Several explanations for the unusual bond lengths in FSSF can be proposed. First, they could be explained in valence bond theory as arising from a large contribution from the $F^-S{=}S^+F$ ionic structure. Such a structure would be energetically favorable on electronegativity grounds while unfavorable for species like HSSH on similar grounds. This argument is further supported by the d(SS) and d(SX) in ClSSCl and BrSSBr which exhibit similar shortening and lengthening but with less drastic effects than in FSSF. A large chemical shift to high fields for the F^{19} n.m.r. absorption also supports this interpretation.[25]

An alternative explanation for the bond lengths is possible with qualitative molecular orbital theory. This method was first suggested by Professor Lipscomb to account for the short d(OO) and long d(FO) in FOOF.[4] By analogy, it is also applicable to FSSF. Just as for O_2, the S_2 molecule is in a $^3\Sigma$ ground state. The two unpaired electrons are in antibonding π-molecular orbitals. A fluorine atom can bond with one of these sulfur electrons giving a resultant three-center bond. This could qualitatively account for the unusual bond lengths and the dihedral angle. The repulsive effect of the fluorine nonbonded electrons is proposed as the reason why this type of bonding is preferred over the normal covalent bonding present in H_2S_2.

A third way of accounting for the bond lengths is by Linnett's theory of "double quartet formulation of the octet." This method was proposed to explain the structure of FOOF.[29] By analogy, it should also be applicable to FSSF although Linnett cautioned against applying it to S_2Cl_2 and S_2Br_2 (and S_2F_2 by inference) on the basis that it is difficult to know whether the number of electrons associated with the sulfur atoms in these molecules should be restricted to eight.

In summary, the S–S and S–F distances in FSSF are anomalously short and long, respectively. They cannot be described as simple covalent single bonds. Simple arguments suffice to show that these unusual bond lengths can be accommodated by the conventional theories of chemical bonds. The arguments are *a posteriori*, nonquantitative, and, particularly in the case of the ionic explanation, not applicable to some other molecules, so that an element of skepticism as to their strength is justified.

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(29) J. W. Linnett, *J. Chem. Soc.*, 4663 (1963).

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The Kinetics of the Exchange of Sulfur-35 between Thiosulfate and Sulfide[1a]

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The rate of exchange of sulfur between sodium sulfide-S-35 and sodium thiosulfate has been measured at temperatures between 100 and 140°. The order in sulfide is less than 1, and that in thiosulfate is greater than 1; however, in the presence of added sulfite, the order in both sulfide and thiosulfate becomes 1.0. Using data obtained in the presence of added sulfite, and also data obtained by adding disulfide, the mechanism of the exchange has been concluded to be a displacement on the outer sulfur of thiosulfate by sulfide ion (eq. 2). (Note that sulfide is shown as S^{-2} rather than HS^- in order to simplify the chemical equations.[2]) However, the mechanism is complicated by a simultaneous exchange of S-35 between disulfide and thiosulfate (eq. 12). Trisulfide and higher polysulfides probably also react in this way, but these reactions are not important in the present system. In addition to these reactions, an exchange occurs between sulfide and disulfide (eq. 5). The rate law for the exchange includes a term in sulfide and one in disulfide (eq. 6). It is shown that this rate law plus the equilibrium reaction (2) explains both the nonintegral kinetic orders in the absence of sulfite and the integral orders produced by the addition of sulfite. The activation energy for k_1 is 17.8 kcal./mole, and the apparent activation energy for the sum of the two terms in eq. 6 is 17.4 kcal./mole. The following values for the rate constants are obtained at 100°, pH 12.46, μ = 2.3, and (Na^+) 1.5 M: $k_1 = 9.8 \times 10^{-5}$, $k_2 = 9.5 \times 10^{-3}$, $k_{-1} = 0.13$ (all in l. mole^{-1} sec.$^{-1}$).

Introduction

An exchange of radiosulfur is known to occur between sulfide[2] and thiosulfate ions.

$$S^{*-2} + {}^-S\text{–}SO_3^- \rightleftharpoons S^{-2} + {}^-S^*\text{–}SO_3^-$$

In 1939, in one of the first papers reporting the use of sulfur-35, Voge and Libby[3] demonstrated that the exchange occurs, and in 1951 Ames and Willard[4] commented on this exchange on the basis of a few preliminary data. This reaction is an example of a nucleophilic displacement at a noncarbon atom, and such reactions are of considerable current interest. In addition, the reaction bears a formal similarity to the reaction of hydroxide with thiosulfate to produce sulfide and sulfate.

$$OH^- + {}^-S\text{–}SO_3^- \longrightarrow HS^- + {}^-O\text{–}SO_3^-$$

This reaction was reported earlier.[5,6] It is slower than

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(2) In all of the reactions in this paper, sulfide ions will be represented as S^{-2}, although at the pH used the chief sulfide species is HS^-. This simplification eliminates the necessity of writing all the fast acid–base reactions which occur, and it in no way affects the final kinetic equations. The reader, however, should bear the simplification in mind.

(3) H. H. Voge and W. F. Libby, *J. Am. Chem. Soc.*, **59**, 2474 (1937); H. H. Voge, *ibid.*, **61**, 1032 (1939).

(4) D. P. Ames and J. E. Willard, *ibid.*, **73**, 164 (1951).

(5) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., New York, N. Y., 1962, pp. 59–70.

(6) W. A. Pryor, *J. Am. Chem. Soc.*, **82**, 4794 (1960).

the reaction reported here, occurring at measurable rates only at 250° and higher, and it was concluded to involve an attack on the inner sulfur atom.

Experimental

Reagents.—Sodium sulfide solutions were prepared by washing large crystals of $Na_2S \cdot 9H_2O$ with distilled water and dissolving them in distilled, boiled water. All solutions were stored under nitrogen. Solutions of sodium disulfide were prepared by heating equimolar amounts of sulfur and sodium sulfide for 15 hr. at 100° under nitrogen. Sodium hydroxide solutions were prepared by the method of Sørensen.[7] The solutions of sodium sulfide and sodium thiosulfate were standardized against potassium iodate. Solutions of radioactive sodium sulfide were prepared by dissolving sodium sulfide-S-35 obtained from Nuclear Chicago Corporation in a solution of inactive sodium sulfide.

pH.—All pH values were measured at 30° with a Beckman Model G pH meter with Type E lithium glass electrodes standardized against buffers of pH 12.5.

Sample Preparation and Counting Technique.—The kinetic runs were followed by measuring the increase of the radioactivity of thiosulfate. Thiosulfate was separated from the solution containing sodium sulfide and any other inactive reagents by precipitation with a solution of nickel ethylenediamine nitrate[4]. The nickel complex was prepared by mixing a solution of nickel nitrate and ethylenediamine (99%). The pink-violet precipitate of $Ni(ethylenediamine)_3S_2O_3$ was transferred as a slurry into a demountable filtration device[8] containing a disk of filter paper. The precipitate was washed twice with water and twice with ethyl alcohol. The filtration device was removed leaving a disk of precipitate on the filter paper. After drying, the sample was counted in a container which exposes a fixed amount of the surface to the counter tube. It was not necessary to separate the two sulfur atoms of thiosulfate since the nonequivalence of those atoms is well established.[4] An infinite thickness technique was used in order to avoid self-absorption and back-scattering corrections. The counter was a proportional flow counter. The samples of every kinetic run were measured within a few hours so that no decay correction was necessary.

A slightly modified procedure was used in the experiments done with added sodium disulfide because of the coprecipitation of the disulfide upon addition of the complexing solution. After addition of the complexing solution, the complex was decomposed by addition of 6 ml. of 0.2 *N* hydrochloric acid, and the solution was filtered to remove the black precipitate of nickel sulfide and disulfide. The filtrate was treated with a few drops of concentrated sodium hydroxide and 0.5 ml. of the complexing solution to obtain the pure nickel ethylenediamine thiosulfate complex.

Procedure Used in Exchange Experiments.—Aliquots of inactive and active sodium sulfide, sodium thiosultate, and other reagents necessary to give the desired concentrations, pH, and ionic strength were added to a volumetric flask and diluted to the mark. The solution was chilled and then aliquots of it were transferred to ampoules. A gentle nitrogen current was passed through the chilled samples for about 15 min. and then the ampoules were sealed. The ampoules were put into an oil bath and removed at regular intervals.

Calculations.—Values of R, the rate of the reaction between sulfide and thiosulfate, were calculated from[9]

$$R = \frac{ab}{a + b} \frac{\ln 2}{t_{1/2}}$$

where a and b are the total concentrations of sulfide and thiosulfate, and $t_{1/2}$ is the half-life (in seconds) for the incorporation of radiosulfur into the thiosulfate. In the presence of added disulfide, the following equation was used.

$$R = \frac{(a + 2c)b}{a + 2c + b} \frac{\ln 2}{t_{1/2}}$$

where c is the total concentration of disulfide. The derivation of these equations is given in the text.

Data and Discussion

Tables I and II give kinetic data in which the concentrations of either sulfide or thiosulfate are varied. These data show the order in thiosulfate to be 1.14 ± 0.03 and in sulfide to be 0.85 ± 0.03 at constant ionic strength, sodium ion concentration, pH, and at 100°. The deviation of these orders from unity is outside experimental error and is significant.

TABLE I

ORDER IN THIOSULFATE[a]

$(Na_2S_2O_3)$, mole l.$^{-1}$	Ionic strength	(Na_2SO_3), mole l.$^{-1}$	$R \times 10^6$, moles l.$^{-1}$ sec.$^{-1}$	$k \times 10^4$, l. mole^{-1} sec.$^{-1}$
0.0403[c]	2.28	..	0.792	2.47
0.0805[c]	2.28	..	1.59	2.48
0.322[c]	2.28	..	8.88	3.46
0.483[c]	2.28	..	12.4	3.23
0.0402[c]	2.28	0.20	0.318	0.994
0.0805[c]	2.28	0.20	0.647	1.01
0.161[c]	2.28	0.20	1.43	1.12
0.322[c]	2.28	0.20	2.78	1.08
0.485[c]	2.28	0.20	4.27	1.11
0.0405[b]	1.88	..	0.861	2.67
0.081[b]	1.88	..	1.916	2.97
0.162[b]	1.88	..	4.11	3.18
0.324[b]	1.88	..	9.23	3.58
0.486[b]	1.88	..	14.1	3.64

[a] In all runs, (Na_2S) = 0.0796 *M*, 100.0°, pH 12.46. [b] Ionic strength adjusted with sodium chloride. [c] Ionic strength adjusted with sodium sulfate, and (Na^+) = 1.52 *M*.

TABLE II

ORDER IN SULFIDE[a]

(Na_2S), mole l.$^{-1}$	Ionic strength	(Na_2SO_3), mole l.$^{-1}$	$R \times 10^6$, moles l.$^{-1}$ sec.$^{-1}$	$k \times 10^4$, l. mole^{-1} sec.$^{-1}$
0.0382[c]	2.05	..	1.18	3.82
0.0764	2.05	..	1.88	3.04
0.153[c]	2.05	..	3.43	2.77
0.305[c]	2.05	..	6.95	2.81
0.0382[c]	2.05	0.20	0.312	1.01
0.0764[c]	2.05	0.20	0.698	1.13
0.153[c]	2.05	0.20	1.61	1.30
0.305[c]	2.05	0.20	3.10	1.26
0.0145[b]	2.28	0.20	0.129	1.10
0.0362[b]	2.28	0.20	0.289	0.985
0.0796[b]	2.28	0.20	0.647	1.00
0.152[b]	2.28	0.20	1.40	1.14
0.304[b]	2.28	0.20	3.78,	1.51

[a] In all runs, $(Na_2S_2O_3)$ = 0.081 *M*, 100.0°. [b] Ionic strength adjusted with sodium sulfate; $(Na^+) \doteq 1.52$ *M*; pH not adjusted. [c] Ionic strength adjusted to 2.05 and (Na^+) to 1.48 *M* using sodium chloride and sodium sulfate; pH adjusted to 13.1 using sodium hydroxide.

Since it was possible that disulfide ions were present as an impurity and were responsible for the nonintegral kinetic orders observed, experiments were performed in which the disulfide concentration was systematically varied. In addition, experiments were done with added sodium sulfite, since sulfite is known to react with disulfide to produce thiosulfate and sulfide.

Table III gives data on the effect of added sodium disulfide. The presence of disulfide ions produces a much faster rate of exchange. For example, the addi-

(7) H. T. S. Britton, "Hydrogen Ions," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 319.

(8) F. C. Henriques, G. B. Kistiakowsky, C. Margenetti, and W. G. Schneider, *Ind. Eng. Chem., Anal. Ed.*, **18**, 349 (1946).

(9) For the definition of the rate of exchange R, its determination, the relation between R, the rate constant k, and the order of the reaction with respect to the reagents, see: (a) R. M. Duffield and M. Calvin, *J. Am. Chem. Soc.*, **68**, 557 (1946); (b) G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, New York, N. Y., 1949, p. 285; (c) ref. 4.

TABLE III

EFFECT OF SODIUM DISULFIDE ON THE RATE OF THE EXCHANGE

(Na_2S), mole $l.^{-1}$	(Na_2S_2), mole $l.^{-1}$	$R \times 10^6$, moles $l.^{-1}$ $sec.^{-1}$
0.0796[a]	0.0	1.59
0.0796[a]	0.0101	7.44
0.0796[a]	0.0203	16.40
0.0796[a]	0.0304	22.7
0.0796[a]	0.0405	32.1
0.0[b]	0.0290	7.22
0.0[b]	0.0145	3.7

[a] $(Na_2S_2O_3)$ = 0.0805 M, 100.00°, ionic strength is adjusted to 2.28 with sodium sulfate, (Na^+) = 1.52 M. [b] $(Na_2S_2O_3)$ = 0.0403 M, ionic strength adjusted to 2.16, T = 100.00°.

tion of 0.04 M disulfide to 0.08 M sulfide increases the rate 20-fold.

The data given in the last two lines of Table III show that an exchange occurs between disulfide and thiosulfate in the absence of sulfide. This exchange is a direct exchange and does not involve a mechanism in which disulfide is first converted to sulfide which then undergoes exchange. This follows from the fact that the exchange of disulfide with thiosulfate is actually *faster* than the exchange of sulfide with thiosulfate. For example, for 0.04 M thiosulfate and 0.03 M disulfide, the rate of exchange is 7×10^{-6} (sixth line in Table III), whereas for 0.04 M thiosulfate and 0.08 M sulfide the rate of exchange is only 0.8×10^{-6} (first line of Table I). This eliminates a mechanism in which disulfide exchanges with thiosulfate by going through the disproportionation

$$2\ {}^-S\text{-}S^- \rightleftharpoons S^{-2} + {}^-S\text{-}S\text{-}S^-$$

Table IV shows the effect of added sodium sulfite. The presence of sulfite ions strongly retards the rate. For example, the addition of 0.02 M sulfite reduces the rate to about half its value, and further additions of sulfite ion reduce the rate still further. Since these concentrations of sulfite greatly exceed the possible concentrations of a disulfide impurity, it is clear that the effect of sulfite is not merely to convert disulfide impurities to sulfide. In fact, the data of Table IV show that the

TABLE IV

EFFECT OF SODIUM SULFITE ON THE RATE OF THE EXCHANGE[a]

(Na_2SO_3), mole $l.^{-1}$	$R \times 10^6$, mole $l.^{-1}$ $sec.^{-1}$
0.0	1.59
0.003	1.29
0.006	1.18
0.012	0.945
0.02	0.868
0.04	0.729
0.06	0.688
0.2	0.647

[a] In all runs: (Na_2S) = 0.0796 M, $(Na_2S_2O_3)$ = 0.0806 M, pH 12.46, 100.0°; the ionic strength was adjusted to 2.28 using sodium sulfate; and (Na^+) = 1.52 M.

rate is proportional to the inverse of the sulfite concentration. Figure 1 is a graph of R *vs.* $1/(SO_3^{-2})$ and a linear relationship is obtained above 0.01 M sulfite. Therefore, the rate is related to the sulfite ion concentration as in eq. 1.

$$R = A + \frac{B}{(SO_3^{-2})} \qquad (1)$$

The Mechanism of the Exchange.—As we have seen, the rate is decreased by the addition of sulfite, and both the kinetic law (eq. 1) and the amounts of sulfite

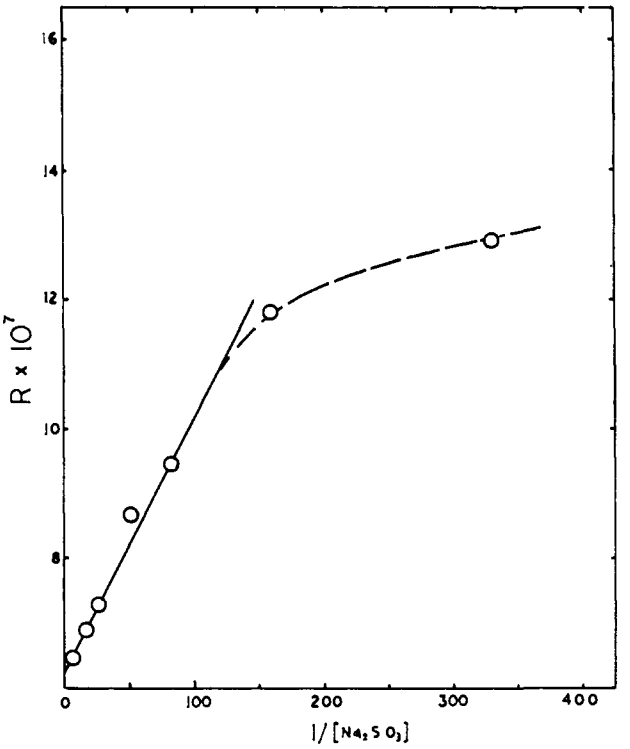

Fig. 1.—Effect of sodium sulfite.

involved indicate that the effect of sulfite is not merely due to the removal of impurities. This rate effect of sulfite can be explained if disulfide ions are produced in some equilibrium reaction. The retarding effect of sulfite would then arise from its known reaction with disulfide to convert it to sulfide. Since disulfide has been shown to exchange faster than sulfide, the conversion of disulfide to sulfide would slow the exchange reaction.

We therefore postulate the mechanism for this exchange which is shown below.

$$S^{-2} + S_2O_3^{-2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S_2^{-2} + SO_3^{-2} \qquad (2)$$

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{(S_2^{-2})(SO_3^{-2})}{(S^{-2})(S_2O_3^{-2})} \qquad (3)$$

The effect of disulfide on the rate arises from the direct exchange of disulfide with thiosulfate

$$\overset{*}{S}_2^{-2} + S_2O_3^{-2} \overset{k_2}{\rightleftharpoons} S_2^{-2} + \overset{*}{S}_2O_3^{-2} \qquad (4)$$

(We will discuss the mechanism of this direct exchange below.) The disulfide becomes radioactive through its known rapid exchange with sulfide.

$$\overset{*}{S}^{-2} + {}^-S\text{-}S^- \overset{\text{fast}}{\rightleftharpoons} S^{-2} + {}^-\overset{*}{S}\text{-}S^- \qquad (5)$$

The routes which sulfur-35 follows, therefore, can be schematically indicated as is shown below, where the dotted lines show the additional path for incorporation of sulfur-35 which is provided by eq. 4 and 5.

$$S^{*-2} + S_2O_3^{-2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{*}{S}_2^{-2} + SO_3^{-2} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} S^{-2} + \overset{*}{S}_2O_3^{-2}$$

fast ... k_2

Derivation of the Kinetic Law for the Exchange.—Let the concentrations be given as[10]

x radioactive sulfide
y radioactive thiosulfate
z radioactive disulfide
a total sulfide
b total thiosulfate
c total disulfide

The rate of appearance of radioactivity in thiosulfate is given by the following equations.[9a]

$$\left(\frac{dy}{dt}\right)_1 = k_1(S^{-2})(S_2O_3^{-2})(x/a - y/b)$$

$$\left(\frac{dy}{dt}\right)_2 = k_2(S_2^{-2})(S_2O_3^{-2})(z/2c - y/b)$$

The first equation accounts for the exchange between sulfide and thiosulfate and the second for the exchange between disulfide and thiosulfate. A direct result of the assumption that disulfide exchanges rapidly with sulfide is

$$\frac{x}{a} = \frac{z}{2c}$$

The over-all exchange is then given by

$$\left(\frac{dy}{dt}\right) = \left(\frac{dy}{dt}\right)_1 + \left(\frac{dy}{dt}\right)_2 =$$

$$[k_1(S^{-2})(S_2O_3^{-2}) + k_2(S_2^{-2})(S_2O_3^{-2})](x/a - y/b)$$

If we define

$$R = k_1(S^{-2})(S_2O_3^{-2}) + k_2(S_2^{-2})(S_2O_3^{-2}) \quad (6)$$

we can write

$$\left(\frac{dy}{dt}\right) = R\left(\frac{x}{a} - \frac{y}{b}\right)$$

With the aid of the following (see also Duffield and Calvin[9a])

$$x + y + z = x_\infty + y_\infty + z_\infty$$

$$\frac{x_\infty}{a} = \frac{y_\infty}{b} = \frac{z_\infty}{2c}$$

the following equation can be derived.

$$R = \frac{(a + 2c)b}{a + 2c + b}\,\frac{\ln 2}{t_{1/2}} \quad (7)$$

Except in the case where disulfide has been added, this equation can be reduced to

$$R = \frac{ab}{a + b}\,\frac{\ln 2}{t_{1/2}} \quad (8)$$

without any appreciable error in the results.

Confirmation of the Proposed Mechanism.—Four sets of experiments confirm this mechanism. The first is the dependence of the rate on $1/(SO_3^{-2})$. The substitution of eq. 3 into eq. 6 gives

$$R = k_1(S^{-2})(S_2O_3^{-2}) + k_2K_{eq}\,\frac{(S^{-2})(S_2O_3^{-2})^2}{(SO_3^{-2})} \quad (9)$$

(10) The symbol z represents the concentration of disulfide which has one labeled sulfur. The amount of S-35 is so small that the concentration of disulfide with two labeled sulfur atoms can be ignored.

Equation 9 predicts that a graph of R *vs.* $1/(SO_3^{-2})$ will be a straight line at any given concentration of sulfide and thiosulfate. As we have already seen (Fig. 1), such a plot is linear for concentrations of sulfite greater than 0.01 M. For concentrations of sulfite smaller than 0.01 M, the actual amount of sulfite present is somewhat greater than the amount added because of equilibrium (2).

The second set of experiments confirming this mechanism concerns the rate dependence on disulfide. Equation 6 predicts a linear relationship between R and the concentration of disulfide. This is verified by the data of Table III. A graph of R *vs.* the concentration of disulfide gives a straight line with slope 7.7×10^{-4}. (In calculating R for these runs, eq. 7 must be used. The use of eq. 8 does not yield a straight line relationship.)

The third set of experiments concerns the nonintegral kinetic orders observed. In the absence of externally added sulfite or disulfide, the concentration of disulfide equals that of sulfite. Therefore, eq. 3 can be rearranged to give

$$(S_2^{-2}) = K_{eq}^{1/2}(S^{-2})^{1/2}(S_2O_3^{-2})^{1/2} \quad (10)$$

Under these conditions, the rate of exchange is given by

$$R = k_1(S^{-2})(S_2O_3^{-2}) + k_2K_{eq}^{1/2}(S^{-2})^{1/2}(S_2O_3^{-2})^{1/2} \quad (11)$$

Thus in the absence of externally added sulfite or disulfide, the proposed mechanism predicts that the exchange should have a dependence on the thiosulfate concentration which is between 1 and 1.5. The actual value observed is 1.14. The proposed mechanism predicts that the order in sulfide should be between 0.5 and 1.0. The actual value is 0.85.

The fourth confirmation of the mechanism concerns experiments done in the presence of added concentrations of sulfite. Equation 9 leads to the prediction that the presence of an infinite concentration of sulfite should lead to a first-order rate dependence on both sulfide and thiosulfate. Experiments done in the presence of 0.2 M sulfite show that the order in thiosulfate becomes 1.04 ± 0.02, and the order in sulfide increases from 0.85 to 1.0 for concentrations of sulfide below 0.15 M. For concentrations of sulfide greater than this, the order increases further to about 1.1 (see Fig. 2); the explanation for this is not understood.

Temperature Dependence.—Table V gives data on the temperature dependence of the rate both in the presence and absence of 0.2 M added sodium sulfite. The Arrhenius activation energy is 17.8 ± 0.2 kcal./mole in the presence of sulfite and 17.4 ± 0.2 kcal./mole in its absence. The activation energy obtained

TABLE V

TEMPERATURE DEPENDENCE[a]

Temp., °C.	$k \times 10^4$[b]	$k \times 10^4$[c]
100	2.44	0.925
110	4.25	2.01
120	8.49	3.36
130	14.4	5.77
140	23.9	10.1

[a] In all runs, $(Na_2S_2O_3) = 0.0808$ M, $(Na_2S) = 0.0796$ M, ionic strength adjusted to 2.05 with sodium sulfate. [b] No sodium sulfite added. [c] In presence of 0.2 M sodium sulfite.

in the presence of sulfite is that for the first term of eq. 6 specifically, while that obtained in its absence is the apparent activation energy for the sum of the two terms.

Specific Values for the Rate Constants.—Since experiments were done at 100° using added sulfite and disulfide, all of the rate constants can be calculated at that temperature. The value of k_1 in eq. 9 can be calculated from the intercept of Fig. 1. The value obtained is $k_1 = 9.8 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$. The slope of the graph of R *vs.* the concentration of disulfide is equal to $k_2(S_2O_3^{-2})$ as given in eq. 6, and k_2 is obtained[11] from this graph as 9.5×10^{-3} l. mole^{-1} sec.$^{-1}$. The slope of the straight line portion of Fig. 1 is equal to $k_2K_{eq}(S^{-2})(S_2O_3^{-2})^2$, as is shown in eq. 9. Using the previously calculated value of k_2 and the slope from Fig. 1, K_{eq} can be found to be 7.6×10^{-4}. The value of 0.13 l. mole^{-1} sec.$^{-1}$ can then be calculated for k_{-1} from the above values of k_1 and K_{eq}. (All these rate constants are at 100°, pH equal to 12.46, ionic strength of 2.3, and a sodium ion concentration of 1.5 M.) These constants lead to correct values of R if eq. 6 or 9 is used. (Equation 6 is useful if disulfide is in excess and 9 if sulfite is in excess.) However, if eq. 11 is used, it is found that the experimental values of R are from 12% larger to 45% smaller than calculated. Equation 11 was derived by assuming that the concentrations of disulfide and sulfite are identical. This is not true if there are any impurities present or if the equilibrium given in eq. 12 occurs (eq. 12 is given below). At the point where the difference between the calculated and the experimental values of R is as large as 45%, an alteration in the concentration of disulfide as small as 1×10^{-3} M (*i.e.*, 0.25% of the concentration of the reagent in excess) would be sufficient to explain this difference.

Effect of pH.—Table VI gives data showing the effect of pH. Solutions more acidic than a pH of 11.9 could not be investigated due to hydrogen sulfide being evolved. Over the range 11.91 to 13.3, the rate is independent of pH. At higher values of pH, the rate increases; in these solutions, a strong yellow color rapidly appears at 100° which remains after the solutions are cooled. Evidently some decomposition occurs in these very alkaline solutions.

TABLE VI

EFFECT OF pH[a]

pH	Ionic strength	$R \times 10^6$, mole l.$^{-1}$ sec.$^{-1}$
11.91[b]	1.88	1.82
12.04[b]	1.88	1.82
12.18[b]	1.88	1.88
12.33[b]	1.88	1.88
12.46[b]	1.88	1.92
12.46[c]	1.31	1.34
12.91[c]	1.31	1.32
13.14[c]	1.31	1.33
13.39[c]	1.31	1.65
13.41[c]	1.31	1.90
13.67[c]	1.31	2.73

[a] In all runs $(Na_2S_2O_3) = 0.0805$ M, $(Na_2S) = 0.0796$ M, and the temperature is 100.0°. [b] Ionic strength adjusted with sodium chloride, $(Na^+) = 1.72$ M, pH adjusted with hydrochloric acid. [c] Ionic strength adjusted with sodium chloride, $(Na^+) = 1.53$ M, pH adjusted with sodium hydroxide.

(11) A value of k_2 can also be obtained from the last two lines in Table III. The value obtained in this way is 6.3×10^{-3}, in fair agreement with the above value. The value from the slope of the graph of R *vs.* (S^{-2}) is the most accurate.

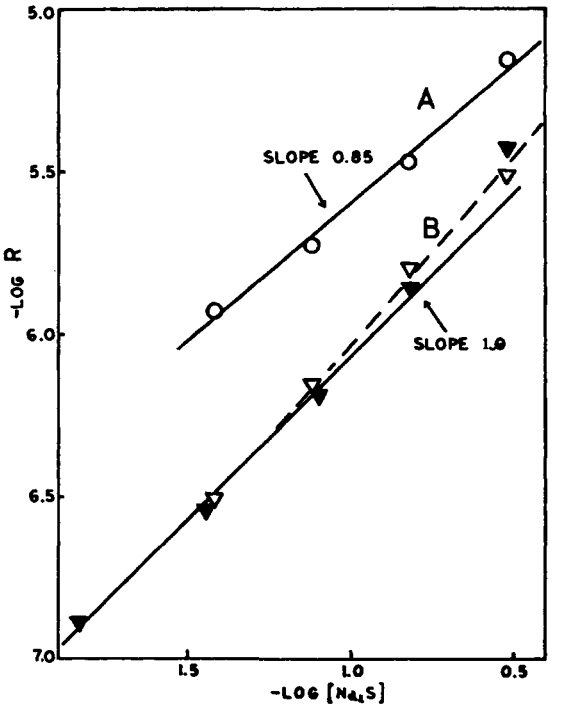

Fig. 2.—Order in sulfide: line A, pH adjusted to 13.1; line B, sodium sulfite added; ▼, pH not adjusted; ▽, pH adjusted to 13.1 (in this region the rate does not depend on the pH).

It should be pointed out that Table VI gives pH values measured at 30° and rates measured at 100°. Based on the values of the two dissociation constants of hydrogen sulfide at 25°, HS^- is the only species of importance between the pH values of 10 and 13. However, it is conceivable that either the pH values of these solutions are different or that the dissociation constants of hydrogen sulfide are different at 100°, and that the amount of S^{-2} begins to become appreciable above 13.3. If that were true, and if S^{-2} undergoes the exchange reaction some 50 times faster than HS^-, then the increase in rate observed above pH 13.3 could be ascribed to the onset of reaction by sulfide in addition to bisulfide. We do not favor this alternative, and prefer to regard the increase in rate as a spurious result of an unidentified decomposition reaction, but this is an alternative not excluded by our data.

Effect of Ionic Strength and of Positive Ions.—Table VII gives data on the variation in the rate of exchange produced by changing the ionic strength and the concentration of sodium ions. (Ionic strengths were calculated on the basis of molarities.) A plot of log R *vs.* the square root of the ionic strength is linear,

TABLE VII

EFFECT OF IONIC STRENGTH AND CONCENTRATION OF SODIUM IONS[a]

(Inert salt)	(Na^+)	Ionic strength	$R \times 10^6$, mole l.$^{-1}$ sec.$^{-1}$
0.7[b]	1.02	1.18	1.21
1.4[b]	1.721	1.88	1.91
2.1[b]	2.421	2.58	2.65
0.1[c]	0.521	0.78	0.859
0.2[c]	0.720	1.08	0.924
0.6[c]	1.52	2.28	1.57
0.8[c]	1.92	2.88	1.82

[a] In all runs $(Na_2S) = 0.0796$ M, $(Na_2S_2O_3) = 0.0810$ M, pH 12.46, 100.0°. [b] Sodium chloride. [c] Sodium sulfate.

although these experiments were done at concentrations where the Brønsted–Christiansen–Scatchard equation does not apply. However, the slope of the graph of log R *vs.* $\mu^{1/2}$ is not the same when the ionic strength is adjusted with sodium chloride as when it is adjusted with sodium sulfate. The two slopes are 0.646 and 0.431, respectively.

A graph of log R *vs.* the square root of the sodium ion concentration is also linear, with slopes of 0.582 and 0.537 when the adjustment is made with sodium chloride and sodium sulfate, respectively. It is clear that the concentration of sodium ions correlates the rates better than does the ionic strength. At the same value of the ionic strength, the rate constant may differ by as much as 60% for runs in which sodium chloride or sodium sulfate is used; at the same sodium ion concentration, however, the rates do not differ by more than 15%. It is not unexpected that the rate is correlated better by the concentration of positive ions than by the ionic strength in a reaction between two negative ions.[12]

One further feature of the rate behavior in the presence of inert salts is worth pointing out. The order of the exchange in thiosulfate was measured with both sodium sulfate and sodium chloride as the inert salt. In the former case, the sodium ion concentration as well as the ionic strength could be held constant; however, when sodium chloride was used, the ionic strength was held constant but the sodium ion concentration varied (last five lines of Table I). Nevertheless, the order in thiosulfate was observed to be almost the same regardless of which inert salt was used. The orders were 1.14 and 1.13 for sodium chloride and sodium sulfate runs, respectively.

Conclusions

It has been shown that sulfide attacks thiosulfate on the outer sulfur atom.

$$S^{-2} + {}^{-}S\text{–}SO_3^{-2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^{-}S\text{–}S^{-} + SO_3^{-2}$$

We suggest that the the mechanism of eq. 4 also involves attack on the outer sulfur atom.

$$ {}^{-}S\text{–}S^{-} + {}^{-}S\text{–}SO_3^{-} \overset{k_2}{\rightleftharpoons} {}^{-}S\text{–}S\text{–}S^{-} + SO_3^{-2} \qquad (12)$$

It is reasonable to postulate that this reaction is a general one for polysulfides

$$S_n^{-2} + {}^{-}S\text{–}SO_3^{-} \rightleftharpoons S_{n+1}^{-2} + SO_3^{-2}$$

and that the rate for any given polysulfide species is governed by its concentration and its thiophilicity towards thiosulfate. Attack by all of the polysulfides probably occurs, but the concentration of the higher polysulfides is small and their reactions are not measurable here. In addition, the reaction of the higher polysulfides is complicated by the fact that polythionates can be formed by an attack on an inner sulfur atom.

$$ {}^{-}S_n\text{–}S_m^{-} + SO_3^{-2} \rightleftharpoons {}^{-}S_n\text{–}SO_3^{-} + S_m^{-2}$$

There is positive evidence for the attack of sulfide on the outer sulfur of thiosulfate. However, since the attack on either sulfur atom would give the same rate law, there is the possibility that a fraction of the exchange which is represented by the first term of eq. 6 could be an attack on the inner sulfur atom of the thiosulfate. Since K_{eq} is known, a direct measurement of the rate constant for the reaction between disulfide and sulfite (k_{-1}) would allow the calculation of k_1. The value obtained in this way should agree with that found above. A smaller value of k_1 would indicate that the k_1 found above is a composite, containing some contribution from attack on the inner sulfur. We believe that this possibility is unlikely since this mechanism would be expected to have a much higher activation energy than obtained here. The reaction of hydroxide with thiosulfate, which may involve attack on the inner sulfur of thiosulfate, has an activation energy of 57 kcal./mole.[6]

(12) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

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Multilayer Membrane Electrodes. V. Biionic Potentials across Nonpressurized Membranes

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Nonpressurized calcium stearate electrodes have been used to measure the biionic potentials of mixed calcium and sodium chloride solutions. The results showed that sodium ions can enter the membrane and set up a diffusion potential, E_{Na}. By applying the Nernst–Planck diffusion equation, it was possible to derive the following relationship between the diffusion potential and the activities of calcium and sodium ions in solution: $E_{Na} = (RT/\mathfrak{F}) \ln [1 + \lambda a_{Na}/a_{Ca}^{1/2}]$. The experimental results fitted this equation with $\lambda = 2.0$. Earlier results with calcium or barium and potassium chloride solutions were re-examined and found also to obey this equation with $\lambda = 2.9$ for $CaCl_2$–KCl and $\lambda = 1.2$ for $BaCl_2$–KCl. Provided that the sodium/calcium ratio is not too high and the sodium content of the solution is known, these nonpressurized electrodes can be used for the direct determination of calcium ion activities, by applying the above equation. For example, in the determination of the calcium ion activity in milk which has an average sodium plus potassium content of 0.06 M and a calcium content of 0.03 M, a variation in the alkali metal content of ±5% leads to a calcium ion activity error of ±5%.

Introduction

The preparation and properties of multilayer membrane electrodes composed of alkaline earth stearates have been described in earlier papers.[1-3] As prepared or "unprotected" these electrodes are reversible to the cationic species only in the presence of the corresponding alkaline earth salts. They are not reversible to the alkaline earth cations only when used in mixed electrolytic solutions containing appreciable amounts of alkali metal cations. These membranes can be pressurized or "protected" by containing the multi-

(1) H. P. Gregor and H. Schonhorn, *J. Am. Chem. Soc.*, **79**, 1507 (1957).
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(3) H. Schonhorn and H. P. Gregor, *ibid.*, **83**, 3576 (1961).