acetate to which 20 ml of hexane was added to yield 2.33 g (59%) of yellow crystals: mp 82–82.5°; $\nu_{max}^{KBr}$ 1654 (m, C=N), 1535 (s), 1352 $cm^{-1}$ (s, $NO_2$).

*Anal.* Calcd for $C_{15}H_{13}N_3O_4S$: C, 54.36; H, 3.95; N, 12.68. Found: C, 54.50; H, 4.08; N, 12.45.

**Registry No.**—**1Aa**, 4569-82-8; **5**, 7782-02-7; **6**, 7738-96-7; **8**, 7738-97-8; **7a**, 7738-98-9; **1Ac**, 7738-99-0; **10**, 7739-00-6; **12**, 7739-01-7; **7c**, 7739-02-8; **7b**, 7739-03-9.

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# The Oxidation of Organic Divalent Sulfur by Iodine. I. Alternative Pathways for Thiols as Determined by Structure[1]

JAMES P. DANEHY AND MICHAEL Y. OESTER

*Department of Chemistry, University of Notre Dame, Notre Dame, Indiana*

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While many water-soluble thiols are oxidized terminally to disulfides by iodine in aqueous potassium iodide, thiols which have a free β-carboxyl group are strongly inclined to further oxidation, apparently without going through the disulfide stage, and the ratio of higher oxidation product to disulfide increases with increasing initial dilution of the thiol. For 3-mercaptopropionic acid, mercaptosuccinic acid, and *o*-mercaptobenzoic acid the higher oxidation products are the corresponding sulfonic acids. For cysteine the higher oxidation product is 3-sulfinoalanine, the corresponding sulfinic acid. *o*-Mercaptobenzoic acid gives particularly high ratios of sulfonic acid to disulfide since the latter is unusually sensitive to further oxidation. It is suggested that a sulfenyl iodide is first formed in all cases, and that this intermediate is either attacked by thiol to give disulfide, or undergoes an intramolecular displacement reaction to form a five-membered cyclic intermediate which undergoes hydrolysis and further oxidation.

It has long been known that water-soluble thiols are rapidly oxidized by iodine in aqueous potassium iodide to disulfides, which are then resistant to further oxidation by small concentrations of iodine over a wide range of temperature and pH. Klason[2] first used the reaction as the basis for a quantitative procedure for the determination of thiols, but occasional reports have appeared of the overoxidation of certain thiols, *i.e.*, of the consumption of more than 1 equiv of iodine per mole of thiol. Dowler[3] reported that cysteine is not oxidized to cystine with iodine, "... provided but a small amount of cysteine is present and further provided that cysteine is added to the solution of iodine" (rather than *vice versa*). Bierich and Kalle[4] observed that the apparent SH values as determined iodometrically for solutions of cysteine and of reduced glutathione of known concentrations agreed approximately with the theoretical when sodium nitroprusside was used as indicator, but when starch was used as indicator consumptions of iodine were greater, the extent of the difference increasing with decreasing initial concentration of cysteine. Shinohara[5] demonstrated the much slower but ultimately complete oxidation of cystine to cysteic acid by the use of a large excess of iodine, but Lavine[6] has shown that cystine is completely resistant to iodine in water at 25–30°, provided the concentration of HI is molar or higher.

Lucas and King[7] made a study of the influences of several factors on the oxidation of a number of thiols by aqueous iodine. While their data on the effects of temperature and of pH are very interesting, the results are not definitive since they failed to realize that initial concentration is the overriding factor in those cases where the thiol is sensitive to overoxidation. They did demonstrate clearly, however, that individual thiols differ quite markedly in their behavior toward iodine. Simonsen[8] did realize the primary importance of concentration, insofar as cysteine is concerned, and attempted, though unsuccessfully, to isolate cysteinesulfinic acid (3-sulfinoalanine) as a reaction product. More recently Larrouquere[9] has studied the reaction of iodine with several thiols, but substantially all of the work was done with solutions of one initial concentration (0.005 *M* RSH).

Tables I and II give the experimental evidence for the two empirical generalizations: that initial concentration of thiol is of primary importance in determining the degree of overoxidation observed with a given thiol, and that thiols vary greatly in their susceptibility to overoxidation. The 12 thiols examined in the present study are easily divided into two groups: (A) those rather resistant to overoxidation, and (B) those highly susceptible to it. All of the members of group A could be satisfactorily assayed iodometrically in 0.01 *M* solution, but with further dilution each exhibits a small but significant degree of overoxidation. Even under the forcing conditions of inverted addition, however, the highest observed value (2.20) is far from the maximal value of 6, which would correspond to oxidation to sulfonic acid. The members of group B, though they differ among themselves, are all quite prone to overoxidation, even without resort to inverted addition.

There appear, then, to be two distinct, but closely related questions of chemical interest here. First,

(1) Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 14, 1966. Based on the M.S. dissertation of M. Y. Oester.

(2) P. Klason, *Ber.*, **14**, 409 (1881); **39**, 738 (1906).

(3) V. B. Dowler, *Proc. Am. Soc. Biol. Chem.*, **XXII**, XXXVIII (1928); with *J. Biol. Chem.*, **78** (1928).

(4) R. Bierich and K. Kalle, *Z. Physiol. Chem.*, **175**, 115 (1928).

(5) K. Shinohara, *J. Biol. Chem.*, **96**, 285 (1932).

(6) T. F. Lavine, *ibid.*, **109**, 141 (1935).

(7) C. C. Lucas and E. J. King, *Biochem. J.*, **26**, 2076 (1932).

(8) D. G. Simonsen, *J. Biol. Chem.*, **101**, 35 (1933).

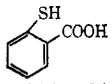
(9) J. Larrouquere, *Ann. Chim.* (Paris), **6**, 733 (1961).

TABLE I
CONSUMPTION OF IODINE BY THIOLS AS A FUNCTION OF INITIAL CONCENTRATION OF THIOLS[a] (GROUP A)

| Thiol | Molarity | Direct addn, I/SH | Inverted addn, I/SH |
|---|---|---|---|
| $HSCH_2COOH$ | 0.100 | 1.00 | ... |
| | 0.010 | 1.00 | 1.26 |
| | 0.001 | 1.04 | 1.30 |
| | 0.0001 | 1.13 | 1.44 |
| $CH_3CHCOOH$ (SH) | 0.100 | 1.00 | 1.12 |
| | 0.010 | ... | 1.18 |
| | 0.001 | 1.02 | 1.34 |
| | 0.0001 | 1.09 | 1.80 |
| $HSCH_2COOMe$ | 0.100 | 1.00 | 1.00 |
| | 0.010 | 1.01 | 1.04 |
| | 0.001 | 1.09 | 1.40 |
| | 0.0001 | 1.20 | 2.00 |
| $HSCH_2CH_2OH$ | 0.100 | 1.00 | 1.00 |
| | 0.010 | 1.01 | 1.00 |
| | 0.001 | 1.02 | 1.08 |
| | 0.0001 | 1.07 | 1.27 |
| 1-Thiosorbitol | 0.100 | 1.00 | 1.05 |
| | 0.010 | 1.00 | 1.03 (?) |
| | 0.001 | 1.20 | 1.50 |
| $HSCH_2CH_2NH_3^+ Cl^-$ | 0.100 | 1.00 | 1.03 |
| | 0.010 | 1.01 | 1.09 |
| | 0.001 | 1.02 | 1.34 |
| | 0.0001 | 1.03 | 2.20 |
| $HSCH_2CHCOOMe$ ($NH_3^+ Cl^-$) | 0.100 | 1.00 | 1.16 |
| | 0.010 | 1.05 | 1.24 |
| | 0.001 | 1.14 | 1.67 |
| $HSCH_2CH_2COOMe$ | 0.100 | ... | 1.03 |
| | 0.010 | ... | 1.06 |
| | 0.001 | ... | 1.08 |
| | 0.0001 | ... | 1.28 |

[a] Room temperature; self-pH; 0.1, 0.01, or 0.001 *N* iodine.

TABLE II
CONSUMPTION OF IODINE BY THIOLS AS A FUNCTION OF INITIAL CONCENTRATION OF THIOLS[a] (GROUP B)

| Thiol | Molarity | Direct addn, I/SH |
|---|---|---|
| $HSCH_2CH_2COOH$ | 0.100 | 1.00 |
| | 0.010 | 1.30 |
| | 0.004 | 1.70 |
| | 0.002 | 2.00 |
| | 0.001 | 2.53 |
| $HSCHCH_2COOH$ (COOH) | 0.100 | 1.10 |
| | 0.010 | 2.50 |
| | 0.001 | 4.5 |
| | 0.0001 | 5.8 |
|  | 0.200 | 1.85 |
| | 0.020 | 2.35 |
| | 0.010 | 2.50 |
| Acid insol in $H_2O$; dissolved in $AcO^-$ buffer at pH 6 | 0.004 | 2.79 |
| | 0.001 | 3.30 |
| | 0.0001 | 5.9 |
| $HSCH_2CHCOOH$ ($NH_3^+ Cl^-$) | 0.100 | 1.00 |
| | 0.050 | 1.03 |
| | 0.025 | 1.13 |
| | 0.0125 | 1.35 |
| | 0.0063 | 1.63 |

[a] Room temperature; self-pH; 0.1, 0.01, or 0.001 *N* iodine.

how does initial concentration of thiol affect the extent of overoxidation? Second, why are some thiols so much more sensitive to overoxidation than others?

## Discussion

**Mechanistic Suggestions.**—The literature contains little on a possible mechanism of oxidation of thiol to disulfide by aqueous iodine other than the reasonable suggestion by Kharasch,[10] corresponding to the first two reactions in the scheme below. The results presented here, however, suggest that the hypothetical sulfenyl iodide has at least two possible fates: attack

$$RSH + I_2 \longrightarrow RSI + HI$$

$$RSI \xrightarrow{RSH} RSSR + HI$$

$$RSI \xrightarrow{H_2O} RSOH + HI$$

$$RSOH + 2I_2 + 2H_2O \longrightarrow RSO_3H + 4HI$$

by another thiol, or thiolate anion, to give disulfide, or attack by water to give a sulfenic acid. In the latter case further oxidation to at least the sulfinic, and probably the sulfonic, acid stage would be expected. Support for the intermediacy of the sulfenyl iodide is furnished by Rheinboldt[11] and by Kolthoff and Harris[12] who showed that oxidation of tertiary thiols by iodine does not proceed beyond the formation of tertiary sulfenyl iodides which are stable, presumably, for the same reason that neopentyl halides are stable.

The remarkable favoring of disulfide formation among the thiols of group A, or for that matter even among those of group B, is simply an excellent example of the well-established generalization that thiols, or thiolate ions, are much more nucleophilic than water toward a common substrate. Nevertheless, as the likelihood of a sulfenyl iodide encountering a thiol decreases, as initial concentration of thiol decreases, the probability of hydrolysis increases, and this corresponds to our results. But why should some thiols be particularly susceptible to overoxidation?

Consideration of the four compounds whose pronounced tendency to overoxidation has been demonstrated reveals that they have a common structural feature: a carboxyl group on a carbon atom $\beta$ to the sulfur atom. The positional requirement for the carboxyl group is emphasized by the fact that mercaptoacetic acid and 2-mercaptopropionic acid belong in group A. That the free carboxyl group, or carboxylate anion, is involved is indicated by the fact that, while cysteine and mercaptosuccinic acid belong in group B, their esters belong in group A.

An intramolecular displacement reaction involving a five-membered cyclic intermediate, as illustrated in Scheme I, is suggested as a possible interpretation of the results. The initial attack of carboxylate anion, or of carboxyl group, on sulfur would have to be very rapid since it competes successfully with thiol. But one or more of the subsequent reactions would have to be slower, since titrations in which overoxidation is significant are characterized by fading end points. Alternatively, and not shown in Scheme I, further oxidation of the cyclic intermediate may precede the ultimate hydrolysis.

**Product Analysis and Kinetic Studies.**—The validity of the mechanistic suggestions has been checked, both from the standpoints of product analysis and of kinetics.

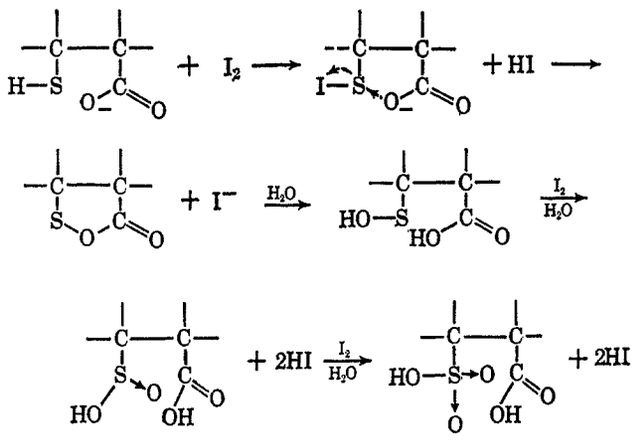
It has been assumed so far that terminal products of oxidation are disulfide, sulfonic acid, and no others. It is practical to determine disulfide quantitatively by reducing it to thiol, and determining the latter spectro-

(10) N. Kharasch, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Oxford, 1961, p 387.

(11) H. Rheinboldt and E. Motzkus, *Ber.*, **72**, 657 (1939); H. Rheinboldt and E. Mott, *ibid.*, **72**, 668 (1939).

(12) I. M. Kolthoff and W. E. Harris, *Anal. Chem.*, **21**, 963 (1949).

SCHEME I



photometrically after reaction with phosphotungstic acid.[13] It is possible to calculate what the ratio of disulfide to sulfonic acid should be from the experimentally determined [I]/[SH] ratio if the assumptions made are correct. The relationship between [RSSR]/[$RSO_3H$] and [I]/[SH] is shown.

$$RSH + I \longrightarrow 0.5RSSR$$

$$RSH + 6I \longrightarrow RSO_3H$$

$$I = 2RSSR + 6RSO_3H \quad (1)$$

$$RSH = 2RSSR + RSO_3H \quad (2)$$

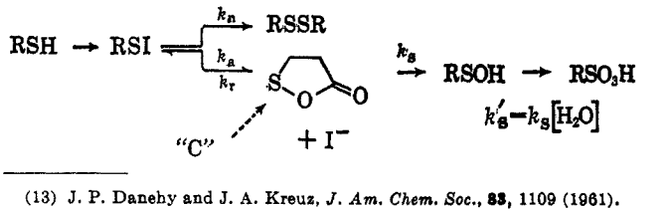
$$I = ([I]/[SH])RSH \quad (3)$$

Substituting eq 1 and 2 into eq 3, $2[RSSR] + 6\cdot[RSO_3H] = 2[RSSR]([I]/[SH]) + [RSO_3H]([I]/[SH])$, or $6[RSO_3H] - [RSO_3H]([I]/[SH]) = 2[RSSR]\cdot([I]/[SH]) - 2[RSSR]$, or $[RSO_3H](6 - [I]/[SH]) = [RSSR][2([I]/[SH]) - 2]$, or $[RSSR]/[RSO_3H] = (6 - [I]/[SH])/[2([I]/[SH]) - 2]$.

From the following additional considerations it is possible to calculate the number of millimoles of disulfide obtained from a given number of millimoles of thiol for a given [I]/[SH]. If $n[RSH] = 2m[RSSR] + p\cdot[RSO_3H]$ and $[RSSR]/[RSO_3H] = m/p = x$, then, since $p = m/x$ and $p = n - 2m$, $m/x = n - 2m$, or $m = nx - 2mx$, or $nx = 2mx + m = m(2x + 1)$, or $m = nx/(2x + 1)$.

In the case of 3-mercaptopropionic acid, for several concentrations of thiol the experimentally determined amounts of disulfide corresponded closely to the amounts calculated from the relationships just derived.

In addition to the over-all ratio of [RSSR] to [$RSO_3H$], calculable at the end of each reaction from the experimentally determined [I]/[SH] value, one can consider the instantaneous ratios of [RSSR] being formed to [$RSO_3H$] being formed, which, for a given initial concentration of RSH, will be maximal at the beginning of a titration, and zero at the end of the titration. It is possible to establish a definite relationship between the over-all [RSSR]/[$RSO_3H$] and the instantaneous [RSSR]/[$RSO_3H$] in the following way.



(13) J. P. Danehy and J. A. Kreuz, *J. Am. Chem. Soc.*, **83**, 1109 (1961).

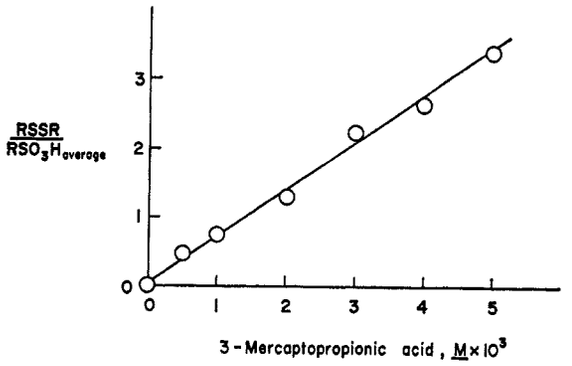



Figure 1.—[RSSR]/[$RSO_3H$]$_{av}$ *vs.* [RSH]$_{orig}$/2 in 0.5 *M* KI at pH 7.0.

The above diagram summarizes the assumptions and defines the terminology. Two possibilities must be considered: that in which the reverse reaction governed by $k_r$ is ignored, and that in which it is taken into account. If $k_r$ is negligible, then

$$R_i = \frac{[RSSR]}{[RSO_3H]_{inst}} = \frac{\frac{d[RSSR]}{dt}}{\frac{d[RSO_3H]}{dt}} = \frac{k_n[RSI][RSH]}{k_a[RSI]} = \frac{k_n}{k_a}[RSH]$$

If $k_r$ is not negligible, then

$$\frac{d[RSO_3H]}{dt} = k_a[RSI] - k_r["C"][I^-]$$

and

$$R_i = \frac{k_n[RSI][RSH]}{k_a[RSI] - k_r["C"][I^-]}$$

On the assumption of the steady state for the hypothetical cyclic intermediate

$$k_a[RSI] = k_r["C"][I^-] + k_s'["C"]$$

and

$$["C"] = \frac{k_a[RSI]}{k_r[I^-] + k_s'}$$

Substitution for ["C"] in the expression for $R_i$ gives

$$R_i = \frac{k_n[RSI][RSH]}{k_a[RSI] - \frac{k_ak_r[RSI][I^-]}{k_r[I^-] + k_s'}}$$

and simplifying

$$R_i = \frac{k_n}{k_a}[RSH]\left(\frac{k_r[I^-]}{k_s'} + 1\right)$$

From the relationships derived it is clear that when the reverse reaction is negligible the plot of $R_i$ *vs.* [RSH] should be linear with intercept at the origin. Even when the reverse reaction is not negligible the plot of $R_i$ *vs.* [RSH] should still be linear, provided only that the [$I^-$] is sufficiently high so as to remain substantially constant. From these linear relationships it follows that the over-all (or average) values for [RSSR]/[$RSO_3H$], calculated from the experimental values for [I]/[SH], should be precisely equal to the values for $R_i$ when the concentrations of thiol have fallen to exactly half of their initial values. In the case of 3-mercaptopropionic acid such a plot conforms to the expectations (Figure 1). It should also follow from the final expression derived that when iodide ion concentration is varied in a series of experiments in which the initial concentrations of thiol are the same, the plot of average values of [RSSR]/[$RSO_3H$] *vs.* iodide ion concentration should also be linear, though the intercept

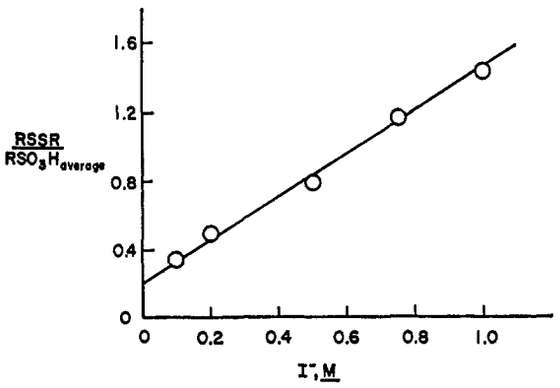



Figure 2.—[RSSR]/[$RSO_3H$]$_{av}$ *vs.* [$I^-$] at initial concentration of $10^{-3}$ *M* 3-mercaptopropionic acid at pH 7.0.

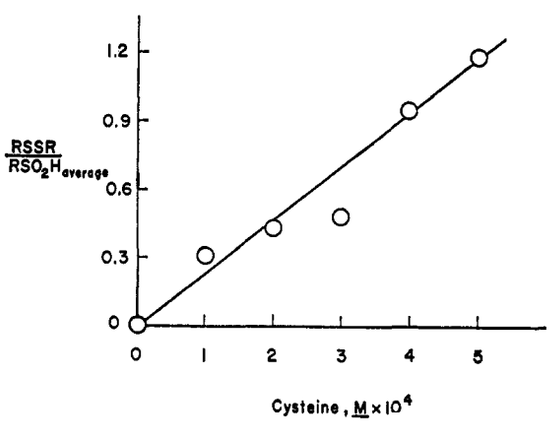



Figure 3.—[RSSR]/[$RSO_2H$]$_{av}$ *vs.* [RSH]$_{orig}$/2 in 0.02 *M* KI at pH 7.0.

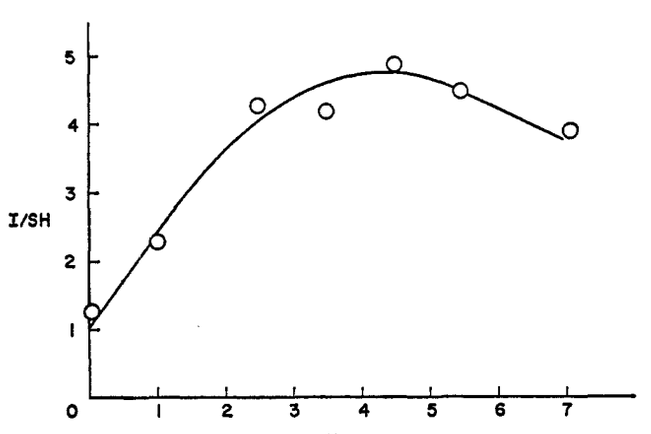



Figure 4.—[I]/[SH] *vs.* pH for 3-mercaptopropionic acid initially $10^{-3}$ *M*.

should depend on the exact initial concentration of thiol chosen. For 3-mercaptopropionic acid this expectation is also realized (Figure 2) and furnishes evidence in support of the view that the reverse reaction governed by $k_r$ is a reality.

In the case of cysteine, however, this treatment of the data does not give a linear plot. Nor did analytical determinations of disulfide (cystine) agree with the values calculated from the expressions derived. Moreover, the [I]/[SH] values obtained by inverted addition level off at 4, not 6. All these data are consistent with the conclusion reached 30 years ago by Lavine:[14] that 3-sulfinoalanine is an uncommonly stable

(14) T. F. Lavine, *J. Biol. Chem.*, **117**, 309 (1937).

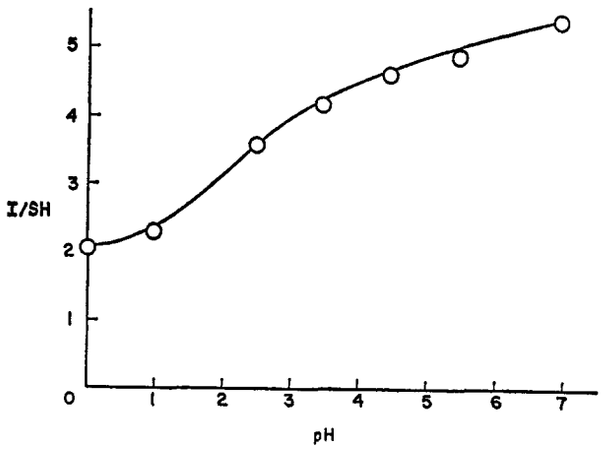



Figure 5.—[I]/[SH] *vs.* pH for mercaptosuccinic acid initially $10^{-3}$ *M*.

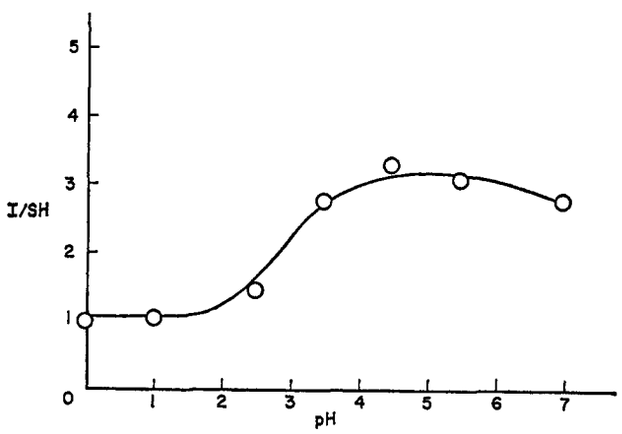



Figure 6.—[I]/[SH] *vs.* pH for 3-mercaptopropionic acid initially $10^{-3}$ *M* in 0.2 *M* KI.

sulfinic acid. Specifically, he stated that it could not be titrated directly with iodine, though it could be oxidized with an excess of iodine, as well as reduced to cystine in 1–2 *M* hydriodic acid. A plot of [RSSR]/[$RSO_2H$]$_{av}$ *vs.* [RSH]$_{orig}$/2 is linear (Figure 3).[15] Within the framework of the present investigation cysteine is atypical only in that oxidation does not appear to proceed beyond the sulfinic acid stage.

**pH Studies.**—Some experiments have been carried out in which [I]/[SH] ratios have been determined as a function of pH at a constant initial concentration of thiol sufficiently low ($10^{-3}$ *M*) to ensure appreciable overoxidation. The data in Figures 4 and 5 suggest, as might have been expected, that the carboxylate anion is the more actively participating species though the carboxyl group may participate when the ratio of the latter to the former is overwhelming. Specific differences in this respect are seen by comparing the two figures.

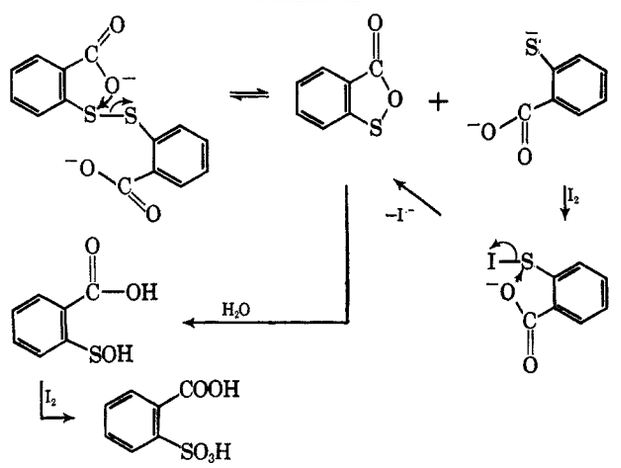
Experiments similar to those just described were carried out in the presence of 0.2 *M* KI. Comparison of Figure 4 with Figure 6, and of Figure 5 with Figure 7, gives additional evidence for the reality of the reverse reaction in which iodide ion participates, and suggests that the carboxyl group is less able to compete with the reverse reaction than is the carboxylate anion.

Figure 8 records the situation for cysteine, for which no convincing explanation can be offered.

(15) [RSSR]/[$RSO_2H$] = (4 − [I]/[SH])/[2([I]/[SH]) − 2].

**o-Mercaptobenzoic Acid.**—o-Mercaptobenzoic acid is more sensitive to overoxidation than any other thiol yet examined. Since the carboxyl group and sulfhydryl group are constrained in one plane with their adjacent carbon atoms by the aromatic ring the formation of the five-membered cyclic intermediate is sterically favored. But that is not the whole story. Suspicions aroused by the difficulty of obtaining final, stable end points in the titration of o-mercaptobenzoate with iodine led to the discovery that the corresponding disulfide reacts much more slowly than, but just as completely as, the thiol with iodine. A possible interpretation of these facts is suggested by Scheme II. Since

SCHEME II



iodine is in no way involved in the first step, it may well be that 2,2′-dithiodibenzoate ion is intrinsically unstable in aqueous solution. This possibility is under experimental investigation.

## Experimental Section

**Materials.**—We are grateful to Evans Chemetics, New York, N. Y., for generous gifts of mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, mercaptosuccinic acid, and 2-mercaptoethylammonium chloride; and to the Toni Company, Chicago, Ill., for generous gifts of cysteine hydrochloride methyl ester and 1-thiosorbitol. Cysteine hydrochloride monohydrate was purchased from Sigma Chemical Co., St. Louis, Mo. 2-Mercaptoethanol and methyl mercaptoacetate were purchased as Eastman Organic Chemicals from Distillation Products Industries, Rochester, N. Y. In each case it was ascertained that several samples could be titrated iodometrically in water over a range of concentrations to give a constant ratio of milliequivalents of iodine to milligrams of sample, and the purity of the samples was calculated on the assumption that this ratio corresponded to an [I]/[SH] ratio of one. In the case of o-mercaptobenzoic acid, also purchased from Distillation Products Industries, the product was recrystallized from benzene to a constant melting point of 164°.

Methyl 3-mercaptopropionate was synthesized as follows. 3-Mercaptopropionic acid (27.5 g), 75 ml of chloroform, 50 ml of methanol, and 1 ml of concentrated sulfuric acid were placed in a 200-ml, round-bottom flask under a Soxhlet extractor containing anhydrous magnesium sulfate and refluxed for 25 hr under a slight positive pressure of nitrogen. The reaction mixture was washed with water and held under vacuum at 35° to remove volatile liquids, and the remaining liquid was distilled at approximately 27 mm to give a main fraction boiling at 79–80°. The yield was 17.4 g of ester (56%).

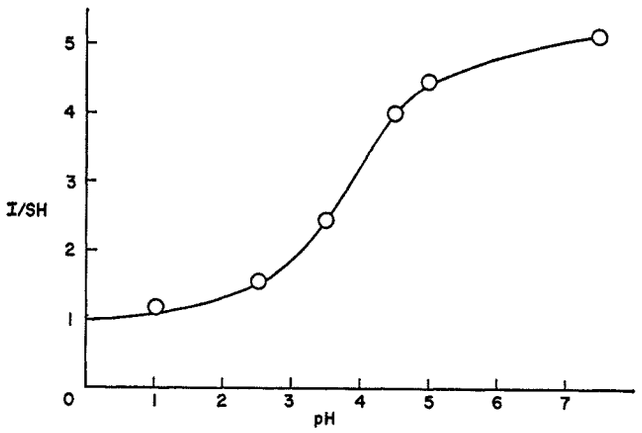



Figure 7.—[I]/[SH] *vs.* pH for mercaptosuccinic acid initially $10^{-3}$ *M* in 0.2 *M* KI.

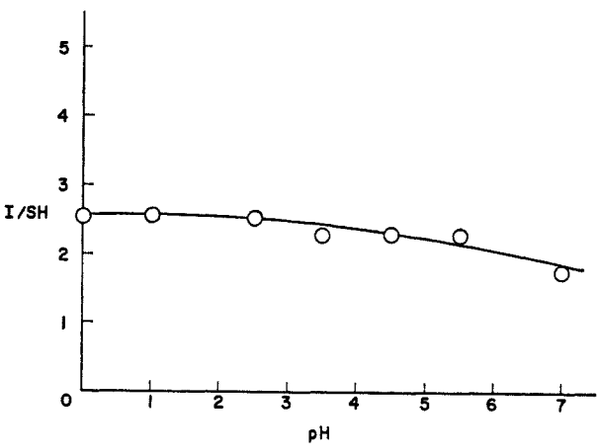



Figure 8.—[I]/[SH] *vs.* pH for cysteine initially $10^{-3}$ *M*.

**Titrations.**—For direct addition, thiol solutions varying in concentration from 0.5 to $10^{-4}$ *M* were titrated with solutions of iodine in aqueous potassium iodide either 0.1, 0.01, or 0.001 *N* I. All solutions were stirred magnetically and freshly prepared starch sols were used as indicator. For inverted addition aliquots of 0.1, 0.01, or 0.001 *N* I were titrated with thiol solutions varying in concentration from 0.1 to $10^{-4}$ *M*. Starch sol was added just before the color of the iodine became imperceptible.

In obtaining the data on which Figures 1 and 3 are based the iodide ion concentration was maintained constant by adding a suitable volume of a concentrated stock solution of potassium iodide and maintaining the pH value at 7.0 by adding 5 or 10 ml of 1 *M* phosphate buffer. The thiol concentration was varied by adding a suitable aliquot of a stock solution and the volume finally adjusted to 50 or 100 ml with boiled and cooled distilled water before starting the titration. By appropriately varying this procedure the studies on the effect of varying iodide ion concentration and pH were made.

**Registry No.**—Mercaptoacetic acid, 68-11-1; 2-mercaptopropionic acid, 79-42-5; mercaptoacetic acid methyl ester, 2365-48-2; 2-mercaptoethanol, 60-24-2; 1-thiosorbitol, 10036-50-7; 2-aminoethanethiol hydrochloride, 156-57-0; cysteine methyl ester hydrochloride, 7319-35-9; methyl 3-mercaptopropionate, 2935-90-2; 3-mercaptopropionic acid, 107-96-0; 2-mercaptosuccinic acid, 70-49-5; o-mercaptobenzoic acid, 147-93-3; cysteine hydrochloride, 10036-48-3.