OH addition rate coefficients, k_H and k_{OH}, were measured: the average of all H addition rate coefficients in Table 2 is $k_{H,av} = 5.2 \times 10^9 mol^{-1} dm^3 s^{-1}$. The average value for OH addition, $k_{OH,av} = 6.1 \times 10^9 mol^{-1} dm^3 s^{-1}$, is just slightly higher. (We collected most of the OH radical addition rate coefficient values from our former publication.[1] In cases when no data were available, we made new measurements with the same technique as before.) When we interpret the relation between H and OH radical addition rate coefficients we have to take into account that all rate coefficients fall in the so-called near-diffusion-controlled rate coefficient region and, due to the much lower diffusion constant of OH radicals than H atoms (2.2×10^{-9} and $7 \times 10^{-9} m^2 s^{-1}$ at 25°C) the encounter rate coefficient for OH radicals is much smaller than for H
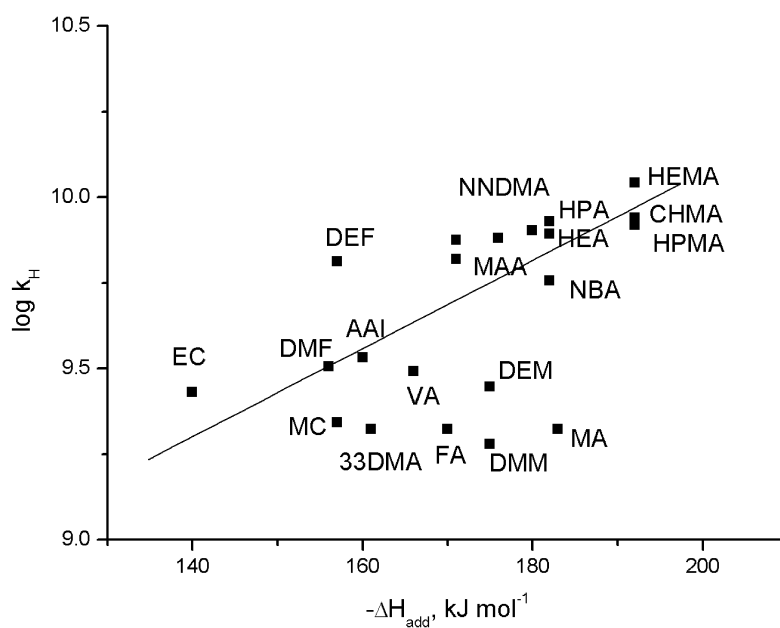
Figure 2. Correlation between the rate coefficients and the reaction enthalpies.
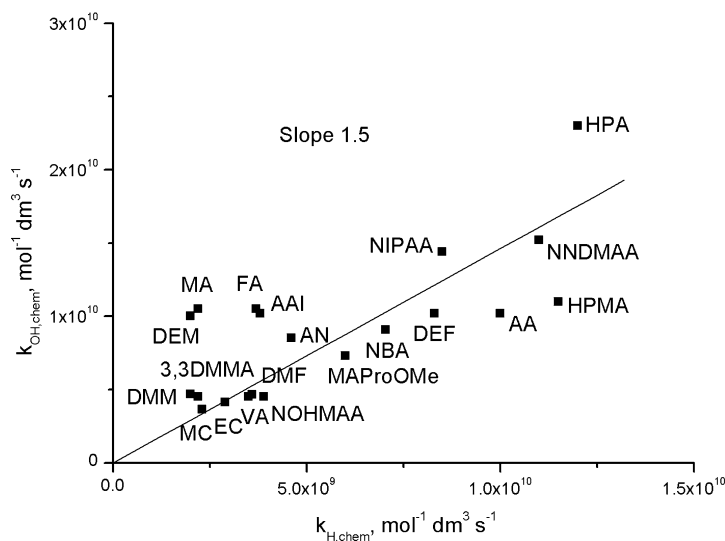
Figure 3. Correlation between $k_{H,chem}$ and $k_{OH,chem}$ rate coefficients. The solid line was obtained by linear fit.

atoms.[30] Using for our systems the method described in Ref. 30 and taking the average diffusion constant and reaction radius for acrylates as 1×10^{-9} m^2 s^{-1} and 0.36 nm, the encounter rate coefficients for the OH and H reactions are estimated as $k_{OH,diff}\approx1.4\times10^{10}$ and $k_{H,diff}\approx3\times10^{10}$ mol^{-1} dm^3 s^{-1}, respectively. The rate coefficient of the chemical reaction separated from the diffusion, that would be measured if the diffusion of the species was not rate influencing, $k_{H,chem}$ or $k_{OH,chem}$, can be estimated using an equation that we show on the example of H reaction:[31]

$$\frac{1}{k_H} = \frac{1}{k_{H,diff}} + \frac{1}{k_{H,chem}} \tag{7}$$

In the case of the lower rate coefficients $k_{H,chem}$ and $k_{OH,chem}$ are just slightly higher than k_H or k_{OH}, however, closer to the diffusion controlled limit the differences between the two values are high. A critical point is the selection of the diffusion limited rate coefficient especially in the case of OH reactions where the measured rate coefficients are very close to the encounter rate coefficient. In the further analysis we disregarded the olefins with very high k_{OH} values (HEA, HEMA, CHMA, MAA).

In Figure 3 we show that similarly to the k_H- and k_{OH}-values there is also some correlation between the $k_{H,chem}$ and $k_{OH,chem}$ rate coefficients. After the correction using Eq. (7), the OH radicals appear to be slightly more reactive in addition reaction to acrylate type olefins than the H atoms.

3. Summary

In the radiolysis of acidic aqueous solutions containing 0.1–0.8 mmol dm^{-3} acrylate type olefin and 0.3–0.5 mol dm^{-3} tert-butanol the H atoms react with comparable rate with the two solutes. The two reactions were separated by systematic variation of the solute concentrations. The rate coefficients of the H atom addition reaction to the double bond of the olefins are in the so-called near-diffusion-controlled region: they are between 1.9×10^9

and 1.1×10^{10} mol^{-1} dm^3 s^{-1}. The k_Hs are the smallest for the crotonates, maleates and fumarates and the largest for the methacrylic acid esters. It seems that the reaction enthalpies basically determine the magnitude of the rate coefficients. An analysis showed that the reactivity of OH radicals towards these olefins is somewhat higher than the reactivity of H atoms.

4. Experimental

The compounds were freed from the inhibitors by recrystallisation (AA and MAAm) or column treatment (acrylic acid esters, NNDMAA) and the solutions were freshly prepared before the experiments. The structural formulas of acrylate type monomers discussed in this work are collected in Table 1. The pH was set by perchloric acid to 1.1–1.5. Ar bubbling deoxygenated the solutions. Monomer concentrations ranged from 0.1 to 0.8 mmol dm^{-3}. tert-Butanol (analytical grade) was purchased from Fluka and was purified as recommended in the book of Perrin and Armarego.[32] The concentration of tert-butanol was 0.3 or 0.5 mol dm^{-3}.

Pulse radiolysis measurements were conducted with 20 ns pulses of 12 MeV electrons of the LINAC in Bologna.[13] The detection set-up had an overall rise-time of 2.5 ns. The temperature of the solutions was 25±3°C. The dose/pulse was generally ~50 Gy on a 5 cm optical path cell.

References

1. Bíró, A.; Takács, E.; Wojnárovits, L. *Macromol. Rapid. Commun.* **1996**, *17*, 353–357.

2. Chambers, K. W.; Collinson, E.; Dainton, F. S. *Trans. Faraday Soc.* **1970**, *66*, 142–162.

3. Madhavan, V.; Lichtin, N. N.; Hayon, E. *J. Am. Chem. Soc.* **1975**, *97*, 2989–2995.

4. Takács, E.; Sáfrány, Á.; Wojnárovits, L.; Martellini, L. F.; Yoshida, M.; Katakai, R.; Emmi, S. S.; Beggiato, G.; Carenza, M. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 21–32.

5. Strauss, P.; Knolle, W.; Naumov, S. *Macromol. Chem. Phys.* **1998**, *199*, 2229–2235.

6. Wojnárovits, L.; Takács, E.; Dajka, K.; D'Angelantonio, M.; Emmi, S. S. *Radiat. Phys. Chem.* **2001**, *60*, 337–343.

7. Neta, P.; Fessenden, R. W.; Schuler, R. H. *J. Phys. Chem.* **1971**, *75*, 1654–1666.

8. Beckert, D.; Mehler, K. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 587–591.

9. Neta, P.; Schuler, R. H. *Radiat. Res.* **1971**, *47*, 612–627.

10. Hayon, E.; Simic, M. *J. Am. Chem. Soc.* **1973**, *95*, 2433–2439.

11. Buxton, G. V.; Green, J. C. *Faraday Trans. 1* **1978**, *74*, 697–714.

12. Wojnárovits, L.; Takács, E.; Dajka, K.; Emmi, S. S.; Russo, M.; D'Angelantonio, M. *Phys. Chem.* **2003**, in press.

13. Emmi, S. S.; Beggiato, G.; Casalbore-Miceli, G. *Radiat. Phys. Chem.* **1989**, *33*, 29–37.

14. Kumar, M.; Rao, M. H.; Moorthy, P. N.; Rao, K. N. *Radiat. Phys. Chem.* **1989**, *33*, 219–222.

15. Sabharwal, S.; Das, T. N.; Chaudhari, C. V.; Bhardwaj, Y. K.; Majali, A. B. *Radiat. Phys. Chem.* **1998**, *51*, 309–315.

16. Buxton, G.; Ellis, P. G.; McKillop, T. F. W. *J. Chem. Soc., Faraday Trans.* **1978**, 1050–1066.

17. Cabelli, D. E.; Bielski, B. H. J. *Z. Naturforsch. B, Anorg. Chem., Org. Chem.* **1985**, *40B*, 1731–1737.

18. Kumar, M.; Rao, M. H.; Moorthy, P. N.; Rao, K. N. *Radiat. Eff. Express.* **1988**, *1*, 167–173.

19. Maruthamuthu, P. *Macromol. Chem., Rapid Commun.* **1980**, *1*, 23–25.

20. Appleby, A.; Schoes, G.; Simic, M. *J. Am. Chem. Soc.* **1963**, *85*, 3891–3892.

21. Acharia, A.; Mohan, H.; Sabharwal, S. *Radiat. Phys. Chem.* **2002**, *65*, 225–232.

22. Gilbert, B. C.; Schmith, J. R. L.; Milne, E. C.; Whitwood, A. C.; Taylor, P. *J. Chem. Soc., Perkin. Trans. 2* **1993**, 2025–2031.

23. Ficher, H.; Radom, L. *Angew. Chem. Int. Ed.* **2001**, *40*, 1340–1371.

24. Denisov, E. T. *Uspehi Himii* **2000**, *69*, 166–177.

25. Tumanov, V. E.; Kromkin, E. A.; Denisov, E. T. *Russ. Chem. Bull.* **2002**, *51*, 1641–1650.

26. Denisov, E. T.; Khursan, S. L.; Russ, *J. Phys. Chem.* **2000**, *74*, S491–S497.

27. Héberger, K.; Fischer, H.; Int, *J. Chem. Kinet.* **1993**, *25*, 913–920.

28. Héberger, K.; Lopata, A. *J. Org. Chem.* **1998**, *63*, 8646–8653.

29. Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886, Updated version: http://www.rcdc.nd.edu.

30. Elliot, A. J.; McCracken, D. R.; Buxton, G. V.; Wood, N. D. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1539–1547.

31. Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129–160.

32. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed. Pergamon: Oxford, 1988.