

PULSE RADIOLYSIS OF ACRYLOYL-L-PROLINE METHYL ESTER IN DILUTE AQUEOUS SOLUTION

E. TAKÁCS,* Á. SÁFRÁNY, and L. WOJNÁROVITS

Institute of Isotopes of the Hungarian Academy of Sciences
H-1525 Budapest, P.O. Box 77, Hungary

F. MARTELLINI

Comissão Nacional de Energia Nuclear
Instituto de Pesquisas Energéticas e Nucleares
IPEN/CNEN-SP
Sao Paulo, Brazil

M. YOSHIDA

Department of Material Development
Takasaki Radiation Chemistry Research Establishment
JAERI
1233 Watanuki, Gunma 370-12, Japan

R. KATAKAI

Department of Chemistry
Faculty of Engineering
Gunma University
Kiryu, Gunma 376, Japan

S. S. EMMI and M. CARENZA

Istituto di Fotochimica e Radiazioni d'Alta Energia
CNR
Via P. Gobetti 101, 40129 Bologna, Italy

ABSTRACT

The reactions of hydroxyl radical, hydrogen atom, and hydrated electron intermediates of water radiolysis with a hydrogel monomer, acryloyl-L-proline methyl ester, were studied by pulse radiolysis in dilute aqueous solutions. In reactions of OH and H, α -carboxyalkyl radicals form; they absorb the light with a maximum at 460–480 nm, $\epsilon_{\max} \approx 1000 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. The electron adduct reversibly protonates, and the protonated form absorbs the light with $\lambda_{\max} = 290 \text{ nm}$ and $\epsilon_{\max} = 8000 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. In addition to the reversible protonation, there is also an irreversible protonation which produces also α -carboxyalkyl radicals. These radicals at low concentration ($0.1\text{--}1 \text{ mmol} \cdot \text{dm}^{-3}$) and high dose/pulse ($10\text{--}100 \text{ Gy}$) decay in second-order self-termination reactions with $2k = 3 \times 10^8 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$.

INTRODUCTION

The reactions of several acrylic and methacrylic esters (ethyl acrylate, hydroxyethyl acrylate, cyclohexyl methacrylate) with the hydrated electron, hydroxyl radical, and hydrogen atom intermediates of water radiolysis were studied previously by means of pulse radiolysis combined with optical spectroscopy [1–4]. The electron adducts formed in the reaction with the hydrated electron were found to protonate reversibly. In the cases of ethyl and hydroxyethyl acrylate, in addition to the reversible protonation an irreversible one was also found that takes place on the β -carbon atom, thus forming α -carboxyalkyl radicals. Similar radicals directly form in the reaction with OH radicals and H atoms. The α -carboxyalkyl radicals have a characteristic light absorption in the UV region with a flat maximum at about 310 nm and an extinction coefficient of $\approx 400 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. In dilute aqueous solutions and at high dose/pulse values the radicals mostly disappear in bimolecular self-termination reactions. However, at higher monomer concentrations ($\geq 1 \text{ mmol} \cdot \text{dm}^{-3}$) and lower dose/pulse values, some oligomerization reactions were also noted [4].

In recent years thermoresponsive polymers have received much attention. When such a polymer is crosslinked, a hydrogel is obtained that shows a volume phase transition in aqueous solution, changing from a highly swollen network at lower temperature to a collapsed phase above a certain critical level [5–7]. These hydrogels have been proposed for a wide variety of biomedical applications including controlled drug delivery, bioseparation processes, and artificial organs. The hydrogel may be produced by radiation-induced polymerization and crosslinking in aqueous solution. The hydrogel produced from acryloyl-L-proline methyl ester (A-ProOMe) in aqueous solution shows especially good thermoresponsive characteristics [6–8]. In the present work we investigate the radiolytic processes of this monomer.

EXPERIMENTAL

A-ProOMe was obtained by condensation of L-proline methyl ester hydrochloride ($\text{HCl} \cdot \text{HProOMe}$) and acrylic acid by the method as described in Ref. 8. The monomer solutions were freshly prepared using triply distilled water. The ma-

jority of the investigations were carried out at the neutral pH of the solution (pH 6.0–6.4); the others in buffered solutions. The pH was set by HCl, phosphate buffers, or NaOH.

Pulse radiolysis with optical detection in Bologna, Italy, was performed by using the 12-MeV linear accelerator of the FRAE Institute of CNR [9]. The pulse irradiations (10–50 ns) were made on samples in Suprasil cells of 5 cm optical path length. The solutions were protected from the analyzing light by means of a shutter and appropriate cut-off filters. The radiation dose per pulse (10–100 Gy) was monitored by means of a charge collector placed behind the irradiation cell and calibrated with a O₂ saturated solution containing 0.01 M KSCN and by taking $G_{\epsilon_{500\text{nm}}} = 2.15 \times 10^4 (100 \text{ eV})^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$.

In Budapest, Hungary, the pulse radiolytic measurements were carried out with the 4-MeV linear accelerator of the Institute of Isotopes of the HAS with pulse durations of 80 ns or 2.5 μs and dose per pulse values of 10 Gy or 40–100 Gy in a 1-cm cell [10].

The absorbances were calculated from the oscilloscope traces. They were generally converted to $G\epsilon_\lambda$ by dividing the absorbances by the dose (Gy) and the cell length (cm) and multiplying by a conversion factor of $9.65 \times 10^6 \text{ Gy} (100 \text{ eV})^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$.

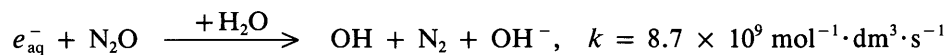
The solutions were deoxygenated by bubbling with dry He or N₂. When the reactions of OH radicals were investigated, the solutions were saturated with N₂O. The solution in the cell was changed after each shot.

All measurements were made at room temperature.

RESULTS AND DISCUSSION

Reaction of the Monomer with OH Radicals

The radiolysis of water generates hydroxyl radical, hydrogen atom, and hydrated electron reactive intermediates. The G -values (number of species formed per 100 eV of energy absorbed by the solution) of these intermediates in the reaction with solutes at the $\text{mmol} \cdot \text{dm}^{-3}$ concentration level are usually taken as 2.7, 0.55, and 2.7, respectively [11, 12]. If the concentration of the solute is considerably higher, somewhat higher $G(\text{OH})$ and $G(e_{\text{aq}}^-)$ values are used because at higher concentrations the solute may interfere with the spur processes. When the reaction of the OH radicals is investigated, the e_{aq}^- is usually converted to OH radicals by the reaction



Therefore, in a N₂O saturated solution ($0.025 \text{ mol} \cdot \text{dm}^{-3}$) the intermediates that react with the solute present in a concentration of $\approx 1 \text{ mmol} \cdot \text{dm}^{-3}$ are OH radicals ($G = 5.4$) and H atoms ($G = 0.55$). The reactions of the H atoms are usually similar to the reactions of OH radicals [11–14].

The reaction between these species and A-ProOMe leads to a transient absorption with a broad maximum at 480 nm (Fig. 1). The absorbance at the pH of the solution (6.0–6.4) builds up quickly, with a time period of about 1 μs , and then it disappears within a few milliseconds (Fig. 2). We obtained the build-up of the signal

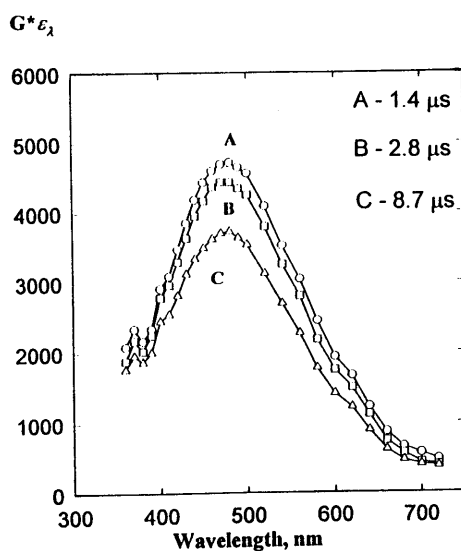
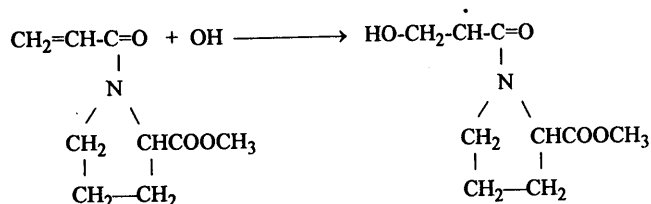


FIG. 1. Absorption spectra obtained in N_2O saturated $1 \text{ mmol} \cdot \text{dm}^{-3}$ A-ProOme solution at neutral pH. Dose/pulse: 63 Gy. (A) $1.4 \mu\text{s}$, (B) $2.8 \mu\text{s}$, and (C) $8.7 \mu\text{s}$ after 50 ns pulse.

by fitting a second-order rate constant of $6.5 \times 10^9 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$. This value agreed reasonably well with the rate constant of the reaction of OH radicals with the solvent, $5.5 \times 10^9 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$, as measured in competition with the OH + SCN^- reaction. The rate constant of the latter reaction was taken as $1.1 \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ [11].

The very wide absorption band centered at 480 is similar to that of the α -carboxyalkyl radical $\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$ obtained by the radiolysis of α -chloro-*N,N*-dimethylacetamide in a hydrated electron scavenging reaction [14]. On the basis of both this similarity and the analogous reaction of OH with acrylic acid derivatives [1-4, 13], the reaction between the OH radical and A-ProOme could take place with OH radical addition to the double bond:



Similar radicals play a decisive role in the radical polymerization of acrylic acid esters and acrylamide. Assuming that all the OH radicals and H atoms react in producing the α -carboxyalkyl radical, the extinction coefficient at 480 nm is estimated as $860 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. In the work of Hayon et al. [14], the extinction coefficient in the absorbance maximum of α -carboxyalkyl radical was estimated to be $1000 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$.

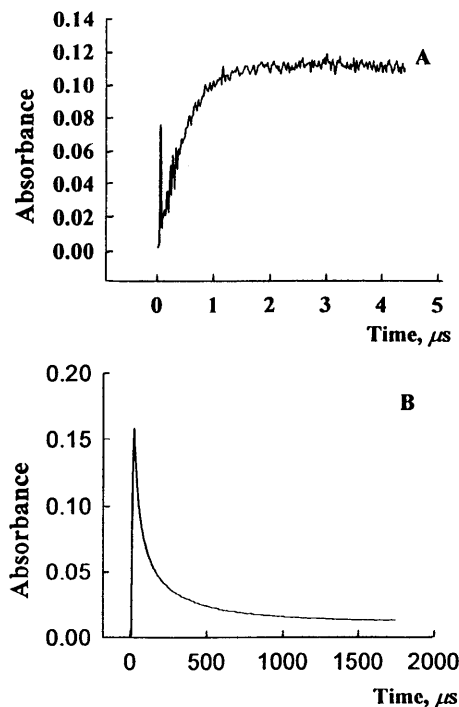


FIG. 2. Time profiles of absorbance at 480 nm after 50 ns pulse in the 0–5 μs (A) and 0–1800 μs (B) time interval as obtained in N_2O saturated $0.2 \text{ mmol} \cdot \text{dm}^{-3}$ A-ProOMe solution at neutral pH. In Fig. 2(A) the spike just after the pulse is due to the absorbance of the solvated electron. Dose/pulse: 43 Gy.

The decay of the absorbance at 480 nm under the conditions applied (monomer concentration $0.05\text{--}1 \text{ mmol} \cdot \text{dm}^{-3}$, dose/pulse $10\text{--}100 \text{ Gy}$, pH6) occurred with second-order kinetics: $2k = 5 \times 10^8 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$.

The absorption spectrum in slightly alkaline solution (in Fig. 3 the spectrum at pH 9.2 is shown), taken just after the nanosecond or microsecond pulses, was similar to the spectrum found in neutral solution. The shape of the transient signal in the UV region, however, was completely different when the measurements were made at $\text{pH} \geq 9$. During the first 100 μs , instead of the decrease observed at lower pH, an increase in the absorbance followed by a leveling off was found. The time scale of the increase agreed with the time scale of the decrease of the transient signal observed in neutral solutions (Fig. 4). On the basis of similar studies with ethyl acrylate, hydroxyethyl acrylate [4] and acrylamide [15], we assume that the increasing absorbance (at long times) is due to the formation of a stable end-product, β -hydroxyl acryloyl-L-proline methyl ester. It forms in the disproportionation reaction of two OH adduct radicals. In alkaline solution the OH group in the product ionizes, and the conjugated system thus formed has a strong absorbance in the UV. The maximum in the spectrum on Fig. 3, taken at $[\text{A-ProOMe}] = 0.1 \text{ mmol} \cdot \text{dm}^{-3}$, 350 μs after the pulse, is at 280 nm and $G_{\epsilon_{280 \text{ nm}}} \approx 6000 (100 \text{ eV})^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. The analogous derivative of acrylic acid ethyl ester has $\lambda_{\text{max}} = 268 \text{ nm}$

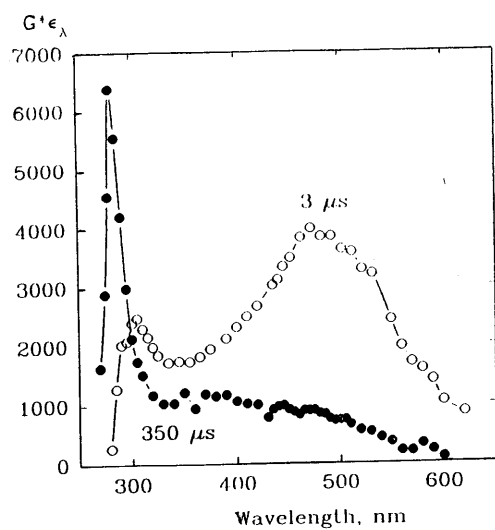


FIG. 3. Absorption spectra obtained in N_2O saturated $0.1 \text{ mmol} \cdot \text{dm}^{-3}$ A-ProOMe solution at pH 9.2. Dose/pulse: 32 Gy. (\circ) $3 \mu\text{s}$, (\bullet) $350 \mu\text{s}$ after $2.5 \mu\text{s}$ pulse.

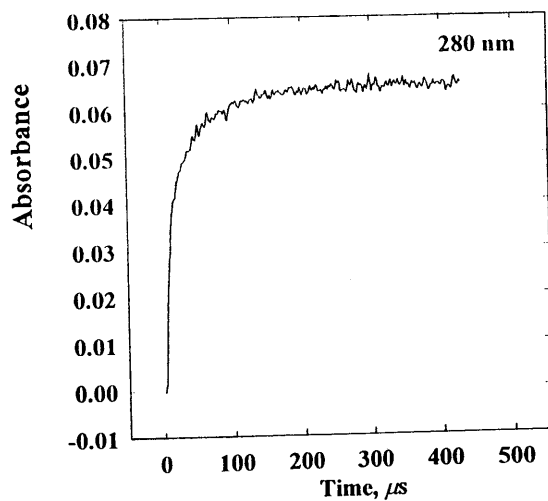
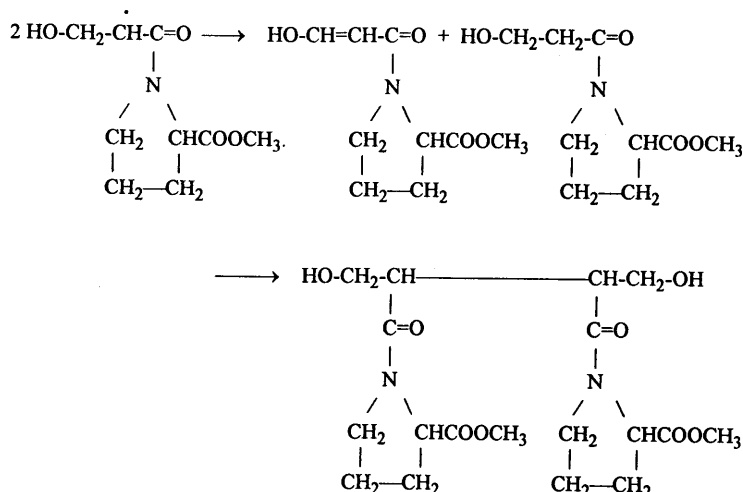


FIG. 4. Time profile of absorbance at 280 nm after 20 ns pulse as obtained in N_2O saturated $0.05 \text{ mmol} \cdot \text{dm}^{-3}$ A-ProOMe solution at pH 9.7. Dose/pulse: 25 Gy.

and $\epsilon_{\max} = 6600 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$ [4]. If the extinction coefficient of the product formed in A-ProOMe solutions is around the latter value, the G -value of disproportionation should be around 1. Since the yield of the OH adduct is equal to $G(\text{OH}) = 5.4$, it is probable that some part of the radicals disappears during self-termination by dimerization:



Reaction of the Monomer with H Atoms

The measurements were carried in $1 \text{ mmol} \cdot \text{dm}^{-3}$ A-ProOMe solution containing $0.5 \text{ mol} \cdot \text{dm}^{-3}$ *tert*-butanol in order to convert the OH radicals into less reactive *tert*-butanol radicals. The pH was 1.7. About 98% of hydrated electrons react with hydroxonium ions producing H atoms at this pH [11]:



At this relatively high H_3O^+ concentration the yield of H atoms formed through this reaction or directly is $G(\text{H}) \approx 3.8$ [12]. The H atoms add to the double bond in a reaction similar to the OH radicals, and the spectral and kinetic characteristics of the intermediate radical formed are similar to those of the OH adduct. The maximum of the spectrum is at about 460 nm (Fig. 5) and the extinction coefficient is ca. $970 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. The rate constant of H atom addition to the monomer is of the order of $2 \times 10^9 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$.

Reaction of the Monomer with e_{aq}^-

These measurements were also carried out in the presence of $0.5 \text{ mol} \cdot \text{dm}^{-3}$ *tert*-butanol, $\text{pH} \geq 4$. In such solutions the primary reaction occurs between the e_{aq}^- and H intermediates of water radiolysis ($G = 2.7$ and 0.55 , respectively) and the monomer. The transient absorption spectrum taken after $2.5 \mu\text{s}$ pulse of electrons at pH 4.2 (Fig. 6) shows a strong absorption peak at 290 nm with $G\epsilon_{290 \text{ nm}} = 20,000$ (100 eV) $^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. There is also some light absorption in the 330–500 nm wavelength range without resolved structure. The build-up of the absorbance in

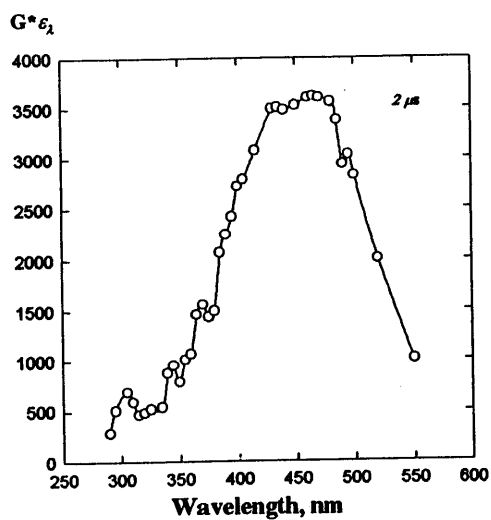


FIG. 5. Absorption spectrum obtained in N_2 saturated $1 \text{ mmol} \cdot \text{dm}^{-3}$ A-ProOMe solution containing $0.5 \text{ mol} \cdot \text{dm}^{-3}$ *tert*-butanol at pH 1.7. The spectrum was taken $2 \mu\text{s}$ after the $2.5 \mu\text{s}$ electron pulse. Dose/pulse: 80 Gy.

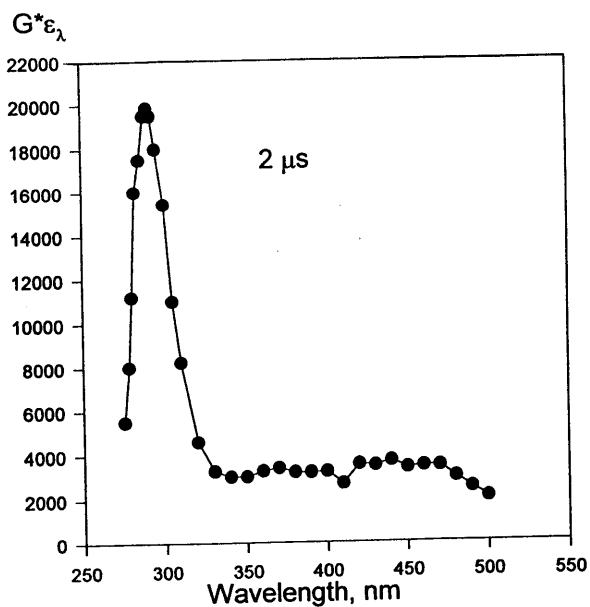
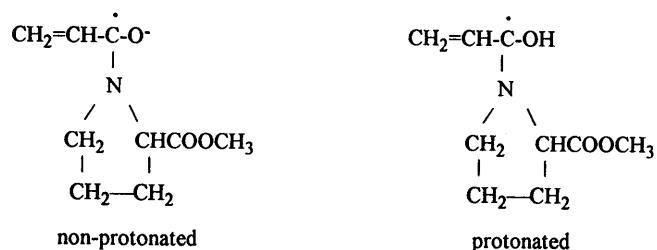


FIG. 6. Absorption spectrum taken $2 \mu\text{s}$ after $2.5 \mu\text{s}$ pulse in N_2 saturated $1 \text{ mmol} \cdot \text{dm}^{-3}$ A-ProOMe solution containing $0.5 \text{ mol} \cdot \text{dm}^{-3}$ *tert*-butanol at pH 4.2. Dose/pulse: 80 Gy.

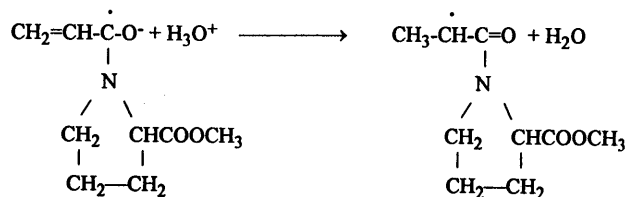
[A-ProOMe] = 1 mmol·dm⁻³ solutions was completed within 1 μs. The decay was found to be second order ($2k/\epsilon_{290\text{ nm}} = 1.6 \times 10^5 \text{ cm}^3 \cdot \text{s}^{-1}$), and its characteristics did not change with the wavelength. It was also independent of the pH in neutral and slightly acidic solutions.

The carbonyl groups are known to have good electron-accepting characteristics. The rate constant of the e_{aq}^- reaction with saturated carboxylic acid esters is of the order of $9 \times 10^7 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ [16]. For acrylamide [17] and *N,N*-dimethylacrylamide [18], 1.8×10^{10} and $1.6 \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ were found, respectively. For A-ProOMe, following the decay of e_{aq}^- at 650 nm, we measured a rate constant of $1.0 \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$. The large difference between the values for saturated carboxylic acid esters and acrylamides suggests that the electron capture occurs on the acryloyl part of the molecule. There are two probable structures, the nonprotonated and protonated forms:



On the basis of analogous reactions with acrylamides and acrylic acid esters, the electron adduct in acidic and slightly alkaline media is mainly in the protonated form [18]. The extinction coefficient in the maximum is calculated to be $\epsilon_{290\text{ nm}} = 8000 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. For the protonated electron adduct of *N,N*-dimethylacrylamide, $\lambda_{\text{max}} = 285 \text{ nm}$ and $\epsilon_{\text{max}} = 6400 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$ were reported [18]. The H atoms, formed with low yield as detailed in the previous section, react in radical addition to the double bond to produce a relatively weak absorbance in the 300–500 nm region: The decay of A-ProOMe protonated electron adduct takes place with a rate constant of about $2k \approx 1.3 \times 10^9 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$.

The shape of the transient signal taken at pH 9.0 (the pH was set by NaOH) was different from the signals obtained at lower pH values. After a fast decaying spike, a slow decay was observed. The spectrum left after the spike disappears (Fig. 7) is similar to the spectrum obtained in the addition reaction of H atoms (see previous section). This suggests that the electron adduct undergoes an irreversible protonation at the β-carbon atom on the acryloyl part of the molecule:



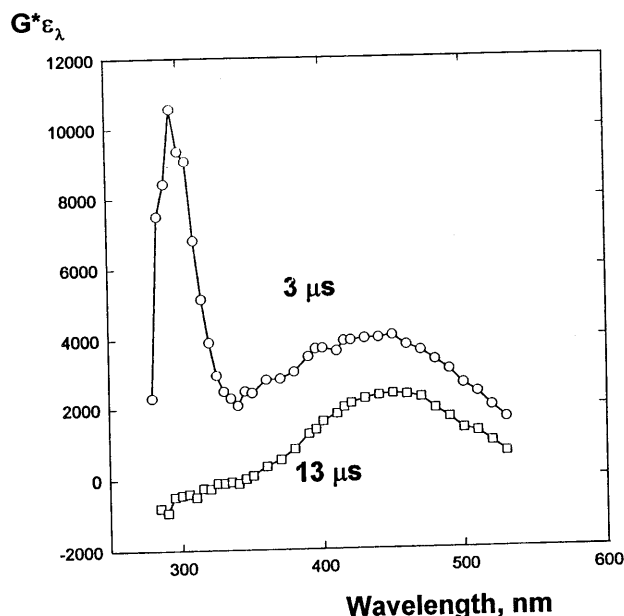


FIG. 7. Absorption spectra obtained in N_2 saturated $1 \text{ mmol} \cdot \text{dm}^{-3}$ A-ProOMe solution containing $0.5 \text{ mol} \cdot \text{dm}^{-3}$ *tert*-butanol at pH 9.0. The spectra were taken 3 and 13 μs after the 2.5 μs electron pulse. Dose/pulse: 80 Gy.

Due to the fast irreversible protonation, it was impossible to determine the exact pK_a value of the electron adduct; we suspect it is ≈ 8 . As the pH of the solution increased, the spike became sharper. This may indicate that the NaOH added to set the pH catalyzes the protonation, as has been found with several acrylate derivatives [2, 14, 18].

CONCLUSIONS

The OH, H, and e_{aq}^- intermediates of water radiolysis react with the solute A-ProOMe present in a $0.1\text{--}1 \text{ mmol} \cdot \text{dm}^{-3}$ concentration in very fast reactions ($k = 10^9\text{--}10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$). In the reaction of OH and H, the α -carboxyalkyl radicals formed show a light absorption with $\lambda_{\text{max}} \approx 460\text{--}480 \text{ nm}$ and $\epsilon_{\text{max}} \approx 900 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. These spectral characteristics are similar to the characteristics of other α -carboxyalkyl radicals produced from acrylamide-type compounds and differ greatly from the characteristics of the radicals produced from acrylic esters ($\lambda_{\text{max}} \approx 310 \text{ nm}$ and $\epsilon_{\text{max}} \approx 400 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$). The e_{aq}^- adds to the C=O group, and there is some indication that here, as with several other acrylate derivatives, the intermediate can both reversibly (on the C-O⁻ group) and irreversibly (on the β -carbon atom) protonate. In the latter reaction the same intermediate α -carboxyalkyl radical forms as in the H atom addition reaction. Under the conditions applied (low concentration, $0.1\text{--}1 \text{ mmol} \cdot \text{dm}^{-3}$; high dose/pulse, 10–100 Gy), these

radicals decay in second-order self-termination reactions. In connection with the OH adducts, there is some indication that both disproportionation and dimerization occur.

ACKNOWLEDGMENTS

E. T. and M. C. wish to express their thanks to the C.N.R.-H.A.S. Agreement (O3/6), and E.T. to the Hungarian Research Fund (OTKA No. T017081) for support of this work.

REFERENCES

- [1] M. Kumar, M. H. Rao, P. N. Moorthy, and K. N. Rao, *Radiat. Phys. Chem.*, **33**, 219 (1989).
- [2] Á. Sáfrány and L. Wojnárovits, *Ibid.*, **41**, 531 (1993).
- [3] Á. Sáfrány, Á. Bíró, and L. Wojnárovits, *Ibid.*, **42**, 1027 (1993).
- [4] L. Wojnárovits, E. Takács, and Á. Bíró, *J. Macromol. Sci. - Pure Appl. Chem.*, **A32**, 443 (1995).
- [5] A. S. Hoffman, *Macromol. Symp.*, **98**, 645 (1995).
- [6] A. Safran, M. Yoshida, H. Omichi, and R. Katakai, *Langmuir*, **10**, 2954 (1994).
- [7] M. Yoshida, A. Safran, H. Omichi, M. Miyajima, and R. Katakai, *Radiat. Phys. Chem.*, **46**, 181 (1992).
- [8] M. Yoshida, H. Omichi, and R. Katakai, *Eur. Polym. J.*, **28**, 1141 (1992).
- [9] S. S. Emmi, G. Begato, and G. Casalbore-Micelli, *Radiat. Phys. Chem.*, **33**, 29 (1989).
- [10] G. Földiák, P. Hargittai, L. Kaszanyicki, and L. Wojnárovits, *J. Radioanal. Nucl. Chem., Articles*, **125**, 19 (1989).
- [11] A. J. Swallow, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis* (J. H. Baxendale and F. Busi, Eds.), Reidel, Dordrecht, 1982, p. 289.
- [12] G. V. Buxton, in *Radiation Chemistry, Principles and Applications* (Farhataziz and M. A. J. Rodgers, Eds.), VHC Publishers, New York, 1987, p. 321.
- [13] M. Simic, P. Neta, and E. Hayon, *J. Am. Chem. Soc.*, **92**, 4763 (1970).
- [14] E. Hayon, T. Ibata, N. N. Lichtin, and M. Simic, *Ibid.*, **92**, 3898 (1970).
- [15] K. W. Chambers, E. Collinson, and F. S. Dainton, *Trans. Faraday Soc.*, **66**, 142 (1970).
- [16] E. J. Hart, E. M. Fielden, and M. Anbar, *J. Phys. Chem.*, **71**, 3993 (1967).
- [17] E. J. Hart, G. Sheffield, and J. K. Thomas, *Ibid.*, **68**, 1271 (1964).
- [18] V. Madhavan, N. N. Lichtin, and E. Hayon, *J. Am. Chem. Soc.*, **97**, 2989 (1975).

Received February 8, 1996