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Electron Adducts of Acrylic Acid and Homologues. Spectra, Kinetics, and Protonation Reactions. A Pulse-Radiolytic Study

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Pulse radiolysis–kinetic absorption spectrophotometry has been employed to study the addition of electrons to acrylic acid and to several of its homologues in aqueous solution as well as spectral properties and subsequent chemical transformations of the electron adducts. Specific rates of reaction of e_{aq}^- with the acid anions at room temperature in units of 10^{10} M^{-1} s^{-1} are acrylate, 0.53 ± 0.05; methacrylate, 0.45 ± 0.4; *trans*-crotonate, 0.13 ± 0.01; β,β-dimethylacrylate, 0.059 ± 0.002; *trans,trans*-sorbate, 0.58 ± 0.03; *trans*-cinnamate, 1.4 ± 0.1. The specific rates of reaction of e_{aq}^- with the corresponding un-ionized carboxylic acids are all in the range $(1.5–2.9) \times 10^{10}$ M^{-1} s^{-1}. Spectra of reversibly diprotonated (i.e., uncharged) and monoprotonated (mononegative) electron adducts were characterized for all six acids. The main features of the spectra of the diprotonated adducts are an intense band, λ_{max} ~250–350 nm, ϵ_{max} ~$(1–4) \times 10^4$ M^{-1} cm^{-1}, and a weaker band, λ_{max} ~350–490 nm, ϵ_{max} ~10^3 M^{-1} cm^{-1}. Spectra of the monoprotonated adducts are red shifted ~10–40 nm relative to corresponding diprotonated adducts. The spectrum of the unprotonated (dinegative) adduct could be determined only for cinnamate; it is additionally red shifted ~25 nm. Values of pK_a (radical) for the process $RCO_2H_2\cdot \rightleftarrows RCO_2H\cdot^- + H^+$ fall in the range 5–8 for the six acids; pK_a (radical) for the second dissociation of the electron adduct of cinnamic acid is 11.6. An anomalous spectral change was observed with acrylic acid around pH 5. Decay of the diprotonated electron adducts of all the acids except β,β-dimethylacrylic is second order, $2k \sim (1–7) \times 10^9$ M^{-1} s^{-1}. Decay of the monoprotonated electron adducts of all the acids in the absence of catalytic species is first order, $k_{H_2O} \sim (0.1–2) \times 10^5$ s^{-1}. α-Carbon radicals, $RR'CH\dot{C}HCO_2^-$, were identified spectrally as the products of irreversible decay of the monoprotonated electron adducts of acrylic, methacrylic, β,β-dimethylacrylic, and crotonic acids; catalysis of the decay process by OH^- was observed for all the adducts except that of cinnamic acid. More detailed investigation of the decay of $CH_2CHCO_2H\cdot^-$ established general acid (Bronsted $\alpha = 0.43 \pm 0.04$) and general base catalysis as well. Electron transfer from the monoprotonated electron adducts of acrylic and crotonic acids to a number of acceptors was studied as a function of $E^{0\prime}$ of acceptor and pH. Spectra of α-carbon radicals generated by addition of H atoms to each of the acids (except cinnamic) at pH ~1 have λ_{max} ~290–300 nm, ϵ_{max} ~450–1800 M^{-1} cm^{-1}, and $2k_{decay} \sim (1–2) \times 10^9$ M^{-1} s^{-1}. Results of these studies are compared with those of a similar investigation involving acrylamide and its homologues.

In a recent communication,[2a] we described two types of protonation reactions of the electron adduct of acrylic acid in aqueous solution. We now report a detailed study of the reactions of electron adducts of several substituted acrylic acids by the technique of pulse radiolysis–kinetic spectrometry.

Pulse radiolytic studies of α,β-unsaturated acids have been reported for acrylic acid,[2,3] benzoic acid,[4] and maleic and fumaric acids.[5] A number of related studies by ESR technique have also been reported. In the reaction of e_{aq}^- with acrylic acid at pH 12,[6] only the C-protonated electron adduct, $CH_3\dot{C}HCO_2^-$, was observed. The electron adducts of a large number of α,β-unsaturated acids produced by the reaction of ammoniated electrons have also been characterized by means of the ESR technique.[7]

An ESR spectrum observed when neat acrylic acid was irradiated with ^{60}Co γ rays at 77 K was attributed to the electron adduct.[8] Exposure of neat acrylic acid to externally generated H atoms under the same conditions gave a product which was identified as the H atom adduct to the β carbon.[9] ^{60}Co γ ray irradiation of acrylic acid at 77 K in frozen solutions in several aprotic solvents, e.g., triethylamine, methyltetrahydrofuran, or 3-methylhexane, gave stable electron adducts, while the species observed in frozen protic solutions was the same as that resulting from addition of H to β carbon.[10] An optical absorption spectrum attributed to the electron adduct of cinnamic acid has also been measured in solution at 77 K in 2-methyltetrahydrofuran.[11]

Experimental Section

Radiolysis of water produces e_{aq}^- along with other species, eq 1.

$$H_2O \xrightarrow{\quad} e_{aq}^-,\ OH,\ H,\ H_2O_2,\ H_2,\ \text{and}\ H_3O^+ \qquad (1)$$

Hydroxyl radicals were scavenged by the addition of *tert*-butyl alcohol to the solutions, eq 2.

$$OH + (CH_3)_3COH \rightarrow \dot{C}H_2C(CH_3)_2OH + H_2O \qquad (2)$$

$$k_2 = 5.2 \times 10^8\ M^{-1}\ s^{-1}\ (\text{ref } 12)$$

The alcohol radicals formed in reaction 2 are generally unreactive and do not have significant absorption in the wavelength region involved in this work.[13] The contribution of transient species formed from the reaction of H atoms (yield ~20% that of e_{aq}^-) to the net observed spectra and kinetics is considered to be relatively small (see below).

Single pulses of 30-ns duration from a Febetron 705 machine were employed to produce the short-lived electron adducts. The technique employed has been described in detail.[13,14]

Materials. The following chemicals were used as received: Ma-

Table I. Specific Rates of Reaction of Hydrated Electrons

Registry no.	Acid	k, 10^{10} M^{-1} s^{-1}	
		Anion[a]	Undissociated acid[b]
79-10-7	Acrylic	0.53 ± 0.05	2.4 ± 0.1
79-41-4	Methacrylic	0.45 ± 0.04 0.84[c]	1.9 ± 0.1
107-93-7	*trans*-Crotonic	0.13 ± 0.01[d]	1.8 ± 0.2
541-47-9	β,β-Dimethylacrylic	0.059 ± 0.015	1.5 ± 0.1
22500-92-1	*trans,trans*-Sorbic	0.58 ± 0.03	2.9 ± 0.1
140-10-3	*trans*-Cinnamic	1.4 ± 0.12[d] 0.72[c]	2.2 ± 0.1

[a] Uncertainties are mean deviations. [b] Uncertainties are standard deviations. [c] From ref 16. [d] Determined by monitoring both kinetics of decay of e_{aq}^- and of formation of the transient.

theson N_2O and gold label Ar; Mallinckrodt 70% AR $HClO_4$ and *tert*-butyl alcohol; Baker and Adamson AR KOH, NaH_2PO_4, KH_2PO_4, Na_2HPO_4, K_2HPO_4, $Na_2B_4O_7\cdot 10H_2O$, KSCN, and NH_4Cl; Fisher or G. Frederick Smith $NaClO_4\cdot H_2O$; G. Frederick Smith-$Ba(ClO_4)_2$; Baker and Adamson K_2SO_4; Aldrich Analyzed 99.9+% zone refined *trans*-cinnamic acid.

Eastman or Matheson Coleman and Bell acrylic acid was recrystallized from the melt, distilled twice under ~20 Torr of N_2, and the middle fraction of the distillate recrystallized again from the melt. The resulting crystals were stored in a refrigerator. Purified acid was used to make up solutions for radiolysis for no more than 2 weeks after purification. Eastman or Matheson Coleman and Bell methacrylic acid was purified and handled in the same way as acrylic acid. Aldrich 98% *trans*-crotonic acid was recrystallized from 30–60 °C petroleum ether, mp found 71–72 °C (uncorrected) (lit.[15] 71.5 °C). Aldrich β,β-dimethylacrylic acid was recrystallized twice from petroleum ether, mp found 67.5–68.5 °C (uncorrected) (lit.[15] 70 °C). Eastman sorbic acid was recrystallized twice from ethyl acetate, then once from hot distilled water and dried by storing in a vacuum desiccator, mp found 130–131.5 °C (uncorrected) (lit.[15] 134.5 °C).

Dosimetry. The concentration of electron adducts produced in solution was calculated from measured doses based on $G(e_{aq}^-) = G(OH) = 2.8$. Doses per pulse were calculated from the measured absorbance at 500 nm due to $(SCN)_2\cdot^-$ produced upon irradiation of N_2O-saturated 0.04 M aqueous KSCN solutions,[13] taking $\epsilon_{500} = 7600$ M^{-1} cm^{-1}. Initial concentration of e_{aq}^- was usually 3–20 μM, but sometimes as much as 10^{-4} M. Under all conditions, the concentration of the substrates was high enough to scavenge >95% of e_{aq}^-.

Results

Reactivity with e_{aq}^-. The specific rates of reaction of e_{aq}^- with acid anions and undissociated acids are presented in Table I. The solutions were deaerated by sweeping with Ar, contained 0.10 M *tert*-butyl alcohol (10^2–10^3-fold excess over substrate) and were buffered at pH 9.2 with ~1 mM borate. The rates of reaction of the anions were determined by following the decay of absorbance of e_{aq}^- at 700 nm under pseudo-first-order conditions. In two cases, growth of absorbance of the electron adduct was also followed.

Rates of reaction of the undissociated acids with e_{aq}^-, eq 3, could not be measured directly at pH ⩽ 3 because of the competition of H_3O^+ for hydrated electrons, eq 4.

$$R_2C{=}CRCO_2H + e_{aq}^- \rightarrow \text{adduct} \tag{3}$$

$$H_3O^+ + e_{aq}^- \rightarrow \cdot H \tag{4}$$

$$k_4 = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}\ (\text{ref } 16)$$

Such low pH values are required to keep the acids (pK_a = 4.25–5.15, see Table II) largely undissociated. The rates were determined, however, from experiments based on the competition between reactions 3 and 4. In these experiments, 2–5 mM acid solutions were irradiated at several pH values in the range 2.0–3.7, and the initial absorbance was measured at wavelengths where absorbance was due primarily to the electron adducts. Absorbance values obtained with a given acid decreased with decrease in pH. The ratio of the absorbance at the highest pH to absorbance at the lower values of pH varied linearly with the ratio $(H_3O^+)/(\text{substrate acid})$. The slopes can be shown to be equal to k_4/k_3.[17] With solutions at the lower end of the pH range, a small correction for absorbance by H atom adducts was necessary.[17]

As seen in Table I, rates of reaction of the undissociated acids with e_{aq}^- do not vary with structure as much as those of the anions. With the anions, the most prominent effect is the lowering of reactivity by substitution of β hydrogen by methyl. β-Phenyl increases reactivity of the anion while β-vinyl does not lead to any significant change. As expected, the anions are less reactive than the undissociated acids.

Absorption Spectra of Initially Formed Transient Species. Spectra of initially formed transients were usually

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

Acid	pK_a of parent acid[a]	Diprotonated electron adduct				pK_a[e] of radical	Monoprotonated electron adduct			
		pH	λ_{max}, nm	ϵ_{max}, mM^{-1} cm^{-1}	$2k$, 10^9 M^{-1} s^{-1}		pH	λ_{max}, nm	ϵ_{max}, mM^{-1} cm^{-1}	k,[g] 10^4 s^{-1}
Acrylic	4.25	3.7	255	19.	4.0	5.0,[f] 7.0[f]	6.0[f]	265	7.7	4.0
			265[b]	16.				350[c]	1.0	
			350[c]	0.7			9.5	285	9.7	3.0
								350[c]	1.3	
Methacrylic	4.36	3.2	255	14.4	4.0	5.3	9.0	290	4.7	20.
			380	0.8				380[c]	1.0	
Crotonic	4.69	3.8	250	18.	0.7	7.5	10.4	280	11.4	1.0
			400	0.6				380[c]	1.0	
β,β-Dimethylacrylic	5.12	3.8	<255	9.5	($k = 6.0 \times 10^3\ s^{-1}$)[d]	8.0	11.0	270	8.8	0.9
								420	0.75	
trans,trans-Sorbic	4.76	4.2	292	33.	2.6	6.4	11.1	320	27.	5.0
								450[c]	0.5	
trans-Cinnamic	4.44	3.7	340	36.	7.2	5.6,[f] 11.6[f]	9.5	375	36.	0.2[h]
			490	1.0				500	2.5	
							13.0	395	37.	8.[i]
								530	4.6	

[a] From ref 15. [b] From ref 2. [c] Shoulder. [d] *first*-order decay. [e] Uncertainties are 0.1–0.2. [f] See discussion of assignment. [g] Extrapolated to zero concentration of buffer and added OH^-. [h] At pH 7.5. [i] Independent of concentration or buffer and OH^-.

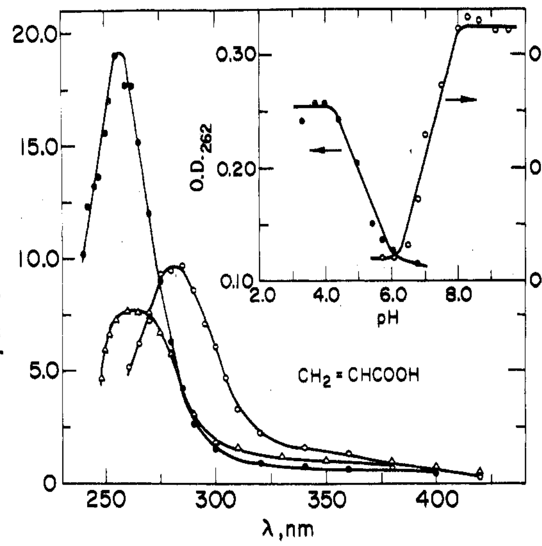

Figure 1. Initial transient absorption spectra produced by the reaction of e_{aq}^- with 2–8 mM acrylic acid at pH 9.5 (○), 6.0 (△), and 3.8 (●) in 1–1.5 M aqueous *t*-BuOH under 1 atm of Ar; dose ~8 krad/pulse. Insert: Change in absorbance with pH at 262 and 280 nm.

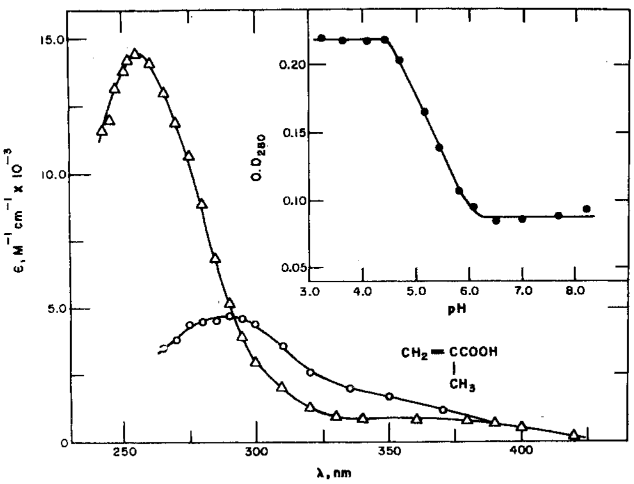

Figure 2. Initial transient absorption spectra produced by the reaction of e_{aq}^- with 3–8 mM methacrylic acid at pH 9.0 (○) and 3.7 (△) in 1.0 M aqueous *t*-BuOH under 1 atm of Ar; dose ~8 krad/pulse. Insert: Change in absorbance with pH at 280 nm.

measured at pH 3.5, 6.0, 9.5, and 12.2, or similar pH values. Absorbances were either measured "immediately," i.e., ~0.1 μs after the pulse, or were extrapolated to zero time from measurements made up to several μs after the pulse. All spectral measurements were corrected for depletion of substrate. Spectral data are presented in Figures 1–6. pK_a values for the *reversible* protonation of the electron adducts were determined by measuring absorbance of irradiated solutions at a fixed wavelength at several different pH values. The resulting titration curves are shown as inserts in Figures 1–6. Values of λ_{max}, ϵ_{max}, and pK_a of the initial transients formed by electron addition are collected in Table II.

The main features of all the initial transient spectra are a prominent absorption band at short wavelengths, centered ~280–300 nm in most cases, and a relatively weak band ~100 nm to the red of the main band. The main band is shifted to longer wavelengths at higher pH values. Acrylic and *trans*-cinnamic acids gave rise to three distinct transient spectra as pH was varied. The other acids, namely, methacrylic, crotonic, β,β-dimethylacrylic, and sorbic, gave rise to only two distinct spectra. The apparent large difference between the second pK_a of the acrylic acid and *trans*-cinnamic acid radicals is discussed below.

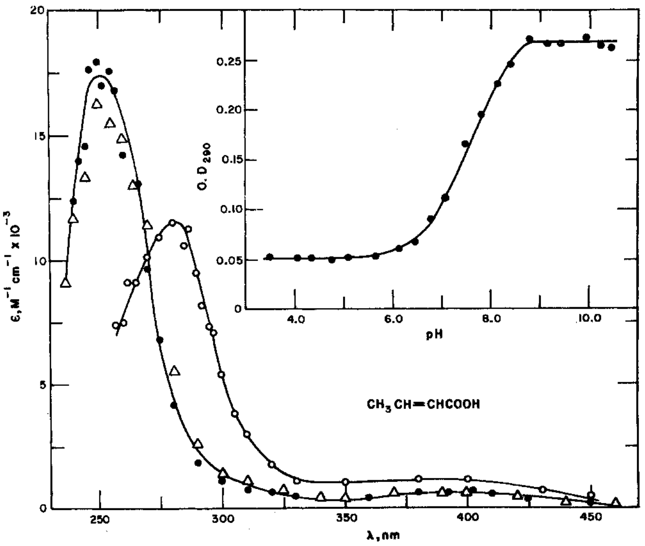

Figure 3. Initial transient absorption spectra produced by reaction of e_{aq}^- with 5 mM *trans*-crotonic acid at pH 9.2 (○), 6.3 (△), and 4.0 (●) in 1.0–1.5 M aqueous *t*-BuOH under 1 atm of Ar; dose ~4 krad/pulse. Insert: Change in absorbance with pH at 290 nm.

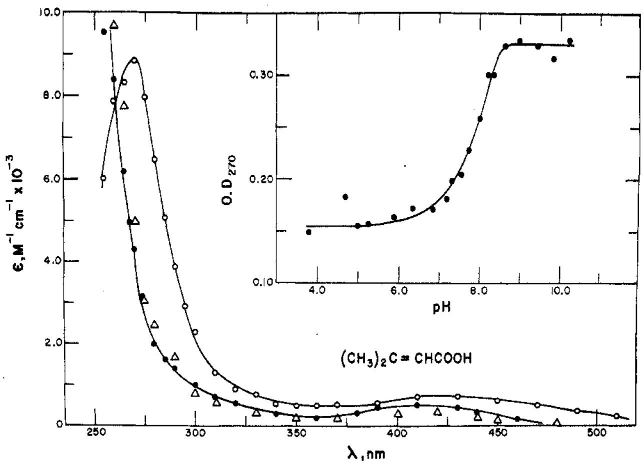

Figure 4. Initial transient absorption spectra produced by the reaction of e_{aq}^- with 5 mM β,β-dimethylacrylic acid at pH 9.7 (○), 6.6 (△), and 3.8 (●) in 1.0 M aqueous *t*-BuOH under 1 atm of Ar; dose ~8 krad/pulse. Insert: Change in absorbance with pH at 270 nm.

Kinetics of Decay of Initially Formed Transient Species. Kinetic data summarized in Table II were obtained by following change in absorbance as a function of time at several pH values. Kinetics were generally followed to ~80–90% decay of initial transient spectra. Spectra of secondary transients were also characterized.

Acrylic Acid. Decay of the electron adduct of acrylic acid in the pH range 8.2–11.5 was cleanly first order, independent of initial concentrations of e_{aq}^- (1–2.5 × 10^{-5} M) and acrylic acid (2–5 mM). At pH 8–9 (1 mM borate buffer) the first-order rate of decay was also independent of the ionic strength (0.01–0.10 M $NaClO_4$). At pH above 9, decay rates depended significantly on the concentration of hydroxide ion (see below) and also on the nature and concentration of buffers. The roles of buffer acids and their conjugate bases in these rate effects were determined by varying buffer ratios at constant total buffer concentration and constant ionic strength.[17,18]

The second-order catalytic constant for each active buffer species was evaluated from the linear dependence of the first-order decay constant on the concentration of the active

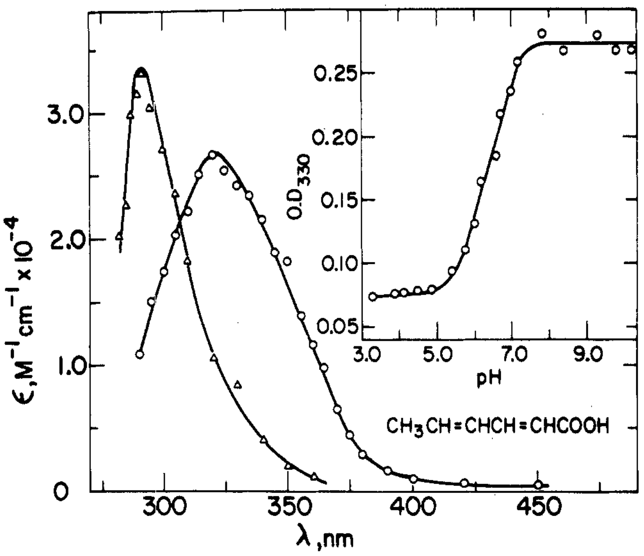

Figure 5. Transient absorption spectra produced by the reaction of e_{aq}^- with 10 mM sorbic acid at pH 9.2 (○) and 3.1 (△) in 1.5 M aqueous *t*-BuOH under 1 atm of Ar; dose ~2 krad/pulse. Insert: Change in absorbance with pH at 330 nm.

species at constant pH and nearly constant ionic strength. In solutions at pH above 9, and at constant ionic strength and low buffer concentration, the first-order decay rate varied linearly with $[OH^-]$. The second-order catalytic constants for buffer components and OH^- were derived from the slopes of such linear plots and are given in Table III.

The rate constants for the reaction of buffer acids with the electron adduct of acrylic acid adhere to the Bronsted catalysis equation $k_{cat.} = (qK_a/p)^\alpha$ with $\alpha = 0.43 \pm 0.04$.[17]

Primary salt effects on the first-order rate constant for the reaction of the electron adduct with OH^- ions were examined in 1 mM tetraborate buffer at pH 10.5 with the objective of determining the overall charge on the electron adduct, i.e., its state of protonation. Linear plots of log k_{decay} vs. $\mu^{1/2}/(1 + \mu^{1/2})$ were obtained for several inert salts but their slopes depended on the nature of the anion. Thus, the apparent magnitude of the negative charge of the electron adduct calculated from the data for various salts was 2.5 ± 0.4 from experiments with $NaClO_4$, 2.4 ± 0.5 for $Ba(ClO_4)_2$, 1.2 ± 0.3 for K_2SO_4, and 0.8 ± 0.2 for $(n\text{-}Bu_4N)_2SO_4$.

Decay of the electron adduct at pH 6.0, i.e., between its two apparent pK_a values, 5.0 and 7.0, adhered to first-order kinetics, as it did at pH 6.0 and 9.5, while at pH 3.1 its decay was second order (see Table II).

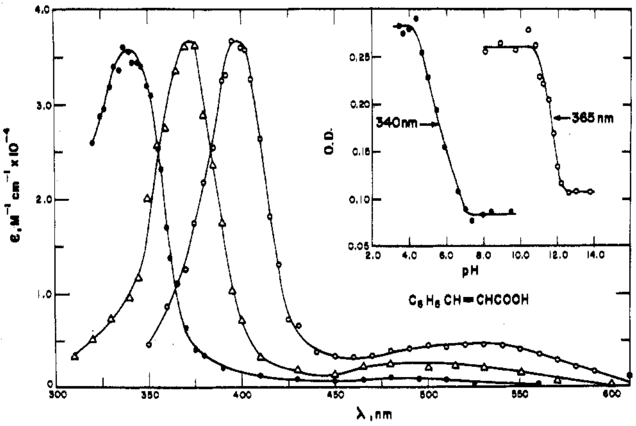

Figure 6. Transient absorption spectra produced by the reaction of e_{aq}^- with 0.2–2 mM *trans*-cinnamic acid at pH 13.0 (○), 9.3 (△), and 3.7 (●) in 1.0 M aqueous *t*-BuOH under 1 atm of Ar; dose ~2 krad/pulse. Insert: Change in absorbance with pH at 340 and 365 nm.

Methacrylic Acid. The initial transient formed by electron addition to methacrylic acid at pH 8–9 was also found to decay by first-order kinetics with the rate independent of radiation dose, initial concentration of the substrate, and pH. As can be seen from Table II, the uncatalyzed first-order rate of decay of the electron adduct of methacrylic acid is considerably higher than that of acrylic acid. Substitution of hydrogen attached to α-carbon atom by a methyl group apparently accelerates decay of the electron adduct.

At higher pH values, viz., 10.1–11.1, the rate was found to be linearly dependent on the concentration of OH^-, with $k = 1.0 \times 10^9\ M^{-1}\ s^{-1}$ (see Table III), a value only slightly higher than for the electron adduct of acrylic acid.

At pH 3.2, the presumably doubly protonated electron adduct decayed completely by a second-order process (see Table II).

***trans*-Crotonic Acid.** At pH 10.4, the electron adduct of *trans*-crotonic acid decayed by a first-order process the rate of which did not change significantly with threefold variation in concentration of the adduct or a 15-fold variation in the concentration of the substrate. As can be seen from Table II, the uncatalyzed first-order rate of decay of the electron adduct is considerably less than that of acrylic acid. In contrast to α-methyl substitution, β-methylation apparently inhibits decay of the radical.

In the pH range 11.1–12.2, the decay rate was linearly dependent on OH^- concentration, with $k = 1.5 \times 10^8\ M^{-1}\ s^{-1}$

Table III. Rate Constants for Reaction of Electron Adducts with Buffer Components[a] and OH^-

Substrate acid	Buffer species	k_μ, $M^{-1}\,s^{-1}$	μ, M	$k_{\mu=0}$
Acrylic	$H_2PO_4^{-1}$	1.6×10^7	0.22	$5.7 \times 10^{6\,b}$
	$HP_2O_7^{-3}$	1.4×10^6	0.50	$9.1 \times 10^{4\,b}$
	NH_4^+	8.5×10^5	0.10	$1.8 \times 10^{6\,b}$
	$B(OH)_3$	2.8×10^5	0.10, 0.50	$2.8 \times 10^{5\,c}$
	HPO_4^{-2}	4.0×10^4	0.20	$7.0 \times 10^{3\,b}$
	NH_3	$(2.8 \pm 1.0) \times 10^6$	0.10	$2.8 \times 10^{6\,d}$
	$B(OH)_4^-$	$(4.9 \pm 1.5) \times 10^5$	0.10	$2.3 \times 10^{5\,b}$
	OH^-	$(7.7 \pm 0.3) \times 10^8$	0.026	$7.7 \times 10^{8\,b}$
Methacrylic	OH^-	$(1.0 \pm 0.1) \times 10^9$	0.013	$8 \times 10^{8\,b}$
trans-Crotonic	OH^-	$(1.5 \pm 0.1) \times 10^8$	0.005–0.022	$\sim 1.2 \times 10^{8\,b}$
β,β-Dimethylacrylic	OH^-	$(1.9 \pm 0.1) \times 10^7$	0.20	$3 \times 10^{6\,b}$
Sorbic	OH^-	$(3.0 \pm 0.2) \times 10^7$	0.005–0.045	$\sim 2 \times 10^{7\,b}$
trans-Cinnamic	OH^-	$\ll 10^4$	0.1	$\ll 10^4$

[a] All data are at pH greater than first pK_a of electron adducts except for acrylic acid. In latter case pH was greater than apparent second pK_a. [b] Extrapolated to $\mu = 0$ by means of the relationship $\log k = \log k_0 + z_a z_b \mu^{1/2}$, assuming a charge of −1 on every electron adduct. [c] k independent of μ. [d] k assumed to be independent of μ.

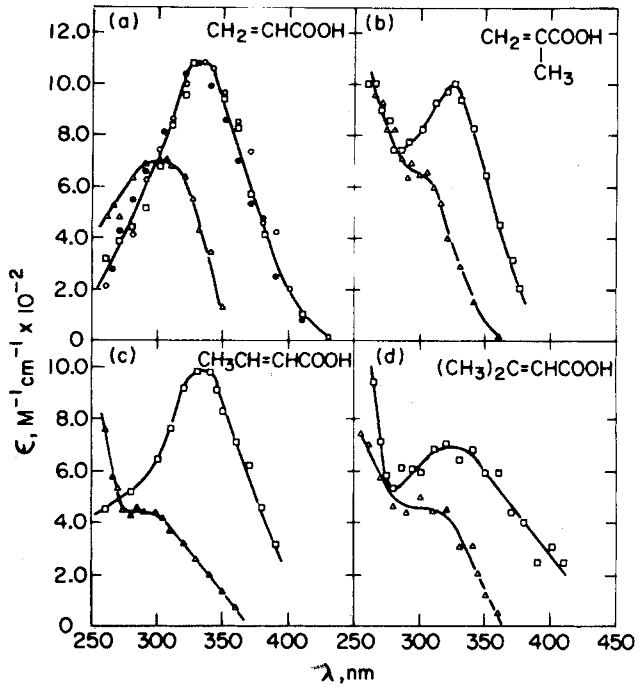

Figure 7. Secondary spectra formed in the decay of electron adducts and primary spectra of H atom adducts of (a) acrylic, (b) methacrylic, (c) crotonic, and (d) β,β-dimethylacrylic acids. Dose per pulse 8–36 krad. (a) 2 mM acrylate, 1.0 M *t*-BuOH, under 1 atm of Ar read 0.2 μs (pH 12.0) (○) and 20 μs (pH 10.0) after the pulse (●); spectrum of $CH_3\dot{C}HCO_2^-$ radical from reaction 5 at pH 9.2 (□); 2 mM acrylic acid, 0.5 M *t*-BuOH, under 1 atm Ar, pH 0.5 (△). (b) 2 mM methacrylate, 1.0 M *t*-BuOH, under 1 atm of Ar, measured at pH 12.2 ~0.2 μs after the pulse (□); 0.4 mM methacrylic acid, 0.4 M *t*-BuOH under 1 atm of Ar, pH 1.0 (△). (c) 5 mM crotonate, 1.5 M *t*-BuOH under 1 atm of Ar, measured at pH 12.9 ~0.2 μs after the pulse (□); 2 mM crotonic acid, 1 M *t*-BuOH, under 1 atm Ar, pH 0.9 (△). (d) 5 mM β,β-dimethylacrylic acid, 1.0 M *t*-BuOH, under 1 atm Ar, measured at pH 13.1, 0.2 μs after the pulse (□); 1 mM β,β-dimethylacrylic acid, 0.4 M *t*-BuOH, under 1 atm Ar at pH 0.7 (△).

(Table III), considerably lower than that for the electron adducts of acrylic and methacrylic acids.

Using the same electrolytes as with acrylic acid [$NaClO_4$, K_2SO_4, and $Ba(ClO_4)_2$], the results of primary salt effect experiments did not help in establishing the state of protonation of the electron adduct at pH 11.6. Results were essentially the same as those described above for the reaction of the electron adduct of acrylic acid with OH^-.

At pH 3.8, the presumably doubly protonated electron adduct decayed via a second-order process (see Table II).

β,β-Dimethylacrylic Acid. At pH 10.0, the uncatalyzed first-order rate of decay of the electron adduct was the same as the corresponding value for crotonic acid (see Table II). In the pH range 11.0–12.2 the rate of pseudo-first-order decay of the electron adduct of β,β-dimethylacrylic acid (measured in the presence of 0.2 M $NaClO_4$) was linearly dependent on $[OH^-]$. As can be seen from Table III, the second-order rate constant for reaction with OH^- is considerably smaller than the corresponding value for crotonic acid.

At pH 3.8, the presumably doubly protonated electron adduct decayed completely by a first-order process (Table II), the chemical course of which was not investigated.

Sorbic Acid. The uncatalyzed first-order rate of decay of the electron adduct differed relatively little from the corresponding value for acrylic acid. The rate of pseudo-first-order decay of the electron adduct of sorbic acid at pH 11.1–12.3 varied linearly with $[OH^-]$. The second-order rate constant for reaction with OH^- (see Table III) is lower than that of acrylic acid by a factor of ~25.

At pH 4.2, the presumably doubly protonated electron adduct decayed by a second-order process (see Table II).

***trans*-Cinnamic Acid.** At pH 10.1 (1 mM tetraborate-buffer), the singly protonated electron adduct decayed by a first-order process considerably slower than the uncatalyzed rate of decay of the electron adduct of acrylic acid. At lower pH values, the decay was slower and followed mixed kinetics. At pH 13.2, the electron adduct of cinnamic acid, i.e., the radical dianion, decayed by a clean first-order process. In the limited pH range available around 13 (radical $pK_a = 11.6$), its decay was not influenced by changes in OH^-, cinnamic acid concentration, or ionic strength. The first-order character of this decay as well as the absence of catalysis by OH^- is discussed below.

The doubly protonated electron adduct at pH 3.7 decayed via mixed kinetics showing a strong second-order component.

Secondary Transient Species and H Atom Adducts. Acrylic Acid. In alkaline solutions, the decay of the initial electron adduct species was found to produce another transient. This was identified as the radical $CH_3\dot{C}HCO_2^-$ by comparison of its spectrum with that generated[1,19] via reaction 5.

$$CH_3CHClCO_2^- + e_{aq}^- \rightarrow CH_3\dot{C}HCO_2^- + Cl^- \quad (5)$$

In Figure 7a spectra of the secondary transient generated under two different conditions are compared with the spectra produced by reaction 5 and by addition of H atoms to acrylic acid. It is apparent that, after normalization at 330 nm, the secondary spectrum observed 20 μs after the pulse at pH 10.0, the spectrum observed 0.2 μs after the pulse under conditions of accelerated decay of the primary transient, i.e., at pH 12.2, and the spectrum produced by reaction 5 at pH 9.2 do not differ significantly. This spectral similarity indicates that protonation at the β-carbon atom takes place during the decay reaction.

The spectrum resulting from addition of H atoms to acrylic acid at pH 0.5 is similar to one which has been reported for the $CH_3\dot{C}HCO_2H$ radical.[19] The shift of λ_{max} to shorter wavelength is consistent with the behavior of a number of radical acid–base pairs.[19]

The decay of the spectra of the secondary transient generated at pH 12.2 and of the H atom adduct generated at pH 0.9 followed second-order kinetics.

Other Acids. The secondary spectra formed from the decay of the electron adducts at pH ~12, as well as the spectra of the H atom adducts of methacrylic, crotonic, and β,β-dimethylacrylic acid at pH ≤ 1, are shown in Figures 7b–d. The secondary spectra have maxima around 325 nm, with another peak below 260 nm. The spectra of the H atom adducts have a poorly defined band at ~300 nm, with another stronger absorption below ~260 nm. Spectra of H atom adducts were generated under conditions of pH and concentration of the acid substrates such that >99% of e_{aq}^- reacted directly with H^+. From these spectra, one can conclude that decay of the electron adduct results in protonation at the β-carbon atom in these cases.

The secondary spectrum from the decay of the electron adduct of cinnamic acid was very weak, with no characteristic features above 320 nm. The two corresponding spectra of sorbic acid were also weak and featureless above 300 nm.

Oxidation Reactions of the Electron Adducts of Acrylic and Crotonic Acids. The oxidation reactions of the electron adducts of acrylic and crotonic acids with several oxidants of known redox potential were examined by a technique which is described in detail elsewhere.[20] Experiments were done at pH ~3.4, 6.0, and 8–9. The extent of reaction 6 can be represented by the percent electron transfer

$$S\cdot^- + Ox \rightarrow S + Ox\cdot^- \quad (6)$$

Table IV. λ_{max}, ϵ_{max}, and Decay Kinetics of α-Carbon Radicals of Acrylic Acids in Aqueous Solution

	From decay of electron adducts				From H atom adduct			
Acid	pH	λ_{max} nm	ϵ_{max}, $M^{-1}\,cm^{-1}$	$2k$, $M^{-1}\,s^{-1\,a}$	pH	λ_{max}, nm	ϵ_{max}, $M^{-1}\,cm^{-1}$	$2k$, $M^{-1}\,s^{-1\,a}$
Acrylic	12.2	330	1100	1.3×10^9	0.9	300	700	2.0×10^9
		335^b	950^b	$1.2 \times 10^{9\,b}$		300^b	700^b	$2.2 \times 10^{9\,b}$
Methacrylic	12.2	325	1000	5.7×10^8	1.0	300	600	1.0×10^9
Crotonic	12.9	330	1000	9.3×10^8	1.0	290^c	450	1.2×10^9
β,β-Dimethylacrylic	13.1	330	650		0.7	300^c	450	1.2×10^9
Sorbic	13.2	380^d	~60		0.8	295^c	1800	
Cinnamic	13.0	300^d	4000					

[a] Mean deviations ~20%. [b] Reference 19 for $CH_3\dot{C}HCO_2^-$ and $CH_3\dot{C}HCO_2H$ radicals. [c] Well-developed shoulder masked by a strong tail absorption. [d] Absorption tail poorly characterized.

where S and $S\cdot^-$ represent the solute and its electron adduct, respectively, while Ox and $Ox\cdot^-$ represent the oxidant and the reduced oxidant.

The maximum absorbance at a characteristic wavelength of the reduced oxidant was measured for a pulse-radiolyzed solution containing an excess of acrylic or crotonic acid (5–10 mM) and a small known concentration of oxidant (0.05–0.1 mM). This absorbance was compared with that produced via reaction 7, taken as 100% reduction.

$$e_{aq}^- + Ox \rightarrow Ox\cdot^- \qquad (7)$$

The results are shown in Figure 8. From the middle point of these curves an apparent oxidation potential value for the electron adduct can be derived. The values at various pH's do not differ appreciably, 1.1 ± 0.1 V, and are with reference to two-electron redox potential values of the oxidants.

There is a noticeable difference in the behavior of the electron adducts of acrylic and crotonic acids, Figures 8a and 8b. Whereas the electron adduct of crotonic acid was nearly completely oxidized by oxidants of suitable potential at all pH values, electron transfer from the electron adduct of acrylic acid at pH 6.0 and 8.2 apparently proceeded to only 50–60% of completion.

The results of experiments where the oxidant was maintained the same but where the pH of the solution was continuously varied are shown in Figure 8c. The pK_a values determined from these sigmoidal curves agree well with the values determined directly from the dependence of the absorbance of the electron adduct on pH. The pK_a values obtained in these experiments validates the assumption that protonation equilibria of the electron adducts are established well within the time required for the electron transfer reaction. This assumption is important as a primary objective in doing these experiments was to help determine the number of distinct states of protonation of the electron adducts in question.

The rates of these electron transfer reactions, determined from rates of formation of transient absorption of the reduced oxidants, were generally $\leq 4 \times 10^9\ M^{-1}\,s^{-1}$.

Discussion

Rates of Reaction with e_{aq}^-. The specific rates of reaction of the undissociated acids, $(1.5\text{–}2.9) \times 10^{10}\ M^{-1}\,s^{-1}$, are near the diffusion controlled limit. The observed variations of reactivity with structure are similar in sign but smaller in magnitude compared to those observed[18] in the reaction of acrylamides with e_{aq}^-. Rates of the latter reaction are also near the diffusion-controlled limit. The somewhat slower reactions of the acid anions with e_{aq}^- display a larger variation of rate with structure. In all three cases the most prominent effect is deceleration by β-methyl. This effect is an example of the frequently observed systematic dependence upon structure of reaction rates near the diffusion-controlled limit.

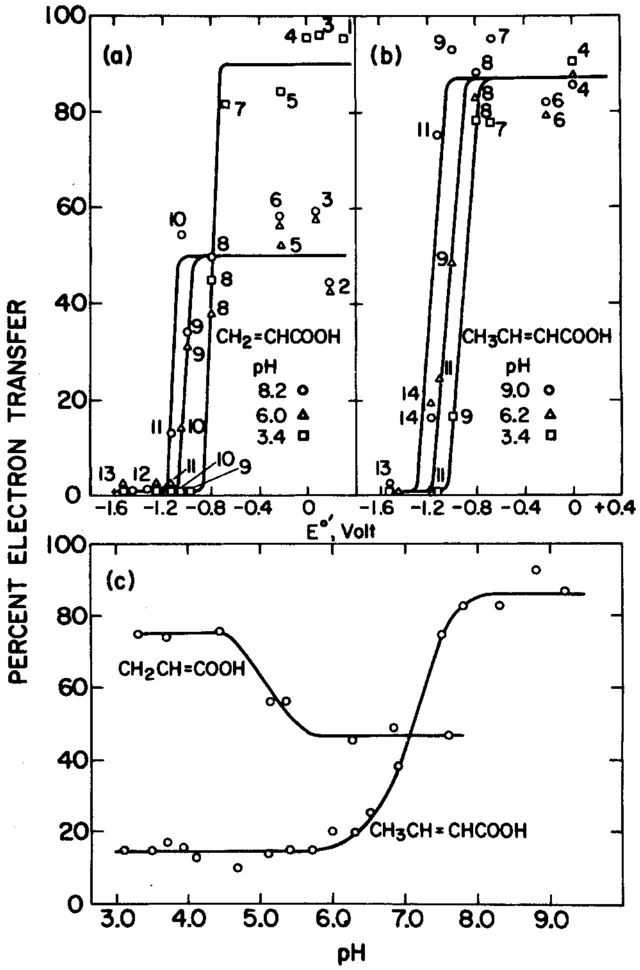

Figure 8. Plot of percent electron transfer from electron adducts of (a) acrylic and (b) crotonic acid to various oxidants vs. $E^{0\prime}$ values for two-electron reduction of the oxidants at various pH values. Solutions contained 10 mM crotonic acid, 1.5 M t-BuOH, and 0.05 mM oxidant or 10 mM acrylic acid, 1.5 M t-BuOH, and 0.1 mM oxidant both under 1 atm of Ar: 1, benzoquinone; 2, 2,5-dimethylbenzoquinone; 3, duroquinone; 4, 2-methyl-1,4 naphthoquinone; 5, 9,10-anthraquinone-1-sulfonate; 6, 9,10-anthraquinone-2-sulfonate; 7, fluorenone; 8, p-cyanoacetophenone; 9, benzophenone; 10, 4,4-dimethoxybenzophenone; 11, 4,4-dihydroxybenzophenone; 12, p-chlorobenzophenone; 13, benzamide; 14, fumaric acid. (c) Variation of percent electron transfer with pH: 10 mM crotonic acid and 0.05 mM benzophenone, or 10 mM acrylic acid and 0.1 mM 2-methyl-1,4-naphthoquinone.

Initial Transient Spectra. The main feature in the spectra of the electron adducts is the band at ~300 nm with ϵ_{max} of ~$10^4\ M^{-1}\,cm^{-1}$. The longer wavelength bands are not well characterized and have a small contribution from the spectra of H atom adducts. Change of initial transient spectra with pH can reasonably be attributed to rapid reversible protonation of the electron adducts at the oxygen atom.[18] A linear relationship which exists[17] between the reciprocals of the wavelength maxima of the electron adducts and those of the corresponding parent molecules includes the amides,[18] carboxylic acids, and carboxylate anions.

pK_a (Radical) Values. The number of distinct spectra and pK_a values measured is important in the context of spectral assignment. Only for the electron adducts of acrylic and cinnamic acids were two pK_a (radical) values (see Table II) observable. Transients from electron adducts of the other acids gave rise to single pK_a values in the range 5.3–8.0. These pK_a values of electron adducts can be compared with pK_a = 5.3 and 12.0 for the electron adduct of benzoic acid[4] as well as 10.9 and 13.5, respectively, for the last stage of deprotonation of the electron adducts of fumaric and maleic acids.[5] By comparison with these cases, the electron adducts of acrylic acids in this study can be expected to have pK_a values for the last stage of deprotonation above 10. This equilibrium has not been observed for most of the substituted acrylic acids, presumably because the electron adducts undergo fast irreversible protonation at β carbon at pH values above 9.

Thus, the following assignments can be made: (a) the electron adduct spectra around pH 9 are probably those of the *singly protonated* mononegative electron adducts; (b) the spectra around pH 3.5 are probably those of the *doubly protonated* uncharged electron adducts and (c) the spectrum of cinnamic acid at pH 13.2 is that of the *unprotonated dinegative electron adduct.*

These assignments do not account for the three spectra and two pK_a values (5.0 and 7.0) observed with acrylic acid. The origin of these observations is not understood at present. Fessenden and Chawla[5] have presented evidence for the monoprotonated mononegative nature of the electron adduct of acrylic acid at pH 9.5 by measuring the conductance of a solution of acrylate ions at this pH after a pulse of radiation.

Using a generalized formula for the electron adducts, the dissociation equilibria can be represented as

$$\mathrm{R_2CCRCO_2H_2\cdot} \underset{\mathrm{p}K_a\ 5\text{–}8}{\rightleftarrows} \mathrm{R_2CCRCO_2H\cdot^-} + \mathrm{H^+} \qquad (8)$$

$$\mathrm{R_2CCRCO_2H\cdot^-} \underset{\mathrm{p}K_a\ >10}{\rightleftarrows} \mathrm{R_2CCRCO_2\cdot^{2-}} + \mathrm{H^+} \qquad (9)$$

(No attempt is made here to represent delocalization of the odd electron.) Reaction 9 was observed in this work only with cinnamic acid. The rate of reaction 10

$$\mathrm{R_2CCRCO_2H\cdot^-} \xrightarrow[\text{or buffer}]{\mathrm{OH^-}} \mathrm{R_2CHCRCO_2\cdot^-} \qquad (10)$$

with all the other monoprotonated radicals is very high. Hence equilibrium 9 cannot be achieved.

Decay Kinetics of Electron Adducts and Formation of β-Carbon Protonated Radicals. The dependence on structure of rate of isomerization of O-monoprotonated (mononegative) electron adducts of the acrylic acids into their β-protonated isomers parallels the behavior of the mononegative electron adducts of the corresponding amides.[18] The trends in both uncatalyzed (Table II) and hydroxide ion catalyzed (Table III) reactions are k(α-methyl) > k(unsubstituted) > k(β-methyl). These relative reactivities have been discussed previously.[18] Acid catalysis of protonation at β carbon has been observed with the electron adducts of both acrylic amides[18] and acrylic acids. Base catalysis has only been observed with electron adducts of acrylic acids. The magnitude of the Bronsted coefficient, α, characterizing catalysis by oxo acids and NH_4^+ is the same for the electron adducts of acrylamide[18] and acrylic acid. Failure to observe base catalysis of β-protonation of the electron adducts of acrylamides can be ascribed to the relatively low pK_a values of their monoprotonated forms (7–9.5).[18] Presumably base catalysis acts by deprotonation of the functional group which is either concerted with or is rapidly followed by protonation at β carbon, e.g., eq 11.

$$\mathrm{AH} + \mathrm{CH_2CHCO_2H\cdot^-} + \mathrm{B} \rightarrow \mathrm{A^-} + \mathrm{CH_3CHCO_2\cdot^-} + \mathrm{BH^+} \qquad (11)$$

The role of either AH or B, or both, can be played by H_2O. In the special case of the electron adduct of cinnamic acid, the deprotonated dinegatively charged radical is sufficiently stable to be observed directly (Figure 6). The first-order decay of this species, e.g., at pH 13 (Table II), quite possibly involves protonation at β carbon with water functioning as the acid.

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