References and Notes

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Protonation Reactions of Electron Adducts of Acrylamide Derivatives. A Pulse Radiolytic-Kinetic Spectrophotometric Study

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Abstract: The absorption spectra of electron adducts of a number of α,β-unsaturated carboxamides and of methyl methacrylate, as well as of two isomeric types of protonated electron adducts, have been characterized by means of the technique of pulse radiolysis-kinetic absorption spectrophotometry. Spectra of the electron adducts are characterized by bands in the uv ($\epsilon_{\max} \sim 10^4\ M^{-1}\ \text{cm}^{-1}$) and in the visible ($\epsilon_{\max} \sim 10^3\ M^{-1}\ \text{cm}^{-1}$). The position of the uv band shifts 10-30 nm to shorter wavelength upon reversible protonation. Fast reversible protonation of electron adducts takes place at the carbonyl oxygen. The pK_a values of the electron adducts vary linearly with the pK_a values of the corresponding carboxylic acids: for acrylamide, 7.9; methacrylamide, 8.0; *trans*-crotonamide, 8.5; β,β-dimethylacrylamide, 9.5; *N,N*-dimethylacrylamide, 8.5; *trans*-cinnamamide, 7.2; methyl methacrylate, ~7. Slower irreversible protonation of the electron adducts takes place at the β-carbon atom and is subject to general acid catalysis which obeys the Brønsted catalysis law. Uncatalyzed specific rates of β protonation of anion radicals (in units of $10^5\ \text{sec}^{-1}$) are: for acrylamide, 1.4; for methacrylamide, 13; for *trans*-crotonamide, 0.22; for β,β-dimethylacrylamide, 0.21; for *N,N*-dimethylacrylamide, 3.7; for *trans*-cinnamamide, $\leq\sim$.01; for methyl methacrylate, 4.5. The second-order decay of reversibly protonated electron adducts competes with irreversible β protonation.

The technique of pulse radiolysis-kinetic absorption spectrophotometry is a convenient means for generating electron adducts of various compounds in aqueous solution and studying several aspects of the chemistry of these adducts. The present paper deals with the kinetics of electron addition to acrylamide derivatives, the position and kinetics of protonation of these adducts, the decay of the protonated electron adducts, and the oxidation of certain electron adducts and their protonation products.

Principal chemical equations are exemplified in eq 1-7

$$\mathrm{H_2O} \rightsquigarrow \mathrm{H},\ \cdot\mathrm{OH},\ \mathrm{e_{aq}}^-,\ \mathrm{H_3O^+},\ \mathrm{H_2O_2},\ \mathrm{H_2} \qquad (1)$$

$$\cdot\mathrm{OH} + \mathrm{(CH_3)_3COH} \longrightarrow \cdot\mathrm{CH_2C(CH_3)_2OH} + \mathrm{H_2O} \qquad (2)^2$$

$$\mathrm{e_{aq}}^- + \mathrm{CH_2{=}CHCONH_2} \longrightarrow \mathrm{CH_2CHCONH_2}\cdot^- \qquad (3)$$

$$\mathrm{CH_2CHCONH_2}\cdot^- + \mathrm{H_3O^+} \rightleftharpoons \mathrm{CH_2CH\dot{C}(OH)NH_2} + \mathrm{H_2O} \qquad (4)$$

$$\mathrm{CH_2CHCONH_2}\cdot^- + \mathrm{HB} \longrightarrow \mathrm{CH_3\dot{C}HCONH_2} + \mathrm{B^-} \qquad (5)$$

$$2\mathrm{CH_2CH\dot{C}(OH)NH_2} \longrightarrow \text{products} \qquad (6)$$

$$\mathrm{CH_2CHCONH_2}\cdot^- + \mathrm{A} \longrightarrow \mathrm{CH_2{=}CHCONH_2} + \mathrm{A}\cdot^- \qquad (7)$$

where $k_2 = 5.2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ (ref 2), and A is an oxidant. Cross reactions of the radicals formed in reactions 2-5 are also considered to take place to extents which depend on radicals and conditions.

Under the conditions employed (see below), the hydroxyl radicals reacted with *tert*-butyl alcohol, eq 2. The resulting $\dot{\mathrm{C}}\mathrm{H_2C(CH_3)_2OH}$ radical[3] is known to have a low reactivity toward a wide variety of (nonradical) substrates so that *tert*-butyl alcohol is very widely used as a scavenger for $\dot{\mathrm{O}}\mathrm{H}$. The observations reported below appeared to be free of interference ascribable to use of this scavenger. No scavenger was used to remove H atoms.

Previous pulse radiolytic-kinetic spectrophotometric investigations of electron adducts of α,β-unsaturated carbonyl compounds include the adducts of acrylamide,[4,5] *N*-ethylmaleimide,[6,7] saturated amides,[8] acrylic acid derivatives,[9] and α,β-unsaturated ketones.[10,11]

Experimental Section

Pulse radiolysis experiments were performed using single pulses of 2.3 MeV electrons of ~30 nsec duration (Febetron 705 machine). The technique and conditions have been described previously.[3,12]

The following chemicals were used as such: Polyscience Ultrapure acrylamide; Calbiochem menadione; Aldrich Analysed *p*-cyanoacetophenone; 99.99+% zone refined benzophenone supplied by James Hinton, Columbia, S.C.; Aldrich Analysed 97% 4,4′-dimethoxybenzophenone; Matheson, Gold Label Ar and $\mathrm{N_2O}$; Mallinckrodt A.R. 70% $\mathrm{HClO_4}$ and *tert*-butyl alcohol; Baker and Adamson A. R. KOH, $\mathrm{NaH_2PO_4}$, $\mathrm{KH_2PO_4}$, $\mathrm{Na_2HPO_4}$, $\mathrm{K_2HPO_4}$, $\mathrm{Na_2B_4O_7{\cdot}10H_2O}$, KCNS, and $\mathrm{NH_4Cl}$; Fisher Purified $\mathrm{NaClO_4{\cdot}H_2O}$; Aldrich 98% trimethylamine·HCl; Merck Reagent $\mathrm{NaHCO_3}$; Eastman ethylamine·HCl, diethylamine·HCl and triethylamine; Matheson Coleman and Bell cyclohexylamine; Calbiochem ammonia-free, A grade glycine.

Matheson Coleman and Bell piperidine and K & K Lab. pyrrolidine were freshly distilled before use at ~20 Torr. Eastman practical grade methacrylamide was recrystallized three times from ethyl acetate and then sublimed at 20 Torr; mp 107-108.5° (uncorrected) (lit.[13] 110-111°). Crotonamide was prepared by the reaction of ice cold J. T. Baker ammonia solution with Aldrich 90% crotonyl chloride. The amide was recrystallized once from distilled water and sublimed at 20 Torr: mp 154.5-156° (uncorrected) (lit.[14] 158°). Aldrich β,β-dimethylacrylic acid was converted to the amide by reaction with $\mathrm{SOCl_2}$ in the cold, followed by treat-

Table I. Specific Rates of Reaction of Hydrated Electron

Substrate[a]	k,[b] $10^{10}\ M^{-1}\ sec^{-1}$
Acrylamide	3.1 ± 0.1
Methacrylamide	2.4 ± 0.3
trans-Crotonamide	1.3 ± 0.1
β,β-Dimethylacrylamide	0.56 ± 0.05
N,N-Dimethylacrylamide	1.6 ± 0.02
trans-Cinnamamide	3.0 ± 0.1
Methyl methacrylate	1.3 ± 0.1

[a] At pH 9.2 in the presence of ~0.1 *M* *t*-BuOH. [b] Uncertainties are mean deviations.

ment with ammonia solution. The resulting amide was recrystallized from Eastman spectrograde benzene and then sublimed twice at 20 Torr: mp 106–108° dec (lit.[14] 107–108°). Polyscience *N,N*-dimethylacrylamide was distilled at 15 Torr and a middle fraction boiling at 75° was used. It showed a single peak upon gas chromatography on a 4% SE 30 column. Polyscience methyl methacrylate was shaken with a 5% solution of NaOH containing some Na_2CO_3, washed repeatedly with water, dried over $MgSO_4$, and distilled under 20 Torr of nitrogen. Its NMR spectrum did not differ from that reported in the literature.[15] Aldrich 97% cinnamamide was recrystallized from 90% Eastman spectrograde benzene–10% ethanol.

Dosimetry. Dose per pulse was determined by measuring the absorbance at 500 nm due to $(CNS)_2\cdot^-$ produced by the irradiation of N_2O-saturated 0.04 *M* KCNS solutions, taking $\epsilon_{500} = 7600$ M^{-1} cm^{-1} and $G[(CNS)_2\cdot^-] = 5.6$ molecules/100 eV[3]. $G(e_{aq}^-)$ was taken as 2.8 and G(H) as 0.6.

Results

Kinetics of Addition of Electrons. Specific rates of reaction of the hydrated electron with substrates were determined by following the decay kinetics of e_{aq}^- at 700 nm. Clean pseudo-first-order kinetics was obtained by using concentrations of amide at least ten times as great as the initial concentrations of e_{aq}^-. Measurements were carried out in 10^{-3} *M* borate at pH 9.2 in the presence of ~0.1 *M* *t*-BuOH. Resulting second-order rate constants are assembled in Table I.

Transient Absorption Spectra. The initial spectra were measured directly ~0.1 μsec after the pulse. In some cases, extrapolation to this time was made for short-lived species using first-order decay data. The spectra of electron adducts were measured in ~10^{-3} *M* borate buffer at pH 9–10.5 and those of the protonated electron adducts (see Discussion section) in 2×10^{-3} *M* phosphate buffer at pH 4 – 6. Values of pK_a for the reversible protonation of the electron adducts were determined by measuring the absorbance at a fixed wavelength as a function of pH. Spectra and "titration curves" for acrylamide, methacrylamide, crotonamide, β,β-dimethylacrylamide, cinnamamide, *N,N*-dimethylacrylamide, and methyl methacrylate are shown in Figures 1–7. Values of λ_{max}, ϵ_{max}, and pK_a are assembled in Table II. Two bands are apparent in each spectrum; λ_{max} values of the more intense band observed with electron adducts fall in the range 270–385 nm, with ϵ_{max} in the range 11,000–46,000 M^{-1} cm^{-1}. For each protonated electron adduct, λ_{max} is blue shifted ~25 nm compared to the radical anion and ϵ_{max} is about the same. Maxima of the weaker bands fall 100–150 nm to the red from the more intense maxima with ϵ_{max} in the range 500–4000 M^{-1} cm^{-1}.

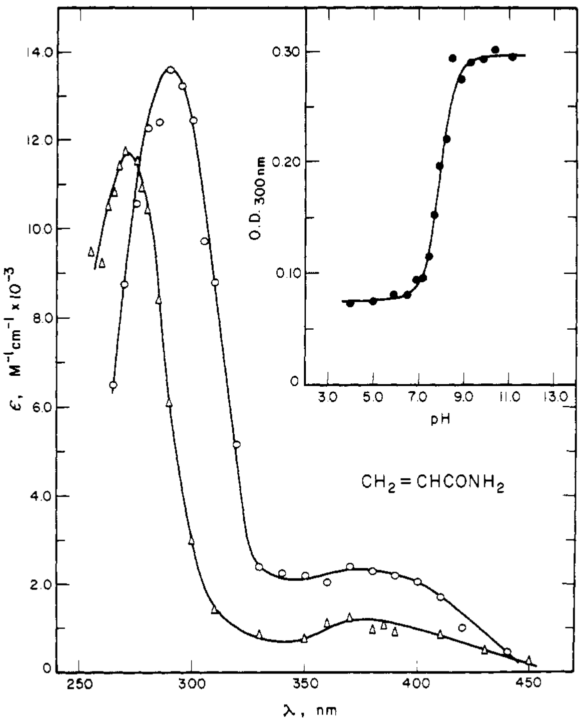

Figure 1. Initial transient absorption spectra produced by reaction of e_{aq}^- with 2 m*M* acrylamide at pH 9.2 (○) and 4.0 (△) in 1.0 *M* aqueous *t*-BuOH under Ar (1 atm). Total dose 4 krads/pulse; absorbance measured ~0.2 μsec after the pulse. Insert: change in absorbance at 300 nm with pH.

Decay Processes. Acrylamide. The decay behavior of the electron adduct was studied in the pH range 9.3 to 13, well above the pK_a of the adduct. Decay of absorbance was followed to ~90% of completion and was found to be cleanly first order over this range, independent of variation of the initial concentrations of e_{aq}^- from 1 to 2.5×10^{-5} *M* and of

Table II. λ_{max}, ϵ_{max}, pK_a, and Decay Kinetics of the Initial Transient Species Produced by Reaction of e_{aq}^- with Acrylamide Derivatives

	Protonated radical				Radical Anion		
Substrate	λ_{max}, nm	ϵ_{max}, mM^{-1} cm^{-1}	$2k$,[a] 10^9 M^{-1} sec^{-1}	pK_a	λ_{max}, nm	ϵ_{max}, mM^{-1} cm^{-1}	k, 10^5 sec^{-1}
Acrylamide	270	11.7	3.0	7.9 ± 0.2	290	13.6	1.4[c]
	375	1.2			380	2.3	
Methacrylamide	275	8.5	4.0	8.0 ± 0.2	300	11.0	13.0[c]
	370	1.3			370	3.8	
trans-Crotonamide	265	13.5	4.0	8.5 ± 0.2	285	12.2	0.2[c]
	410	0.6			410	1.2	
β,β-Dimethylacrylamide	260	13.9	4.0	9.5 ± 0.2	270	13.9	0.2[d]
	430	0.5			440	1.0	
N,N-Dimethylacrylamide	285	6.4	2.4	~8.5[b]	295	13.7	3.7[c]
trans-Cinnamamide	355	37.5	2.4	7.2 ± 0.1	385	46.0	[c,e]
	500	1.0			550	3.0	
Methyl methacrylate	250	11.9	[e]	~7[b]	290	13.7	4.5[c]

[a] Measured second-order specific rate of decay of absorbance. [b] Approximate value due to the relatively fast decay of the product of reversible protonation. [c] 1 m*M* borate buffer or in the absence of any buffer. [d] By linear extrapolation to zero buffer concentration. [e] Mixed kinetics; $k \leqslant 10^3$ sec^{-1} for first-order component.

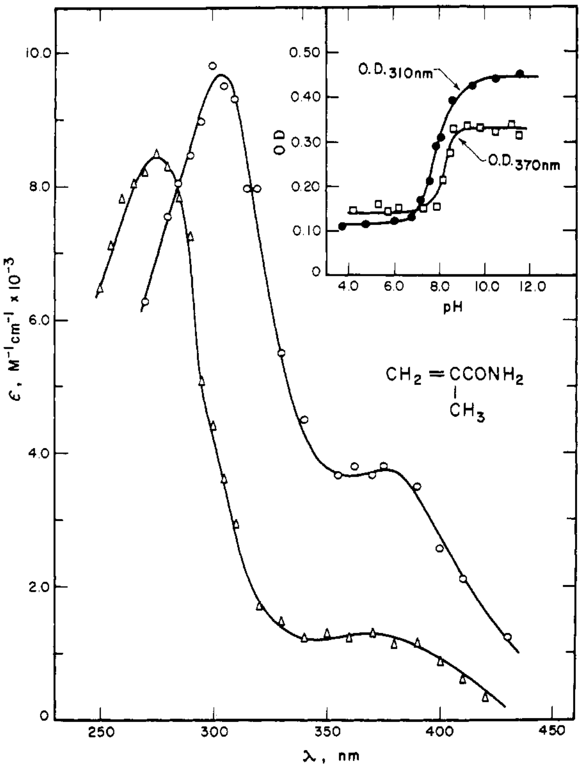

Figure 2. Initial transient absorption spectra produced by reaction of e_{aq}^- with 2 m*M* methacrylamide at pH 10.0 (○) and 4.9 (△) in 1.0 *M* aqueous *t*-BuOH under Ar (1 atm). Insert: change in absorbance with pH at 310 and 370 nm. Absorbances extrapolated to "zero time" at pH above 8.

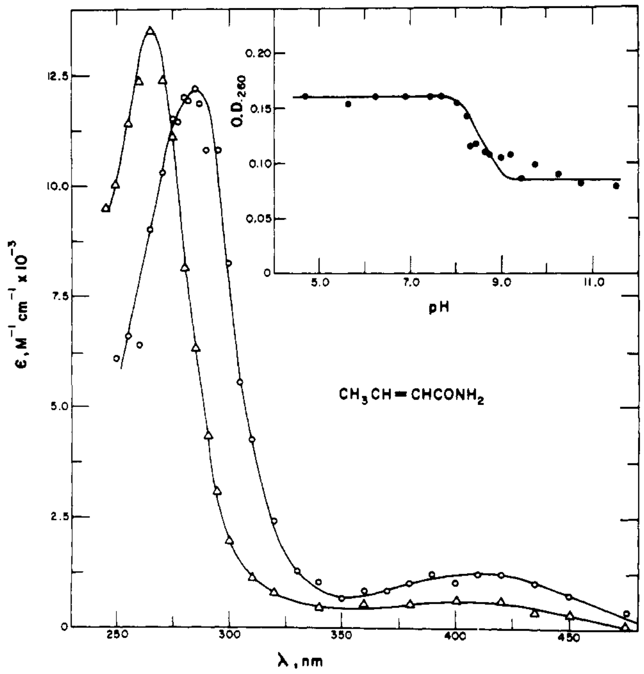

Figure 3. Initial transient absorption spectra produced by reaction of e_{aq}^- with 1 m*M* *trans*-crotonamide at pH 10.2 (○) and 6.0 (△) in 0.5 *M* aqueous *t*-BuOH under Ar (1 atm); total dose 2 krads/pulse. Insert: change in absorbance with pH at 260 nm.

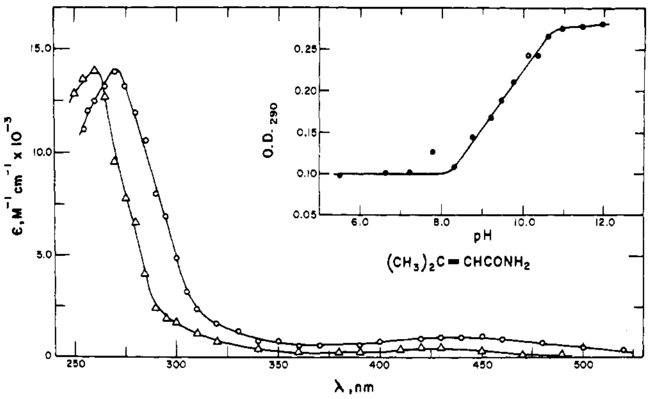

Figure 4. Initial transient absorption spectra produced by reaction of e_{aq}^- with 2 m*M* β,β-dimethylacrylamide at pH 10.4 (○) and 6.7 (△) in 1.0 *M* aqueous *t*-BuOH under Ar (1 atm); total dose 4 krads/pulse. Insert: change in absorbance with pH at 290 nm.

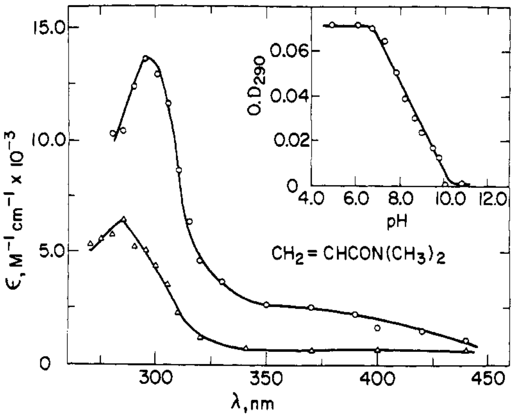

Figure 5. Initial transient absorption spectra produced by reaction of e_{aq}^- with 1 m*M* *N,N*-dimethylacrylamide in 0.5 *M* aqueous *t*-BuOH at pH 9.95 (○) and 6.1 (△) under Ar (1 atm); total dose 6 krads/pulse. Insert: change in absorbance with pH at 290 nm.

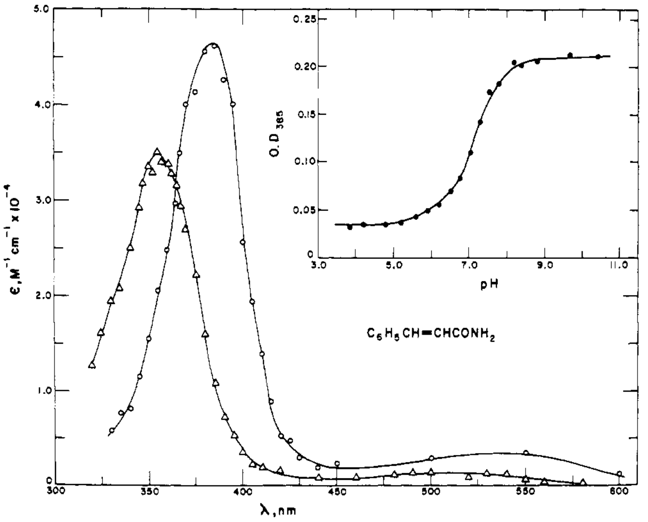

Figure 6. Initial transient absorption spectra produced by reaction of e_{aq}^- with 1 m*M* cinnamamide at pH 10.1 (○) and 5.3 (△) in 0.5 *M* aqueous *t*-BuOH solution under Ar (1 atm); total dose 1 krad/pulse. Insert: change in absorbance with pH at 385 nm.

acrylamide from 10^{-3} to 10^{-2} *M*. The first-order rate of decay was independent of pH over the measured range (Table II). It was also independent of ionic strength, as determined by varying the concentration of $NaClO_4$ from 0.01 to 0.1 *M*. The rate was, however, dependent on the nature and concentration of the buffer. It was demonstrated by variation of buffer ratio at constant buffer concentration and constant ionic strength, e.g., Figure 8a, that catalysis was by the acid components of the buffers. Rate constants for buffers were determined by evaluating the slopes corresponding to eq 8. Three typical plots are shown in Figure 8b.

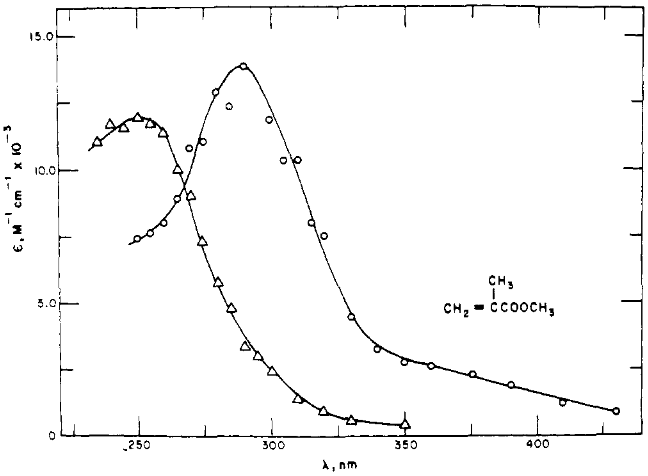

Figure 7. Initial transient absorption spectra produced by the reaction of e_{aq}^- with 1 m*M* methyl methacrylate at pH 9.4 (○) and 4.4 (△) in 1.0 *M* aqueous *t*-BuOH under Ar (1 atm); total dose 4 krads/pulse.

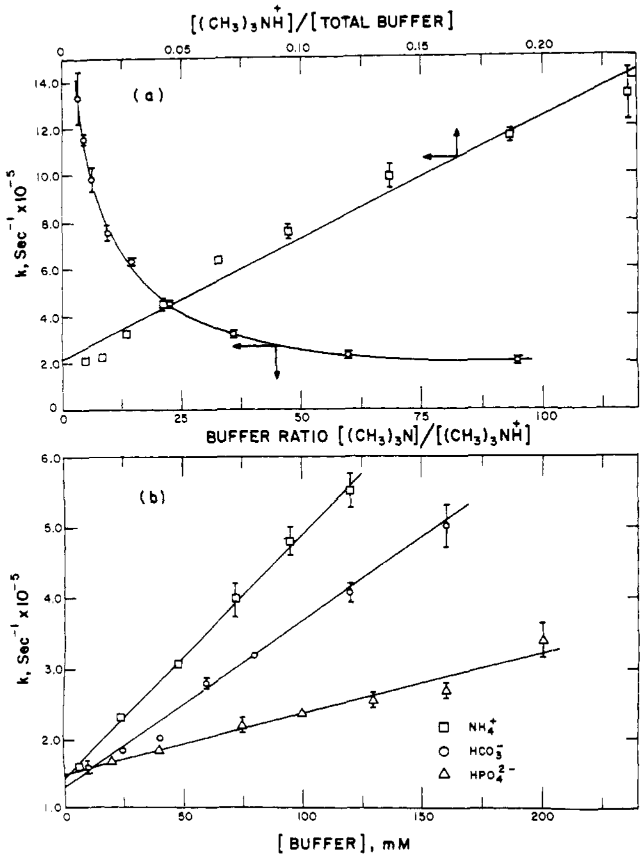

Figure 8. (a) Decay of radical anion of acrylamide catalyzed by trimethylammonium ions. The observed decay constants are plotted against the fraction of acid component of the buffer mixture (total concentration 5 m*M*) over the pH range 10.3 to 11.8; μ = 0.1 *M* ($NaClO_4$). (b) Dependence of the first-order decay constant of the radical anion of acrylamide on the concentration of the acid form of three typical buffers, NH_4^+, HCO_3^-, and HPO_4^{2-}.

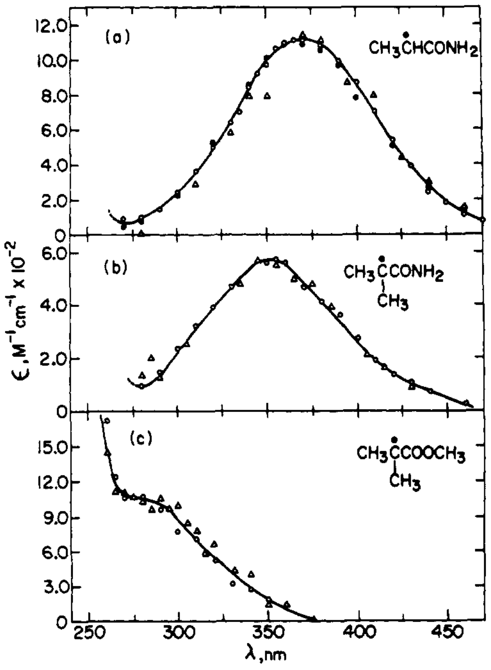

Figure 9. (a) Absorption spectrum of the radical $CH_3CHCONH_2$: formed according to eq 9 (●); normalized transient spectrum measured 35 μsec after the reaction of e_{aq}^- with 0.5 m*M* acrylamide at pH 9.8 in 0.25 *M* aqueous *t*-BuOH under Ar (△); transient spectrum from the reaction of H atoms with 2 m*M* acrylamide (○) at pH 0.9 and in 1.0 *M* aqueous *t*-BuOH under Ar. (b) Secondary transient absorption spectrum produced by decay of electron adduct of 2 m*M* methacrylamide in 1.0 *M* aqueous *t*-BuOH at pH 10.0 (△); spectrum produced by reaction of H atoms with 3 m*M* methacrylamide in 1.0 *M* aqueous *t*-BuOH at pH 0.9 under Ar (○); total dose 19 krads/pulse. (c) Transient absorption spectrum produced by the reaction of H atoms with 0.5 m*M* methyl methacrylate in 0.4 *M* aqueous *t*-BuOH at pH 1.0 under Ar (○); secondary transient absorption spectrum produced by reaction of e_{aq}^- with 0.5 m*M* methylmethacrylate in 0.4 *M* aqueous *t*-BuOH at pH 9.4 under Ar (△); total dose 4 krads/pulse.

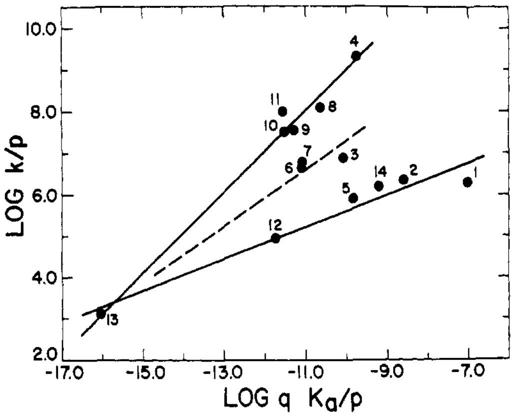

Figure 10. Brønsted correlation of catalytic rate constants for β-protonation of acrylamide anion radical: 1, $H_2PO_4^-$; 2, NH_4^+; 3, $^+H_3NCH_2CO_2^-$; 4, $(CH_3)_3NH^+$; 5, HCO_3^-; 6, c-$C_6H_{11}NH_3^+$; 7, $C_2H_5NH_3^+$; 8, $(C_2H_5)_3NH^+$; 9, $(C_2H_5)_2NH_2^+$; 10, c-$C_5H_{10}NH_2^+$; 11, c-$C_4H_4NH^+$; 12, HPO_4^{2-}; 13, H_2O; 14, $B(OH)_3$

$$k_{\text{obsd}} = k_0 + k_{\text{HB}}[\text{HB}] \quad (8)$$

$$e_{aq}^- + CH_3CHClCONH_2 \longrightarrow CH_3\dot{C}HCONH_2 + Cl^- \quad (9)$$

$$\cdot H + CH_2{=\!=}CHCONH_2 \longrightarrow CH_3\dot{C}HCONH_2 \quad (10)$$

The product of decay was identified as the $CH_3\dot{C}HCONH_2$ radical by comparison of its spectrum with the spectra generated by the reactions shown in eq 9[16] and 10. The resulting spectra are shown in Figure 9. The spectrum produced by the first-order decay of the electron adduct was measured after 7 half-lives of decay at pH 9.8 (in 10^{-3} *M* borate buffer). The same spectrum was obtained when the decay was catalyzed by buffers. The intensity of the spectrum produced by decay of the electron adduct is normalized in Figure 9 to the intensities of the spectra produced by reactions 9 and 10. The catalytic rate constants for 12 buffers are presented in Figure 10. Decay of the spectrum of the α radical was second order, independent of dose over a factor of 2.

The decay of the primary spectrum at pH 4-6, presumed to be that of the protonated electron adduct (see Discussion section), followed mixed kinetics. However, it was possible to show by threefold variation of the dose per pulse, and by tenfold variation of the initial concentration of acrylamide, that the decay was second order in the transient species and independent of the concentration of acrylamide over the first two half-lives (using ~2 × 10^{-3} M phosphate buffer). Under these conditions the spectrum of a second intermediate was not observed during the decay process. Buffer catalysis was observed at this pH as well. In the presence of 5 × 10^{-2} M phosphate buffer, the initial spectrum decayed to a spectrum identical with that shown in Figure 9a.

Methacrylamide. The decay of the electron adduct of methacrylamide obeyed first-order kinetics with a rate independent of pH from 10 to 13 (10^{-3} M borate) and of ionic strength ($NaClO_4$) over the range 0.01 to 0.1 M. As shown in Table II, the rate of decay of the electron adduct was about tenfold faster than that of acrylamide. The product of the first-order decay was identified as $CH_3\dot{C}(CH_3)CONH_2$ by comparison of its spectrum (Figure 9b) with the hydrogen atom adduct produced in reaction 11. The spectrum produced by reaction 11 was measured at the end of the pulse.

$$H + CH_2{=}C(CH_3)CONH_2 \longrightarrow CH_3\dot{C}(CH_3)CONH_2 \quad (11)$$

The spectrum from the first-order decay of the radical anion of methacrylamide was measured after 7 half-lives of decay, i.e., ~4 μsec after the pulse, and was normalized to that of the H atom adduct at 370 nm. The spectrum assigned to the $CH_3\dot{C}(CH_3)CONH_2$ radical decayed by a second-order process.

The decay kinetics at pH 4-6 of the presumed protonated radical anion was mixed in the presence of 2 × 10^{-3} M phosphate buffer. A second-order component of the kinetics was identified by changing the dose per pulse, see Table II. The decay was accelerated and the kinetics became clean first order when the concentration of the phosphate buffer was increased to 0.1 M. Under these conditions, the secondary spectrum was essentially identical with that in Figure 9b.

***trans*-Crotonamide.** The decay of the electron adduct in 10^{-3} M borate buffer at pH 10.2 was cleanly first order over the observed range, i.e., ~90% decay, independent of twofold variation in dose per pulse. The presumed protonated electron adduct decayed completely by a second-order process. As shown in Table II, the rate of decay of the electron adduct of crotonamide was ca. six times slower than that of acrylamide.

***β,β*-Dimethylacrylamide.** In the case of β,β-dimethylacrylamide, both the electron adduct at pH 10.2 (10^{-3} M borate) and the presumed protonated electron adduct at pH 6.7 (2 × 10^{-3} M phosphate) decayed with mixed kinetics. However, the decay of the electron adduct was cleanly first order in the presence of added buffer. Extrapolation of the linear dependence of the pseudo-first-order rate of decay on buffer concentration to zero concentration provided the rate constant which is reported in Table II.

***N,N*-Dimethylacrylamide.** Decays of the electron adduct at pH 10 (0.5 mM borate buffer) and the presumed protonated radical at pH 6.1 were respectively first and second order. Rates are shown in Table II.

***trans*-Cinnamamide.** The kinetics of decay of the radical anion of cinnamamide was mixed in the presence of 1.0 × 10^{-3} M borate buffer at pH 9.2. However, the decay was accelerated and became clean first order upon addition of excess buffer. At pH 4.7 (2 mM phosphate), decay of the presumed protonated radical was second order.

Table III. λ_{max}, ϵ_{max}, and Decay Kinetics of the Radicals Formed by Addition of H Atoms

Substrate	λ_{max}, nm	ϵ_{max},[b] mM^{-1} cm^{-1}	2k,[c] 10^9 M^{-1} sec^{-1}
Acrylamide	370	1.13	3.0
		1.18[d]	3.2[d]
Methacrylamide	350	0.58	2.4
			2.9[e]
Crotonamide	360	0.38	
β,β-Dimethylacrylamide	305	0.63	
N,N-Dimethylacrylamide	460	1.13	2.3
Cinnamamide	380	2.75	2.2
	322	5.00	3.6
Methyl methacrylate	280[a]	1.05	2.7[f]
			2.6[e,f]
			3.2[g]

[a] Shoulder. [b] Assuming that a single species is formed. [c] Measured second-order specific rates of decay of absorbance. [d] α radical formed by reaction 9. See ref 16. [e] α radical formed by β protonation of electron adduct. [f] Measured at 240 nm. [g] Measured at 290 nm.

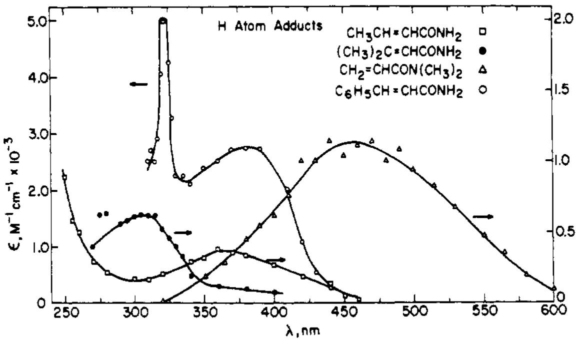

Figure 11. Spectra formed by reaction of H atoms with 1 mM crotonamide, β,β-dimethylacrylamide, N,N-dimethylacrylamide, and cinnamamide in 1 M aqueous t-BuOH at pH 1.0 ($HClO_4$) under Ar. Total dose 8-19 krads/pulse.

Methyl Methacrylate. The decay of the electron adduct of methyl methacrylate was first order over the observed period, i.e., to ~90% decay. The rate was independent of

$$H + CH_2{=}C(CH_3)COOCH_3 \longrightarrow CH_3\dot{C}(CH_3)COOCH_3 \quad (12)$$

pH (10^{-3} M borate) in the range 9.8-12.8 and of ionic strength ($NaClO_4$) in the range 0.01-0.2 M. The resulting species was identified as the $CH_3\dot{C}(CH_3)COOCH_3$ radical by comparing its spectrum with that of the H atom adduct formed in acid solution by reaction 12 (Figure 9c). The hydrogen adduct spectrum was measured at the end of the pulse while the secondary spectrum produced from the decay of the electron adduct was measured after 4 half-lives of decay of the primary spectrum, i.e., 7.6 μsec after the pulse. The spectra shown in Figure 9 were obtained with identical doses per pulse and are not normalized. Their kinetics of decay were identical. Kinetics of decay of the reversibly protonated electron adduct was mixed but the rate of a second-order component could be determined over the first two half-lives in 2 × 10^{-3} M phosphate buffer at pH 4.4 by variation of dose per pulse over a twofold range.

H Atom Adducts. Table III summarizes spectral characteristics of the H atom adducts of the acrylamide derivatives measured in the presence of 1.0 M t-BuOH at pH ≤1. Extinction coefficients were derived taking G(H) = 3.4.

Redox Properties. Redox properties of the electron adducts of acrylamide and crotonamide were examined by the technique reported recently.[17] Data are presented in Figure

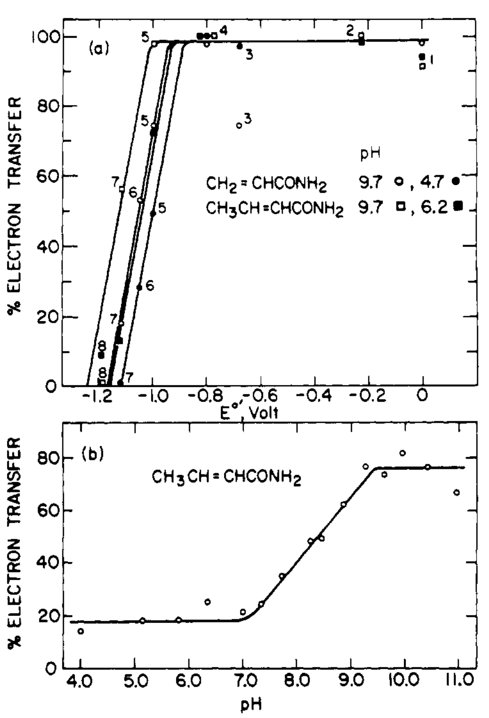

Figure 12. (a) Dependence of the efficiency of electron transfer in the oxidation reactions of the acrylamide and crotonamide electron adducts on the two-electron reduction potentials of oxidants at pH 7.0 ($E^{0\prime}$): 10 mM acrylamide and $\sim 10^4$ M or 5×10^{-4} M oxidant at pH 9.7 (○) or 4.7 (●); 5 mM crotonamide and 10^{-4} M oxidant at pH 9.7 (□) or 6.2 (■). Experiments carried out in 1.5 M *t*-BuOH, see also ref 15. (1) Menaquinone, (2) 9,10-anthraquinone-2-sulfonate, (3) fluorenone, (4) *p*-cyanoacetophenone, (5) benzophenone, (6) *p*-chlorobenzophenone, (7) 4,4′-dimethoxybenzophenone, (8) fumaric acid. (b) Dependence upon pH of the effiwiency of electron transfer from the electron adduct of crotonamide to 4,4′-dimethoxybenzophenone; conditions as above.

12. In this method the concentration of the substrate, e.g., acrylamide or crotonamide, and of the standard oxidant are adjusted so that virtually all e_{aq}^- is initially captured by the substrate. The quantity plotted as ordinate in Figure 12 is the percent of electron transfer from the initial electron adduct species to the oxidant evaluated by measurement of absorbance at a wavelength characteristic of the oxidant anion radical. The dependence of percent electron transfer upon pH is shown for crotonamide in Figure 12b. The value of the pH at 50% electron transfer, ~8.25, is very similar to the pK_a of the protonated electron adduct given in Table II.

$$A\cdot^- + Ox \longrightarrow A + Ox\cdot^- \qquad (13)$$

The rate of electron transfer, eq 13, was determined for a number of oxidants with sufficient excess of oxidant to give pseudo-first-order kinetics. The rate constants fell in the range $0.7\text{-}5 \times 10^9$ M^{-1} sec^{-1}

Discussion

Rates of Reaction with Electrons. All the rate constants presented in Table I are close to the diffusion controlled limit. Experimentally significant differences among them are, however, apparent. Substitution of hydrogen by a methyl group decreases the rate regardless of where the methyl group is introduced into the acrylamide structure. The effect is, however, largest for substitution at the β position; a second β-methyl group reduces the rate by virtually exactly the same factor as the first methyl group does, i.e., 2.3-2.4. In contrast to the methyl group, the phenyl group does not significantly affect the rate of electron addition.

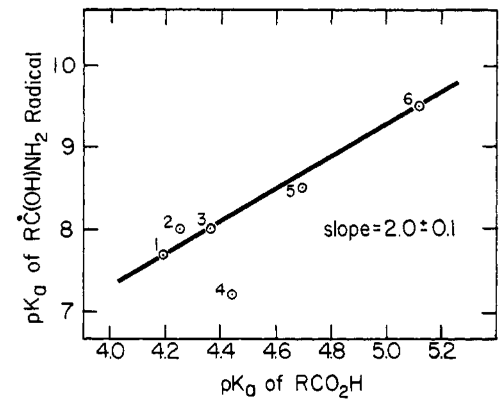

Figure 13. Correlation of pK_a of protonated electron adducts of unsaturated amides $R\dot{C}(OH)NH_2$ with pK_a of corresponding RCO_2H. R: 1, C_6H_5; 2, CH_2CH; 3, CH_2CCH_3; 4, *trans*-C_6H_5CHCH; 5, *trans*-CH_3CHCH; 6, $(CH_3)_2CCH$.

Spectra. The principal characteristic feature of the spectra of electron adducts is the band in the vicinity of 300 nm with ϵ_{max} of the order of 10^4 M^{-1} cm^{-1}. Values of λ_{max} of the much weaker longer wavelength absorption bands are also presented in Table II (these include a small contribution due to the radical produced by H atom addition, (G(H) = 0.6 at pH >4).

It can reasonably be assumed that spectral changes in the initial spectra observed as the pH is changed are due to a rapid reversible protonation process. The major difference between the spectra of the neutral radical and the radical anion is a small shift toward the uv of the shorter wavelength absorption band. Such a shift is characteristic of the difference between the spectra of a large number of radical anions and their conjugate acids.[18] Spectral data presented above exclude the possibility that fast reversible protonation of the anion radical takes place principally at the β-carbon atom, eq 14, since the radical produced by β protonation would be the same species as is produced by addition of H atom and would have a very different spectrum. Similarly, protonation at the α-carbon atom, eq 15, would leave an isolated unpaired electron at the β position. The resulting spectrum would be expected to be similar to that of simple alkyl radicals, i.e., short wavelength end absorption.[18]

$$H^+ + CH_2CHCONH_2\cdot^- \underset{\text{reversible}}{\overset{\text{fast}}{\rightleftharpoons}} CH_3\dot{C}HCONH_2 \qquad (14)$$

$$H^+ + CH_2CHCONH_2\cdot^- \underset{\text{reversible}}{\overset{\text{fast}}{\rightleftharpoons}} \dot{C}H_2CH_2CONH_2 \qquad (15)$$

It is suggested that fast reversible protonation takes place at oxygen, eq 4. The difference between the spectra of electron adducts and of protonated electron adducts in the present work is similar to the difference between the spectra of α-hydroxyalkyl radicals, e.g., $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$, and those of their conjugate bases.[3]

pK_a Values for Reversible Fast Protonation of Electron Adducts. A limited correlation of pK_a values for reversible protonation of electron adducts of unsaturated amides with the pK_a values of corresponding carboxylic acids is demonstrated in Figure 13.

Rates of β Protonation of Electron Adducts. The rates of decay of radical anions, summarized in Table II, were shown to be the rates of protonation at the β position. These rates show a relatively strong dependence on the structure of the amide which can be interpreted qualitatively on the basis of simple resonance considerations. Thus, the methyl group of methacrylamide cannot be significantly involved in resonance stabilization of the electron adduct. In contrast, the terminal methyl group of crotonamide does participate in such stabilization through hyperconjugation. In the β-protonated radicals, $(CH_3)_2\dot{C}CONH_2$ and $CH_3CH_2CHCONH_2$, the α-methyl group in the product from methacrylamide participates in stabilization of the radical but the β-methyl group in the product from crotonamide does not. Consistent with this difference, the electron adduct of methacrylamide is protonated about ten times as fast as that of acrylamide while the electron adduct of crotonamide is protonated about one seventh as rapidly as the acrylamide anion radical. The even slower rate of β protonation of the electron adduct of cinnamamide can be ascribed to a combination of loss of delocalization energy and the electron withdrawing effect of the phenyl group.

The fact that irreversible protonation at β carbon is much slower than reversible protonation at oxygen can be ascribed to the requirement for rehybridization of the β-carbon atom and the absence of this need in the case of protonation at oxygen.

Effect of Reversible Protonation on Rate of Bimolecular Decay. Reversible protonation at oxygen produces a species which undergoes bimolecular decay so much faster than does its conjugate base that this mode of decay becomes dominant. Two factors contribute to this increased reactivity: elimination of electrostatic repulsion, which can account for only a small part of the difference and reduction of resonance stabilization resulting from protonation.

Brϕnsted Correlation of Acid Catalysis of β Protonation of $CH_2CHCONH_2{}^{\cdot -}$ Radical. Adherence of catalytic rate constants, k_{HB}, to the Brϕnsted relationship, eq 16, is demonstrated in Figure 10.

$$\log (k_{HB}/p) = k_{H_2O} + \alpha \log (qK_a/p) \qquad (16)$$

Two values of α correlate most of the data. One of these, 1.0 ± 0.1, correlates the data for conjugate acids of tertiary and secondary amines. The other, 0.4 ± 0.1, correlates the data for oxoacids and NH_4^+ ion. Points for the conjugate acids of three primary amines fall between the two correlation lines. An intermediate value of α, ~0.7, is apparently appropriate for the latter group of acids. Essentially normal Brϕnsted correlation is thus observed in a reaction characterized by specific rates only a few orders of magnitude slower than the diffusion controlled limit.

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Kinetics of Deprotonation of Organic Free Radicals in Water. Reaction of $HO\dot{C}HCO_2^-$, $HO\dot{C}HCONH_2$, and $HO\dot{C}CH_3CONH_2$ with Various Bases

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Abstract: The technique of pulse radiolysis was used to observe the radicals $HO\dot{C}HCO_2^-$ (I), $HO\dot{C}HCONH_2$ (II), and $HO\dot{C}CH_3CONH_2$ (III) in aqueous solution at 22 ± 1°. The radicals were produced by hydrogen-atom abstraction from the respective parent compounds by OH radicals. Rate constants are reported for that reaction, as well as for the decay of the free radicals and of their conjugate bases. The transient absorptions of the radicals and of their conjugate bases are sufficiently different to permit monitoring of the deprotonation reactions, which take place with loss of the OH proton. The radicals are relatively acidic; pK_a is 8.8 for I, 5.5 for II, and 6.5 for III. Second-order rate constants are reported for deprotonation of the radicals by OH^-, NH_3, $B(OH)_4^-$, HPO_4^{2-}, $HP_2O_7^{3-}$, and $P_2O_7^{4-}$. In each case, $\Delta G° < 0$. Typical rate constants ($\sec^{-1} M^{-1}$) at 22 ± 1° are: $OH^- + I$, 3.9×10^9; $OH^- + II$, 1.1×10^{10}; $OH^- + III$, 1.1×10^{10}; $NH_3 + I$, 7.5×10^8; $NH_3 + II$, 1.2×10^9; $NH_3 + III$, 9.7×10^8; $P_2O_7^{4-} + I$, 5.8×10^6; $P_2O_7^{4-} + III$, 8.5×10^8. The rate constants for deprotonation of the radicals are similar to those for deprotonation (with $\Delta G° < 0$) of stable and of electronically excited oxygen acids.

There is now a substantial body of information on the ionization constants of organic free radicals in aqueous solutions.[2] In some cases, reaction rate constants were measured[3,4] for proton transfer to hydroxide ion, where $\cdot RH$

$$\cdot RH + OH^- \xrightarrow{k_{OH}} \cdot R^- + HOH \qquad \Delta G° < 0 \qquad (1)$$

and $\cdot R^-$ are the acid and base forms of the free radicals, and the standard free energy change $\Delta G° < 0$. These rate