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Nucleophilic Displacements at Sulfur. III. The Exchange of Oxygen-18 between Sodium Thiosulfate-^{18}O and Water[1]

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Abstract: The exchange of oxygen-18 between water and thiosulfate ions has been measured in aqueous solutions at 60 to 100° and pH from 5.3 to 6.5. The rate is first order in thiosulfate ions and first order in protons, is catalyzed by the proton specifically, does not show general acid catalysis, and does not show catalysis by chloride ions. The slope of the graph of log k *vs.* $\mu^{1/2}$ is zero both in regions of high and low ionic strength. The exchange is faster in D_2O than in normal water, with k_{H_2O}/k_{D_2O} being equal to 0.63. The temperature parameters are E_a = 13.4 kcal/mole, log A = 9.9, and $\Delta S^{\ddagger} = -16$ eu at 80°. A mechanism for the exchange is proposed in which a water molecule attacks the inner sulfur of $HO-SO_2-S^-$ in an S$_N$2 reaction. This mechanism is analogous to the A-2 hydrolysis of esters and is supported by the solvent isotope effect and by the negative value of $\Delta S^{\ddagger}$. This ^{18}O exchange of thiosulfate is compared to two other reactions to which it has superficial similarity; they are a disproportionation to sulfide and sulfate and sulfur-35 exchange with bisulfide ion. (These three similar reactions are shown as eq 13–15 in the text.) In the ^{35}S exchange reaction, HS^- attacks thiosulfate at the outer sulfur (eq 15), whereas in the ^{18}O exchange and the disproportionation water attacks at the inner sulfur (eq 13 and 14). In comparing the latter two processes, the displacement of HS^- from $HS-SO_2-O^-$ by water (eq 14) occurs with an activation energy which is 40 kcal/mole less than the displacement of HO^- from $HO-SO_2-S^-$ by the same nucleophile (eq 13). These remarkable differences between these reactions are discussed and rationalized. The exchange of oxygen-18 in the sulfur oxyanions probably occurs in the order thiosulfate > sulfite > sulfate, and reasons for this are proposed.

Displacement reactions on atoms other than carbon are of great current interest, due to the general renaissance in inorganic chemistry, and also because of the insights to be gained from a broadened understanding of this key transformation in organic chemistry. Displacements on silicon,[3] phosphorus,[4] nitrogen,[5] sulfur,[6] other metalloids,[7] and on metals[8] have been reviewed. Recently, considerable attention had been directed to the oxygen exchange reactions between water and the salts or esters of inorganic oxyanions with the aim of learning the factors which determine the rate of attack by the nucleophile water on the central metalloid atom.[9]

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[1] (a) This research was supported in part by a grant from the U. S. Air Force Office of Scientific Research AFOSR(SRC)-OAR, Grant No. 540-66; (b) parts I and II: *J. Am. Chem. Soc.*, **82**, 4794 (1960); **86**, 3621 (1964).

[2] Postdoctoral student supported on an AFOSR grant.

[3] L. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[4] F. H. Westheimer, Special Publication No. 8, The Chemical Society, London, 1957, pp 1–15; C. A. Vernon, *ibid.*, pp 17–32.

[5] R. Boschan, R. T. Merrow, and R. W. Van Dolah, *Chem. Rev.*, **55**, 485 (1955).

[6] W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; p 67.

[7] J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964.

[8] R. G. Pearson, *J. Chem. Educ.*, **38**, 164 (1961); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958; H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959); H. Taube, *Ann. Rev. Nucl. Sci.*, **6**, 280 (1956); C. K. Ingold, "Substitution at Elements Other than Carbon," Weizmann Science Press of Israel, Jerusalem, 1959; F. Basolo, "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, pp 1–55; Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965; C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

[9] Examples of recent papers include: (a) D. Samuel and B. L.

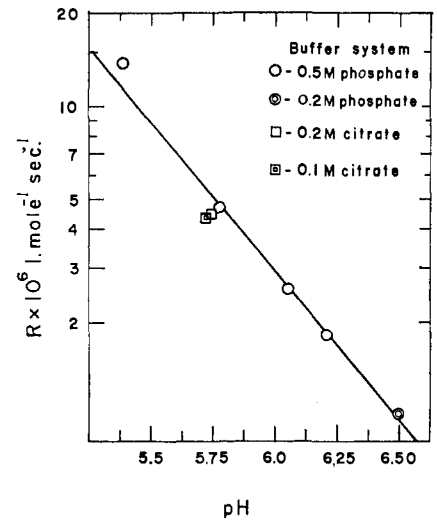

Figure 1. Log R *vs.* pH at 80°.

In this paper we report the kinetics of the oxygen exchange between thiosulfate-^{18}O and water in aqueous buffers at 65 to 100° and pH 5.3 to 6.5. Some of the earliest publications describing the use of oxygen-18 had reported qualitative evidence that thiosulfate does exchange with water,[10] and we have confirmed this and have studied the mechanism of the exchange.

Experimental Section

Materials and Apparatus. Sodium thiosulfate-^{18}O, enriched to about 45%, was obtained from YEDA Research and Development Co., Ltd., and used without further purification. Analytical reagent grade inorganic salts were oven dried at 110° where necessary and stored over P_2O_5 until used. Freshly boiled demineralized distilled water was used to prepare solutions. Deuterium oxide, 99.7%, was supplied by Nuclear Research Chemicals, Inc.

The pH values were measured at 65 and 80° using a Beckman Model G pH meter, Beckman No. 3501 and Sargent S-30141-10B buffers which are calibrated from 10 to 90°, and a thermostated bath. Isotopic analyses were made on a Consolidated Engineering Corp. Model 21-260 mass spectrometer.

Sample Preparation and Isotopic Analysis. The kinetic runs were followed by measuring the decrease of the oxygen-18 enrichment of thiosulfate. Aqueous solutions of enriched $Na_2S_2O_3$ with added salts at the desired concentration were transferred in aliquots to ampoules. After a gentle nitrogen current was passed through the chilled samples for about 5 min, the ampoules were sealed and put in a thermostated oil bath.

Thiosulfate was precipitated from the solution with lead nitrate; lead thiosulfate was filtered, washed, and dried in a vacuum desiccator over P_2O_5 for 4 hr and then in a vacuum oven at 60° for about 30 min. Lead thiosulfate was obtained with a different procedure from solutions containing anions which give insoluble lead salts. Tris(ethylenediamine)nickel(II) nitrate was used to precipitate thiosulfate, and the tris(ethylenediamine)nickel(II) thiosulfate was filtered and washed with cold water.[11] The filtrate was removed and dissolved in water with dilute hydrochloric acid. Thiosulfate was then precipitated with lead nitrate at a controlled pH of about 4. It was dried as described above. Finally, dry lead thiosulfate was decomposed by heat under vacuum to give sulfur dioxide on which the isotopic analyses were made. We have neglected any isotopic effect on the decomposition of lead thiosulfate and have assumed that the sulfur dioxide has the same isotopic enrichment of the parent thiosulfate.

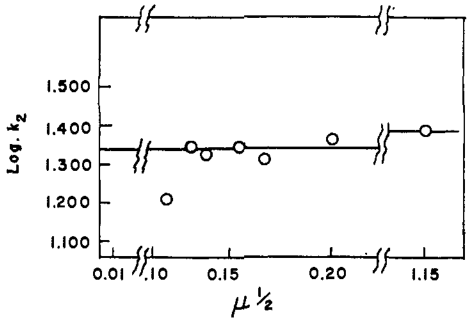

Figure 2. Log k_2 *vs.* $\mu^{1/2}$ at 80°.

Relative abundances of oxygen-18 in sulfur dioxide were calculated from the ratios of peak heights at m/e 64 and 66 assuming the natural distribution of sulfur isotopes, that is, 95.0% ^{32}S, 0.76% ^{33}S, and 4.22% ^{34}S. The mass spectra due to the isotopic molecules were scanned enough times to reduce the errors in peak height measurement to less than 1%. The relatively high oxygen-18 enrichment of the samples made SO_2 a suitable gas for oxygen isotopic analysis; pump-out times of 15 to 30 min were required to reduce memory[12] effects due to absorption in the spectrometer to a negligible extent. The rate of the reaction which leads to isotopic exchange was calculated by the reduced equation[11,13]

$$R = 3(S_2O_3{}^{2-}) \ln (1 - F)$$

where F is the fraction exchanged and $(1 - F)$ is given by the expression

$$1 - F = (^{18}O)_t/(^{18}O)_0$$

i.e., the ratio of the oxygen-18 enrichment of thiosulfate at time t and the enrichment at time zero.

Results

Kinetic Order. Table I gives kinetic data for experiments carried out in buffers of differing pH at 80°. A plot of log R *vs.* pH (runs 1 through 7) is shown in Figure 1; a straight line results with slope −0.99. Thus, the exchange rate is proportional to the hydrogen ion concentration at constant thiosulfate, ionic strength, and sodium ion concentration. The rate is relatively unaffected either by changing the nature of the buffer system or by increasing the total buffer concentration (runs 2, 3, and 6); this behavior suggests specific hydrogen ion catalysis. No catalysis by chloride ion was observed (runs 2 and 3); sulfate and perchlorate also do not affect the rate. Table II gives data showing that the exchange is first order in thiosulfate. Therefore, the rate equation is given by

$$R = k_1(S_2O_3{}^{2-}) = k_2(H^+)(S_2O_3{}^{2-}) \qquad (1)$$

where k_1 is the observed pseudo-unimolecular rate constant at a fixed pH. The data in Table II also show that log k_2 is independent of the square root of the ionic strength in a region where the Brønsted–Bjerrum–Christiansen–Scatchard law can be applied. Figure 2 shows a plot of log k_2 *vs.* $\mu^{1/2}$; the slope is approximately zero over an unusually wide range of ionic strengths.

Temperature Dependence. From the data in Table I, the Arrhenius activation energy can be calculated to be 13.4 kcal/mole. Taking k_2 as 25.7 M^{-1} sec^{-1}, log A is 9.9 and $\Delta S^{\ddagger}$ is −16 eu at 80°.

Runs with Added Sulfite. It is important to establish whether sulfite is an intermediate since sulfite and

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Silver, *J. Chem. Soc.*, 1049 (1964); (b) M. Anbar and S. Guttmann, *J. Am. Chem. Soc.*, **83**, 781 (1961); (c) B. Keisch, J. W. Kennedy, and A. C. Wahl, *ibid.*, **80**, 4778 (1958); (d) C. A. Burton, D. R. Llewellyn, C. A. Vernon, and V. A. Welch, *J. Chem. Soc.*, 1363 (1961); (e) I. Pech and Z. Luz, *J. Am. Chem. Soc.*, **87**, 4068 (1965).

(10) (a) G. A. Mills, *ibid.*, **62**, 2833 (1940); (b) N. F. Hall and O. R. Alexander, *ibid.*, **62**, 3455 (1940).

(11) E. Ciuffarin and W. A. Pryor, *ibid.*, **86**, 3621 (1964).

(12) T. C. Hoering and J. W. Kennedy, *ibid.*, **79**, 56 (1957).

(13) R. B. Duffield and M. Calvin, *ibid.*, **68**, 557 (1946).

Table I. Hydrogen Ion and Temperature Dependence

Run[a]	Temp, °C	Type of buffer[d]	(Buffer), M	pH	$R \times 10^6$ M sec^{-1}
1[b]	80.0	P	0.50	5.93[e]	13.7
2[b]	80.0	C	0.10	5.72[e]	4.38
3	80.0	C	0.20	5.75[e]	4.45
4[b]	80.0	P	0.50	5.78[e]	4.66
5[b]	80.0	P	0.50	6.06[e]	2.57
6[c]	80.0	P	0.20	6.21[e]	1.81
7[b]	80.0	P	0.50	6.50[e]	1.01
8[b]	65.C	P	0.50	6.08[f]	1.22
9[b]	100.0	P	0.50	6.09[g]	7.70

[a] In all runs ($Na_2S_2O_3$) = 0.1 M, ionic strength = 1.3, (Na^+) = 0.6 M. [b] Ionic strength adjusted with NaCl. [c] Ionic strength adjusted with NaCl and KCl. [d] P is phosphate ($H_2PO_4^-$–HPO_4^{2-}), and C is citrate. [e] Measured at 80°. [f] Measured at 65°. [g] Measured at 80°; a value of 6.04 at 100° is obtained by extrapolation of the lower temperature values.

Table II. Unbuffered Runs at 80°

Run	($Na_2S_2O_3$) $\times 10^3$ M	($NaClO_4$) $\times 10^3$ M	$\mu^{1/2}$	$R \times 10^9$ M sec^{-1}	k_2,[b] M sec^{-1}	Log k_2
10	4.00	0	0.109	6.47	16.2	1.210
11	4.02	3.52	0.124	8.93	22.2	1.344
12	6.01	0	0.134	12.76	21.2	1.324
13	8.03	0	0.155	17.83	22.2	1.344
14	3.99	17.62	0.172	8.17	20.5	1.312
15	4.02	34.2	0.215	9.25	23.0	1.362
5[a]	1000	0	1.15	2570	25.7	1.41

[a] See Table I for concentrations. [b] The pH value for runs 10 through 15 was assumed to be 7.0. This is obviously not strictly correct. However, the actual pH values of these unbuffered solutions, which were carefully and uniformly prepared under a nitrogen atmosphere, should be very similar. If the actual pH value were slightly different from 7 it would not affect the appearance of Figure 2. If it is assumed that the pH values of these solutions is 7, the derived values of k_2 agree with the values from buffered solutions (see the last two columns in the table). These experiments were done in unbuffered solutions since that was the only way of achieving the low ionic strengths necessary.

thiosulfate are known[14a] to exchange oxygen-18, and thiosulfate can decompose to form sulfite.[14b] A mechanism for oxygen exchange between water and thiosulfate, therefore, can be written in which sulfite is the actual species undergoing exchange.

$$S_2\overset{*}{O}_3{}^{2-} \rightleftarrows S\overset{*}{O}_3{}^{2-} + S \qquad (2)$$

$$S\overset{*}{O}_3{}^{2-} + H_2O \rightleftarrows SO_3{}^{2-} + H_2\overset{*}{O} \qquad (3)$$

$$SO_3{}^{2-} + {}^-S\text{–}S\overset{*}{O}_3{}^- \rightleftarrows {}^-SO_3\text{–}S^- + S\overset{*}{O}_3{}^{2-} \qquad (4)$$

In our previous study[11] of sulfur-35 exchange between sulfide and thiosulfate, sulfite was in fact shown to be a critical intermediate. However, sulfite is not an intermediate in this oxygen-18 exchange. This was shown by studying the rate of exchange of thiosulfate in the presence of added sulfite. Figure 3 shows the results of a run in which a 0.1 molar equivalent of sulfite was added to $S_2O_3{}^{2-}$-^{18}O. There is a relatively rapid exchange of oxygen-18 between sulfite and thiosulfate through eq 4. (From the data of Ames and Willard, complete exchange would be predicted to occur in 3 hr under our conditions.) This exchange reduces the oxygen-18 content of the thiosulfate to about 90% of its original value. The thiosulfate then exchanges with water at nearly[15] the same rate that it would have in the absence of sulfite. We also have duplicated this result using ($S_2O_3{}^{2-}$) = 0.10, ($SO_3{}^{2-}$) = 0.015, phosphate buffer 0.50, (KCl) = 0.161, μ = 1.35, (Na^+) = 0.575, and pH 5.82 at 80° (concentrations in mole l^{-1}). It is conceivable that sulfite does not have a pronounced effect on the exchange rate because sulfite is destroyed under our conditions. This does not appear likely, since sulfite does exist long enough to exchange oxygens with thiosulfate. However, this is an important point, and we, therefore, studied the stability of sulfite under our conditions. The concentration of sulfite is substantially unchanged after 17 hr at 80°.

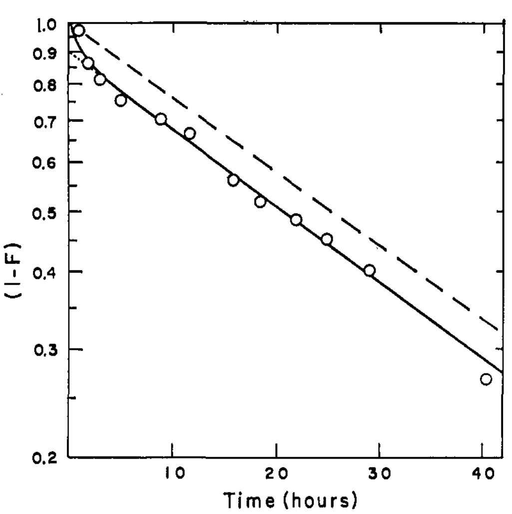

Figure 3. Effect of added sulfite on the exchange of thiosulfate-^{18}O at 80°: ($Na_2S_2O_3$) = 0.1 M; (Na_2SO_3) = 0.01 M; phosphate buffer = 0.5 M; pH 6.11; μ = 1.3; - - - -, in the absence of SO_3.

Our results, therefore, demonstrate unequivocally that, in the presence of thiosulfate, sulfite exchanges oxygens with water at least as slowly as does thiosulfate at 80° and pH 6.[15] This is one more fact in the rather confusing story on the exchange of sulfite. Mills[10a] found that K_2SO_3 did not exchange with water at all at 100° for 24 hr, whereas Alexander and Hall[10b] reported that it completely exchanged in 8 hr; both of these early workers used very low enrichments. Halperin and Taube[16a] passed SO_2 into water at 25° and immediately oxidized the SO_2 to sulfate using iodine. They found that the oxygen atoms in the sulfate had completely exchanged with water when the water was initially either 0.1 M in HCl or 0.4 M in NaOH. However, this result does not necessarily imply that sulfite exchanges oxygens with water rapidly at room tempera-

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(14) (a) D. P. Ames and J. E. Willard, *J. Am. Chem. Soc.*, **73**, 164 (1951); (b) R. E. Davis, *ibid.*, **80**, 3565 (1958); F. Foerster and R. Vogel, *Z. Anorg. Allgem. Chem.*, **155**, 161, 184 (1926).

(15) If oxygen exchange between sulfite and thiosulfate is rapid and exchange between water and sulfite is slow, then the 0.1 M thiosulfate plus 0.1 M sulfite mixture should be observed to exchange at 90% of the rate observed for 0.1 M thiosulfate alone (see ref 13). The rate would be unaltered only if sulfite and thiosulfate coincidentally exchange with water at exactly the same rate under our conditions. We believe that sulfite exchanges more slowly than thiosulfate, and, therefore, the slope of the solid line in Figure 3 should be 90% of that of the dashed line. However, our data are not sufficiently precise to permit a distinction between these two possibilities.

(16) (a) J. Halperin and H. Taube, *J. Am. Chem. Soc.*, **74**, 375 (1952); (b) H. Taube, private communications; (c) N. N. Lichtin, I. Laulicht, and S. Pinchas, *Inorg. Chem.*, **3**, 537 (1964); (d) M. Eigen, K. Kustin, and G. Maass, *Z. Physik. Chem.* (Frankfurt), 30, 130 (1961).

ture over this pH range, since Lichtin, Laulicht, and Pinchas[16c] have found that SO_2 and $\overset{*}{S}O_2$ exchange ^{18}O even in the gas phase.

Taube and Anbar and Taube and Espenson have studied the exchange of sulfite with water under alkaline conditions where SO_3^{2-} is the most important species and the exchange is slow.[16b] Eigen[16d] has measured a relaxation phenomenon in sulfite solutions at pH values near 5 at 20°. He believes that the reaction he has studied is

$$H^+ + HSO_3^- \rightleftarrows SO_2 + H_2O$$

and the rate constants are $10^8\ M^{-1}\ sec^{-1}$ and $10^6\ sec^{-1}$ in the forward and reverse directions, respectively. It seems clear that H_2SO_3 exchanges very rapidly with water at 20° and SO_3^{2-} exchanges rather slowly at 100°. Unquestionably, under our conditions sulfite exchanges more slowly than does thiosulfate, and it is difficult to see how thiosulfate could affect the rate of exchange of sulfite. We conclude that HSO_3^-, the most important species present under our conditions, exchanges with water more slowly than does $HS_2O_3^-$.

Solvent Isotope Effect. The rate of exchange was measured in D_2O and H_2O solutions of the same composition [$(Na_2S_2O_3) = 0.10\ M$, $(NaCl) = 0.20\ M$, $(KCl) = 0.1\ M$; phosphate buffer $= 0.50\ M$; $\mu = 1.3$; $(Na^+) = 0.60\ M$, pH 5.78 in H_2O at 80°]. After dissolving the salts, the D_2O was approximately 98.8% enriched. At 80°, $R \times 10^6$ values were 7.41 and 4.66 in D_2O and H_2O. Therefore $k_{H_2O}/k_{D_2O} = 0.63$.

Discussion

Mechanism of the Exchange. There are two mechanisms which have unimolecular rate-determining steps; both involve the unlikely species S_2O_2. The first involves a rate-determining proton transfer (eq 5 and 6).

$$H^+ + S_2O_3^{2-} \xrightarrow{\text{slow}} HO\text{–}SO_2\text{–}S^- \tag{5}$$

$$HO\text{–}SO_2\text{–}S^- \xrightarrow{\text{fast}} HO^- + S_2O_2 \tag{6}$$

This can be eliminated as inherently improbable and also since it predicts general acid catalysis. The second possibility is analogous to the A-1 hydrolysis of esters (eq 7 and 8). This can be eliminated by the solvent isotope data and the entropy of activation; these criteria are discussed below.

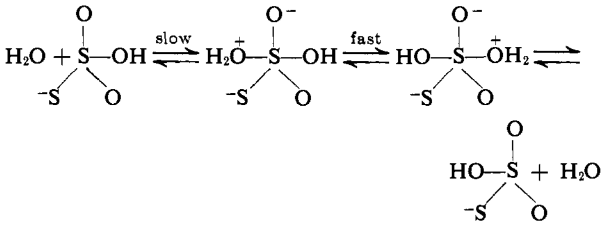
$$H^+ + S_2O_3^{2-} \rightleftarrows HO\text{–}SO_2\text{–}S^- \tag{7}$$

$$HO\text{–}SO_2\text{–}S^- \xrightarrow{\text{slow}} HO^- + S_2O_2 \tag{8}$$

$$S_2O_2 + H_2O \rightleftarrows \text{exchange}$$

There are three possible mechanisms with bimolecular rate determining steps. The first (a) is a process analogous to the A-2 hydrolysis of esters (eq 7 and 9).

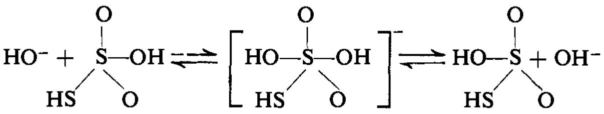
$$H^+ + S_2O_3^{2-} \overset{\text{fast}}{\rightleftarrows} HS_2O_3^- \tag{7}$$



(9)

A second (b) may be formulated as a SN2 reaction between a hydroxide ion and $H_2S_2O_3$ (eq 10 and 11).

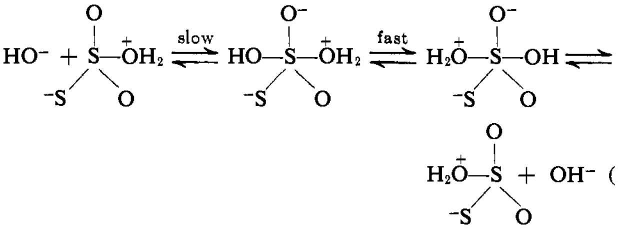
$$2H^+ + S_2O_3^{2-} \overset{\text{fast}}{\rightleftarrows} H_2S_2O_3 \tag{10}$$



(11)

A third mechanism (c) would involve a nucleophilic attack of the hydroxide ion on the zwitterionic complex shown in eq 12. Of the three bimolecular mechanisms represented above, we prefer mechanism (a) involving attack by water on $HS_2O_3^-$ as the determining step.

$$2H^+ + S_2O_3^{2-} \overset{\text{fast}}{\rightleftarrows} {}^-S\text{-}SO_2\text{-}\overset{+}{O}H_2$$



(12)

Both eq 11 and 12 involve improbable species for the pH range 5–7. For example, the ratio of the concentrations of reactants for eq 9 and 11 is[17] (at room temperature)

$$\frac{(H_2O)(HOSO_2S^-)}{(HO^-)(H_2S_2O_3)} = \frac{(H_2O)}{(H^+)(HO^-)}\,\frac{(HS_2O_3^-)(H^+)}{(H_2S_2O_3)} \cong 10^{16}\cdot 10^{4} = 10^{20}$$

Hydroxide ion is, of course, a better nucleophile than is water, but the ratio of their nucleophilic activities in this reaction is less than a factor of 10^{20}. We shall argue below that k_{HO^-}/k_{H_2O} is approximately 10^{12}, and it is certainly extremely doubtful that it is any larger than 10^{15}. Therefore, the ratio of the rates of reactions 9 and 11 is approximately

$$\frac{R_9}{R_{11}} = \frac{k_{H_2O}}{k_{OH^-}}\,\frac{(H_2O)(HS_2O_3^-)}{(HO^-)(H_2S_2O_3)} \cong 10^{-12}\cdot 10^{20} = 10^{8}$$

The activated complex for eq 12 is even less probable in this pH range. However, zwitterionic activated complexes of this sort have been proposed for the hydrolysis of esters of various inorganic oxyanions.[18] We shall return to a discussion of this point below.

A choice therefore must be made between the A-1 mechanism represented by eq 7 and 8 and the A-2 mechanism of eq 7 and 9. Table III compares the data for this exchange reaction with data for the acid-catalyzed hydrolysis of organic sulfate and selenate

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(17) The first dissociation constant for $H_2S_2O_3$ has not been measured but it can be calculated to be 10^7 by the method of J. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp 206–207. This method also gives 10^7 for K_1 for sulfuric acid, which is known to be too high as is discussed by Branch and Calvin. The value for thiosulfuric acid also is probably too high, and the correct value is probably between 10^3 and 10^5. The values of K_2 for both sulfuric and thiosulfuric acids are about 10^{-2}. The value of K_2 for thiosulfuric acid is given, for example, by R. H. Dinegar, R. H. Smellie, and V. K. La Mer, *J. Am. Chem. Soc.*, **73**, 2050 (1951); T. O. Denny and C. B. Monk, *Trans. Faraday Soc.*, **47**, 992 (1951); see also F. M. Page, *J. Chem. Soc.*, 1719 (1953). J. L. Kice, *J. Org. Chem.*, **28**, 957 (1963), has concluded from kinetic evidence that $C_2H_5\text{-}S\text{-}SO_2\text{-}OH$ is a very strong acid.

(18) See, for example, B. D. Batts, *J. Chem. Soc., Sect. B*, 547, 551 (1966).

esters. A-1 and A-2 type reactions can frequently be distinguished by use of the solvent isotope effect. Values of k_{H_2O}/k_{D_2O} for reactions of the A-1 type generally lie in the range of 0.39 to 0.53; the solvent isotope effect is normally 0.59 to 0.77 for A-2 reactions.[19]

Table III. Comparison of A-1 and A-2 Hydrolysis Reactions[a]

Transition state	Mechanism	Acidity dependence	k_{H_2O}/k_{D_2O}	$\Delta S^{\ddagger}$, eu	Ref
$[Ar{-}\overset{H^+}{O}{-}SO_2{-}O^-]$	A-1	$(h_0)^{1.0}$	0.41	...	21a
$[Me{-}\overset{H^+}{O}{-}SO_2{-}O^-]$	A-1	$(h_0)^{0.7}$	...	7	18
$[H_2O + Me\overset{H^+}{O}{-}SeO_2{-}O^-]$	A-2	Molarity of acid	0.73	−23	22
$[H_2O + HO{-}SO_2{-}S^-]$	A-2	$(H^+)^{1.0}$	0.63	−16	...

[a] Me indicates a methyl group.

Reactions which involve solvent water as a nucleophile often have a more negative entropy of activation than do A-1 reactions because of the entropy necessary to localize one (or several) water(s) in the activated complex.[20] This difference in entropy should be at least 5 eu and frequently is as large as 25 eu.

The data in Table III show that the reaction reported here is of the A-2 type as judged both by its value for $\Delta S^{\ddagger}$ and by its solvent isotope effect. This appears particularly convincing in comparison with the data on the other reactions shown in the table. The hydrolyses of both alkyl[18] and aryl[21a] sulfate esters follow the Hammett acidity function and can be concluded to be A-1 reactions,[21b] and these processes have solvent isotope effects and entropy of activation values which lie in the expected range. The hydrolysis of sodium methyl selenate[22] follows the molarity of the catalyzing acid and is not linear in H_0. By this criterion this hydrolysis can be concluded to be an A-2 reaction, and its solvent isotope effect, position of bond scission in hydrolysis, and entropy of activation values reinforce this conclusion. The oxygen-18 exchange of thiosulfate seems quite clearly to fit the A-2 pattern.

Microscopic Reversibility. An exchange such as that represented by eq 9 must be symmetrical.[23] Therefore, eq 9 can be described more completely and exactly as in (9a). Ignoring kinetic isotope effects, the energy profile for this reaction is as shown in Figure 4. It is clear that the pentacovalent species shown in eq 9a must be *actual intermediates* rather than transition states, in contrast with the situation applicable to displacement reactions at saturated carbon atoms. Westheimer recently has postulated pentacovalent, trigonal bipyramid intermediates in the hydrolysis of some phosphorus esters.[21c]

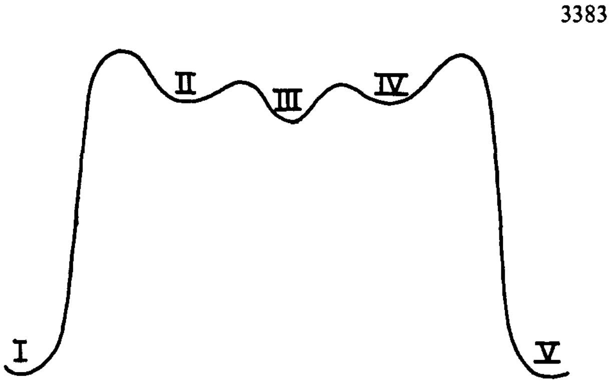
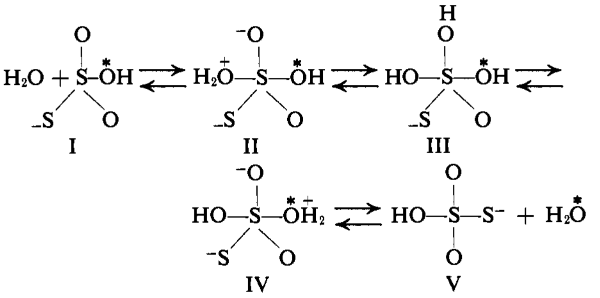


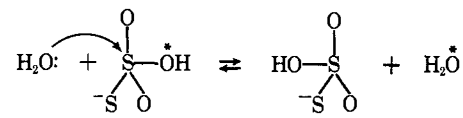
Figure 4. The free-energy-reaction coordinate diagram for eq 9a.



(9a)

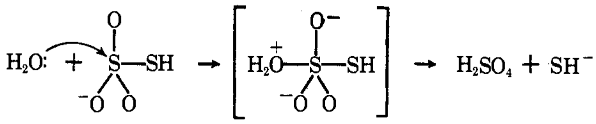
Related Reactions of Thiosulfate. The O-18 exchange forms an interesting trio with two other reactions of thiosulfate (eq 13–15). Our original purpose

oxygen-18 exchange



(13)

disproportionation



(14)

sulfur-35 exchange

$$HS^- + {}^-S{-}SO_3^- \rightleftharpoons HS{-}S^- + SO_3^{2-} \quad (15)$$

in studying the oxygen-18 exchange was to aid in the elucidation of the mechanisms of all three of these processes.[6]

Reaction 14 was reported previously;[24] it is superficially extremely similar to eq 13. *These two reactions, however, differ in activation energy by over 40 kcal/mole.* They are compared in detail below. Reaction 15, sulfur-35 exchange between sulfide and thiosulfate,[11] has an activation energy very similar to that for oxygen-18 exchange. However, it has a rate which is independent of pH and involves sulfite as a critical intermediate. It, therefore, involves attack by sulfide on the *outer* sulfur atom, in contrast to the attack on the *inner* sulfur atom by water as in eq 13 and 14.

This difference between the site of attack by HS^- and water can be explained most easily in terms of the four-

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(19) J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **78**, 6008 (1956); **80**, 4162 (1958); also see K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955), and C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3207, 3214 (1961).

(20) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 26 (1963).

(21) (a) J. L. Kice and J. M. Anderson, *J. Am. Chem. Soc.*, **88**, 5242 (1966) (we thank Professor Kice for communicating his results to us prior to publication); (b) see also the discussion and the earlier literature cited by E. T. Kaiser, M. Panar, and F. H. Westheimer, *ibid.*, **85**, 602 (1963); (c) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3431, 3432 (1966).

(22) C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, 3130 (1963).

(23) R. L. Burwell and R. G. Pearson, *J. Phys. Chem.*, **70**, 30 (1966).

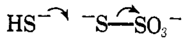
(24) W. A. Pryor, *J. Am. Chem. Soc.*, **82**, 4794 (1960).

parameter equation for displacement reactions. This equation predicts the rate constant for the reaction of a nucleophile Y^- with a substrate relative to the rate of reaction of water as the standard nucleophile

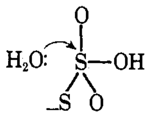
$$\log (k_{Y^-}/k_{H_2O}) = \alpha E + \beta H \qquad (16)$$

where α and β are parameters characteristic of the substrate, and E and H are determined by the nature of Y^-. (Values of E and H are defined as zero for $Y^- = H_2O$.) This equation was originally proposed by Edwards[25,26] and has been extended by Edwards and Pearson[27] and by Davis.[28,29] In eq 16, α measures the reducibility of the substrate (and its associated leaving group[29]), E measures the oxidizability of the nucleophile Y^-, β measures the electropositivity ("acidity") of the center being attacked, and H measures the basicity of the nucleophile.[30] That is, αE is a term which measures the ease of electron transfer from Y^- to the substrate and can be correlated either with polarizability[26] or with oxidation–reduction potentials,[28] and βH measures the interaction due to the basicity of the nucleophile and the acidity of the substrate.

Comparison of Eq 13 and 15. The attack by HS^- on the outer sulfur and H_2O (or HO^-) on the inner sulfur of thiosulfate is explained in terms of eq 16 as follows.



(15*a*)



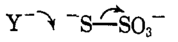
(13a)

The E and H values for the nucleophiles in question are shown below[28]

	E	H
HS^-	2.40	8.88
OH^-	1.65	17.48
H_2O	0	0

The inner sulfur of thiosulfate is certainly considerably more positive than is the outer and therefore has a larger β. For hydroxide ion, with its extremely large H value, the βH term is overwhelmingly large for attack at the inner sulfur and attack occurs exclusively at this position. Since water is the standard and both its E and H are taken as zero, the extent to which its attack at the inner sulfur is favored cannot be calculated. However, it seems clear by analogy with the hydroxide ion that water will attack thiosulfate at the inner sulfur. If we assume a value of β for the inner sulfur, we can calculate the relative rates of attack by hydroxide and by water. If β is taken as about 0.7, then $k_{OH^-}/k_{H_2O} \cong 10^{12.5}$. This is the basis of our earlier statement that oxygen-18 exchange occurs by attack by water, eq 9, rather than by attack by hydroxide, eq 11. Hydroxide is a better nucleophile by 10^{12}, but the activated complex for its attack is less probable by 10^{20} (see discussion above).

For attack by HS^-, the situation is reversed. This nucleophile is less basic than hydroxide but is more easily oxidized. It, therefore, is relatively insensitive to the high β value of the inner sulfur, but it is quite sensitive to sites of high α values. The outer sulfur of thiosulfate has a high α value since it is easily reduced and is joined to a good leaving group.



The inner sulfur is less reducible and is joined to a poorer leaving group and, therefore, should have a smaller α value.[31]

Comparison of Eq 13 and 14. Reactions 13 and 14 both have the same rate law and neither involves sulfite as an intermediate.[32] In eq 13 the leaving group is H_2O and in eq 14 it is HS^-. Reaction 14 was studied at 270° using pH values measured at 22 and 75°. Table IV compares the rates of these two reactions using a rate constant for eq 14 which was extrapolated from 270 to 80° using an activation energy of 57 kcal/mole.

Table IV. Comparison of Eq 13 and 14

	Eq 13 ^{18}O exchange	Eq 14 Dispropor-tionation
k_1 (80°, pH 6.0), sec^{-1}	2.6×10^{-5}	$(2 \times 10^{-17})^a$
E_a, kcal/mole	13.7	57
Log A (at pH 0)	10^b	25^b

[a] Extrapolated from 270 to 80°. The apparent pH at 270° was obtained by extrapolation from 22 and 75° assuming an Arrhenius-type graph and found to be 5.20. The rate dependency on protons was assumed to be first order, although 0.8 was found.[24] The rate constant at 270° and pH 5.20 (3.1×10^{-4} sec^{-1}) was then extrapolated to 80° and pH 6.00 using the experimental 57-kcal/mole activation energy. [b] At 80°.

Table IV shows that eq 13 is approximately 10^{12} faster than eq 14. Before attempting to explain this difference, the nature of the activated complex for eq 14 must be discussed.

A unimolecular A-1 type reaction is much more plausible for the disproportionation (reaction 14) than it is for the oxygen exchange process (eq 13), since the disproportionation would involve the known species, SO_3, as the intermediate

$$H^+ + S_2O_3^{2-} = HS_2O_3^-$$

$$HS{-}SO_3^- \xrightarrow{\text{slow}} HS^- + SO_3$$

$$SO_3 + H_2O = H_2SO_4$$

Because of the difficulty in studying the disproportionation reaction at the high temperatures required, no conclusive evidence is available which rules on whether it is A-1 or A-2. We will formulate it as an A-2 reaction

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

(26) J. O. Edwards, *ibid.*, **78**, 1819 (1956).

(27) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(28) R. E. Davis, "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, pp 199-212.

(29) R. E. Davis, *J. Am. Chem. Soc.*, **87**, 3010 (1965).

(30) See ref 27 and 29, and especially pp 207-209 of ref 28.

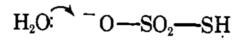
(31) R. E. Davis has discussed this (see ref 28, p 217). He points out that CN^- (E = 2.79, H = 10.88) and SO_3^{2-} (E = 2.57, H = 9.00) have E and H values very near those of HS^-, and both are known to attack the outer sulfur of thiosulfate. Professor Davis has estimated (private communication) the following values for thiosulfate: inner sulfur $\beta \sim 0.7$, $\alpha \sim 0.2$; outer sulfur $\beta \sim 0.3$, $\alpha \sim 2.5$. These values lead to the following values for $\log (k_{Y^-}/k_{H_2O})$ for the two sulfur atoms of thiosulfate.

Y^-	Outer S	Inner S
HS^-	8.7	6.7
HO^-	9.4	12.5
H_2O	0	0

(32) Because of the lower basicity of sulfur relative to oxygen, we have not formulated eq 14 analogously to eq 13 (or eq 9), but rather have postulated that the leaving group is HS- rather than H_2S^+.

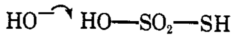
in this discussion in analogy with the oxygen exchange reaction. However, the relative rates for the two processes can be rationalized by the same reasoning regardless of whether the disproportionation is of the A-1 or A-2 type.

If reaction 14 is bimolecular, then the same three choices arise for the makeup of the activated complex as were discussed for the oxygen exchange. In the original paper[24] on the disproportionation we suggested that the activated complex (i) is more probable than is the


$H_2O{:}\ {}^{-}O{-}SO_2{-}SH$

i

tautomeric activated complex (ii). This is likely for the


$HO^{-}\ HO{-}SO_2{-}SH$

ii

same reason that water was preferred over hydroxide as the nucleophile in the oxygen exchange reaction. Attack by hydroxide appears to occur when the species being attacked is neutral. A number of examples of SN2 attack by hydroxide could be cited; perhaps the most relevant are the basic hydrolysis of dialkyl sulfites studied by Bunton and by Davis.[33]

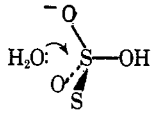
It is reasonable, therefore, to formulate the disproportionation and the oxygen exchange in a similar way as shown in eq 13 and 14. The ratio of 10^{12} for the rate constants for these two reactions is much smaller than would be expected for the 40-kcal/mole difference between their activation energies. The preexponential term for the disproportionation is 10^{25}, and the entropy of activation is 52 eu, but these values should not be taken too seriously since they are calculated assuming that the activity of protons can be extrapolated to 270°. However, it is clear that the entropy of activation is much more favorable for the disproportionation than it is for the oxygen exchange.

If eq 13 and 14 are correctly formulated as shown, then the large difference in their rates must be ascribed to the main two distinctions between them: the altered site of protonation and the change in the leaving group. Both the features act to make the oxygen exchange faster than the disproportionation.

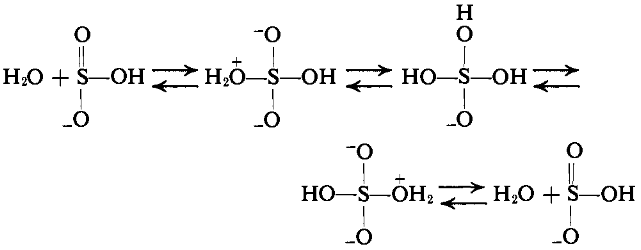
The site of protonation for oxygen exchange is at the more basic position of thiosulfate. It is difficult to estimate how much more basic the oxygen atom is than is the sulfide sulfur; however, it does not appear improbable, considering the difference in pK between water and H_2S, that the ratio of $(HOSO_2S^-)/(^-OSO_2SH)$ could be as large as 10^8.

The oxygen exchange involves $-OH_2^+$ as the leaving group whereas the disproportionation involves the much poorer leaving group –SH. In terms of the four-parameter equation, $-OH_2^+$ is the better (*i.e.*, more reducible) leaving group.[29] The E values given above (2.4 and 0) imply that HS– is less reducible than $-OH_2^+$ by 2.4 v, or 58 kcal/mole. Clearly, then, either the difference in the site of protonation or the superiority of $-OH_2^+$ as a leaving group could explain the difference in the rates of oxygen exchange and disproportionation; probably both factors play a role.

Stereochemistry. It appears most reasonable to postulate a Walden inversion-type process[34] for the initial attack involved in eq 9.



Similar Reactions of Other Sulfur Oxyanions. We have already pointed out that sulfite exchanges oxygens with water more slowly than does thiosulfate under our conditions, although SO_2 exchanges oxygens extremely rapidly at room temperature either with water or with itself. The relatively slow exchange by sulfite can be explained in terms of eq 16. Sulfurous acid is a much weaker acid than is either sulfuric or thiosulfuric acid; its two acidity constants are about 10^{-2} and 10^{-8}. Clearly, this is because of the lower oxidation state of the central sulfur atom,[35] and this implies a much smaller charge on that atom. The method of Branch and Calvin,[17] taking this smaller charge into account, predicts the correct value for both pK_a values for sulfurous acid. This smaller charge on the sulfite sulfur implies a smaller value of β for SO_3^{2-} than for the central sulfur of $S_2O_3^{2-}$, and, since the βH term is the dominant term in attack by OH^- or by H_2O, this implies that sulfite should exchange oxygens with water more slowly than does thiosulfate. It is interesting that the effect of a smaller β value outweighs the fact that the central sulfur of sulfite is sterically far more accessible than is that of thiosulfate. In fact, sulfite can exchange by an addition–elimination type mechanism



However, since the central atom can expand its octet, this distinction between displacements at a trivalent and a tetravalent sulfur is apparently not significant. This contrasts greatly with the situation for carbon, where RCOX is a much more reactive substrate than is RCH_2X.

Sulfate exchanges oxygens with water only in rather concentrated sulfuric acid solutions;[12] it exchanges with a half-life of about 1 hr in 3.5 M acid at 100°, in 12.5 M acid at 25°, or in 14 M acid at 10°. There are apparently at least two mechanisms for the exchange since from 60 to 100° in 3.6 M acid the activation energy is 31.3 kcal/mole, whereas in 13 M acid from 10 to 25° it is 20.4 kcal/mole. Hoering and Kennedy suggested an SN1 mechanism as one possibility for the exchange.

$$2H^+ + SO_4^{2-} = H_2SO_4$$

$$H_2SO_4 = H_2O + SO_3$$

An alternative suggestion would be an SN2 displacement by water.

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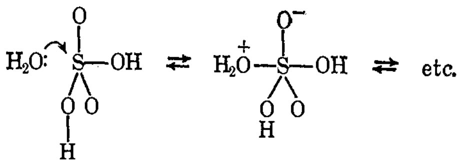
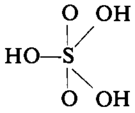
[33] These references are reviewed in ref 6, p 66.

[34] See ref 6, p 63; K. K. Anderson, W. Goffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Am. Chem. Soc.*, **86**, 5637 (1964).

[35] L. Pauling, "College Chemistry," 2nd ed, W. H. Freeman and Co., San Francisco, Calif., 1956, p 433; R. P. Bell, "The Proton in Chemistry," Meuthen and Co., Ltd., London, 1959, p 93.



Since the acid constants for thiosulfuric and sulfuric acids are so similar, it is perhaps initially surprising that sulfate exchanges only as the free acid whereas thiosulfate exchanges as the monoanion. A reasonable explanation of this can be given in terms of the suggestion made by Branch and Calvin concerning the unexpectedly small value for pK_1 for sulfuric acid. If it is postulated that sulfate exists in aqueous solution as the hydrate, then the accessibility of its sulfur to a nucleophile, its value of β, and its acidity constant will all be reduced.



For thiosulfate, with its larger HS^- as an attached ligand, the ion may exist unhydrated as $HS_2O_3^-$; if so, thiosulfuric acid should have a larger value for pK_1 than does sulfuric acid and a larger value for β, and would be expected to be attacked by water faster as is observed.

Acknowledgment. We wish to thank Dr. Ennio Ciuffarin for the exploratory research on an analytical method, which he conducted several years ago in these laboratories, and the Atomic Energy Commission for the support of that initial work. We also thank the Conference Board of the Associated Research Councils of the Committee on International Exchange of Persons for a travel grant for Dr. Tonellato. We are pleased to acknowledge extremely helpful discussions with Professors Robert E. Davis, John O. Edwards, John Kice, Donald S. Noyce, V. J. Shiner, Henry Taube, and Frank H. Westheimer during the preparation of the manuscript.

Electrochemistry of Organophosphorus Compounds. I. Electroreduction of Tris(*p*-nitrophenyl) Phosphate

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Received November 17, 1966

Abstract: The electroreduction of tris(*p*-nitrophenyl) phosphate has been investigated by polarography, cyclic voltammetry, coulometry, and esr. A mechanism for the reduction based on an initial two-electron transfer followed by cleavage of the oxygen–carbon bond is proposed. The cleaved nitrophenyl rings condense to give 4,4′-dinitrobiphenyl as a product during controlled-potential reduction.

Although the electrochemical oxidation and reduction of organic nitrogen compounds have been widely investigated, relatively few studies have been concerned with phosphorus compounds. Because of the widespread use of organophosphorus compounds as biocides, plasticizers, and additives, and a fundamental interest in the mechanisms of oxidation and reduction of this class of compounds, for example, in biological systems, we have undertaken a systematic investigation of their electrochemical behavior. Tris(*p*-nitrophenyl) phosphate (TNP) $[(NO_2C_6H_4O)_3P{=}O]$ was chosen as a model compound for an initial study, because of the well-known behavior of nitro aromatic compounds in aprotic media,[2] and because of the practical interest in nitro-substituted organosphorus compounds as insecticides. Recently Gulick and Geske[3] have reported the polarographic reduction of a number of nitrophenyl phosphates in nonaqueous media during a study of the electron spin resonance (esr) spectra of anion radicals derived from these compounds. No investigation of the mechanism of the reaction or of reactions following the electron transfer was reported.

A few electrochemical studies concerned with the development of polarographic methods for the analysis of such compounds as Malathion [S-(1,2-dicarbethoxyethyl) O,O-dimethyl dithiophosphate] and Parathion (O,O-diethyl O-*p*-nitrophenyl thiophosphate) have also been reported.[4–7]

Results

Polarography. The polarographic reduction of TNP in N,N-dimethylformamide (DMF) solution containing 0.1 *M* tetra-*n*-butylammonium iodide (TBAI) showed five waves (Figure 1): a small prewave followed by one well-defined and three ill-defined waves, with half-wave potentials ($E_{1/2}$) of −0.83, −1.07, −1.9, −2.2, and −2.5 v *vs.* an aqueous saturated calomel electrode (sce). The value of $E_{3/4} - E_{1/4}$ for the well-defined wave (wave 2) (Tômes criterion for reversibility) of 0.08 v suggested

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[1] To whom correspondence and request for reprints should be directed.

[2] See, for example, (a) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960); (b) J. Q. Chambers and R. N. Adams, *J. Electroanal. Chem.*, 10, 400 (1965), and references contained therein.

[3] W. M. Gulick, Jr., and D. H. Geske, *J. Am. Chem. Soc.*, **88**, 2928 (1966).

[4] M. K. Saikina, *Uch. Zap. Kazansk Gos. Univ., Obshch. Sb.*, **116**, 121 (1956); *Chem. Abstr.*, **52**, 296 (1958).

[5] W. H. Jura, *Anal. Chem.*, 27, 525 (1955).

[6] C. V. Bowen and F. I. Edwards, Jr., *ibid.*, 22, 706 (1950).

[7] D. E. Ott and F. A. Gunther, *Analyst*, **87**, 70 (1962).