

are not correlated. The actual structure is probably some combination of these possibilities. We know, for example, that a structure involving exclusively i or ii is ruled out for the 1:1 mixture, since about 12% of the C<sub>21</sub> chains are end-gauche. We have no direct evidence for the interlayer correlations that characterize structure i. However, the presence of such correlations is consistent with the observed deviation of the plot of  $\delta H_g$  vs. concentration from what is predicted for random mixing alone.

(4) *The Integrity of Phase II and an Additivity Model for Conformational Disorder.* Phase II exists for all C<sub>19</sub>/C<sub>21</sub> mixtures. Our earlier studies on the neat *n*-alkanes have shown that phase II is much more conformationally disordered than is phase I. The situation for the mixtures is very similar: phase II is more conformationally disordered than phase I at all compositions.

These facts suggest that to a first approximation the structural disorder in the phase II mixture may be separated into two parts. One part is associated with the effect of mixing and depends on composition; the second part is associated with disorder that is inherent to phase II and therefore should be relatively independent of composition.

Evidence supporting a model in which the conformational disorder is additive is found in the behavior of the difference in the gauche bond concentrations between phase I and II with

respect to composition. (This difference is designated  $\Delta f_g^{19}$  ( $= f_g^{19}(\text{II}) - f_g^{19}(\text{I})$ ), for C<sub>19</sub> and  $\Delta f_g^{21}$  for C<sub>21</sub>.) We find (Figure 9)  $\Delta f_g^{19}$  to be nearly constant for all compositions. Similarly,  $\Delta f_g^{21}$  is found to be constant over most of the composition range. This constancy of  $\Delta f_g$  provides strong evidence that the increase in conformational disorder that occurs in going to phase II from phase I is associated with the inherent structure of phase II.

However, in certain situations, mixing effects can dominate. Such a case arises for C<sub>21</sub> at low concentrations. In the limit of infinite C<sub>21</sub> dilution,  $f_g^{21}$  approaches its maximum possible value, 0.5, indicating that all the C<sub>21</sub> chains are gauche at one end (Figure 9). As discussed earlier, this occurs because C<sub>21</sub>/C<sub>21</sub> and C<sub>21</sub>/C<sub>19</sub> pairs interact differently at the chain ends. This is a "mixing" effect since in this case the end-gauche concentration is highly dependent on composition (Figure 10).

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**Registry No.** *n*-C<sub>19</sub>H<sub>40</sub>, 629-92-5; *n*-C<sub>21</sub>H<sub>44</sub>, 629-94-7.

## Kinetics and Mechanism of the Oxidation of 2-Mercaptoethanol by Hydrogen Peroxide in Aqueous Solution

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The kinetics of oxidation of 2-mercaptoethanol by H<sub>2</sub>O<sub>2</sub> to 2-hydroxyethyl disulfide in aqueous solution has been studied. Over the pH range 9 to 13, the rate law for the oxidation of 2-mercaptoethanol was found to be

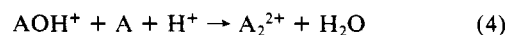
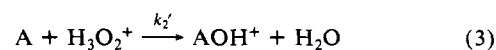
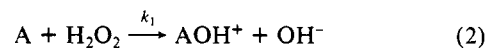
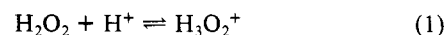
$$\nu = \frac{-d[\text{RS}^-]}{dt} = \frac{[\text{H}_2\text{O}_2]_T[\text{RS}^-]}{\left(1 + \frac{K'}{a_{\text{H}^+}}\right)\left(1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}}\right)}(k_1 + K'k_2/a_{\text{H}^+})$$

where R is HOC<sub>2</sub>H<sub>4</sub>,  $K'$  is the apparent acid dissociation constant of H<sub>2</sub>O<sub>2</sub>,  $K'_{a1}$  and  $K'_{a2}$  are the apparent acid dissociation constants of HOC<sub>2</sub>H<sub>4</sub>SH and HOC<sub>2</sub>H<sub>4</sub>S<sup>-</sup>, respectively, and  $a_{\text{H}^+}$  is the hydrogen ion activity. A nonlinear least-squares fit of experimental data to the above rate law gave values of  $k_1 = 12.64 \pm 0.54 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_2 = 0.93 \pm 0.39 \text{ M}^{-1} \text{ s}^{-1}$  at 20 °C. The rate law and other data indicate that the reaction proceeds via a nucleophilic displacement by thioethanol on hydrogen peroxide with the formation of HOCH<sub>2</sub>CH<sub>2</sub>SOH as an intermediate.

### Introduction

The kinetics of oxidation of a variety of reductants such as hydrogen sulfide,<sup>1</sup> aqueous sulfur dioxide,<sup>2</sup> thiourea,<sup>3</sup> substituted thioureas,<sup>3</sup> thioxane,<sup>4</sup> thiocyanate,<sup>5,6</sup> and halides<sup>7</sup> by hydrogen peroxide in aqueous solution have been studied. In general, two-term rate laws of overall second and third order have been

observed. A common mechanism for the acid-catalyzed nucleophilic attack of reductant A on H<sub>2</sub>O<sub>2</sub> is as follows:

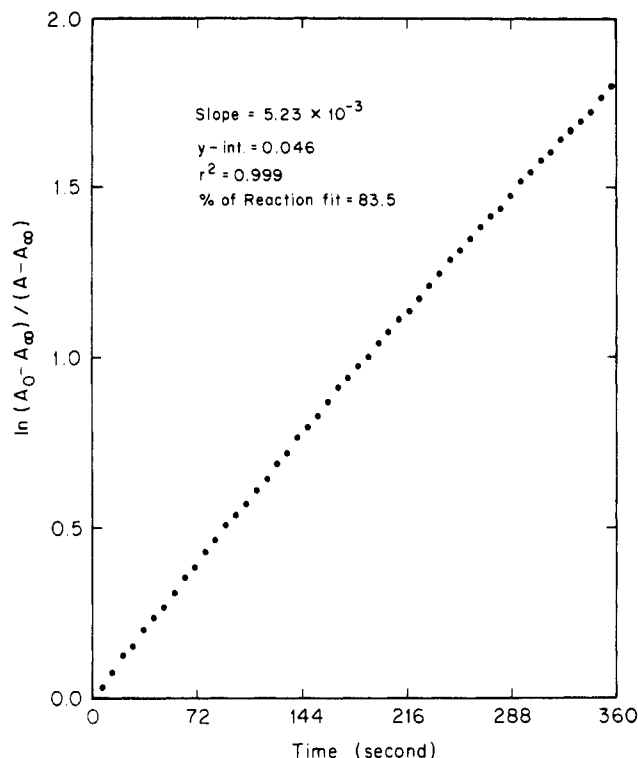


where A denotes the nucleophile. This mechanism gives a rate expression of the following form:

$$\nu = k_1[\text{H}_2\text{O}_2][\text{A}] + k'_2K[\text{H}_2\text{O}_2][\text{H}^+][\text{A}] \quad (5)$$

In the above mechanism, the oxygen-oxygen bond of hydrogen peroxide is cleaved heterolytically with the release of either hy-

- (1) Hoffmann, M. R. *Environ. Sci. Technol.* **1977**, *11*, 61.
- (2) McArdle, J. V.; Hoffmann, M. R. *J. Phys. Chem.* **1983**, *87*, 5425.
- (3) Hoffmann, M. R.; Edwards, J. O. *Inorg. Chem.* **1977**, *16*, 3333.
- (4) Dankleff, M.; Curci, R.; Edwards, J. O.; Pyun, H. Y. *J. Am. Chem. Soc.* **1968**, *90*, 3209.
- (5) Wilson, I. R.; Harris, G. M. *J. Am. Chem. Soc.* **1960**, *82*, 4515.
- (6) Wilson, I. R.; Harris, G. M.; *J. Am. Chem. Soc.* **1961**, *83*, 286.
- (7) (a) Liebhafsky, H. A.; Mohammed, A. *J. Am. Chem. Soc.* **1933**, *55*, 3977. (b) Liebhafsky, H. A. *Ibid.* **1934**, *56*, 1680.



$A_0$  = Initial Absorbance = 1.208  
 $A$  = Absorbance at time  $t$   
 $A_\infty$  = Absorbance at infinity = 0.03

## EXPERIMENTAL CONDITIONS:

pH = 10.43  
 $\mu$  = 0.10 M  
 Temp. = 20.5 °C  
 $[EDTA] = 1 \times 10^{-5}$  M  
 $[H_2O_2]_0 = 4.52 \times 10^{-4}$  M  
 $[RS]_0 = 2.9 \times 10^{-5}$  M

**Figure 1.** First-order kinetic plot of the oxidation of 2-mercaptoethanol by  $H_2O_2$ .

dioxide ion or water as the leaving group. The "hydroxy intermediate" subsequently reacts with either a second molecule of A to form a dimer as the final product or with an additional  $H_2O_2$  via a different pathway.<sup>1</sup>

According to Edwards<sup>8</sup> the nucleophilic reactivity of  $RS^-$  toward  $H_2O_2$  should exceed that of  $CN^-$ ,  $S_2O_3^{2-}$ , and  $(NH_2)_2CS$ , respectively. With this in mind, we decided to examine in detail the kinetics of the reaction of 2-mercaptoethanol ( $RS^-$ ) in a pH domain where  $pH > pK_{a1}$ . Furthermore, we have observed hydrogen peroxide as an intermediate during the oxidation of 2-mercaptoethanol and sulfur dioxide<sup>9</sup> by  $O_2$  catalyzed by 4,4',4'',4'''-tetrasulfocobalt(II)phthalocyanine. Mercaptans such as 2-mercaptoethanol are odorous constituents of sour refinery wastes. Catalytic autooxidation or oxidation by  $H_2O_2$  of mercaptans may be used for odor and wastewater quality control.

### Experimental Procedure

Stock solutions were prepared from redistilled 99% reagent grade 2-mercaptoethanol (Aldrich) and 3.23% hydrogen peroxide (Mallinckrodt). Buffer solutions were prepared with reagent grade sodium hydroxide (Mallinckrodt), sodium chloride (J. T. Baker), sodium bicarbonate (Mallinckrodt), and 18 M $\Omega$ -cm resistivity water (Millipore). Ionic strength was held constant at  $\mu = 0.1$  M with NaCl.

**TABLE I: Kinetic Data for Oxidation of 2-Mercaptoethanol by Hydrogen Peroxide in Carbonate Buffer at 20 °C<sup>a</sup>**

pH	$k_{obsd}$	$k_{calcd}$	% diff
12.61	$0.31 \pm 0.02$	0.28	8.34
12.32	$0.55 \pm 0.04$	0.65	-18.28
12.09	$1.36 \pm 0.12$	1.24	8.60
11.10	$8.20 \pm 0.13$	7.71	5.89
10.76	$9.20 \pm 0.18$	9.62	-4.67
10.58	$9.95 \pm 0.10$	10.20	-2.51
10.43	$10.96 \pm 0.46$	10.45	4.67
10.26	$10.38 \pm 0.29$	10.47	-0.89
10.14	$9.97 \pm 0.06$	10.31	-3.44
9.98	$10.17 \pm 0.05$	9.92	2.45
4.8	$b$	$3.73 \times 10^{-4}$	

<sup>a</sup>  $1.53 \times 10^{-4} M \leq [H_2O_2] \leq 3.057 \times 10^{-4} M$  and  $[HOC_2H_4S^-]$  is at least tenfold less than  $[H_2O_2]$ . <sup>b</sup> Very small.

**TABLE II: Stoichiometry Determination of the Oxidation of 2-Mercaptoethanol by Hydrogen Peroxide**

$H_2O_2$ used, mmol	initial $RS^-$ , mmol	$RS^-$ unreacted, mmol	$RS^-$ reacted, mmol	$\Delta[RS^-]/\Delta[H_2O_2]$
0.24	0.73	0.20	0.53	2.24
0.24	0.73	0.22	0.51	2.13
0.24	0.73	0.20	0.53	2.19

Pseudo-first-order kinetic data were obtained with a Hewlett Packard Model 8450 spectrophotometer linked to a DEC MINC 23 minicomputer. A minimum of four data sets was obtained for each value of  $k_{obsd}$ . Constant temperature was maintained at 20 °C with a Haake HK2 circulating water bath, while pH was determined with a Beckman Altex  $\Phi$  71 pH meter and Radiometer glass electrodes. EDTA was used (10  $\mu$ M) to minimize the influence of trace-metal catalysis (i.e., Fenton's reagent). For  $pH \geq 9.4$  the reaction was monitored at  $\lambda = 233$  nm (the absorbance maximum for  $HOC_2H_4S^-(aq)$ , the  $pK_{a1} = 9.4^{10}$ ), whereas when  $pH \leq 9.4$ , the reaction was monitored at  $\lambda = 220$  nm.

Stoichiometry was established by determination of the residual 2-mercaptoethanol after 99% of hydrogen peroxide had reacted in alkaline solution. 2-Mercaptoethanol was analyzed by titration with  $I_2^{11,12}$  hydrogen peroxide was standardized according to the method given by Wilson and Wilson.<sup>11</sup>

Reaction products were extracted into chloroform, concentrated by evaporation under nitrogen, and analyzed by HPLC (HP1080B) using deionized doubly distilled water with 15% of methanol as the solvent carrier.

### Results

Pseudo-first-order plots, ( $[H_2O_2] \gg [HOC_2H_4SH]$ ), Figure 1) of  $\ln(A_t - A_\infty)/(A_0 - A_\infty)$  vs.  $t$  were linear ( $r^2 \geq 0.999$ ) for up to 85% of the reaction which indicates that the reaction is, in fact, first order with respect to 2-mercaptoethanol. The dependence of  $k_{obsd}$  on  $[H_2O_2]$  was determined at pH 10.4. A plot of  $k_{obsd}$  vs.  $[H_2O_2]$  ( $d \log k_{obsd}/d \log [H_2O_2] = 1.0$ ) up to (1.2 mM) yields a straight line ( $r^2 \geq 0.99$ ) with a slope of  $10.96 \pm 0.45 M^{-1} s^{-1}$  and an intercept of zero, as shown in Figure 2. Thus, the rate of disappearance of 2-mercaptoethanol is first order in both  $H_2O_2$  and  $HOC_2H_4SH$ .  $k_{obsd}$  exhibits a pH dependency as shown in Figure 3 and Table I. For the pH range of 10.4 to 12,  $1/k_{obsd}$  vs.  $1/a_{H^+}$  was linear with  $r^2 = 0.99$ ,  $d(1/k_{obsd})/d(1/a_{H^+}) = 5.31 \times 10^{-13}$  and  $1/k_{obsd} = 0.078$ . At pH 4.8 and  $pH \geq 13$ , the oxidation rate was negligible. In the absence of buffer, the pH rose continuously during the course of reaction (Figure 4), whereas a variation of ionic strength over the range of  $0.05 M < \mu < 0.4$  M had no effect on the rate of reaction.

(10) "Stability Constants of Metal-Ion Complexes"; The Chemical Society: London, 1971; Supplement No. 1, Spec. Publ. No. 25.

(11) Wilson, C. L., Wilson, D. W., Eds. "Comprehensive Analytical Chemistry"; Elsevier: New York, 1960; Vol. 1B, p 278.

(12) Fritz, J. S.; Schenk, G. H. "Qualitative Analytical Chemistry"; Allyn and Bacon: Boston, 1974; 3rd ed, p 264.

(8) Edwards, J. O. "Peroxide Reaction Mechanisms", Edwards, J. O., Ed.; Interscience: New York, 1962; pp 78 and 79.

(9) Boyce, S. D.; Hoffmann, M. R.; Hong, P. A.; Moberly, M. *Environ. Sci. Technol.* **1983**, *17*, 602.

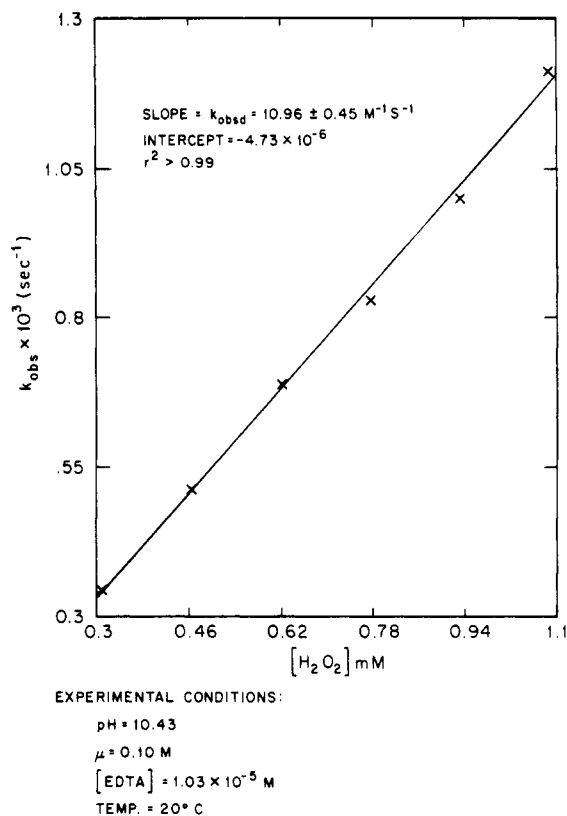


Figure 2. Hydrogen peroxide dependence analysis of the oxidation of 2-mercaptoethanol by H<sub>2</sub>O<sub>2</sub>.

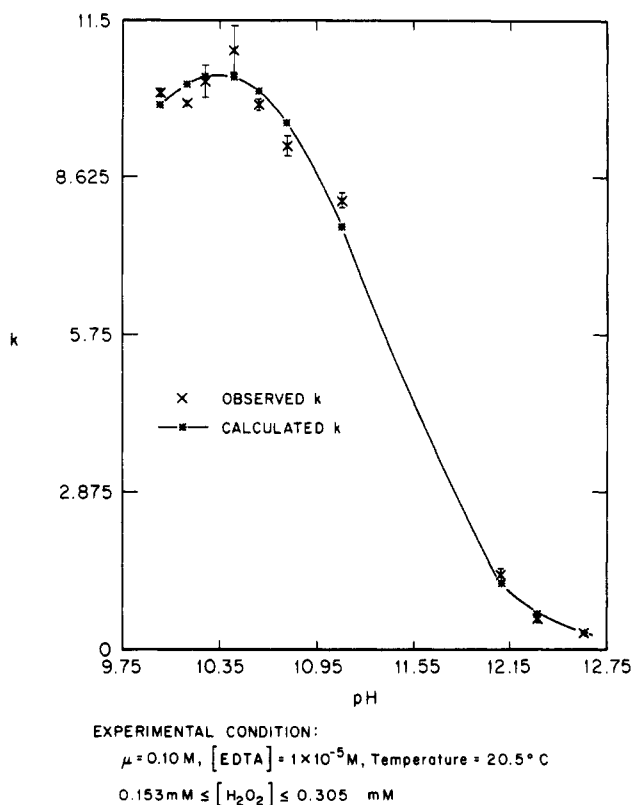


Figure 3. pH dependence analysis of the oxidation of 2-mercaptoethanol by H<sub>2</sub>O<sub>2</sub>.

The stoichiometry (Table II) was established to be 1 mol of H<sub>2</sub>O<sub>2</sub> to 2 mol of HOC<sub>2</sub>H<sub>4</sub>SH (eq 6). The sole oxidation product was determined to be 2-hydroxyethyl disulfide by HPLC analysis.

Thus, the overall reaction is

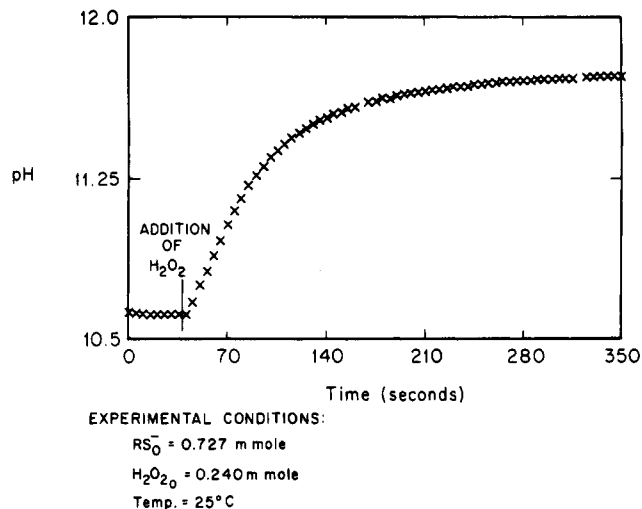
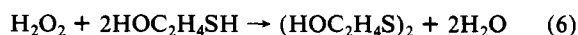
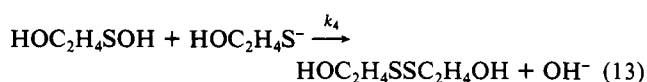
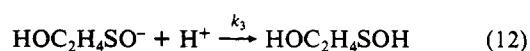
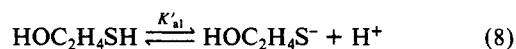
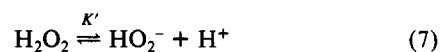


Figure 4. Evidence for the formation of OH<sup>-</sup> on the oxidation of 2-mercaptoethanol by H<sub>2</sub>O<sub>2</sub>.

The above kinetic information is consistent with the following mechanism:



This mechanism is similar to the general mechanism for nucleophilic displacements on H<sub>2</sub>O<sub>2</sub> as discussed by Hoffmann and Edwards.<sup>3</sup> According to this mechanism, the rate of disappearance of the 2-mercaptoethanol is given by

$$\nu = -d[\text{RSH}]_T/dt = k_1[\text{H}_2\text{O}_2][\text{HOC}_2\text{H}_4\text{S}^-] + k_2[\text{HO}_2^-][\text{HOC}_2\text{H}_4\text{S}^-] + k_4[\text{HOC}_2\text{H}_4\text{SOH}][\text{HOC}_2\text{H}_4\text{S}^-] \quad (14)$$

where

$$[\text{RSH}]_T = [\text{HOC}_2\text{H}_4\text{SH}] + [\text{HOC}_2\text{H}_4\text{S}^-] + [\text{OC}_2\text{H}_4\text{S}^-]$$

If we assume that  $k_4[\text{HOC}_2\text{H}_4\text{SOH}] \ll k_1[\text{H}_2\text{O}_2]$  and  $k_2[\text{HO}_2^-]$ , the rate expression reduces to

$$\nu = [\text{HOC}_2\text{H}_4\text{S}^-]\{k_1[\text{H}_2\text{O}_2] + k_2[\text{HO}_2^-]\} \quad (15)$$

Expressing the concentration of H<sub>2</sub>O<sub>2</sub> and 2-mercaptoethanol in terms of their total concentrations,  $[\text{H}_2\text{O}_2]_T = [\text{H}_2\text{O}_2] + [\text{HO}_2^-]$  and  $[\text{HOC}_2\text{H}_4\text{SH}]_T = [\text{HOC}_2\text{H}_4\text{SH}] + [\text{HOC}_2\text{H}_4\text{S}^-] + [\text{OC}_2\text{H}_4\text{S}^-]$ , yields

$$\nu = \frac{-d[\text{HOC}_2\text{H}_4\text{S}^-]}{dt} = [\text{H}_2\text{O}_2]_T[\text{HOC}_2\text{H}_4\text{S}^-] \left( \frac{k_1 + K'k_2/a_{\text{H}^+}}{\left(1 + \frac{K'}{a_{\text{H}^+}}\right) \left(1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}}\right)} \right) \quad (16)$$

where  $K'$  is the apparent acid dissociation constant for H<sub>2</sub>O<sub>2</sub>;  $K'_{a1}$

is the apparent acid dissociation constant for 2-mercaptoethanol;  $K'_{a2}$  is the apparent acid dissociation constant for  $\text{HOC}_2\text{H}_4\text{S}^-$ .  $k_{\text{obsd}}$  in this case is given by

$$k_{\text{obsd}} = \left( k_1 + \frac{K'k_2}{a_{\text{H}^+}} \right) / \left( 1 + \frac{K'}{a_{\text{H}^+}} \right) \left( 1 + \frac{a_{\text{H}^+}}{K'_{a1}} + \frac{K'_{a2}}{a_{\text{H}^+}} \right) \quad (17)$$

Initial values for the constants of eq 17 can be obtained by analyzing kinetic data over the pH range of 10.4 to 12. The observed linear behavior between  $1/a_{\text{H}^+}$  and  $1/k_{\text{obsd}}$  over this pH range requires that  $k_1 \gg k_2K'/a_{\text{H}^+}$  and  $1 \gg a_{\text{H}^+}/K'_{a1} \gg K'_{a2}/a_{\text{H}^+}$ . Given these constraints, eq 17 reduces to

$$k_{\text{obsd}} = k_1 / \left( 1 + \frac{K'}{a_{\text{H}^+}} \right) \quad (18)$$

or

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{K'}{a_{\text{H}^+}(k_1)} \quad (19)$$

where  $k_1 = 12.82 \text{ M}^{-1} \text{ s}^{-1}$  and  $\text{p}K' = 11.18$  at  $\mu = 0.1 \text{ M}$  and  $T = 20^\circ \text{C}$ .

The variation of  $k_1$  with temperature at pH 10.4 gave  $\Delta H_1^\ddagger = 46.5 \pm 0.09 \text{ kJ/mol}$  and  $\Delta S_1^\ddagger = -65.5 \pm 5.3 \text{ J/(deg}\cdot\text{mol)}$ . The temperature dependence of  $K' = K(\gamma_{\text{HO}_2^-})^{-1}$  can be determined from the thermodynamic data of Evan and Uri<sup>13</sup> and the appropriate value of  $\gamma_{\text{HO}_2^-}$  determined from the Davies equation.<sup>14</sup>

The constants  $k_2$  and  $K'_{a2}$  were obtained by the nonlinear least-squares analysis of the following function:<sup>15</sup>

$$\Phi = \sum_{i=1}^n [(k_{\text{obsd}} - k_{\text{calcd}}) \text{ wts}(i)]^2 \quad (20)$$

$$\text{wts}(i) = \sigma(i)^{-1} \quad (21)$$

$\sigma(i)$  = sample standard deviation of data point  $i$

The constants  $k_1$  and  $K'$  were further refined by the same function, while the values of  $k_{\text{calcd}}$  were determined according to eq 17. Values obtained by this method were  $k_1 = 12.64 \pm 0.54 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\text{p}K' = 11.45 \pm 0.19$ ,  $\text{p}K'_{a2} = 11.92 \pm 0.56$ .  $k_2$  was calculated as  $0.93 \pm 0.39 \text{ M}^{-1} \text{ s}^{-1}$ . Calculated values of pseudo-first-order rate constant ( $k_{\text{calcd}}$ ) are compared to the experimental values in Table I and shown in Figure 3.

## Discussion

The mechanism presented above is similar to the generalized mechanism for nucleophilic displacements on  $\text{H}_2\text{O}_2$  as discussed by Hoffmann and Edwards.<sup>3</sup> However, in this study, the acid-catalyzed term is unimportant. Equations 7, 8, and 9 are pre-equilibria that give  $\text{HO}_2^-$ ,  $\text{HOC}_2\text{H}_4\text{S}^-$ , and  $^-\text{OC}_2\text{H}_4\text{S}^-$ , respectively. The slow rate of oxidation above and below the pH range of 9 to 12 indicates that  $\text{HOC}_2\text{H}_4\text{S}^-$  is the reactive mercaptan species for the rate-determining steps of eq 10 and 11.  $\text{HOC}_2\text{H}_4\text{S}^-$  reacts with  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^-$ , respectively, via nucleophilic displacements in which hydroxide serves as the leaving group. The rapid decrease of oxidation rate above pH 10.5 indicates that  $\text{H}_2\text{O}_2$  is clearly more reactive than  $\text{HO}_2^-$ . The value of  $k_1$  for thioethanol oxidation is consistent with those reported for other mercaptides.<sup>16</sup>

Large negative values of  $\Delta S^\ddagger$  are generally observed for reactions between singly charged ions and neutral molecules; this has been attributed to bond formation between substrate and nucleophile before departure of the leaving group.<sup>17</sup> Some typical

TABLE III: Some Kinetic Data for Oxidations by Peroxides<sup>a</sup>

R	N <sup>k</sup>	$k_1^l$	$\Delta H_1^\ddagger, ^m$	$\Delta S_1^\ddagger, ^n$	$E_{\text{rxn}}$	H	ref
H	i	16.24	47	-65	1.98	11.07	o
H	g	0.094	56	-75	2.22	0.43	3
H	h	0.086	56	-80	2.21		3
H	f	0.07	62	-59	2.18	0.55	3
H	$\text{S}_2\text{O}_3^{2-}$	0.025			1.68	3.60	24, 25
H	$\text{I}^-$	0.011	54	-67	1.22	-9.00	7
H	c	$2.6 \times 10^{-3}$	54	-113			4
H	b	$2.2 \times 10^{-3}$					26
H	$\text{SCN}^-$	$5.2 \times 10^{-3}$	62	-105	0.99	1.06	5, 6
H	d	$5.3 \times 10^{-5}$	73	-71			27
H	e	$4.6 \times 10^{-5}$					28
H	$\text{NO}_2^-$	$5 \times 10^{-7}$			0.90	5.09	8
H	$\text{Br}^-$	$3.8 \times 10^{-7}$	86	-46	0.67	-6.00	7
H	$\text{Cl}^-$	$1.8 \times 10^{-9}$	96	-54	0.40	-3.00	7
t-Bu <sup>j</sup>	b	$1.4 \times 10^{-4}$	59	-121			4
t-Bu <sup>j</sup>	c	$1.4 \times 10^{-4}$	56	-130			29

<sup>a</sup> All data are for ROOH oxidation of N at  $25^\circ \text{C}$  in aqueous solution. <sup>b</sup> N is bis(2-hydroxyethyl)sulfide. <sup>c</sup> N is thioxane. <sup>d</sup> N is the thiocyanatopentaamminecobalt(III) cation. <sup>e</sup> N is the thiocyanatonitrotris(ethylenediamine)cobalt(III) cation. <sup>f</sup> N is thiourea. <sup>g</sup> N is  $N,N'$ -dimethylthiourea. <sup>h</sup> N is  $N,N'$ -diethylthiourea. <sup>i</sup> N is  $\text{HOC}_2\text{H}_4\text{S}$ . <sup>j</sup> t-Bu =  $(\text{CH}_3)_3\text{C}$ . <sup>k</sup> N = nucleophile. <sup>l</sup>  $k_1$  in  $\text{M}^{-1} \text{ s}^{-1}$ . <sup>m</sup>  $\Delta H^\ddagger$  in  $\text{kJ mol}^{-1}$ . <sup>n</sup>  $\Delta S^\ddagger$  in  $\text{J mol}^{-1} \text{ K}^{-1}$ . <sup>o</sup> This study.

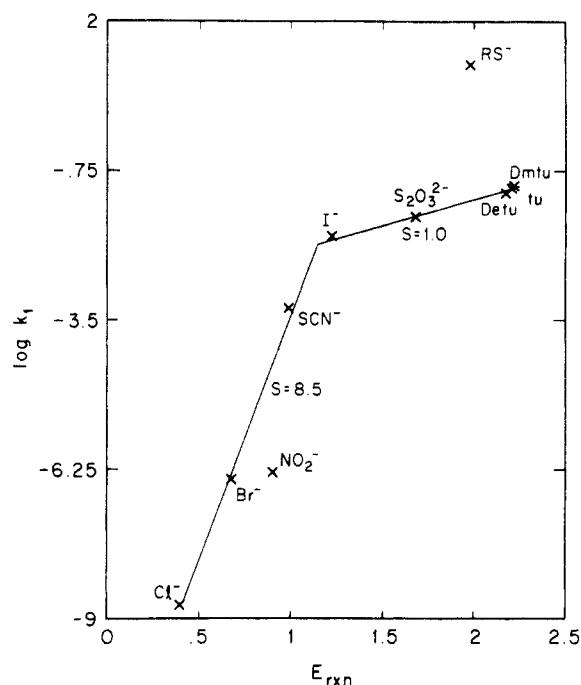


Figure 5. Linear free energy relationship.

values of  $\Delta S^\ddagger$  for nucleophilic displacements on peroxides are given in Table III.

The order of nucleophilic reactivity as listed in Table III is similar to the order predicted by Edwards and Pearson<sup>18</sup> (i.e.,  $\text{RS}^- > \text{R}_3\text{P} > \text{C}_6\text{H}_5\text{S}^- \sim \text{SCN}^- > \text{SO}_3^{2-} > \text{OH}^- > \text{S}_2\text{O}_3^{2-} > \text{SC}(\text{NH}_2)_2 > \text{SCN}^- > \text{Br}^- > \text{Cl}^-$ ), with the exception of the relative order of  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SC}(\text{NH}_2)_2$ .

Three important factors have been considered by Edwards and Pearson<sup>18</sup> in determination of nucleophilic reactivity. They are basicity, polarizability, and the  $\alpha$  effect.<sup>18</sup> In Figure 5, a linear free energy relationship of  $\log k_1$  vs. the  $E_{\text{rxn}}^\circ$  ( $E_{\text{rxn}}^\circ = E_{\text{H}_2\text{O}_2}^\circ - E_{\text{N}}^\circ$ ), where  $E_{\text{H}_2\text{O}_2}^\circ$  is the electrode potential for the half-reaction of  $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$ , and  $E_{\text{N}}^\circ$  is the electrode potential of the nucleophile (N) for the half-reaction of  $(\text{N})_2 + 2\text{e}^- \rightleftharpoons 2\text{N}$ , shows that there are two independent linear free energy relationships for the nucleophiles listed in Table III. The reduction

(13) Evans, M. G.; Uri, N. *Faraday Soc. Trans.* **1949**, *45*, 224.

(14) Stumm, W.; Morgan, J. J. "Aquatic Chemistry"; Wiley: New York, 1981; 2nd ed, pp 134-137.

(15) Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969; p 205.

(16) Hering, D. L.; Sloan, C. P.; Cabral, A. W.; Krueger, J. H. *Inorg. Chem.* **1978**, *17*, 1649.

(17) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism"; Wiley: New York, 1981; 3rd ed, pp 260-272.

(18) Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16.

potential of 2-hydroxyethyl disulfide to 2-mercaptoethanol ( $E_0 = -0.22$  V) can be calculated from the half-wave potential reported by Stricks et al.<sup>19</sup> The thioureas,  $S_2O_3^{2-}$ , and  $I^-$  appear to cluster as a distinct group exhibiting a slope of 1.0, while  $Cl^-$ ,  $Br^-$ , and  $SCN^-$  cluster as another distinct group with a steeper slope of 8.5. However, 2-mercaptoethanol does not appear to correlate with either group of nucleophiles.

A linear free energy relationship of the following form can be written:

$$\log k_1 = \frac{2.3SRT}{nF} \log K_{\text{reac}} + C \quad (22)$$

where  $S$  is the slope,  $C$  is the intercept and  $K_{\text{reac}}$  ( $\log K_{\text{reac}} = nFE_{\text{rxn}}/2.3RT$ ) is the equilibrium constant of the overall reaction. Equation 22 is similar in form to the Edwards equation<sup>20</sup>

$$\log (k_1/k_0) = \alpha E_n + \beta H \quad (23)$$

where  $k_0$  corresponds to the rate constant for water as a nucleophile,  $E_n$  is a nucleophilic constant characteristic of the particular electron donor,  $H$  is the relative basicity of the donor to protons which has been defined at  $H = \text{pH}_a + 1.74$ , and  $\alpha$  and  $\beta$  are the substrate constants.  $E_n$ , which depends on the polarizability,<sup>21</sup> is calculated from the electrode potential of the nucleophile.

Comparison of eq 22 to 23 suggests that  $E_{\text{rxn}}$  should be comparable to  $E_n$ , that  $S$  is equivalent to the substrate constant, and that  $C$  can be equated to  $(\beta H + \log k_0)$ .

The minimal contribution (i.e.,  $\alpha E_n \gg \beta H$ ) of the basicity term to relative reactivity and the existence of two apparently inde-

pendent linear free energy domains as shown in Figure 5 may be explained within the context of Pearson's HSAB theory.<sup>22</sup> The observed order of nucleophilic reactivity should be similar to the order of softness of bases. The relative order of softness for various nucleophiles is thiourea  $> SO_3^{2-} > SCN^- > I^- > Br^- > NO_2^- > Cl^- > F^-$  which is similar to the observed order to nucleophilic reactivity. Since  $H_2O_2$  is soft center,<sup>23</sup> polarizability rather than basicity should be the more important factor. Thiosulfate and  $I^-$  are considered as soft bases, whereas  $Cl^-$ ,  $Br^-$ ,  $F^-$ , and  $NO_3^-$  are considered to be hard bases. As a consequence, the former group will have higher polarizabilities and hence greater nucleophilic reactivities than the latter group. The departure of 2-mercaptoethanol from this correlation implies that its rate of the oxidation also depends strongly on its basicity. The relative basicity of 2-mercaptoethanol ( $H = 11.1$ ) is significantly higher than all other nucleophiles listed in Table III. This indicates that the addition of 2-mercaptoethanol to hydrogen peroxide is energetically more favorable than the other listed sulfur compounds.

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**Registry No.**  $HOC_2H_4SH$ , 60-24-2;  $(HOC_2H_4S)_2$ , 1892-29-1.

(22) Pearson, R. G., Ed. "Hard and Soft Acids and Bases"; Dowden, Hutchinson & Ross: New York, 1973.

(23) Pearson, R. G. *Chem. Brit.* **1967**, 3, 103.

(24) Abel, E. *Monatsch. Chem.* **1907**, 28, 239.

(25) Sandved, K.; Holte, J. B. *Chem. Abstr.* **1939**, 33, 4856.

(26) Ross, S. D. *J. Am. Chem. Soc.* **1946**, 68, 1484.

(27) (a) Schung, K.; Gilmore, M. D.; Olson, L. A. *Inorg. Chem.* **1967**, 6, 2180. (b) Schung, K.; Miniatas, B.; Sadowski, A. J.; Yano, T.; Veno, K. *Ibid.* **1968**, 7, 1669.

(28) Caldwell, S. M.; Norris, A. R. *Inorg. Chem.* **1968**, 7, 1667.

(29) Edwards, J. O.; Fortnum, D. H. *J. Org. Chem.* **1962**, 27, 407.

(19) Stricks, W.; Frischmann, J. K.; Mueller, R. G. *J. Electrochem. Soc.* **1962**, 109, 518.

(20) Edwards, J. O. *J. Am. Chem. Soc.* **1954**, 76, 1540.

(21) Edwards, J. O. *J. Am. Chem. Soc.* **1956**, 78, 1819.

## Activation Energy for the Reaction $H + OH^- \rightarrow e_{\text{aq}}^-$ . Kinetic Determination of the Enthalpy and Entropy of Solvation of the Hydrated Electron

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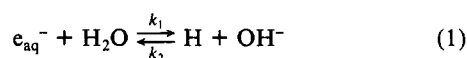
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The reaction between atomic hydrogen and hydroxide ion in aqueous solutions  $H + OH^- \rightarrow e_{\text{aq}}^- + H_2O$  has been studied by pulse radiolysis. The rate constant was measured at pH 11.7 and 12 by following the growth of the hydrated electron absorption at 600 nm. The activation energy of the reaction has been determined over the temperature range 15–60 °C as  $6.3 \pm 0.6$  kcal/mol ( $26.4 \pm 2.5$  kJ/mol). From this value and the activation energy of the reverse reaction, the  $e_{\text{aq}}^-$  enthalpy of formation  $\Delta H_f^\circ = -32.6 \pm 1.6$  kcal/mol ( $-136.4 \pm 6.7$  kJ/mol) and its standard entropy  $S^\circ = 16.7 \pm 5.4$  cal/(mol deg) ( $69.8 \pm 22.5$  J/(mol deg)) were calculated. The high entropy of solvation  $\Delta S_s^\circ = 11.7 \pm 5.4$  cal/(mol deg) ( $49 \pm 22.6$  J/(mol deg)) when electrons are transferred from gas phase into aqueous solution indicates that the hydrated electron is a structure breaker.

### Introduction

In water the hydrated electron is not stable; nevertheless, some of its thermodynamic properties have been derived from the equilibrium constant of the reaction<sup>1-3</sup>



At room temperature  $k_1 = 890 \text{ s}^{-1}$  and  $k_2 = 1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>5</sup> From this the equilibrium constant

$$K = [H][OH^-]/[e_{\text{aq}}^-]$$

can be found by assuming  $K = k_1/k_2$ . The standard free energy of reaction 1 is  $\Delta G_1^\circ = 5.9$  kcal/mol if the standard state of water

(1) Baxendale, J. H. *Radiat. Res. Suppl.* **1964**, 4, 139.

(2) Marcus, R. A. *J. Chem. Phys.* **1965**, 43, 3477.

(3) Jortner, J.; Noyes, R. M. *J. Phys. Chem.* **1966**, 70, 770.

(4) Hart, E. J.; Gordon, S.; Fielden, E. M. *J. Phys. Chem.* **1966**, 70, 150.

(5) Matheson, M. S.; Rabani, J. *J. Phys. Chem.* **1965**, 69, 1324.