in such stabilization through hyperconjugation. In the β-protonated radicals, $(CH_3)_2\dot{C}CONH_2$ and CH_3CH_2-$CHCONH_2$, 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

Table I. Rate Constants for Reaction of Parent Compounds with OH and e_{aq}^- at 22 ± 1°

Parent compd	pH	k_4, $\sec^{-1} M^{-1}$ (OH + HROH)[a]	k_5, $\sec^{-1} M^{-1}$ (e_{aq}^- + HROH)[b]
$HOCH_2CO_2H$	5.5	$8.6 \pm 0.7 \times 10^8$	
	7.0		$8.2 \pm 0.8 \times 10^6$ [c]
$HOCH_2CONH_2$	8.5	$1.1 \pm 0.1 \times 10^9$	
	8.5		$2.9 \pm 0.2 \times 10^8$
$HOCHCH_3CONH_2$	4.5	$1.3 \pm 0.3 \times 10^9$	
	7.0		$1.9 \pm 0.2 \times 10^8$
N_2O			8.7×10^9 [d]

[a] 25–75 m*M* parent compound; 5 m*M* CNS^-; uncertainties are standard errors of slopes of kinetic plots. [b] 0.3 and 0.15 *M* glycolic acid; 2.5 and 5 m*M* amide; uncertainties are mean deviations. [c] Unexpectedly high value may be due to trace impurity in sample. [d] From reference 17.

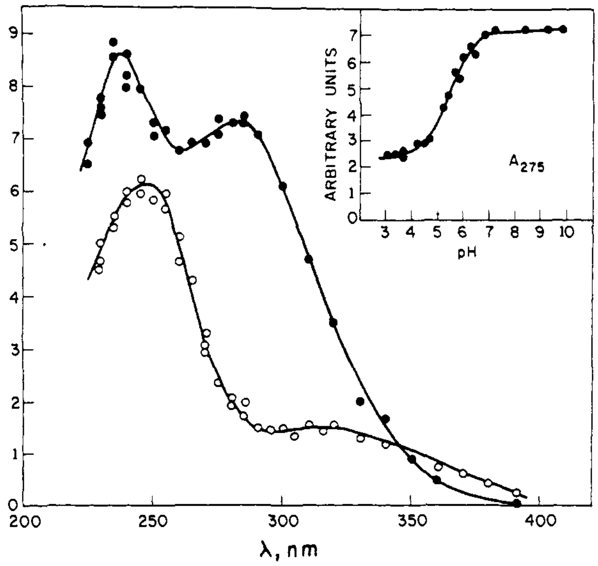


Figure 1. Absorption spectra of intermediates produced from the reaction of OH radicals with glycolamide (10^{-2} M, 1 atm N_2O) in aqueous solutions at pH 4.0 (○) and pH 8.0 (●). Insert: change in absorbance at 275 nm with pH. Total dose 2-4 krads/pulse.

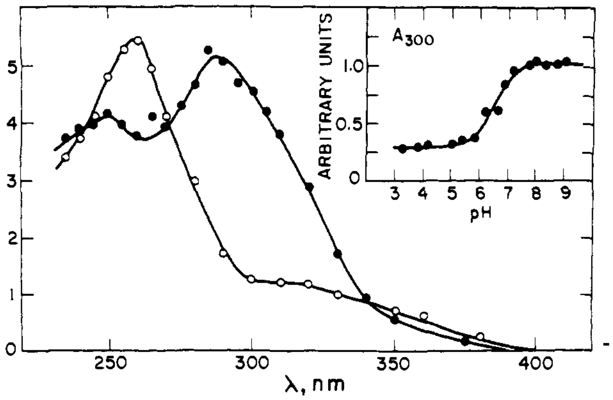


Figure 2. Absorption spectra of intermediates produced from the reaction of OH radicals with lactamide (10^{-2} M, 1 atm N_2O) in aqueous solutions at pH 4.6 (○) and pH 9.2 (●). Insert: change in absorbance at 300 nm with pH. Total dose 2-4 krads/pulse.

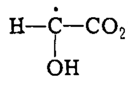
constants were on the order of 10^{10} $\sec^{-1}$ M^{-1}, similar to rate constants of ordinary oxygen and nitrogen acids with hydroxide ion.[5]

We now report a detailed kinetic study of exoergic proton transfer to a variety of inorganic bases which vary in charge and base strengths. The free radical substrates used are glycolate (I), glycolamide (II), and lactamide (III). These free radicals will be denoted by ·ROH to indicate that the OH proton is the acidic proton. They were chosen for study because: (a) the nature of the glycolate free radical is known from optical absorption[6] and ESR[7] studies (similar α-hydroxyalkyl radicals are expected[8] to be formed from glycolamide and lactamide, and our data confirm this); (b) the ·ROH radicals are readily produced by reaction of the parent compounds with OH radicals and their transient absorption spectra observed using the technique of pulse radiolysis; (c) deprotonation of ·ROH leads to marked changes in the uv spectrum, which can be monitored readily in a convenient pH range.

Table II. Transient Absorption, pK'_q, and Decay Rate Constants of α-Hydroxyalkyl Radicals in Water at 22 ± 1°

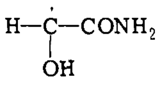
Radical	pH	λ_{max}, nm	ε,[b] $M^{-1} cm^{-1}$	pK_A	2*k*, $M^{-1} \sec^{-1}$
$HO\dot{C}HCONH_2$	4.0	247	6100	5.5	1.2×10^9
		320	1600		
$^-O\dot{C}HCONH_2$	8.0	238	8500		2.5×10^8
		285	7300		
$HO\dot{C}CH_3CONH_2$	4.6	257	5400	6.5	7.2×10^8
		315	1200		
$^-O\dot{C}CH_3CONH_2$	9.3	250	4100		9.4×10^7
		290	5100		
$HO\dot{C}HCO_2H$[a]	1	245		4.6	1.1×10^9
$HO\dot{C}HCO_2^-$[a]	7.2	245	5700	8.8	8.5×10^8
$^-O\dot{C}HCO_2^-$[a]	12	255	5400		1.5×10^7
$HO\dot{C}CH_3CO_2^-$[a]	8.9	245	5100	9.8	1.6×10^8

[a] Reference 6. [b] ± 15%.


$\mathrm{H{-}\underset{\displaystyle OH}{\underset{|}{\dot{C}}}{-}CO_2^-}$

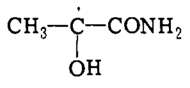
I

p*K*a 8.8 (radical)


$\mathrm{H{-}\underset{\displaystyle OH}{\underset{|}{\dot{C}}}{-}CONH_2}$

II

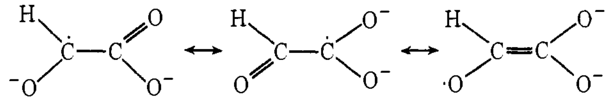
5.5


$\mathrm{CH_3{-}\underset{\displaystyle OH}{\underset{|}{\dot{C}}}{-}CONH_2}$

III

6.5

The low values of pK_a of the radicals I-III (relative to pK_a for typical alcohols)[9,10] indicate that the conjugate bases have extra resonance stabilization. For the conjugate base of I, analysis of ESR hyperfine interaction constants[11] suggests that the resonance can be described in terms of the coplanar valence-bond structures IV-VI.



IV V VI

In a parallel investigation, rate constants for the reactions of free radicals as bases have been obtained.[12,13] In particular the rate of the exoergic protonation of $\cdot R^-$ radicals by H_3O^+ appears to be diffusion controlled, with $k \sim 2\text{-}6 \times 10^{10}$ $\sec^{-1}$ M^{-1}.

Experimental Section

Instrumentation for Pulse Radiolysis. The Febetron 705 pulsed radiation source was used to generate the ·ROH radicals and monitor the deprotonation kinetics they undergo. The pulse radiolysis technique and experimental conditions have been described.[14] Doses used were in the range 0.5-10 krads/pulse. The oscilloscope waveforms of transmitted light intensity versus time were photographed, the decay curves were smoothed visually, and the smoothed intensity versus time curves were processed with a Gerber Digital Data Reduction System, Model 3B.

Materials and Solution Preparation. Glycolic acid (Aldrich), glycolamide (Sigma), and lactamide (K & K Laboratories) were commercial products of high purity whose sharp melting points agreed with literature values. Buffer materials, potassium hydroxide, perchloric acid, and *tert*-butyl alcohol were analytical reagent chemicals.

Solutions were prepared fresh before each experiment. Stock buffer solutions were adjusted to the desired pH, and aliquot portions of the buffer and parent compound were mixed and diluted to the chosen concentrations. Buffer concentrations were typically 0.5–10 m*M*. The nature of the bases selected was based on their relative inertness to reaction with OH radicals and e_{aq}^-.

A Corning Digital 112 Research pH Meter with Beckman electrodes (glass and fiber junction calomel reference) was used for pH measurements. Fisher certified buffers were used for standardizing the meter; two buffers were used to bracket the pH range being studied. Final adjustment of the pH was made with dilute KOH or $HClO_4$ solution while the sample was being degassed, and the pH was checked after the sample was placed on the radiolysis sample line. The readings agreed to ±0.02 unit.

Results

Characterization of Free Radicals. The free radicals I-III were characterized by measuring their specific rates of formation and decay, spectra, and pK_a values.

Rates of formation were measured in aqueous solutions saturated with N_2O at 1 atm. Under these conditions, hydrated electrons produced in the radiolysis of water (eq 2) are converted to OH radicals (eq 3), which in turn abstract hydrogen atoms from the molecules of the parent compound to form ·ROH (eq 4). The rate constant k_4 for (4) was

$$H_2O \longrightarrow e_{aq}^-, H^+, OH, H_2, \text{ and } H_2O_2 \qquad (2)$$

$$e_{aq}^- + N_2O \longrightarrow OH + N_2 + OH^- \qquad (3)$$

$$OH + HROH \xrightarrow{k_4} \cdot ROH + HOH \qquad (4)$$

measured by competition kinetics with CNS^- ion,[15] using k_4 ($OH + CNS^-$) = 1.1×10^{10} sec^{-1} M^{-1}.[16] These results are presented in Table I.

A possible (and undesirable) side reaction under these conditions is that of the parent compound with e_{aq}^-, which may result in the formation of an intermediate different from ·ROH (eq 5). k_5 was measured for each parent com-

$$e_{aq}^- + HROH \xrightarrow{k_5} \text{electron adduct} \qquad (5)$$

pound by monitoring the decay kinetics of e_{aq}^- at 700 nm, in the presence of 0.1-1.0 *M tert*-butyl alcohol to scavenge the OH radicals. The results are included in Table I. On comparing these values with the rate constant, 8.7×10^9 sec^{-1} M^{-1}, for the reaction of e_{aq}^- with N_2O,[17] one can calculate that if the concentration of the parent compound is less than about 0.05 *M*, reaction 5 will be negligible compared to the reaction of e_{aq}^- with N_2O.

Uv spectra for the glycolate radical (I) and its conjugate base have been reported previously.[6] Transient absorption spectra for the free radicals II and III and their conjugate bases were measured analogously and are shown in Figures 1 and 2.

Absorption maxima and molar extinction coefficients for the various protonated forms of the radicals are listed in Table II. The strong absorption peaks near 250 nm of II (pH 4.0) and III (pH 4.6) resemble that of I (pH 7.2) and of the corresponding lactate radical (pH 8.9), both with respect to λ_{max} and ϵ_{max}, while the weaker absorption peaks near 320 nm of II and III have no counterpart in the spectrum of I. All three spectra are strikingly different from those of radicals derived from corresponding aliphatic alcohols (e.g., $HO\dot{C}HCH_3$)[14] and amides (e.g., $\cdot CH_2CONH_2$ and $CH_3CONH\cdot$).[8] On the whole, for the radicals derived from glycolate, glycolamide, and lactamide, the qualitative similarities of the spectra seem more important than the differences of detail. Thus the spectra tend to support the assumption that the radicals derived from the amides are primarily the α-hydroxyalkyl radicals II and III, similar to the glycolate radical I.

Figures 1 and 2 also show spectra obtained at basic pH, which are quite different from those obtained at acid pH. It will be shown that this is due to proton removal.

pK_A for the radicals was determined by measuring the optical density of the transient species at constant dose as a function of pH. Results are shown in the inserts in Figures 1 and 2. Before each measurement, enough time was allowed to elapse for the attainment of acid-base equilibrium among the transient species. The data show the typical sigmoid relationship with pH characteristic of simple proton transfer. pK_a values deduced from the data are listed in Table II, as well as results obtained previously for the glycolate and lactate radicals.[6] For both amides, pK_a is lower by 3.3 units than pK_a for the corresponding glycolate or lactate radical, reflecting in part the effect of the negative charge of the latter.

Decay rates were measured for the radicals produced from the amides by monitoring the decrease in transient optical density with time. In the case of the glycolate radicals, decay leads[18] to coupling and disproportionation products, and we assume that similar products are formed here. The decay follows second-order kinetics. Rate constants ($2k$) for the decay of the α-hydroxyalkyl radicals and their conjugate bases are listed in Table II. Values of $2k$ are substantially smaller for the conjugate bases, partly due to the negative charge and probably also due to the greater resonance stabilization. Introduction of a CH_3 group, e.g., glycolate to lactate, consistently lowers the decay rate.

Range of Rate Measurements for Proton Transfer. A kinetic study of proton transfer for free radicals is more intricate than that for longer lived species because the free radicals must first be produced from the parent compounds, and the rate measurements must be made before there is appreciable decay.

In the present case, where we are concerned with the formation of the acidic radicals I-III, the slowest step appears to be the formation of these radicals according to (4). Hydrogen-atom abstraction from the parent compounds, according to rate constants listed in Table I, will proceed with mean times of 0.02-0.04 μsec at the concentrations used in our experiments. Thus we estimate that the formation of the acidic free radicals is practically complete (>99%) in <0.5 μsec. For this reason, and because of transient effects and signal noise immediately after the pulse, measurement of the proton transfer rate could not begin until ~0.5 μsec after the 30 nsec pulse. If we insist that not more than one mean time for proton exchange be lost in this way, then the maximum (pseudo-first-order) rate constant for proton exchange accessible to measurement is 2×10^6 sec^{-1}.

To estimate the minimum rate constant accessible to measurement, we insist that the decay of the free radicals be less than 10% during 8 half-lives for proton transfer. Fortunately, as ·ROH is converted to $\cdot RO^-$, the decay rate slows down because $2k$ is much smaller for $\cdot RO^-$ than for ROH (Table II). A convenient dose, for good accuracy in the measurement of proton transfer, would produce a free radical concentration of $\sim 6 \times 10^{-6}$ *M*. Using this concentration, and taking $2k = 1.2 \times 10^9$ sec^{-1} M^{-1}, we estimate that the minimum rate constant for proton exchange that can be measured with good accuracy is about 1×10^5 sec^{-1}. The error introduced by free-radical decay is to *increase* the apparent rate constant for proton exchange.

Another source of error, which may have been serious in a few of our experiments, is the formation of H^+ and OH^- in the radiolysis (eq 2 and 3). In typical experiments, the amounts thus produced were 3×10^{-6} *M*. These excess amounts must relax to equilibrium concentrations[19,20] in order that our kinetic interpretation of the rates of proton

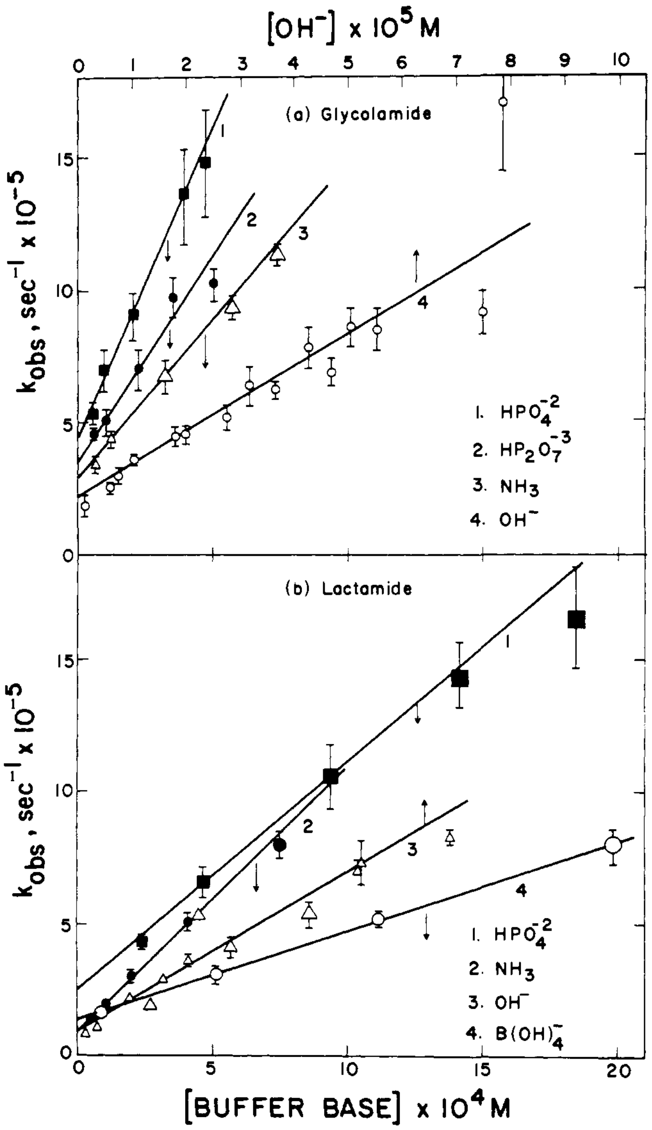


Figure 3. k_{obsd} for reaction of $\mathrm{HO\dot{C}HCONH_2}$ and $\mathrm{HO\dot{C}CH_3CONH_2}$ radicals with different bases. (**a**) Glycolamide (2.5×10^{-2} *M*), 1 atm N_2O: (1) 0.5–4 m*M* phosphate, pH 6.2; (2) 0.3–2.0 m*M* pyrophosphate, pH 6.1; (3) 1.0–13 m*M* NH_4Cl, pH 8.2; (4) 1.5–78.6 μ*M* OH^-, pH 8.3–10.0. (b) Lactamide (2.5×10^{-2} *M*), 1 atm N_2O: (1) 0.25–2.0 m*M* phosphate, pH 8.3; (2) 1.0–2.0 m*M* NH_4Cl, pH 8.0; (3) 0.8–68.2 μ*M* OH^-, pH 8.0–10.2; (4) 1.0–20 m*M* borate pH 8.3. Total dose 0.5–2.5 krads/pulse.

abstraction from ·ROH be strictly correct. Since the latter measurements began ~0.5 μsec after the pulse, it is necessary that the relaxation be sufficiently complete during that time. Calculation using known rate constants[5] indicated that this requirement was met if millimolar concentrations of buffer were present, or if the pH was >9.5. The error introduced by excess H^+ and/or OH^- is to *increase* the apparent rate constant for proton exchange.

Kinetic Data for Proton Transfer. The approach to dynamic equilibrium in the system $\cdot\mathrm{ROH} \rightleftarrows \cdot\mathrm{RO}^- + \mathrm{H}^+$, as monitored by the transmitted light intensity of the solution, is kinetically first order in free radical. Let k_{obsd} be the pseudo-first-order rate constant for approach to equilibrium. The pseudo-first-order rate constants k_f and k_r for the forward and reverse processes are then given by eq 6 and 7, where K_a is the acid dissociation constant of ·ROH.

$$k_{\mathrm{obsd}} = k_f + k_r \qquad (6)$$

$$k_f/k_r = ([\cdot\mathrm{RO}^-]/[\cdot\mathrm{ROH}])_{\mathrm{eq}} = K_a/[\mathrm{H}^+] \qquad (7)$$

Typical data obtained for k_{obsd} are shown in Figure 3. Each value of k_{obsd} is the mean of at least four experiments. In calculating k_{obsd}, a weighted linear least-squares program was used to find the slope k_{obsd} of ln $(A_{\mathrm{eq}} - A_t)$ vs. time. (*A* denotes the optical density.) The statistical weight was set equal to unity for the first measured half-life, then decreased in proportion to $(A_{\mathrm{eq}} - A_t)$, normalized to a point near the first measured half-life.

The wavelength for monitoring the change in absorbance was chosen such that the difference of molar absorptivity between the protonated and deprotonated forms of the radicals was as large as possible in the accessible region of the spectrum. For glycolate radical, this was 270 nm, for glycolamide, 290 nm, and for lactamide radical, 300 nm. Reaction conditions were chosen so that $[\cdot\mathrm{RO}^-]/[\cdot\mathrm{ROH}]$ at equilibrium is greater than 3.

In the kinetic analysis, k_f was calculated from k_{obsd} and the known reaction pH using eq 6 and 7. The resultant data were consistent with a kinetic scheme based on the following reactions (8–10). In (10), B_i denotes the buffer base,

$$\cdot\mathrm{ROH} + \mathrm{H_2O} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \cdot\mathrm{RO}^- + \mathrm{H_3O}^+ \qquad (8)$$

$$\cdot\mathrm{ROH} + \mathrm{OH}^- \overset{k_{\mathrm{OH}^-}}{\rightleftharpoons} \cdot\mathrm{RO}^- + \mathrm{HOH} \qquad (9)$$

$$\cdot\mathrm{ROH} + \mathrm{B_i}^z \overset{k_{\mathrm{B_i}}}{\rightleftharpoons} \cdot\mathrm{RO}^- + \mathrm{HB_i}^{z+1} \qquad (10)$$

the nature of which was varied in different series of experiments. Recalling that the pseudo-first-order rate constant k_f = (rate of deprotonation)/[·ROH], the corresponding rate law is (11). Values obtained for k_{OH^-} and $k_{\mathrm{B_i}}$ are listed

$$k_f = k_a + k_{\mathrm{OH}^-}[\mathrm{OH}^-] + k_{\mathrm{B_i}}[\mathrm{B_i}] \qquad (11)$$

in Table III. The validity of these rate constants was demonstrated as follows: (a) for each radical, the rate constant k_{OH^-} obtained in the absence of buffer agreed with that obtained in the presence of buffer; (b) the rate constant $k_{\mathrm{B_i}}$ for reaction with buffer base for a given buffer was independent of pH.

On the other hand, the intercept in the rate law, which according to (11) should be identified with k_a, was consistently $0.5\text{–}2 \times 10^5$ for all three radicals. On applying the known values of K_a and assuming a diffusion-controlled mechanism for $\mathrm{H_3O^+} + \cdot\mathrm{RO}^-$, with $k_{-a} = 6 \times 10^{10}$ sec^{-1} (this is the largest of the values obtained),[12,13] we predict that $k_a = 1 \times 10^2$, 2×10^5, and 2×10^4 sec^{-1} respectively for radicals I, II, and III. Thus the experimental intercepts are of a plausible magnitude for k_a only in the case of radical II. Because the evaluation of the intercept is based mostly on data near the lower limit of the range of accurate measurement (see preceding section) we feel that the intercepts are inherently inaccurate and shall not discuss them further. On the other hand, the rate constants obtained for k_{OH^-} and $k_{\mathrm{B_i}}$ are based solidly on data in the most accurate portion of the range of measurement and should be not much less accurate than their precision, which is about ±10%.

Ionic strength corrections were made in the calculation of concentrations of hydroxide and of ionic buffer species from the pH and total buffer concentrations, and in the calculation of rate constants for the glycolate free radical.

In all cases, except the pyrophosphate buffers, ionic activity coefficients were approximated by the familiar Davies formula (eq 12), in which *z* denotes charge number, *y* the

$$\log y_z = -Sz^2 I^{1/2}/(1 + I^{1/2}) \qquad (12)$$

Table III. Deprotonation Rate Constants of Free Radicals in Water at 22 ± 1°

Acid	Base	pH	$k_{\mathrm{OH^-}}$ or k_{B},[a] $\mathrm{sec^{-1}}\,M^{-1}$	$\Delta \mathrm{p}K_{\mathrm{a}}$[b]	σ_{app}, A[c]
$\mathrm{HO\dot{C}HCO_2^-}$	$\mathrm{OH^-}$	9.5–10.5	3.9×10^9[d]	6.9	3.12
	$\mathrm{NH_3}$	9.26; 9.75	7.5×10^8	0.6	0.29
	$\mathrm{P_2O_7^{4-}}$	9.26; 9.75	5.8×10^6	0.8	3.25
	$\mathrm{B(OH)_4^-}$	9.16; 9.75	1.4×10^7	0.5	1.06
$\mathrm{HO\dot{C}HCONH_2}$	$\mathrm{OH^-}$	8.3–9.9	1.1×10^{10}	10.2	2.88
	$\mathrm{NH_3}$	8.05; 8.25	1.2×10^9	3.9	0.45
	$\mathrm{B(OH)_4^-}$	8.25	9.1×10^8	3.8	0.57
	$\mathrm{HP_2O_7^{3-}}$	6.10; 6.40	1.1×10^9	1.3	0.84
	$\mathrm{HPO_4^{2-}}$	6.20	1.8×10^9	1.7	1.31
$\mathrm{HO\dot{C}CH_3CONH_2}$	$\mathrm{OH^-}$	8.0–10.2	1.1×10^{10}	9.2	2.30
	$\mathrm{NH_3}$	8.05	9.7×10^8	2.9	0.38
	$\mathrm{B(OH)_4^-}$	8.30	3.1×10^8	2.8	0.21
	$\mathrm{HP_2O_7^{3-}}$	8.1; 9.3	3.7×10^8	0.3	0.29
	$\mathrm{P_2O_7^{4-}}$	8.1; 9.3	8.5×10^8	3.1	0.69
	$\mathrm{HPO_4^{2-}}$	8.30	8.5×10^8	0.7	0.65

[a] Standard error ±10%; corrected to $I = 0$ using eq 13. [b] $\Delta \mathrm{p}K_{\mathrm{a}} = \mathrm{p}K_{\mathrm{a}}(\text{acceptor}) - \mathrm{p}K_{\mathrm{a}}(\text{donor})$; $\mathrm{p}K_{\mathrm{a}}(\mathrm{HOH}) = 15.7$. [c] Equations 14 or 15; diffusion coefficients, $10^5 D$ $\mathrm{cm^2\,sec^{-1}}$: $\mathrm{OH^-}$, 5.32; $\mathrm{NH_3}$, 2.39; $\mathrm{B(OH)_4^-}$, 1.0; $\mathrm{HP_2O_7^{3-}}$, 0.68; $\mathrm{P_2O_7^{4-}}$, 0.64; $\mathrm{HPO_4^{2-}}$, 0.72; $\mathrm{HO\dot{C}HCO_2^-}$, 1.07; $\mathrm{HO\dot{C}HCONH_2}$, 1.1; $\mathrm{HOCC_3CONH_2}$, 1.0. [d] This is the mean $k_{\mathrm{OH^-}}$ obtained by analysis of data in the presence of buffers. In the absence of buffers, $k_{\mathrm{OH^-}} = (3.1 \pm 0.4) \times 10^9\ \mathrm{sec^{-1}}\,M^{-1}$.

molar activity coefficient, I the ionic strength, and S the Debye-Hückel limiting slope, which is 0.501 for water at 22 ± 1°. For pyrophosphate buffers, activity coefficients were estimated according to Edwards et al.[21]

The $\mathrm{p}K_{\mathrm{a}}$ values of buffers were taken from Perrin,[22] except for pyrophosphate for which Edwards et al.'s value at 25° was used.[21] For our solutions, the complexation of $\mathrm{P_4O_7^{2-}}$ with alkali ions[23] and the self-association of boric acid species[24,25] was calculated to be at most a few percent and was considered in calculating buffer concentrations, but not in the kinetic analysis. Ionic strength effects on the rate constants were assumed to be given by the Brønsted-Bjerrum relationship (13), in which z_{A} and z_{B} denote the

$$\log k = \log k_0 + 2Sz_{\mathrm{A}}z_{\mathrm{B}}I^{1/2}/(1 + I^{1/2}) \tag{13}$$

charge numbers of acid and base, respectively. z_{A} differs from zero only for the glycolate radical I, so that ionic strength corrections were included in the kinetic analysis only for that species. Before the ionic strength corrections were made, some of the kinetic plots were slightly curved; making the corrections straightened out the relationships.

In the case of the glycolate radical I, the concentration of the parent compound was varied over a wide range, from 0.025 to 0.25 M. There was no evidence of catalysis of deprotonation by the glycolate ion.

Discussion

Proton transfer reactions may be simple bimolecular processes in which a proton is transferred directly from the acid to the base. However, for oxygen and nitrogen acids and bases in aqueous solution, there is direct evidence from nuclear magnetic resonance that proton transfer reactions are often termolecular or even quatermolecular, involving participation by one or two water molecules.[26] Although, when $\Delta G° < 0$, the second-order rate constants are generally high, the values are not at all uniform but vary over several orders of magnitude, approaching that for diffusion-controlled reaction as an upper limit. We may suppose that the magnitude of the rate constant, and the extent of participation by water molecules, reflect the strength and nature of the hydration of the acid and base at the reactive site. In undertaking the present study, we hoped to find out if the rate constants for a representative sample of acid-base reactions of free radicals are qualitatively different from those for ordinary oxygen and nitrogen acids and bases.

Our results are summarized in Table III. In each case, the positive values of $\Delta \mathrm{p}K_{\mathrm{a}}$ indicate that $\Delta G°$ for the given proton transfer is negative.

For reactions of the same charge type, there is a striking similarity between the present rate constants for proton abstraction from free radicals and available values for proton abstraction with $\Delta G° < 0$ from ordinary oxygen acids. For instance, for $\mathrm{HCO_3^-} + \mathrm{OH^-}$, $k \approx 2 \times 10^9\ \mathrm{sec^{-1}}\,M^{-1}$ ($I = 0$);[5] for phenol + $\mathrm{OH^-}$, $k = 1.4 \times 10^{10}$ (ref 5); for $\mathrm{HCO_2H} + \mathrm{NH_3}$, $k = 8.0 \times 10^8$ (ref 27); for $\mathrm{CH_3CO_2H} + \mathrm{NH_3}$, $k = 6.5 \times 10^8$ (ref 27). The points of similarity include (a) the magnitudes of the rate constants, (b) the apparently low sensitivity of the rate constants to differences in electron delocalization (and resonance energy) between the acid and its conjugate base, and (c) the retarding effect on the rate constant of a $\mathrm{CH_3}$ group near the acidic site (e.g., in reacting with $\mathrm{NH_3}$, III < II and $\mathrm{CH_3CO_2H} < \mathrm{HCO_2H}$). If one may generalize from this limited sample, one must conclude that the rate constants for the acid-base reactions of free radicals are very similar to those for stable molecules and can be predicted or interpreted according to the same rules. A very similar generalization was stated some years ago by Weller[28] for the acid-base reactions, with $\Delta G° < 0$, of electronically excited singlet states of oxygen and nitrogen acids and bases, and the generalization may also apply to electronically excited triplet states. Thus, for the reaction of triplet phenol + $\mathrm{OH^-}$, $k = 1.6 \times 10^{10}$,[29] fitting into the same pattern.

The rate constants in Table III are of such a magnitude as to suggest diffusion-controlled reaction, and a brief analysis in terms of the Smoluchowsky-Debye-Eigen theory[30] will be instructive. If all long-range A-B interactions other than charge-charge interactions may be neglected, the rate constant, k_{e}, for bimolecular encounter formation is given by (14) if A and/or B is uncharged, and by (15) if both A and B are ions. Here σ denotes the "encounter diameter",

$$k_{\mathrm{e}} = 4\pi N_0 \sigma (D_{\mathrm{A}} + D_{\mathrm{B}})/1000 \tag{14}$$

$$k_{\mathrm{e}} = \frac{4\pi N_0 Z_{\mathrm{A}} Z_{\mathrm{B}} e^2 (D_{\mathrm{A}} + D_{\mathrm{B}})}{1000 \epsilon k T [\exp(Z_{\mathrm{A}} Z_{\mathrm{B}} e^2/\epsilon \sigma k T) - 1]} \tag{15}$$

D_{A} and D_{B} are the diffusion coefficients, ϵ is the dielectric constant, and the other symbols have their usual significance.

In the following we shall assume that the observed rate constant $k = k_e$, i.e., that proton transfer is diffusion controlled, and that the steric factor for reaction is unity, and by means of (14) or (15) calculate σ for each reaction. Although these σ values may not represent real encounter diameters, they do represent an index of reactivity that has been corrected for differences in mobility and charge type of the reactants.

The results of the calculation are listed in Table III. The σ values divide themselves roughly into two groups. For all reactions with OH^-, and (surprisingly) for the reaction of I with $P_2O_7^{4-}$, σ is in the range 2.8 ± 0.5 Å, which is of an acceptable magnitude for a real encounter diameter. (Compare with the nearest neighbor O-O distance of 2.76 Å in ice.) The other values are too small, by significant amounts, to represent genuine closest approach distances. Here, if we wish to retain the model of diffusion-controlled reaction with steric factors of unity, we must infer that (14) and (15) overestimate the true value of k_e. A likely reason for this is that in the stepwise diffusion process preceding the formation of the reactive encounter complex, the final step or steps have higher activation free energies than that for diffusion of the far-separated A and B molecules in the bulk solvent. In other words, the formation of the encounter complex is opposed by forces of solvation, since it involves the mutual penetration and distortion of the original solvation shells of the A and B molecules.

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An X-Ray Structure Determination of the 1:1 Charge Transfer Complex of Naphthalene and Tetrachlorophthalic Anhydride at −153°

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Abstract: The crystal structure of the 1:1 charge transfer complex of perdeuterated naphthalene and tetrachlorophthalic anhydride has been determined at −153°. Crystals of the complex grow in the form of light-yellow triclinic needles ($P\bar{1}$; $Z = 2$), with unit cell dimensions $a = 10.042$ (5), $b = 6.701$ (2), $c = 13.872$ (9) Å, $\alpha = 86.34$ (4), $\beta = 90.82$ (5), and $\gamma = 59.63$ (3)°. The structure was solved with Patterson and Fourier techniques and refined by least squares to a conventional R value of 0.048 for 2044 observed reflections collected on a Syntex $P\bar{1}$ autodiffractometer with Mo Kα radiation. Component molecules are stacked alternately in infinite chains along the b axis. Accurate, low temperature, structural parameters obtained for naphthalene and tetrachlorophthalic anhydride in the complex are within experimental error identical to those observed in the pure materials.

Accuracy of X-ray structural determinations for charge transfer complexes of the π-π type has often been limited by the large thermal motion and disorder exhibited by one of the molecular components. Complexes of naphthalene seem to be particularly susceptible to this problem.[1] In both the naphthalene-tetracyanobenzene[2] and naphthalene-tetracyanoethylene[3] complexes the naphthalene molecules are disordered at room temperature. Although detailed structural data are not available, the naphthalene-trinitrobenzene and naphthalene-pyromellitic dianhydride complexes also appear to be disordered.[1]

Because of the theoretical interest in the detailed molecular parameters of naphthalene, a very careful determination of the crystal structure of pure naphthalene has been carried out[4] in which corrections for the thermal motion were applied. An electron diffraction study of gaseous naphthalene has also been reported.[5] Although very few data of comparable accuracy appear to be available for molecular π complexes of naphthalene, structures of two inorganic naphthalene complexes have been determined. In the unusual naphthalene-$AgClO_4$ complex[6] the naphthalene molecule is ordered, but the accuracy of C-C bond lengths ob-