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The Kinetics of the Oxidation of 3-Mercaptopropionic Acid with Potassium Ferricyanide[1]

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The kinetics of the oxidation of 3-mercaptopropionic acid with potassium ferricyanide in aqueous solution have been investigated under a variety of conditions, using a spectrophotometric method. In the *p*H range 3.83–4.78, the rate law $-\mathrm{d}(\text{ferricyanide})/\mathrm{d}t = k(\text{ferricyanide})^2$ was found to apply. The observed rate constant (k) was found to increase with increasing thiol concentration and *p*H, to decrease with increasing initial ferricyanide ion concentration and with added potassium ferrocyanide, and to be unaffected by added dithiodipropionic acid. These results are discussed in terms of a mechanism in which an initial reversible electron transfer is followed by another, irreversible one.

The biologically significant conversion of thiols to disulfides has received much attention. In recent years, kinetic studies of this reaction in homogeneous solution have been made in which potassium persulfate,[2,3] sodium 2,6-dichlorobenzenenone-indophenol[4,5] and hydrogen peroxide[6] were used as oxidants. These investigations indicated that the mechanism of the oxidation depends upon the nature of the oxidant, and that the transformation of the oxidant to a reactive intermediate may be rate-determining.

The simplest mode of oxidation involves the abstraction of one electron by an oxidizing agent. The present investigation was undertaken in order to obtain kinetic evidence for the occurrence of this electron transfer in the oxidation of thiols in aqueous solution. Potassium ferricyanide was chosen as oxidant[7] since it yields a stable reduction product by the gain of a single electron. Further, it was thought that the inert nature of the ferricyanide ion would preclude the formation of complexes with the thiol or disulfide. Orienting experiments showed that reasonable reaction times and freedom for the variation of conditions could be obtained with 3-mercaptopropionic acid (I). The reaction was followed by measuring the decrease in ferricyanide concentration spectrophotometrically.

Results

The oxidation of I with potassium ferricyanide was first carried out on a larger scale in order to establish the course of the reaction. 3,3′-Dithiodipropionic acid was obtained in 95% yield; no other organic product could be isolated.

The spectra of potassium ferricyanide and potassium ferrocyanide show strong absorption in the ultraviolet region.[8] However, whereas the ferrocyanide has only negligible absorption above 375 mμ, the ferricyanide has a strong band at 418 mμ (log ϵ 3.01).[9] At this wave length, which was utilized for analytical purposes, solutions of potassium ferricyanide obeyed Beer's law in the concentration range of the kinetic experiments (to 1×10^{-4} *M*). Neither Compound I nor dithiodipropionic acid show any absorption in this spectral region. Spectral examination of solutions containing relevant combinations of reactants and products showed no evidence of association or complex formation between these compounds. The spectrum of the ferricyanide–thiol mixture was measured at an acidity (*p*H 1.4) at which disulfide formation is extremely slow.[10]

The kinetic runs were carried out in sodium acetate–acetic acid buffered solutions using an excess of I. The reaction became extremely rapid as the *p*H increased, and useful data could only be obtained in the *p*H 4–5 range. To minimize the effects of spurious oxidation by atmospheric oxygen, all the solutions used were deaerated with nitrogen, and the runs were conducted under a nitrogen atmosphere.

Under all the conditions examined, the rate of disappearance of potassium ferricyanide (F) obeyed a second-order law for the initia l60–95% of reaction[11]

$$-\,\mathrm{d}F/\mathrm{d}t = kF^2 \qquad (1)$$

Typical data are shown in Table I, and in Fig. 1, in which the reciprocal of the potassium ferricyanide concentration is plotted against time. The concentrations were calculated from the optical density at 418 mμ and the molar extinction coefficient at that wave length.

The observed pseudo second-order rate constant (k) was found to decrease with increasing initial potassium ferricyanide concentration, and with added potassium ferrocyanide (F'). The pertinent data are presented in Table II. The variation of k with initial ferricyanide concentration can apparently be represented by the equation

$$k = k' + k''/(\mathrm{F})_0 \qquad (2)$$

With added potassium ferrocyanide at constant initial ferricyanide concentration, k was found to vary with the total iron concentration ($(\mathrm{F})_0 + (\mathrm{F}')_0$) in accordance with the equation

$$k = \frac{k'''}{(\mathrm{F})_0 + (\mathrm{F}')_0} \qquad (3)$$

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[1] Presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960 (Abstracts, p. 74-O).

[2] To whom enquiries should be addressed.

[3] R. L. Eager and C. A. Winkler, *Can. J. Research*, **26B**, 527 (1948); I. M. Kolthoff and I. K. Miller, THIS JOURNAL, **73**, 5118 (1951).

[4] R. E. Basford and F. M. Huennekens, *ibid.*, **77**, 3873 (1955).

[5] C. G. Overberger and P. V. Bonsignore, *ibid.*, **80**, 5431 (1959).

[6] I. Pascal and D. S. Tarbell, *ibid.*, **79**, 6015 (1957); this reference also cites much of the pertinent literature on the kinetics of thiol oxidations.

[7] The use of potassium ferricyanide in organic chemistry has recently been reviewed; see B. S. Thyagarajan, *Chem. Revs.*, **58**, 439 (1958).

[8] J. A. Ibers and N. Davidson, THIS JOURNAL, **73**, 476 (1951).

[9] J. Brigando, *Bull. soc. chim. France*, 503 (1957), found log ϵ 2.99 at this wave length.

[10] The spectrum of potassium ferricyanide is unaffected by the addition of strong acid.[8] The three dissociation constants of $H_3Fe(CN)_6$ are those of a strong acid,[9] and consequently only ferricyanide ions exist in aqueous solution.

[11] In some runs the concentrations of the reactants were such that the concentration of I decreased approximately 10% during the course of the reaction. However, taking this variation into account by using a third-order rate law only introduced a negligible correction term, which did not affect the linearity and slope of the plots.

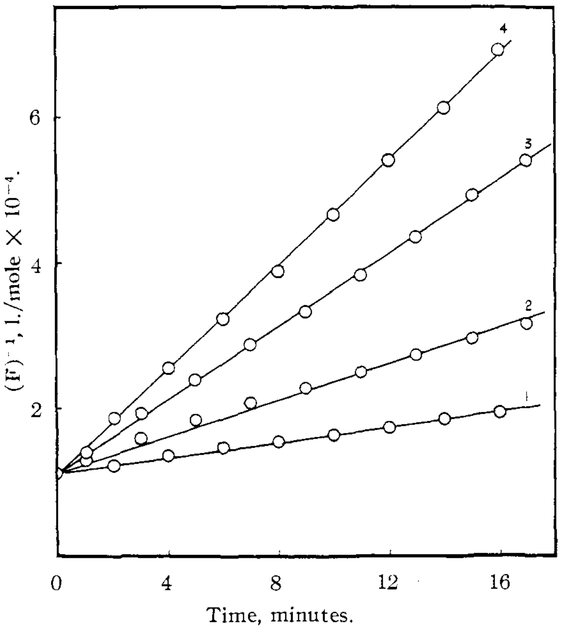

Fig. 1.—Effect of thiol concentration; $(F)_0 = 9.11 \times 10^{-5}\,M$. pH = 3.83, T = 25.0°. $(HRSH)_0$ concentrations: 1, $8.96 \times 10^{-4}\,M$; 2, $17.9 \times 10^{-4}\,M$; 3, $26.9 \times 10^{-4}\,M$; 4, $35.8 \times 10^{-4}\,M$.

These relationships are illustrated in Fig. 2. The slopes (k'' and k''') appear to be the same in the presence and absence of added ferrocyanide. Several of the slow, ferrocyanide-retarded reactions were followed for sufficient time to establish that even under these conditions the oxidation proceeds essentially to completion. Dithiodipropionic acid (HRSSRH) was without effect on the rate, even in the presence of additional potassium ferrocyanide (Fig. 3).

TABLE I

POTASSIUM FERRICYANIDE-3-MERCAPTOPROPIONIC ACID REACTION

(Run 4, Fig. 1) $(RSH)_0$ is $35.8 \times 10^{-4}\,M$, pH is 3.83, T is 25.0°

Time, min.	(F), $M \times 10^5$	$(F)^{-1}$, l./mole $\times 10^{-4}$	k, l. mole^{-1} min.$^{-1} \times 10^{-3}$
0	9.11	1.10	
2	5.26	1.90	4.00
4	3.92	2.55	3.63
6	3.09	3.24	3.57
8	2.58	3.88	3.48
10	2.14	4.67	3.57
12	1.85	5.42	3.59
14	1.63	6.13	3.59
16	1.45	6.91	3.63
		Av.	$3.63 \pm 0.08 \times 10^3$

The reaction rate increased with increasing pH at constant initial thiol and potassium ferricyanide concentrations. The dependency of k on the hydrogen ion concentration (Fig. 4) may be expressed by the equation

$$1/k = k_H + k'_H(H^+) \tag{4}$$

It can be seen that the plot of $1/k$ vs. (H^+) has an apparent negative intercept. This anomaly may in part be due to the change in ionic strength in this series of experiments. The dependency of the rate constant k on the thiol concentration is shown in Fig. 5.

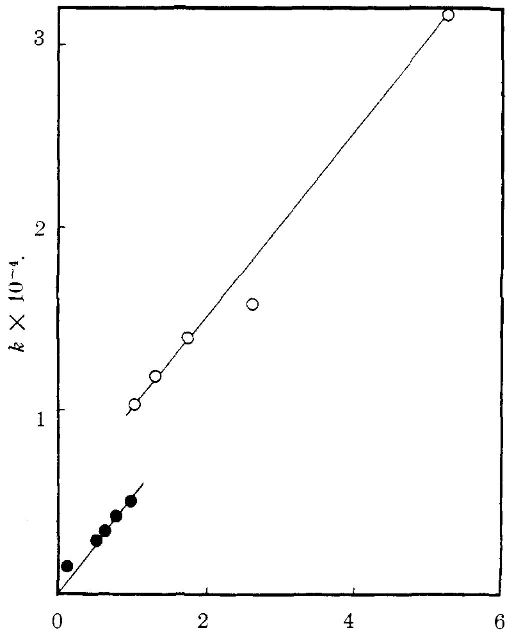

Fig. 2.—Effect of initial ferricyanide concentration and of added ferrocyanide; for conditions see Table II: ●, variation of rate with added ferrocyanide at constant initial ferricyanide concentration; ○, variation of rate with initial ferricyanide concentration in the absence of added ferrocyanide.

Discussion

Before consideration of the kinetic results, it is necessary to examine the acid–base relationships of 3-mercaptopropionic acid (I). In contrast to simple thiols bearing only one SH group, I gives rise to several ionized species. The equilibria involved are shown in Chart 1, which is typical for dibasic acids.[12] In this scheme: HRSH = $HSCH_2CH_2COOH$, HRS^- = $^-SCH_2CH_2COOH$, RSH^- = $HSCH_2CH_2COO^-$, and $RS^=$ = $^-SCH_2CH_2COO^-$. The primed K's represent the individual ionization constants.

TABLE II

EFFECT OF INITIAL POTASSIUM FERRICYANIDE CONCENTRATION AND OF ADDED POTASSIUM FERROCYANIDE

$(RSH)_0 = 8.75 \times 10^{-4}M$ (Runs 5–9), $(RSH)_0 = 9.32 \times 10^{-4}M$ (Runs 10–14), pH = 4.57, T = 25.0°

Run	$(F)_0$, $M \times 10^5$	$(F')_0$, $M \times 10^5$	k, l. mol^{-1} min.$^{-1} \times 10^{-4}$
5	1.89	0	3.16
6	3.79	0	1.58
7	5.69	0	1.39
8	7.58	0	1.19
9	9.48	0	1.04
10	8.35	1.51	0.502
11	8.35	4.52	.429
12	8.35	7.53	.338
13	8.35	10.54	.288
14	9.66	63.12	.148

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[12] J. E. Ricci, "Hydrogen Ion Concentration," Princeton University Press, Princeton, N. J., 1952, Chapter 6.

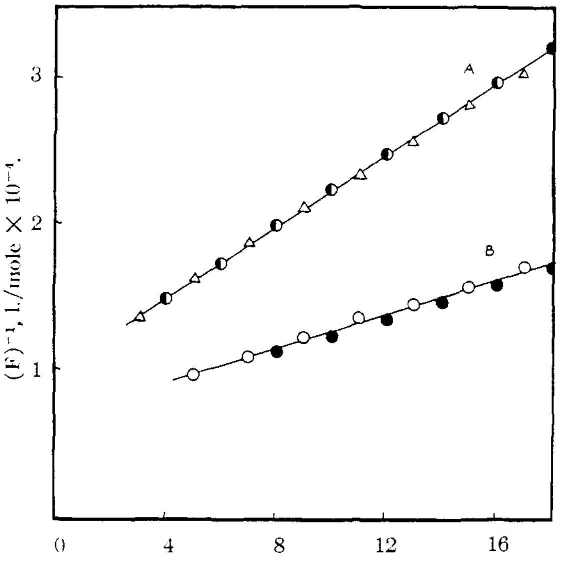

Fig. 3.—Effect of added dithiodipropionic acid; $(HRSH)_0 = 7.33 \times 10^{-4}\ M$, pH = 4.57, $T = 25.0°$; A: no added ferrocyanide, $(F)_0 = 1.12 \times 10^{-4}\ M$; △, no disulfide; ◐, $(HRSSRH)_0 = 1.76 \times 10^{-4}\ M$. B: ferrocyanide added, $(F')_0 = 1.24 \times 10^{-4}\ M$, $(F)_0 = 1.33 \times 10^{-4}\ M$; ○, no disulfide; ●, $(HRSSRH)_0 = 1.76 \times 10^{-4}\ M$.

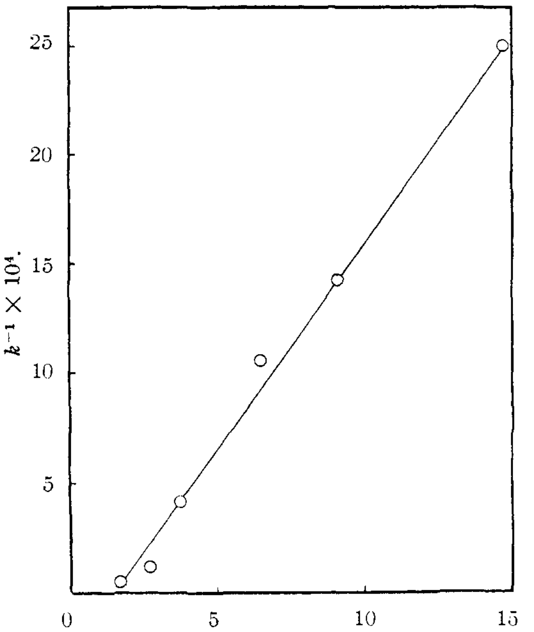

Fig. 4.—Effect of pH: $(F)_0 = 9.41 \times 10^{-5}\ M$; $(HRSH)_0 = 7.30 \times 10^{-4}\ M$, $T = 25.0°$.

Chart 1

$$\begin{tikzcd}
HRSH \arrow[r, "K'_1"] \arrow[dr, "K''_1"'] & HRS^- \arrow[r, "K'_2"] & RS^= \\
& RSH^- \arrow[ur, "K''_2"'] &
\end{tikzcd}$$

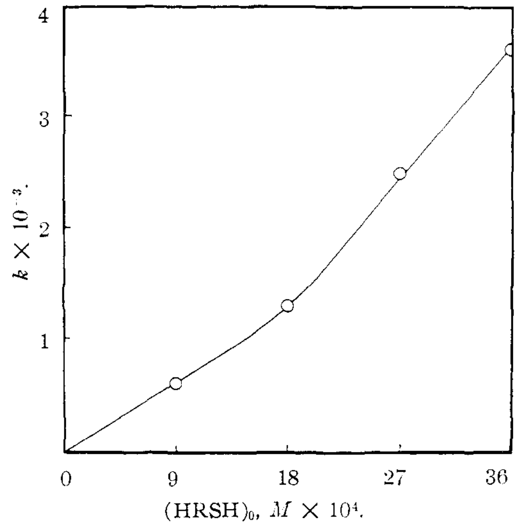

Fig. 5.—Effect of thiol concentration; for conditions see Fig. 1.

The pH dependence of the rate of oxidation of I suggests that only ionized sulfhydryl groups are directly involved in the reaction, *i.e.*, the species HRS^- and $RS^=$. From properly defined observed ionization constants of I (K_1 and K_2), it can be shown[12] that the concentrations of HRS^- and $RS^=$ are

$$(HRS^-) = (HRSH)_0 \left[\frac{1/(1+x)}{1 + (H^+)/K_1 + K/(H^+)}\right] \quad (5)$$

and

$$(RS^=) = (HRSH)_0 \left[\frac{K_2/(H^+)}{1 + (H^+)/K_1 + K/(H^+)}\right] \quad (6)$$

where $x = K''_1/K'_1$, and $(HRSH)_0 = (HRSH) + (HRS^-) + (RSH^-) + (RS^=)$. The value of x cannot be measured. It represents the ratio of the ionization constants of the –COOH and –SH groups. The values of K_1 and K_2 are 4.6×10^{-5} and 2.9×10^{-11}, respectively, at 20–25°.[13] Since these values are not very different from those of the ionization constants of simple carboxylic acids ($\sim 10^{-5}$) and aliphatic thiols ($\sim 10^{-11}$),[14] the assumption that x is equal to the ratio of the observed ionization constants (K_1 and K_2) appears reasonable. It should be realized that this assumption implies that the sulfhydryl group does not affect the ionization of the carboxylic acid group and *vice versa*. On this basis one can calculate that in a $1 \times 10^{-3}\ M$ solution of I the approximate concentrations of the pertinent ionized species are $(HRS^-) = 3 \times 10^{-10}\ M$ and $(RS^=) = 1 \times 10^{-10}\ M$ at pH 4, and $(HRS^-) = 8 \times 10^{-10}\ M$ and $(RS^=) = 2 \times 10^{-9}\ M$ at pH 5. These figures emphasize the extreme rapidity of the elementary processes involved in the oxidation of I.

The kinetic data indicate that the rate-determining processes are considerably more complicated than the simple electron transfer envisioned originally. The disappearance of ferricyanide ion according to a second-order rate law suggests the involvement of an intermediate, the concentration of which is dependent on the ferricyanide concentration. Although the reaction is apparently not detectibly reversible,[15] the decrease in rate affected by

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[13] E. Larsson, *Z. anorg. u. allgem. Chem.*, **172**, 375 (1928).

[14] D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257 (1940).

[15] Even if the reaction involves an equilibrium, its position would

the addition of potassium ferrocyanide provides evidence of the reversibility of one of the rate-determining steps. Dithiodipropionic acid appears not to participate in this process. The most surprising result is the observed decrease in k with increasing initial ferricyanide concentration.

The I–ferricyanide system bears some resemblance to other oxidation reactions. Thus a second-order rate law has been observed to apply to the internal oxidation–reduction of ferric cysteinate[17] and ferric thioglycolate.[18] The analogy appears, however, to be superficial since the rates of these reactions are increased by hydrogen ion and decreased by the thiols. Waters and Fieser have found that the addition of ferrocyanide ion also decreases the rate of oxidation of phenols[19,20] by alkaline potassium ferricyanide. On the other hand, ferrocyanide ion exerts no significant effect in the ferricyanide oxidation of aldehydes, ketones and nitroparaffins.[21]

Many simple schemes which would explain the second-order dependence on ferricyanide ion concentration, fail to account for the observed variation of k with the experimental conditions. The sequence of steps presented in eq. 7–12 offers a reasonable, semi-quantitative interpretation of the data.

$$\mathrm{HRS^- + F} \underset{k'_1}{\overset{k_1}{\rightleftarrows}} \mathrm{HRS\cdot + F'} \qquad (7)$$

$$\mathrm{RS^= + F} \underset{k'_2}{\overset{k_2}{\rightleftarrows}} \mathrm{RS\div + F'} \qquad (8)$$

$$\mathrm{HRS\bullet + F} \xrightarrow[k_3]{} \mathrm{HRS^+ + F'} \qquad (9)$$

$$\mathrm{RS\text{-} + F} \xrightarrow[k_4]{} \mathrm{RS^\pm + F'} \qquad (10)$$

$$\mathrm{HRS^+ + HRSH} \xrightarrow[k_5]{} \mathrm{HRSSRH + H^+} \qquad (11)$$

$$\mathrm{RS^\pm + HRSH} \xrightarrow[k_6]{} \mathrm{HRSSRH} \qquad (12)$$

This scheme is based on a reversible initial electron transfer of the type proposed by Waters and Fieser[19,20] which is followed by another, irreversible, oxidation step.[19] That the ferricyanide–thiol reaction generates thiyl radicals is evidenced by the ability of this system to initiate the polymerization of olefins.[22] Species similar to $\mathrm{HRS^+}$ and $\mathrm{RS^\pm}$, corresponding to the oxidation level of a sulfenic acid, have previously been suggested as intermediates in the oxidation of thiols by Basford and Huennekens.[4] Since sulfenyl halides react rapidly with thiols and their anions,[23] it seems reasonable to assume that steps 11 and 12 are also fast.

Application of the steady state approximation to the radicals HRS· and $\mathrm{RS^-}$ involved in steps 7–10 leads to the expression for the rate of disappearance of ferricyanide ion

$$\frac{-\,\mathrm{d}F}{\mathrm{d}t} = \frac{2k_1(\mathrm{HRS^-})F^2}{rC + (1-r)F} + \frac{2k_2(\mathrm{RS^=})F^2}{r'C + (1-r')F} \qquad (13)$$

In this equation, C = total iron concentration = $(\mathrm{F})_0 + (\mathrm{F'})_0$, $r = k'_1/k_3$, and $r' = k'_2/k_4$. Integration yields an equation in which t is related to the sum of an $(\mathrm{F})^{-1}$ term and complex logarithmic (F) terms, the latter being weighted by $(1 - r)$ and $(1 - r')$ factors. A much simpler expression can be obtained by the assumption that $r = r'$. Since r is the ratio of the specific rates of reduction and oxidation of the radical HRS·, and r' refers to the corresponding processes with RS·, this assumption does not appear unreasonable. Its adoption leads to

$$\frac{-\,\mathrm{d}F}{\mathrm{d}t} = \frac{2F^2[k_1(\mathrm{HRS^-}) + k_2(\mathrm{RS^=})]}{rC + (1-r)F} \qquad (14)$$

which on integration yields

$$\frac{1}{F} - \frac{(1-r)}{rC}\ln F = \frac{2}{rC}\,[k_1(\mathrm{HRS^-}) + k_2(\mathrm{RS^=})]t + \text{Constant} \qquad (15)$$

We have found that under all conditions plots of $(\mathrm{F})^{-1}$ *vs.* t are linear for the major part of the reaction. If the proposed scheme applies, this implies that the value of r (and of r') is very close to 1, *i.e.*, the specific rates of oxidation and reduction of the intermediate radicals are essentially equal. The observed rate constant (k) would then be given by

$$k = \frac{2k_1}{C}\left[(\mathrm{HRS^-}) + \frac{k_2}{k_1}(\mathrm{RS^=})\right] \qquad (16)$$

Equation 16 predicts an inverse relationship between k and the total iron concentration, (C). This is obeyed in the presence of added ferrocyanide iron (Fig. 2). In the absence of additional ferrocyanide, the data imply the occurrence of a process which is independent of C, and which is not predicted by eq. 16. This discrepancy may be a reflection of differences in the steady state radical concentrations under the two sets of conditions, which are not taken into account in deriving the rate law. In agreement with this point of view is the fact that, at equal values of C, the rate is greater where the radical concentration is expected to be larger, *i.e.*, in the absence of added ferrocyanide ion.

The dependence of k on the total thiol concentration is readily derived with the aid of eq. 5 and 6. At constant pH the concentrations of the ions are given by $(\mathrm{HRS^-}) = a(\mathrm{HRSH})_0$ and $(\mathrm{RS^=}) = b(\mathrm{HRSH})_0$, where a and b are constants. Equation 16 then becomes

$$k = \frac{2k_1}{C}\left[a + \frac{k_2}{k_1}b\right](\mathrm{RHSH})_0 \qquad (17)$$

The data of Fig. 5 show that k increases with increasing thiol concentration, but somewhat more rapidly at higher concentrations than is required by eq. 17.

As far as the effect of the hydrogen ion concentration is concerned, the application of eq. 16 is not so clear cut. The experimental data (Fig. 4) indicate a linear relationship between $(k)^{-1}$ and the hydro-

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probably be highly in favor of the disulfide. Thus for cysteine, the equilibrium constant of the reaction $2\mathrm{Fe^{++}} + \mathrm{RSSR} + 2\mathrm{H^+} \rightleftarrows 2\mathrm{Fe^{+++}} + 2\mathrm{RSH}$ has been found to be 5.3×10^{-24} at 25°.[16]

(16) N. Tanaka, I. M. Kolthoff and W. Stricks, THIS JOURNAL, **77**, 2004 (1955).

(17) N. Tanaka, I. M. Kolthoff and W. Stricks, *ibid.*, **77**, 1996 (1955).

(18) D. L. Leussing and L. Newman, *ibid.*, **78**, 552 (1956); H. Lamfrom and S. O. Nielson, *ibid.*, **79**, 1966 (1957).

(19) C. G. Haynes, A. H. Turner and W. A. Waters, *J. Chem. Soc.*, 2823 (1956); this reference cites the earlier literature on this topic.

(20) L. F. Fieser, THIS JOURNAL, **52**, 5204 (1930).

(21) P. T. Speakman and W. A. Waters, *J. Chem. Soc.*, 40 (1955).

(22) I. M. Kolthoff and E. J. Meehan, *J. Polymer Sci.*, **11**, 71 (1953).

(23) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).

gen ion concentration. Thus $[(\mathrm{HRS}^-) + (k_2/k_1)(\mathrm{RS}^=)]^{-1}$ should be linearly related to (H^+). Incorporating the assumption that $x = K_1/K_2 \simeq (1 + x)$, and neglecting the K_1K_2 term,[24] the application of eq. 5 and 6 yields

$$\frac{1}{(\mathrm{HRS}^-) + (k_2/k_1)(\mathrm{RS}^=)} = \frac{(\mathrm{H}^+)[(\mathrm{H}^+) + K_1)]}{K_2(\mathrm{HRSH})_0[(\mathrm{H}^+) + (k_2/k_1)K_1]} \quad (18)$$

Obviously, as (H^+) is always the same order of magnitude as K_1, linearity in (H^+) of eq. 18 depends on k_2/k_1 and can only be expected if this ratio is quite small. This might well be the case since electrostatic repulsion is more important in reaction 8 than in reaction 7, and hence k_2 is probably smaller than k_1. The experimental results are certainly not at variance with a reasonable interpretation of eq. 18, and the conclusion that sulfhydryl anions are the reactive thiol species in the rate-determining processes.

Several variations of the reaction scheme of eq. 7–12 involving the participation of iron–sulfur complexes can be formulated, which lead to similar kinetic expressions. Such paths cannot be ruled out, since the inability to detect these complexes spectroscopically may be due to their low concentration, or other factors. The actual electron transfer is conveniently pictured to proceed *via* a cyanide-bridged transition state.[25] It follows from electrostatic considerations that the transition states of the radical–ferricyanide interactions are more likely to pass into intermediate complexes than the transition states involving sulfhydryl anions. The extremely low radical concentrations would render such complexes undetectible.

It is interesting to note that the oxidation of cysteine with potassium nitrosyl disulfonate $(\cdot\mathrm{ON}(\mathrm{SO_3K})_2)$[26] in aqueous solution is first order in oxidant.[27] It appears likely that in this system a rate-controlling electron transfer is followed by the rapid dimerization of the intermediate thiyl radicals.[28]

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Experimental

Materials.—3-Mercaptopropionic acid (Evans Chemetics, Inc.) was redistilled several times under reduced pressure. The purified material, b.p. 104° (6 mm.) (reported[29] 105–107° (4 mm.)), was stored under nitrogen. Potassium ferricyanide (Baker and Adamson, reagent grade) was recrystallized several times from hot water. The dark-red crystals obtained in this manner were demonstrated to be free of ferric ion by the absence of Prussian Blue formation with ferrous sulfate. Potassium ferrocyanide (Fisher Scientific Co.) was purified according to the procedure of Loftfield and Swift.[30] The pale yellow crystals were stored in the dark under nitrogen.

Preparative-scale Oxidation of I.—A solution of 3-mercaptopropionic acid (3.0 g.) in 80 ml. of water was added slowly, under nitrogen, to a stirred solution of potassium ferricyanide (7.0 g.) in 160 ml. of water. After 2 hours at room temperature, the white precipitate which was formed was filtered (2.0 g., 90%). Recrystallization from ethanol afforded colorless 3,3'-dithiodipropionic acid, m.p. 154° (cor.), reported[31] 154°. No other organic products could be isolated.

Kinetic Experiments.—For all the spectral work, a Beckman model DK-2 recording spectrophotometer equipped with a Beckman no. 92430 time-drive attachment was used. Special milling of a Beckman no. 92527 temperature-regulated cell holder permitted to use of a matched pair of 10-cm. quartz cells. Constant temperature (25.00 ± 0.05°) was maintained in the cell holder by the circulation of water from an Ultra electronically controlled thermostat circulating bath.[32]

Preliminary spectral measurements showed that the spectra of the following mixtures were indistinguishable from the spectral sums of their components: solutions 1, 3.56×10^{-5} M in ferricyanide and 3.14×10^{-5} M in ferrocyanide; 2, 4.28×10^{-5} M in ferricyanide and 1.07×10^{-4} M in dithiodipropionic acid; 3, 3.48×10^{-5} M in ferrocyanide and 3.47×10^{-4} M in I; 4, 3.6×10^{-2} M in HCl, 1.93×10^{-5} M in ferricyanide, and 8.69×10^{-4} M in I. Data on the compliance with Beer's law and the extinction coefficient of potassium ferricyanide are given in Table III.

TABLE III

EXTINCTION COEFFICIENT OF POTASSIUM FERRICYANIDE IN AQUEOUS SOLUTION AT 418 mμ

(F), $M \times 10^5$	9.43	7.54	5.65	3.77
ϵ^a	1021	1042	1043	1029

[a] A 10-cm. cell was used; av. 1033 ± 9.

All the solutions were made up with permanganate-purified, doubly-distilled water.[33] Solutions of reactants were always kept in the dark and under nitrogen, but were never stored overnight. The buffer mixtures[34] were prepared from deaerated stock solutions of 0.2 M sodium acetate and 0.2 M acetic acid, which were stored with a continuous slow stream of moisture-saturated nitrogen bubbling through them.

The kinetic measurements were made directly in a 10-cm. quartz cell. For this purpose the wave length of the spectrophotometer was set at 418 mμ, and the time-drive unit was put into operation. Buffer solution (20.0 ml.), and sufficient distilled water to bring the total volume to 50 ml. after the addition of the reactants, were rapidly delivered into a ground-glass stoppered 125-ml. flask, under a stream of nitrogen. The potassium ferricyanide solution was added next and this mixture, as well as the stock solution of I were allowed to come to temperature equilibrium. The time-drive was started immediately when the solution of I was added. The mixture was briefly swirled, and then rapidly transferred into the absorption cell. The concentration of ferricyanide ion as a function of time was obtained directly from the resulting density–time plot. Each given run was carried out at least in duplicate.

The pH values, which were determined with a calibrated Beckman model G pH meter, were found to be identical before and after the reaction.

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[24] K_1K_2 is smaller by a factor of about 10^6 than the other relevant terms in the pH range used.

[25] *Cf.* H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

[26] *Cf.* E. Fremy, *Ann. chim. phys.*, **15**, [3], 408 (1845).

[27] J. J. Bohning and K. Weiss, unpublished results.

[28] A rate-controlling electron transfer has also been proposed by G. D. Allen and W. A. Waters, *J. Chem. Soc.*, 1132 (1956), to account for the kinetic features of the oxidation of isobutyraldehyde with this oxidizing agent.

[29] L. C. Cheney and J. R. Piening, THIS JOURNAL, **67**, 731 (1945).

[30] R. Loftfield and E. Swift, Jr., *ibid.*, **60**, 3083 (1938).

[31] G. G. Stoner and G. Dougherty, *ibid.*, **63**, 987 (1941).

[32] Manufactured by Colora, G.m.b.H., Lorch, Germany; supplied by Lux Scientific Instrument Corp., New York, N. Y.

[33] Kindly supplied by Dr. S. Lipsky.

[34] I. M. Kolthoff and C. Rosenblum, "Acid–Base Indicators," The Macmillan Co., New York, N. Y., 1937, p. 256.