# Redox Potentials of Free Radicals. III. Reevaluation of the Method

**P. S. Rao and E. Hayon***

*Contribution from the Pioneering Research Laboratory, U.S. Army Natick Laboratories, Natick, Massachusetts 01760.* *Received June 27, 1974*

**Abstract:** A reevaluation of the method described in ref 1 and 2 to determine the redox potentials of free radicals (·RH) in water is presented. This method is based on the dependence of the percentage efficiency for the one-electron oxidation (or reduction) of ·RH radicals upon the redox potentials $E^{\circ 1}$ of the electron acceptors, A. The reaction $\cdot RH + A \rightarrow \cdot A^- + R + H^+$ ($k_{ox}$) is not reversible for most radicals under the experimental conditions used, and the derived potentials are, therefore, not thermodynamic values. A reinterpretation of the results is made on the basis of the kinetic competition between the above reaction and $\cdot RH + A \rightarrow \cdot RHA$ ($k_{add}$) (radical adducts). Based on $k_{ox}$ and $k_{add}$, it is concluded that the observed experimental "titration" curves do represent a measure of the redox property of the free radicals. From the midpoint on the curves, the kinetic potential, $E_k^{\circ 1}$, of the free radicals can be derived based on the known two-electron redox potentials of the electron acceptors. These and other questions are discussed.

We have recently reported[1,2] a new method to determine the redox potentials of free radicals in aqueous solution using the technique of pulse radiolysis and kinetic absorption spectrophotometry. This method is based on the one-electron oxidation (or one-electron reduction) of organic free radicals ·RH to a series of electron acceptor compounds A (or electron donor compounds) whose redox potentials ($E^{\circ 1}$ V at pH 7.0 and 25°) are known:

$$\cdot RH + A \rightleftharpoons R + \cdot A^- + H^+ \quad (1)$$

Depending on the pH at which the experiment is carried out, the ·RH or the ·A⁻ radicals may be present in the acid or base form, according to equilibria 2 and 3.

$$\cdot RH \rightleftharpoons \cdot R^- + H^+ \quad (2)$$

$$\cdot AH \rightleftharpoons \cdot A^- + H^+ \quad (3)$$

It was observed that a plot of the efficiency of the electron transfer reaction, expressed as percentage, versus the $E^{\circ 1}$ values of the acceptors used gave a sigmoidal titration curve. From the midpoint of these curves (i.e., at 50% electron transfer) potentials for the redox couples examined were derived.

Equilibrium 1 was assumed[1,2] and based on the Nernst equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

appropriate corrections for concentration, pH, etc., were made. It has since been found that, under the experimental conditions used, eq 1 is not reversible for the great majority of the free radicals examined. The absence of a thermodynamic equilibrium, therefore, indicates that many of the corrections made are not valid. An important exception is the one-electron oxidation of the superoxide radical $\cdot O_2^-$, where it was found[3,4] that equilibrium 4 is reversible. Indeed, the $\cdot O_2^-$ was the first radical examined using this

$$\cdot O_2^- + A \rightleftharpoons O_2 + \cdot A^- \quad (4)$$

electron transfer method to determine the potential of free radicals.

Presented below are the results obtained which indicate that reaction 1 is not in equilibrium, at the time scale at which the forward reaction is measured, for the majority of the organic free radicals investigated. The experimental observations[1,2] are reinterpreted and discussed. A term kinetic potential is introduced to define this midpoint potential, based on the known two-electron redox potentials of the electron acceptor (or donor) compounds.

## Experimental Section

Complete details of the pulse radiolysis set-up and the electron transfer method used to determine the potentials of free radicals in water have been given in detail elsewhere.[1,2]

## Results

Four different characteristic reactions depicting one-electron transfer redox reactions of free radicals in water were examined to establish whether reversible equilibrium conditions prevailed in the time scale during which measurements were carried out.

$$\cdot RH + A \rightleftharpoons R + \cdot A^- + H^+ \quad (1)$$

In all cases the formation of ·A⁻ (or ·AH) radicals, or the disappearance of A when dyes are used as electron acceptors, is followed. The percentage efficiency for the formation of ·A⁻ radicals was determined based on carrying out the "blank" (equivalent to 100% electron transfer) for each acceptor molecule. This blank, established in a separate experiment, was produced according to reaction 5. See ref 1 and 2 for further details.

$$e_{aq}^- + A \longrightarrow \cdot A^- \quad (5)$$

The following free radical redox reactions were examined.

$$CH_3\dot{C}(OH)COO^- + A \longrightarrow CH_3COCOO^- + \cdot A^- + H^+ \quad (6)$$

(a) The one-electron oxidation of the lactate radical $CH_3\dot{C}(OH)COO^-$, according to reaction 6. This radical

$$OH + CH_3CH(OH)COO^- \longrightarrow CH_3\dot{C}(OH)COO^- + H_2O \quad (7)$$

was produced via reaction 7 in solutions containing 5 m*M* lactic acid, 1 atm $N_2O$ at pH 7.0. In the presence of 50 μ*M* anthraquinone-2,6-disulfonate ($E^{\circ 1} = -0.184$ V) as the electron acceptor, the efficiency of formation of ·A⁻ was 58 ± 3%. This value is in good agreement with earlier results.[1]

If reaction 6 is reversible, i.e., an equilibrium exists, the efficiency of formation of ·A⁻ radicals should be dependent on the presence and concentration of pyruvate ions. In solutions containing up to 5 m*M* pyruvate ions, added initially, no change in the percentage formation of ·A⁻ could be observed. Furthermore, the *observed* rate of formation of ·A⁻

radicals, $k_{obsd} = 3.0 \times 10^9\ M^{-1}\ sec^{-1}$, as well as the second-order decay rate of $\cdot A^-$ ($2k/\epsilon = 9.2 \times 10^4$ cm sec$^{-1}$), were found to be independent of the $CH_3COCOO^-$ concentration.

These results would seem to suggest that since the forward reaction is very fast, $k_{obsd} = 3.0 \times 10^9\ M^{-1}\ sec^{-1}$, the reverse reaction must be relatively very slow ($k \leq 10^6\ M^{-1}\ sec^{-1}$). Hence at the time scale during which the experiments are carried out no equilibrium conditions exist for reaction 6.

(b) The one-electron oxidation of the acetone ketyl radical according to reaction 8. This radical was produced via

$$(CH_3)_2\dot{C}OH + A \longrightarrow CH_3COCH_3 + \cdot A^- + H^+ \qquad (8)$$

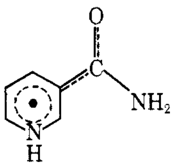
reaction 9 in solutions containing 0.1 $M$ isopropyl alcohol, 1

$$OH + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O \qquad (9)$$

atm $N_2O$, pH 7.0. In the presence of 25 $\mu M$ rhodamine B ($E^{\circ 1} = -0.54$ V) as the electron acceptor, the efficiency of the "bleaching" of A was 87 ± 3%.

The bleaching of A was found to be independent of the concentration of added acetone up to 1 m$M$. Furthermore, the bleaching kinetics of rhodamine B were also independent of the acetone concentration.

(c) The one-electron oxidation of the nicotamide radical $\cdot NH$



according to reaction 10. This radical was produced via

$$\cdot NH + A \longrightarrow N + \cdot A^- + H^+ \qquad (10)$$

reaction 11; the $\cdot N^-$ species produced initially is rapidly

$$e_{aq}^- + N \longrightarrow \cdot NH + OH^- \qquad (11)$$

protonated[5,6] in neutral solutions. Solutions contained 2 m$M$ nicotinamide, 1.5 $M$ *tert*-butyl alcohol (as an OH radical scavenger[5,6]), 1 atm argon, pH 7.0. Using 50 $\mu M$ 4,4′-bipyridyl ($E^{\circ 1} = -0.86$ V) as the electron acceptor, the percentage efficiency of formation of $\cdot A^-$ was found to be independent of nicotinamide concentration over the range 1 to 20 m$M$. The rates of formation and decay of $\cdot A^-$ were also independent of [nicotinamide].

(d) The one-electron oxidation of the $N$-ethylmaleimide radical anion $\cdot NEM^-$, according to reaction 12. This radi-

$$\cdot NEM^- + A \longrightarrow NEM + \cdot A^- \qquad (12)$$

cal was produced via reaction 13 in solutions containing 0.5

$$e_{aq}^- + NEM \longrightarrow \cdot NEM^- \qquad (13)$$

m$M$ NEM, 0.5 $M$ $t$-BuOH, 1 atm argon, pH 7.0. The p$K_a$ of the $\cdot NEM^-$–$H^+$ radical[7] is 2.85. In the presence of 50 $\mu M$ methyl viologen ($E^{\circ 1} = -0.446$ V) as the electron acceptor, the efficiency of reduction of the acceptor was also found to be independent of NEM concentration over the range 0.5–3.0 m$M$.

## Discussion

The above results indicate that the one-electron oxidations of the organic free radicals examined are irreversible processes under the experimental conditions used to monitor these reactions. Hence reaction 1 is not applicable, and reaction 14 must be considered since the reverse reaction 15

$$\cdot RH + A \xrightarrow{k_{ox}} R + \cdot A^- + H^+ \qquad (14)$$

is relatively very slow, $k_{15} \leq 10^6\ M^{-1}\ sec^{-1}$, for most of the systems examined. One must conclude, therefore, that the

$$\cdot A^- + R(+H^+) \longrightarrow \cdot R^-(\cdot RH) + A \qquad (15)$$

thermodynamic redox potentials of free radicals can generally not be deduced from the measurement of the electron transfer efficiency of acceptors of various redox potentials, under these conditions.

The "titration" curves of the percentage efficiencies of electron transfer vs. the redox potentials of the electron acceptors which have been observed[1,2] for the one-electron oxidation of free radicals must be explained. They could be formed as a result of a kinetic competition between (a) reactions 14 and 16, and/or (b) between reactions 14 and 17.

$$\cdot RH + \cdot RH \longrightarrow \text{products} \qquad (16)$$

$$\cdot RH + A \xrightarrow{k_{add}} \cdot RHA \text{ (radical addition)} \qquad (17)$$

Mechanism a does not appear to be important, under the experimental conditions employed,[1,2] since it is found that the percentage efficiency of formation of $\cdot A^-$ radicals is independent of the ratio $[A]/[\cdot RH]$, over the range 15–100, for the above mentioned four free radical systems.

Mechanism b can explain the observed results reasonably well on the basis of the competition between $k_{ox}$ and $k_{add}$, reactions 14 and 17, respectively. From this kinetic competition one can derive[8] expression A, where $k_{obsd}$ is the ex-

$$k_{ox} = k_{obsd}(\%\ \text{electron transfer}) \qquad (A)$$

perimentally observed rate and is equal to ($k_{ox} + k_{add}$). Figure 1a shows the dependence of $k_{ox}$ upon the redox potentials of the acceptors used in the one-electron oxidation of the $CH_3\dot{C}(OH)COO^-$ radical. Figure 1b shows the plot of percent electron transfer vs. $E^{\circ 1}$ obtained for the same system at the same time. The $k_{obsd}$ and the percent electron transfer values were independent of the ratio $[A]/[\cdot RH]$ over the range 15–100.

From Figure 1 and expression A the following conditions seem to prevail. (i) With acceptors where 100% electron transfer occurs, "top-plateau level", $k_{ox}$ values are close to the diffusion-controlled limit. Clearly, reaction 17 is not important, i.e., $k_{ox} = k_{obsd}$ and $k_{add} \ll k_{ox}$. (ii) With acceptors where essentially 0% electron transfer is observed, "bottom-plateau level", $k_{ox} \ll 10^7\ M^{-1}\ sec^{-1}$. Reaction 17 is the predominant mechanism for reaction of the radical, though one cannot exclude some contribution from reaction 16. (iii) In the intermediate region between 0 and 100% electron transfer, the efficiency of electron transfer is dependent on the ratio $k_{ox}/k_{add}$. While $k_{ox}$ is strongly dependent on the two-electron redox potentials of the acceptors, see Figure 1a, it is reasonable to assume that $k_{add}$ varies much less over that relatively narrow $\Delta E^{\circ 1}$ range. It follows, therefore, that the changes observed in the "titration" curves reflect primarily the changes in $k_{ox}$ with the $E^{\circ 1}$ values of the acceptors, hence the changes in the apparent efficiencies for the one-electron transfer reactions (radical oxidation, reaction 14).

It also follows from above that when $k_{add} = k_{ox} \simeq 5 \times 10^9\ M^{-1}\ sec^{-1}$, only a maximum 50% electron transfer will occur. Since one usually observes a maximum of ~100% electron transfer when only one free radical is being oxi-

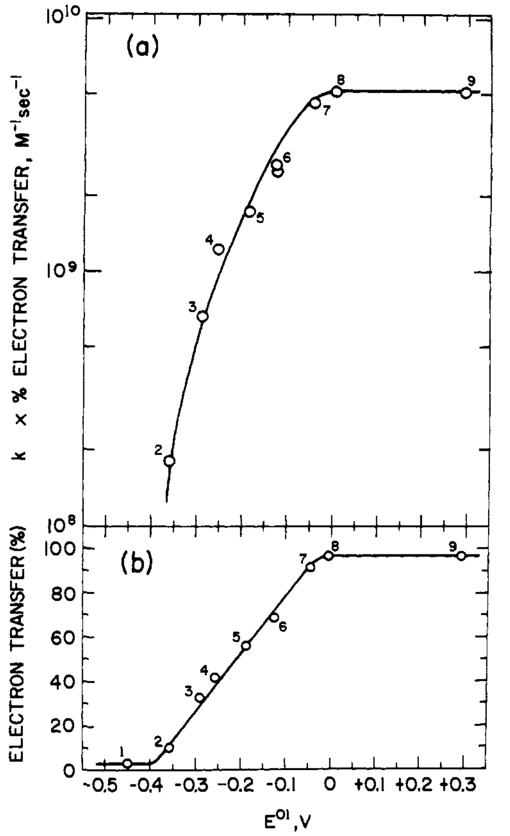


**Figure 1.** One-electron oxidation of the $CH_3\dot{C}(OH)CO_2^-$ radical by various acceptors A in aqueous solution, studied by pulse radiolysis. Solutions contained $5 \times 10^{-3}$ *M* lactic acid, pH 7.0, in the presence of $N_2O$ (1 atm) and 25-50 $\mu M$ concentration of various acceptors. The $[CH_3\dot{C}(OH)CO_2^-] \sim$ 1-2 $\mu M$. (a) Plot of the rate constant $k_{ox}$ for electron transfer to form $A\cdot^-$ radicals, obtained from $k_{obsd}$ multiplied by the percent efficiency of electron transfer vs. the redox potentials $E^{\circ 1}$ of A; (b) plot of the percent efficiency of electron transfer vs. $E^{\circ 1}$. The acceptors used were: (1) Eosin Y (−0.500 V), (2) crystal violet (−0.357 V), (3) safranine T (−0.289 V), (4) phenosafranine (−0.254 V), (5) anthraquinone-2,6-disulfonate (−0.184 V), (6) indigo disulfonate (−0.125 V), (7) indigo tetrasulfonate (−0.046 V), (8) menaquinone (+0.002 V), and (9) *p*-benzoquinone (+0.29 V). See text and ref 1 and 2 for further details.

dized, this hypothetical situation does not occur. When $k_{add} < k_{ox}$, reaction 17 becomes progressively less important. If $k_{add} > k_{ox}$, then again one would not observe 100% electron transfer. The slopes of the titration curves are observed to be different for different radicals.[1,2] This presumably indicates differences in competition between reactions 14 and 17, i.e., $k_{ox}$ and $k_{add}$ values.

From the above results and discussion we conclude that this method does not provide means of directly determining the thermodynamic redox potentials of free radicals. The potential values derived at 50% electron transfer from these titration curves[1,2] will be referred to as "kinetic potentials", $E_k^{\circ 1}$, based on the two-electron redox potentials of the electron acceptor (or electron donor) compounds. Tables I and II show the $E_k^{\circ 1}$ values of the free radicals examined previously.[1,2] These values differ from the $E^{\circ 1}$ values given[1,2] since no corrections based on the Nernst equation have now been made.

The linear free energy change of a reaction correlates ln *k* (*k* = rate constant for electron transfer) with the equilibrium constant *K* of a reversible reaction, which is related through $\Delta G^\circ = RT \ln K$ to the thermodynamic redox potential of the system. Considerable activation energy may be required to bring about the electron transfer reaction and hence the thermodynamic $E^{\circ 1}$ values may not necessarily predict the kinetics of a free radical reaction. It has been found[1,3,6] that for a large number of free radicals the $E_k^{\circ 1}$ values obtained do fit and explain the one-electron redox reactions which these radicals undergo with a variety of electron acceptors or electron donors, including $O_2$. This $E_k^{\circ 1}$ scale for free radicals, relative to the readily available two-electron redox potentials of the reactants, is considered to be more useful in understanding and predicting the kinetics of free radical reactions. One should bear in mind that for one-electron oxidation of free radicals, $E^{\circ 1}$ will usually be more negative than $E_k^{\circ 1}$. Similarly, for one-electron reduction of free radicals $\cdot E^{\circ 1} > E_k^{\circ 1}$.

**Table I.** Kinetic Potentials for the One-Electron Oxidation of Some Simple Aliphatic Free Radicals in Water

| Substrate | $pK_a$ (radical)[a] | Radical form | pH | $E_k^{\circ 1}$, V[b] |
|---|---|---|---|---|
| Lactic acid | 5.3 | $CH_3\dot{C}(OH)COOH$ | 3.2 | ~+0.16 |
| | 9.8 | $CH_3\dot{C}(OH)COO^-$ | 7.0 | −0.20 |
| | | $CH_3\dot{C}(O^-)COO^-$ | 10.8 | ~−0.34 |
| Glycolic acid | 8.8 | $\dot{C}H(OH)COO^-$ | 7.0 | −0.36 |
| | | $\dot{C}H(O^-)COO^-$ | 10.0 | ~−0.48 |
| Glycolamide | 5.5 | $\dot{C}H(OH)CONH_2$ | 3.2 | ~+0.10 |
| | | $\dot{C}H(O^-)CONH_2$ | 7.0 | −0.26 |
| Lactamide | 6.5 | $CH_3\dot{C}(OH)CONH_2$ | 3.2 | ~−0.04 |
| | | $CH_3\dot{C}(O^-)CONH_2$ | 8.5 | −0.34 |
| Isopropyl alcohol | 12.2 | $(CH_3)_2\dot{C}OH$ | 7.0 | −0.90 |
| | | $(CH_3)_2\dot{C}O^-$ | 13.0 | <−1.20 |
| Ethyl alcohol | 11.6 | $CH_3\dot{C}HOH$ | 7.0 | −0.77 |
| | | $CH_3\dot{C}HO^-$ | 13.0 | <−1.20 |
| Methyl alcohol | 10.7 | $\dot{C}H_2OH$ | 7.0 | −0.73 |
| | | $\dot{C}H_2O^-$ | 11.8 | <−1.20 |
| Ribose | | $\cdot C_5H_9O_5$ | 7.0 | −0.05 |
| | | | 7.0 | −0.65 |
| Deoxyribose | 9.8 | $\cdot C_5H_9O_4$ | 7.0 | −0.19 |
| | | | 7.0 | −0.65 |
| Oxaloacetate | 9.2 | $R\dot{C}(OH)COO^-$ | 7.0 | −0.16 |
| | | $R\dot{C}(O^-)COO^-$ | 10.8 | <−0.70 |
| Glycine | 6.6 | $NH_2\dot{C}HCOO^-$ | 8.0 | −0.81 |
| Glycine anhydride | 9.6 | $\underline{NH\dot{C}HCONHCH_2C}O$ | 7.0 | ~+0.40 |
| | | $\underline{\bar{N}\dot{C}HCONHCH_2C}O$ | 10.8 | ~−0.27 |

[a] Data taken from ref 1. [b] Values at pH 7.0 and 25° (see text and ref 1).

**Table II.** Kinetic Potentials for the One-Electron Oxidation of Free Radicals Derived from Pyrimidine Bases in Water[a]

| Substrate[b] | Radical form | pH | $E_k^{\circ 1}$, V[c] |
|---|---|---|---|
| Thymine (9.9, >13.0) | ·T−OH | 7.0 | +0.04 |
| | | 10.8 | ~−0.06 |
| Uracil (9.5, 13.0) | ·U−OH | 7.0 | +0.03 |
| | | 10.8 | ~+0.01 |
| | | 10.8 | ~−0.73 |
| 1-Methyluracil (9.8) | 1-Me−U̇−OH | 7.0 | +0.04 |
| | | 10.8 | ~+0.02 |
| | | 10.8 | ~−0.64 |
| 1,3-Dimethyluracil | 1,3-diMe−U̇−OH | 7.0 | +0.02 |
| | | 10.8 | ~+0.01 |
| Cytosine (4.6, 12.2) | ·C−OH | 7.0 | −0.20 |
| | | 3.2 | ~−0.02 |
| Dihydrothymine | ·TH | 7.0 | −0.26 |
| Dihydrouracil | ·UH | 7.0 | −0.29 |
| Uracil (7.3[d]) | $\cdot U^- - H^+$ | 5.4 | −1.24 |
| | $\cdot U^-$ | 8.5 | −1.36 |
| Thymine (7.2[d]) | $\cdot T^- - H^+$ | 5.4 | −1.24 |
| | $\cdot T^-$ | 8.5 | −1.36 |
| Cytosine | $\cdot C^-$ | 9.2 | ~−1.30 |

[a] Data taken from ref 2. [b] Values in parentheses are the $pK_a$ of the substrates. [c] Values at pH 7.0 and 25° (see text and ref 2). [d] $pK_a$ (radical) values of electron adducts.

**Acknowledgment.** It is a pleasure to acknowledge the numerous and important discussions with Dr. A. Treinin.

## References and Notes

(1) P. S. Rao and E. Hayon, *J. Am. Chem. Soc.*, **96**, 1287 (1974).
(2) P. S. Rao and E. Hayon, *J. Am. Chem. Soc.*, **96**, 1295 (1974).
(3) P. S. Rao and E. Hayon, *Biochem. Biophys. Res. Commun.*, **51**, 468 (1973); *J. Phys. Chem.*, **79**, 397, (1975).
(4) K. B. Patel and R. L. Willson, *J. Chem. Soc., Faraday Trans. 1*, **69**, 814 (1973).
(5) U. Brühlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974).
(6) P. S. Rao and E. Hayon, *J. Phys. Chem.*, submitted for publication.
(7) M. Simic and E. Hayon, *Radiat. Res.*, **50**, 464 (1972).
(8) C. L. Greenstock and I. Dunlop, *J. Am. Chem. Soc.*, **95**, 6917 (1973).

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

**V. Madhavan,[1] N. N. Lichtin,* and E. Hayon***

*Contribution from the Pioneering Research Laboratory, U.S. Army Natick Laboratories, Natick, Massachusetts 01760, and the Department of Chemistry, Boston University, Boston, Massachusetts 02215.* *Received June 29, 1974*

**Abstract:** The absorption spectra of electron adducts of a number of $\alpha,\beta$-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 ($\epsilon_{\max} \sim 10^4\ M^{-1}\ \mathrm{cm}^{-1}$) and in the visible ($\epsilon_{\max} \sim 10^3\ M^{-1}\ \mathrm{cm}^{-1}$). 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 $\mathrm{p}K_a$ values of the electron adducts vary linearly with the $\mathrm{p}K_a$ values of the corresponding carboxylic acids: for acrylamide, 7.9; methacrylamide, 8.0; *trans*-crotonamide, 8.5; $\beta,\beta$-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 $\beta$-carbon atom and is subject to general acid catalysis which obeys the Brønsted catalysis law. Uncatalyzed specific rates of $\beta$ protonation of anion radicals (in units of $10^5\ \mathrm{sec}^{-1}$) are: for acrylamide, 1.4; for methacrylamide, 13; for *trans*-crotonamide, 0.22; for $\beta,\beta$-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 $\beta$ 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

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

$$\cdot\mathrm{OH} + (\mathrm{CH_3})_3\mathrm{COH} \longrightarrow \cdot\mathrm{CH_2C(CH_3)_2OH} + \mathrm{H_2O} \qquad (2)^2$$

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

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

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

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

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

where $k_2 = 5.2 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ (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 $\alpha,\beta$-unsaturated carbonyl compounds include the adducts of acrylamide,[4,5] *N*-ethylmaleimide,[6,7] saturated amides,[8] acrylic acid derivatives,[9] and $\alpha,\beta$-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 $\beta,\beta$-dimethylacrylic acid was converted to the amide by reaction with $\mathrm{SOCl_2}$ in the cold, followed by treat-