This indicates that the radical formed in the first step reacts more quickly with nitric oxide than with styrene. The failure of the reaction to catalyze the polymerization of styrene does not disprove the existence of a radical intermediate since the reaction between the proposed intermediate and nitric oxide is a reaction between two radicals and hence would have a negligible activation energy, whereas the reaction between a radical and styrene and the propagation step in the polymerization of styrene have activation energies of 10 to 20 kcal. per mole.

Experimental

Triethyl phosphite was purified by storing over sodium and distilling at reduced pressure through a Vigreux column. It was found by gas chromatography that after this treatment it contained no significant amount of impurity. Solvents were dried and distilled before use and checked for purity by gas chromatography. The nitric oxide was passed through a bed of Ascarite before entering the reaction flask. This removed the major impurity, nitrogen dioxide, as evidenced by the complete absence of the brown color characteristic of nitrogen dioxide.

The reactions were carried out in a 500-ml., three-neck flask, one neck of which was connected to a vacuum line, the middle neck to a magnetic stirrer and the third neck to a mercury manometer. The teflon stirring blade was cut so that it fitted the contour of the flask. A Mixmaster motor was used to turn the magnet which was coupled to the stirrer. There are ten possible settings of the motor by which one can vary the speed in a stepwise manner. It was found that when the setting was at 6 or higher, the reaction rate was independent of stirring speed. All subsequent runs were made with the setting at 7 or 8.

The appropriate amount of triethyl phosphite was pipetted into a 25-ml. volumetric flask and was diluted with the solvent. The solution was introduced into the reaction flask and allowed to stand in an ice bath for about 30 minutes until temperature equilibrium was achieved. The flask was then evacuated and filled with nitrogen and evacuated again to ensure the complete removal of air. The nitric oxide was then introduced to the desired pressure. The connection between the vacuum line and the reaction flask was closed by a stopcock and the stirrer was started. The manometer was read every 30 seconds until the completion of the reaction.

At the end of the reaction a sample of gas taken and analyzed both by infrared and mass spectrometer. It was found to contain over 99% nitrous oxide. The liquid reaction mixture was then subjected to gas chromatography and yielded three fractions—the solvent, unreacted triethyl phosphite and triethyl phosphate. The last was identified by comparing its infrared spectrum with that of a known sample of triethyl phosphate and by showing that the retention time in the chromatographic column was the same for the reaction product as for the known compound.

It is necessary to know the solubility of the nitric oxide in the various solvents in order to calculate the rate constant. The solubilities were determined in the same apparatus as the rate measurements were made. Fifty ml. of solvent were introduced into the 500-ml. flask which was cooled to 0°. After removal of air and flushing with nitrogen several times, nitric oxide was introduced and the pressure was measured. The stirrer was then started and the solution was stirred until the pressure reached a constant value.

It was assumed that our system obeys Henry's law

$$P = HX$$

where P is the pressure of nitric oxide above the liquid at equilibrium, H is a dimensionless constant and X is the mole fraction of nitric oxide in solution. In dilute solutions such as those used here, X is essentially equal to the concentration. The values of H for the various solvents at 0° which are given in Table II were determined by the relationship

$$P(\text{NO}) \text{ at equilibrium } = \frac{(\text{mm. NO absorbed})(\text{volume of gas})}{(\text{volume of liquid})} H$$

TABLE II

SOLUBILITY OF NITRIC OXIDE IN VARIOUS SOLVENTS AT 0°

Solvent	*H*
Benzene	1.0
Toluene	1.0
n-Butyl ether	0.92
Amyl acetate	0.87
Cyclohexene	1.05
n-Hexane	1.10
Ethanol	1.25

The second order rate constants given in Table I were calculated from the equation

$$\frac{2.303\ \Delta \log (P_t - P_p)\Delta t}{(\text{TEP})\ V_1/(\text{H}V_g + V_1)} = k_2$$

where P_t and P_f are the pressure in the system at time t and the final pressure, respectively, (TEP) is the concentration of triethyl phosphite in moles per liter, H is Henry's constant given in Table II, V_1 is the volume of liquid (25 ml. in our experiments) and V_g is the volume of gas (500 ml.). The numerator was determined from the slope of the first order rate curves such as shown in Fig. 1.

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION, RICHMOND, CALIFORNIA]

The Kinetics of the Disproportionation of Sodium Thiosulfate to Sodium Sulfide and Sulfate

BY WILLIAM A. PRYOR*

RECEIVED FEBRUARY 17, 1960

Sodium thiosulfate has been found to disproportionate irreversibly to form sulfide and sulfate in water or in aqueous buffers at 250–280° (equation 1). The reaction is pseudounimolecular with first order dependence on $S_2O_3^=$. The first order rate constant k_1 measured at 270° is nearly proportional to the hydrogen ion concentration measured at either 22 or 75°, and it seems reasonable to assume k_1 is proportional to the hydrogen ion concentration at 270°. It appears that k_1 is not dependent on the acetate ion concentration in sodium acetate buffers but only on the hydrogen ion concentration. The Arrhenius activation energy is 57 kcal. in sodium phosphate buffers. Sulfite is not an intermediate in this reaction. The mechanism is discussed.

Sodium thiosulfate has been found to undergo irreversible disproportionation in water or in aqueous buffers at 250–280°. The products are mainly sulfide and sulfate but small amounts of sulfur, polysulfide and sulfite are formed

$$S_2O_3^= + OH^- \longrightarrow SO_4^= + HS^- \qquad (1)$$

or

$$S_2O_3^= + H_2O \longrightarrow SO_4^= + HS^- + H^+ \qquad (1A)$$

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* Department of Chemistry, Purdue University, Lafayette, Indiana.

An examination of the behavior of sulfur in basic solution indicated reaction 1 might occur. In aqueous sodium hydroxide, sulfur disproportionates to form sulfide and thiosulfate at 50–100°[1,2]

$$^1/_2S_8 + 4OH^- \longrightarrow S_2O_3^= + 2HS^- + H_2O \quad (2)$$

and sulfide and sulfate at 250–350°[3,4]

$$^1/_2S_8 + 5OH^- = SO_4^= + 3HS^- + H_2O \quad (3)$$

If the reverse of (2) is added to (3), equation 1 results.

Experimental

Reactions were conducted in 16-cc. 316-type stainless steel tubes, $^5/_8$-inch inside diameter, sealed with threaded plugs containing steel gaskets. The thermostat was a stirred KNO_3–$NaNO_2$ eutectic bath. Temperatures were measured with National Bureau of Standards thermometers to 0.1° and were controlled to better than 0.01°. The analytical procedure has been described.[5]

Results

The stoichiometry of the decomposition of sodium thiosulfate supports eq. 1. For example, heating 0.83 *M* $Na_2S_2O_3$ for 8 hr. at 270° and *p*H 6.00 (0.50 *M* phosphate buffer) produces 0.62 *M* sulfide, 0.76 *M* sulfate, 0.00 *M* sulfite, 0.01 *M* polysulfide–sulfur, and 0.07 *M* thiosulfate is recovered. This is a 92% recovery of sulfur. The loss is due to volatilization of H_2S during analysis and possibly also to undetected sulfur species. If sulfide is assumed to be the lost sulfur species and the data are corrected, then 0.76 *M* thiosulfate decomposed to form 0.76 *M* sulfate and 0.74 *M* sulfide in exact agreement with eq. 1. The uncorrected data indicate eq. 1 occurs but may not be the only path for thiosulfate decomposition.

The kinetics of the decomposition of thiosulfate were studied at 260–280° in sodium phosphate buffers, 250–270° in sodium borate buffers and at 270° in sodium acetate buffers and in water. If eq. 1 represents the correct stoichiometry, then thiosulfate disappears at the same rate at which both sulfide and sulfate are formed. Figure 1 confirms that $SO_4^=$ is formed at the same rate at which $S_2O_3^=$ disappears and shows that this rate is first order in $S_2O_3^=$.

$$k_1t = \ln \frac{(S_2O_3^=)}{(S_2O_3^=)_0} = \ln \frac{(S_2O_3^=)_0 - (SO_4^=)}{(S_2O_3^=)_0}$$

Since only $S^=$, $SO_4^=$ and $S_2O_3^=$ are present in appreciable concentrations, oxidation–reduction balance necessitates that $S^=$ also be formed at this rate.

Values of k_1 measured in different buffers show a salt effect. Runs 1 and 1S in Table I show that k_1 increases 32% when 1 *M* sodium chloride is added. Because of this salt effect, or because of a buffering effect of sodium thiosulfate, the rate constant depends on the initial concentration of sodium thiosulfate (runs 1 and 2).

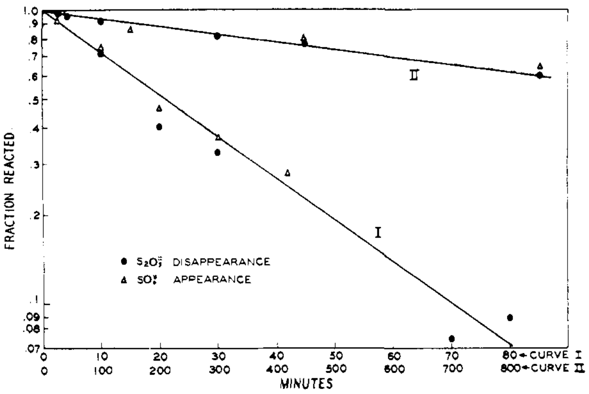

Fig. 1.—The disproportionation of 0.40 *M* $Na_2S_2O_3$ at 270.2°: curve I in water; curve II in 0.75 *M* phosphate buffer of *p*H 7.80.

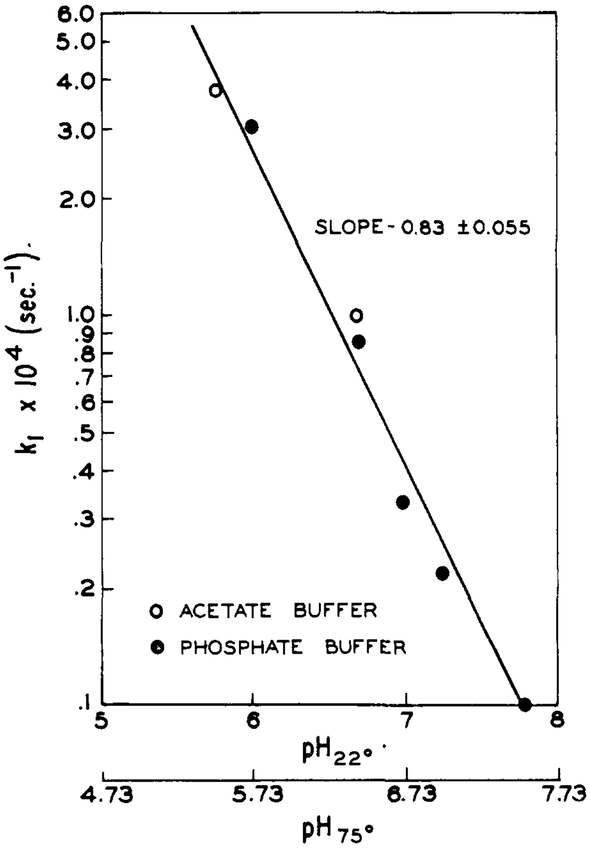

Fig. 2.—The rate constant for the disproportionation of $Na_2S_2O_3$ *vs.* *p*H.

Runs 1 through 6, 11 and 12 compare the value of k_1 measured in buffers of differing $pH_{22°}$ (*p*H measured at 22° with a Beckman *p*H meter). These data are graphed as log k_1 *vs.* $pH_{22°}$ in Fig. 2, and a straight line results with slope −0.85 ± 0.05 (least squares). Thus in both sodium phosphate and acetate buffers, the pseudounimolecular rate constant is almost proportional to the proton concentration, although *p*H is measured at 22° and k_1 at 270°. The correlation of log k_1 with $pH_{75°}$ gives an identical slope with that obtained using $pH_{22°}$. (See Fig. 2.) It seems reasonable to assume that log k_1 might correlate similarly with $pH_{270°}$. This hypothesis is strengthened by noting that run 8 gives a rate 10 times faster than predicted by Fig. 2, and this buffer becomes relatively more acidic than the others when the temperature is increased. Thus, it seems reasonable to suppose that the over-all rate is proportional to the proton concentration. The rate is also proportional to the thiosulfate concen-

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TABLE I

FIRST ORDER RATE CONSTANTS[a] FOR THE DISAPPEARANCE OF SODIUM THIOSULFATE

	Buffer				Rate		
Run	Type[b]	M[c]	$pH_{22°}$	$pH_{75°}$	$(S_2O_3^=)_0$	T, °C.	$k_1 \times 10^4$, sec.$^{-1}$
1	P	0.75	6.00	5.73	0.40	270.2	3.1
1S[d]	P	.75	6.00	..	.40	270.2	4.1
2	P	.75	6.00	5.73	.22	270.2	2.6
3	P	.75	6.70	..	.40	270.2	0.87
4	P	.75	7.00	..	.40	270.2	.33
5	P	.75	7.25	..	.40	270.2	.21
6	P	.75	7.80	..	.40	270.2	.10
7	P	.75	8.39	8.12	.40	270.2	..
8	P	.75	10.55	9.38	.40	270.2	0.002
9	P	.75	7.00	..	.40	260.0	.096
10	P	.75	7.00	..	.40	280.0	.83
11	A	1.50	5.75	5.48	.40	270.2	3.85
12	A	1.50	6.48	6.25	.40	270.2	1.12
13	A	0.75	6.48	6.25	.40	270.2	1.48
14[e]	A	.75	6.48	6.25	.40	270.2	1.25
Na_2SO_3[f]	P	.75	6.00	5.73	.00	270.2	4.6

[a] Pseudounimolecular rate constants in buffers. *p*H was measured using a Beckman *p*H meter, Beckman buffers No. 3505 and 3506, which are calibrated from 10–80°, and a thermostated bath. [b] P is sodium phosphate, A is sodium acetate. [c] Molarity of phosphate or acetate ion in the buffer. [d] Plus 1.00 *M* NaCl. [e] Plus 0.75 *M* NaCl. [f] In this run, 0.40 *M* Na_2SO_3 was the starting material. See discussion in text.

tration, and the chief thiosulfate species is $S_2O_3^=$.[6] Therefore, the rate is

$$\text{rate} = k(S_2O_3^=)(H^+) \qquad (4)$$

The rate constant is relatively insensitive to acetate ion concentration. Runs 12 and 13 show that doubling the concentration of acetate ion at constant *p*H causes the rate to decrease 24%. If the total salt concentration is held constant with sodium chloride (runs 12 and 14), doubling the concentration of acetate ion causes the rate to decrease 10%. This type of behavior in buffers suggests specific hydrogen ion catalysis.[7]

The apparent activation energy for thiosulfate decomposition is 57 kcal. in phosphate buffers (Table I) and 54 kcal. in sodium borate buffers in which the over-all kinetic behavior is similar. The entropy of activation cannot be calculated without a knowledge of the hydrogen ion concentration of these buffers at 270°.

Sodium thiosulfate decomposes to form sulfite and sulfur at 25° in acidic solution,[8] and sulfite is known to disproportionate to sulfide and sulfate.[9] Thus, sulfite could be an intermediate in the reaction reported here. This possibility can be excluded by examining the rate of decomposition of sulfite. Table I gives rate constants for the decomposition of Na_2SO_3 and $Na_2S_2O_3$ in the same phosphate buffer.

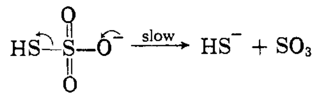
$$\begin{tikzcd} S_2O_3^{=} \arrow[r, "3.1 \times 10^{-4}"] & SO_3^{-} + S \arrow[dr, "4.6 \times 10^{-4}"] & \\ & & SO_4^{-} + S^{-} \end{tikzcd}$$

These constants indicate[10] that 30% of the amount of thiosulfate present initially would be converted to sulfite after 43 minutes if sulfite were an intermediate. However, little or no sulfite or sulfur is found at any time when sodium thiosulfate decomposes.

The kinetics, eq. 4, necessitate a transition complex with a single negative charge. This complex may be formed by a unimolecular reaction of an anion or a bimolecular reaction between a thiosulfate species and an appropriate solvent species.

The unimolecular mechanism must involve either $HS\text{–}SO_3^-$ or $^-S\text{–}SO_3H$. The former is preferable since SH^- is a better leaving group than is $S^=$. Therefore, the unimolecular mechanism would be

$$H^+ + S_2O_3^= = HS_2O_3^- \qquad (5)$$

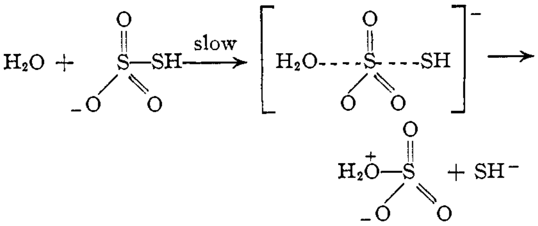


$$HS\text{–}SO_2\text{–}O^- \xrightarrow{\text{slow}} HS^- + SO_3 \qquad (6)$$

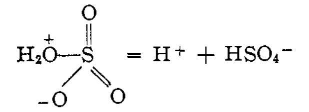
$$SO_3 + H_2O = H_2SO_4 \qquad (7)$$

This unimolecular decomposition is suggestive of the first order, acid catalyzed decomposition of $RS\text{–}SO_2R'$ at 130–200° to produce RSR' and SO_2.[11]

A bimolecular mechanism may be formulated in two ways. The first is the bimolecular counterpart of eq. 6, involving an SN2 reaction with water That is, eq. 5 followed by



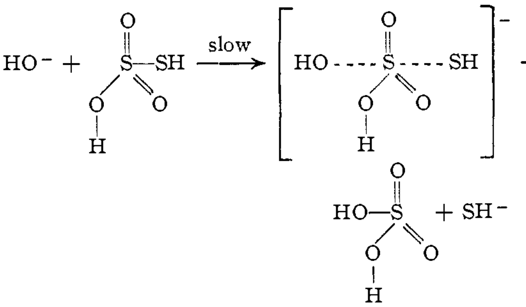
$$H_2O + O_2S(O^-)\text{–}SH \xrightarrow{\text{slow}} \left[H_2O\cdots SO_2(O^-)\cdots SH\right]^- \longrightarrow H_2\overset{+}{O}\text{–}SO_2(O^-) + SH^- \qquad (8)$$



$$H_2\overset{+}{O}\text{–}SO_2(O^-) = H^+ + HSO_4^- \qquad (9)$$

The second formulation involves direct displacement by the hydroxide ion.[12]

$$2H^+ + S_2O_3^= = H_2S_2O_3 \qquad (10)$$



$$HO^- + HO\text{–}SO_2\text{–}SH \xrightarrow{\text{slow}} \left[HO\cdots SO_2(OH)\cdots SH\right]^- \longrightarrow HO\text{–}SO_2\text{–}OH + SH^- \qquad (11)$$

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(6) The second dissociation constant of $H_2S_2O_3$ is 0.02. See F. M. Page, *J. Chem. Soc.*, 1719 (1953); T. O. Denny and C. B. Monk, *Trans. Faraday Soc.*, **47**, 992 (1951); R. H. Dinegar, R. H. Smellie and V. K. La Mer, THIS JOURNAL, **73**, 2050 (1951).

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(12) Equations 10 and 11 can be shown to predict the correct hydrogen ion dependence, eq. 4, by using the relation $K_w = (H^+)(OH^-)$.

Note that (8) and (11) involve activated complexes which are tautomeric. Of the two, (8) is favored since the proton would be expected to be more strongly bound to OH^- than to the weak base $^-SO_3$–SH.

Either (8) or (11) requires nucleophilic attack at a tetra-coördinated atom which is surrounded by electronegative atoms. The existence of direct displacement reactions at such an atom has been reviewed.[13] The limited evidence available indicates that such SN2 reactions can occur.[14]

Distinguishing between reaction 6 and 8 may be possible. The driving force for the decomposition of thiosulfate to sulfide and sulfate possibly can be provided by either high temperatures or by high proton activities at lower temperatues. Thiosulfates liberate variable amounts of H_2S on being dissolved in acid.[15] If reaction 1 occurs in, for example, concentrated sulfuric acid, then eq. 6 predicts the rate constant will depend on Hammett's acidity function and eq. 8 predicts dependence on the molar concentration of acid.[16]

A reaction which is formally similar to (1) occurs when OH^- is replaced by radioactive SH^-. Radioactive sulfide becomes incorporated in the thiosulfate. However, the reaction is faster than the one studied here and may have a different mechanism.[17]

In acid solution, Bunté salts decompose[18] in a manner analogous to HS–SO_3^-

$$\text{RS–SO}_3^- + \text{H}_2\text{O} \xrightarrow[\text{10 hours}]{\text{HCl, }100°} \text{RSH} + \text{HO—SO}_3^-$$

Acknowledgments.—I am grateful to Drs. L. L. Ferstandig, L. E. Miller, P. C. Condit, O. L. Harle and Professor R. E. Powell for helpful criticism of this manuscript and to Mr. Norman D. McNair for assistance with experimental work.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN[1b,c]]

Ion Transport in Sodium–Ammonia Solutions

BY J. L. DYE,[1a] R. F. SANKUER AND G. E. SMITH

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The anion transference number was measured as a function of concentration for sodium-ammonia solutions at −37° by the moving-boundary method. Details of the apparatus are described. The ionic equivalent conductance of Na^+ was calculated from these data and existing conductivity data. Assuming that the conductance of free sodium ions follows the Shedlovsky equation, the degree of dissociation of ion-pairs (or monomers) and the concentration of dimers were calculated. A satisfactory fit of the data was obtained using two equilibrium constants, $K_1 = 9.2 \times 10^{-3}$ for the dissociation reaction, and $K_2 = 18.5$ for the dimerization reaction.

Introduction

Because of the bridge which they form between metals and non-metals, alkali metal–ammonia solutions are of great theoretical interest. Current theories of the dilute solutions are adequately covered elsewhere,[2–4] but a brief description of those features which are important for a discussion of conductance and activity behavior is in order.

It is clear that in very dilute solutions, ($<10^{-3}$ M), it is necessary to view the system in terms of alkali metal cations and solvated electrons. Even the "monomer–dimer" theory[2b] requires dissociation of the monomer in dilute solutions. The recent calculations of Jortner[3] which are refinements of the calculations of Ogg[5] and Lipscomb,[6] afford convincing arguments for the existence of cavities created by electronic polarization of the solvent. This view is supported by the thermal e.m.f. measurements of Dewald and Lepoutre.[7] The mobility of the negative species is too high to involve appreciable migration of solvent molecules along with the electron. Quantum tunnelling of the electron from a cavity to a properly oriented group of solvent molecules in the vicinity of the cavity probably occurs.

In the intermediate concentration range, (10^{-3} to 10^{-1} M), free ions are removed from the solution. Electrostatic considerations demand that, in a solvent of this dielectric constant, a considerable fraction of the ions form pairs or other neutral species. The theory of Becker, Lindquist and Alder[2b] proposes the formation of a monomer unit with a single electron in an expanded orbital about the solvated cation. Nuclear magnetic resonance data[8,9] for fairly concentrated solutions favor such a postulate, but recent spectral data of Clark, Hors-

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[1] (a) To whom correspondence should be addressed. (b) This research was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-312. (c) Presented in part before the Division of Physical Chemistry at the 135th meeting of the American Chemical Society, Boston, Mass., April, 1959.

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