$CF_3SN(CH_3)_2$: yield 95%; IR 3000 (m), 2942 (s), 2890 (s), 2845 (m), 2804 (m), 1460 (s), 1285 (w), 1250 (m), 1202 (s), 1160 (vs), 1130 (vs), 1100 (m, sh), 1040 (m), 976 (s), 747 (m), 668 (m), 560 (m), 465 (m) cm^{-1}; NMR ϕ^* 47.6 (septet, CF_3); τ 7.05 (q, CH_3); $J_{CH_3CF_3} = 1.2$ Hz. The mass spectrum contains a strong molecular ion peak at m/e 145 as well as strong peaks for CF_3SN^+ (m/e 114) and $(CH_3)_2NS^+$ (m/e 76).

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research. We thank Mr. Scott Krueger, Mr. Richard Rankin, and Mr. Stanley Morse for nuclear magnetic resonance and mass spectra.

Registry No. $CF_3SN{=}C(Cl)CF_3$, 62067-05-4; $CF_3SN{=}C(F)CF_3$, 62067-06-5; $CF_3SN{=}C(CF_3)OCH_2CF_3$, 62067-07-6; $CF_3SN{=}C(CF_3)OCH(CF_3)_2$, 62067-08-7; $CF_3SN{=}C(CF_3)NH_2$, 62067-09-8; $CF_3SN{=}C(CF_3)N(H)CH_3$, 62067-10-1; $CF_3SN{=}C(CF_3)N(CH_3)_2$, 62067-11-2; $CF_3SN(H)CH_3$, 62067-12-3; $CF_3SN(CH_3)_2$, 62067-13-4; CF_3CN, 353-85-5; CF_3SCl, 421-17-0; CsF, 13400-13-0; CF_3CH_2OH, 75-89-8; $(CF_3)_2CHOH$, 920-66-1; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3.

References and Notes

(1) H. Ulrich, "The Chemistry of Imidoyl Halides", Plenum Press, New York, N.Y., 1968.
(2) R. Bonnett, *Chem. Carbon–Nitrogen Double Bond*, Chapter 13 (1970).
(3) H. W. Roesky, H. H. Giere, and D. P. Babb, *Inorg. Chem.*, **9**, 1076 (1970).
(4) A. Haas and V. Plass, *Chem. Ber.*, **105**, 2047 (1972).
(5) K. Peterman and J. M. Shreeve, *Inorg. Chem.*, **14**, 1106 (1975).
(6) K. Peterman and J. M. Shreeve, *J. Fluorine Chem.*, **6**, 83 (1975).
(7) N. R. Zack and J. M. Shreeve, *Synth. Commun.*, **4**, 233 (1974).
(8) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).
(9) H. J. Emeléus and S. N. Nabi, *J. Chem. Soc.*, 1103 (1960).
(10) W. L. Reilly and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6032 (1956).
(11) J. F. Bunnett, *Annu. Rev. Phys. Chem.*, **14**, 271 (1963).
(12) For further discussion see J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).
(13) J. F. Bunnett, *J. Am. Chem. Soc.*, **79**, 5969 (1957).
(14) R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967).
(15) J. L. Kice, *Mech. React. Sulfur Compd.*, **3**, 91 (1968).
(16) M. J. Janssen, *Sulfur Org. Inorg. Chem.*, **3**, 355 (1972).

Contribution from the Conoco Coal
Development Company,
Research Division, Library, Pennsylvania 15129

Stoichiometry of the Reaction of Sulfites with Hydrogen Sulfide Ion

GEORGE W. HEUNISCH

Received August 24, 1976 AIC60610H

The aqueous reaction of sulfites with HS^- ion to yield $S_2O_3^{2-}$ ion is dependent upon $[H^+]$, and the stoichiometry of the reaction has been investigated. A molar equivalency of sulfur to hydrogen has been found to be essential for reaction such that if HS^- ion is the sulfide species, the protonated sulfite, HSO_3^- ion, may be considered the sulfite species, and the equation for the reaction should be written $2HS^- + 4HSO_3^- \rightarrow 3S_2O_3^{2-} + 3H_2O$. Free SO_3^{2-} ion will not react with HS^- ion at room temperature.

Introduction

Generally, the reaction of sulfites with sulfides in aqueous solution is considered to produce thiosulfate ion with the possibility of additional, more complex polythionates. Furthermore, the reaction appears to proceed by a stepwise mechanism and involves an unstable thiosulfurous ion intermediate.[1] The dependency of the overall reaction upon hydrogen ion concentration, however, has not been adequately determined.

Isotopic labeling experiments indicate the stepwise nature of the reaction.[2,3] Thiosulfate ion produced by the reaction of H_2S^{35} with HSO_3^- ion, SO_3^{2-} ion, and SO_2 in NaOH has been hydrolyzed in acid solution to recover the elemental sulfur. Of the elemental sulfur recovered, $^2/_3$ was ^{35}S promoting the conclusion that $^2/_3$ of the sulfur originated from the H_2S, while the remaining $^1/_3$ was provided by the sulfite species. Equations 1 and 2 were suggested whereby elemental sulfur is generated initially followed by subsequent addition of the sulfur to excess sulfite ions.

$$2H_2{}^{35}S + SO_3{}^{2-} \rightarrow 2H_2O + 2{}^{35}S + S \qquad (1)$$

$$3SO_3{}^{2-} + 2{}^{35}S + S \rightarrow 2{}^{35}SSO_3{}^{2-} + SSO_3{}^{2-} \qquad (2)$$

Foerster et al,[4,5] had shown earlier that thiosulfate ion, $S_2O_3^{2-}$, decomposes in acid solution to yield HSO_3^- ion and elemental sulfur by an equilibrium reaction. Consequently, sulfur adds to HSO_3^- ion to produce $S_2O_3^{2-}$ ion, and eq 2 may involve HSO_3^- ion instead of the nonprotonated form, SO_3^{2-}.

The two-step mechanism given by eq 3 and 4 is proposed and has been investigated. The noteworthy feature of this mechanism is that HSO_3^- is necessary in both steps. Adding eq 3 and 4 leads to the overall reaction given by eq 5.

$$2HS^- + HSO_3{}^- \rightarrow 3S + 3{}^-OH \qquad (3)$$

$$S + HSO_3{}^- \rightarrow S_2O_3{}^{2-} + H^+ \qquad (4)$$

$$2HS^- + 4HSO_3{}^- \rightarrow 3S_2O_3{}^{2-} + 3H_2O \qquad (5)$$

Hydrogen sulfide ion, HS^-, has been chosen as the sulfide species for this investigation because it is the predominant sulfide species present in solution in the pH range (~5–9) of interest.

Experimental Section

A Fisher Accumet Model 120 pH meter in conjunction with a combination electrode was used for all pH measurements. The pH measurements were made without undue delay to avoid contamination of the electrode by HS^- ion.

Precipitated sulfur was identified from infrared spectra measured using a Perkin-Elmer Model 457 infrared spectrophotometer. Carbon disulfide solvent and a 0.1 mm NaCl cell were used. Spectra were obtained with respect to air reference in the spectral region of 600–400 cm^{-1} to observe the characteristic sulfur absorption at 466 cm^{-1}.

Potassium Hydrogen Sulfide, KHS, Solution. The KHS solution used throughout this study was prepared by neutralizing H_2S with an equivalent amount of standard aqueous KOH.

The H_2S was bubbled through KOH solution with nitrogen carrier gas until the weight of the solution increased by a weight equivalent to the neutralization products dictated by eq 6. Nitrogen carrier gas was used as a diluent to slow the neutralization reaction.

$$H_2S + KOH \rightarrow KHS + H_2O \qquad (6)$$

The KHS was determined by reacting the sulfide with excess standard iodine solution and back-titrating the excess I_2 with standard $Na_2S_2O_3$ solution using starch indicator for end point detection. Standard HCl solution was used to acidify the iodine solution, and the KOH was determined by back-titration of the acid with standard NaOH to the phenolphthalein end point. Any HCl not recovered was considered to have been consumed by the KOH and directly equivalent to the KOH concentration. Since the determination of KHS produces hydriodic acid, HI, which is also titrated by NaOH, compensation

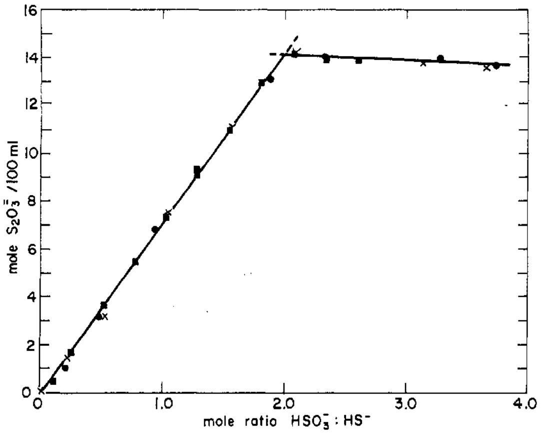

Figure 1. Mole Ratio plots: (●) $[H^+] = 1.1[SO_3^{2-}]$; (■) $[H^+] = 0.55[SO_3^{2-}]$, adjusted for available $[H^+]$; (×) $[H^+]$ = variable.

was necessarily made for that acidic component as predicted by eq 7.

$$KHS + I_2 \rightarrow S + HI + KI \tag{7}$$

The titrations for KHS and KOH showed the solution to be 0.9580 M with respect to KHS and 0.0361 M with respect to KOH. The concentration of KOH was considered insignificant and was not included in subsequent calculations.

Potassium Sulfite, K_2SO_3, Solution. Reagent grade K_2SO_3 was dissolved in water and standardized by titration with standard I_2 solution to the starch end point. The standardization yielded 0.9000 M K_2SO_3.

The standard solutions of HCl, KOH, NaOH, I_2, and $Na_2S_2O_3$ used throughout this investigation were prepared and standardized by classical methods.

Reaction Mixtures. Sulfide/sulfite reaction mixtures were prepared by pipetting appropriate volumes of standard KHS, K_2SO_3, and HCl solutions in that order into 100-mL volumetric flasks, diluting as necessary with water, and mixing. An aliquot from each mixture was treated with zinc acetate to precipitate excess sulfide ion followed by reaction with formaldehyde to complex excess sulfite ion. The $S_2O_3^{2-}$ ion remaining was titrated with standard I_2 to the starch end point.[6,7]

An additional aliquot was reacted with excess standard I_2 to measure the total I_2 oxidizable species for a material balance in terms of total sulfur. The excess I_2 was back-titrated with standard $Na_2S_2O_3$ to the starch end point. The concentrations of sulfide ion and sulfite ion were not determined individually because $ZnSO_3$ precipitates nonquantitatively with the ZnS during the zinc acetate treatment.

Results and Discussion

Mole Ratio $H^+/SO_3^{2-} = 1.1$. Consider the reaction given by eq 5. If aliquots of HSO_3^- ion are added to a stock solution of HS^- ion, $S_2O_3^{2-}$ ion will be produced in direct proportion to the added HSO_3^- ion until all of the HS^- ion has been consumed. At the point when all of the HS^- ion has been consumed, no additional $S_2O_3^{2-}$ can be generated even though more HSO_3^- ion is added. Also at that point, the ratio of the molar concentration of HSO_3^- ion to the molar concentration of HS^- ion will be 2:1.

The proportionality constant between the concentration of HSO_3^- ion added and the concentration of $S_2O_3^{2-}$ ion produced as defined by eq 5 is $^3/_4$ or 0.75. Therefore, if the concentration of $S_2O_3^{2-}$ ion generated is plotted with respect to the concentration of HSO_3^- ion reacted, a linear curve should be obtained with a slope of 0.75. The slope should go to zero after the point when all of the HS^- ion has been consumed. The change from a slope of 0.75 to 0 will occur more or less abruptly with the degree of curvature dependent upon the equilibrium constant for the overall reaction. No curvature at all indicates a quantitative reaction.

Figure 1 shows the plot obtained when 9.58 mmol of HS^- ion were reacted with increasing concentrations of HSO_3^- ion. The HSO_3^- ion was prepared with approximately equimolar quantities of HCl and K_2SO_3. The mole ratio of HSO_3^- ion to HS^- ion has been plotted vs. the measured concentration of $S_2O_3^{2-}$ ion produced.

Table I. Pertinent Data for $nH^+/nSO_3^{2-} = 1.1$

nSO_3^{2-}/nHS^-	$nS_2O_3^{2-}$	nS found	nS added	pH
0			9.58	10.60
0.187	1.00	11.10	11.38	9.46
0.469	3.16	13.89	14.08	8.35
0.939	6.75	18.13	18.58	7.99
1.409			23.08	7.50
1.879	13.06	27.58	27.58	
2.348	14.00	28.06[a]	32.08	5.21
2.818			36.58	3.14
3.288	13.92	39.06[a]	41.08	2.82
3.757	13.66	42.68[a]	45.58	2.99

[a] S precipitated.

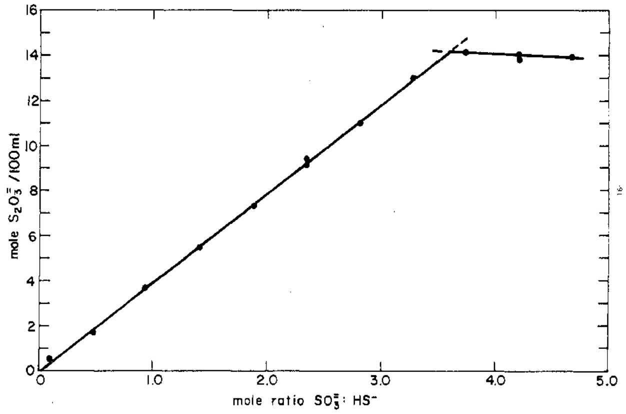

Figure 2. Mole ratio plot, $[H^+] = 0.55[SO_3^{2-}]$.

The point of discontinuity at which the slope goes to zero occurs when the mole ratio of HSO_3^- ion to HS^- ion is 2. The initial slope of the curve as plotted is 7.19. Mathematically eliminating the HS^- ion term gives a slope of 7.19/9.58 = 0.75_1. The measured concentrations of $S_2O_3^{2-}$ ion, the pH of the final solutions, and the material balances are given in Table I.

Mole Ratio $H^+/SO_3^{2-} = 0.55$. Equation 8 has also been considered. If this equation takes place, the concentration

$$2HSO_3^- + 2SO_3^{2-} + 2HS^- \rightarrow 3S_2O_3^{2-} + H_2O + 2\,^-OH \tag{8}$$

of HCl does not need to be equimolar with SO_3^{2-} ion to obtain the same results defined above. In this case, only $^1/_2$ of the SO_3^{2-} ions need to be protonated to fully react with the HS^- ions. In addition, the pH would necessarily increase because hydroxyl ions, ^-OH, are produced.

Figure 2 shows the plotted results when the fraction of hydrogen ions added is 0.55 of the SO_3^{2-} ions added. Instead of the slope going to zero at a mole ratio of 2, the mole ratio is 3.6 and the initial slope, corrected for HS^- ion, is 3.91/9.58 = 0.40_8. Table II gives the measured concentration of $S_2O_3^{2-}$, the pH of the initial solutions, and the material balance. Note that the pH does not increase as would be expected by eq 8, but in fact decreases.

Reconsider eq 5 once again. If the HSO_3^- ion is the reactive sulfite species, only that species should be considered in the mole ratio calculation. Assuming that all of the HCl added protonates an equivalent amount of SO_3^{2-} ions to generate HSO_3^- ions, a plot of the mole ratio of hydrogen ions, H^+, to HS^- ions added vs. the concentration of $S_2O_3^{2-}$ ion produced should yield the expected curve with a discontinuity at mole ratio 2 and an initial slope of 0.75.

The curve has been plotted in Figure 1 with the data for the mole ratio = 1.1 case for comparison. The slope in fact

Table II. Pertinent Data for $nH^+/nSO_3^{2-} = 0.55$

nSO_3^{2-}/nHS^-	$nS_2O_3^{2-}$	nS found	nS added	pH
0			9.58	10.60
0.187	0.447	11.09	11.38	9.88
0.469	1.62	13.99	14.08	10.25
0.939	3.62	18.75	18.58	10.60
1.409	5.43	23.20	23.08	10.22
1.879	7.29	27.63	27.58	9.28
2.348	9.32., 9.15	31.22, 32.27	32.08	9.19
2.818	10.96	36.75	36.58	9.15
3.288	12.97	41.61	41.08	8.90
3.757	14.11	46.09	45.58	8.27
4.227	13.92, 13.73	48.35, 45.95	50.08	8.11, 8.00
4.697	13.87	52.00	54.58	7.73

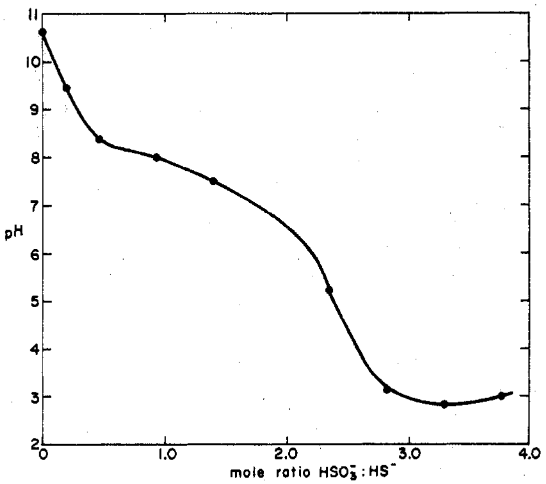

Figure 3. Mole ratio vs. pH, $[H^+] = 1.1[SO_3^{2-}]$.

is 0.74_4, while the point of slope change occurs at mole ratio = 2.

The inference to be gained, then, is that only the HSO_3^- ion reacts with HS^- ion. Any SO_3^{2-} ion present will not react.

The pH values for the equimolar case, $[H^+] = [SO_3^{2-}]$, have been plotted with respect to the mole ratio of HSO_3^- ion to HS^- ion and further substantiate that conclusion. The curve is shown in Figure 3. Equation 5 predicts that the pH of the solution should approach the pH of thiosulfate ion in water. The pH of 14.25 mmol of $K_2S_2O_3$ in 100 mL of water has been measured at 7.27. Close examination of Figure 3 shows that the pH appears to approach a value between 7 and 8 before all of the HS^- is consumed ($[HSO_3^-]/[HS^-] = 2$). After the HS^- ion has been consumed, excess HSO_3^- ion is added, and the pH decreases rather rapidly. The initial drop in pH is probably a result of neutralizing the strongly basic HS^- ion.

Incremental Addition of HCl. The validity of eq 5 and its dependence upon hydrogen ion concentration has been shown conclusively by placing HS^- ion and excess SO_3^{2-} ion together and adding increments of H^+ ion to the mixture. A plot of the H^+ ion concentration added with respect to the concentration of HS^- ion vs. the $S_2O_3^{2-}$ ion generated yielded a curve identical with those given in Figure 1.

Table III. Pertinent Data for nH^+/nSO_3^{2-} = Variable

nH^+/nHS^-	$nS_2O_3^{2-}$	nS found	nS added	pH
0	0.047	43.63	45.58	10.68
0.209	1.45	43.21	45.58	9.62
0.523	3.71	43.69	45.58	9.59
1.047	7.50	44.88	45.58	9.43
1.570	11.08	44.56	45.58	9.13
2.094	14.16	44.89	45.58	8.12
2.617	13.82	42.41	45.58	7.31
3.141	13.73	41.41	45.58	6.70
3.664	13.56	40.44	45.58	5.95

For comparison, the data have been plotted on Figure 1 with the data obtained for the $[H^+]/[SO_3^{2-}] = 1.1$ case. Very close agreement is apparent. The $S_2O_3^{2-}$ ion concentrations, pH of the final solutions, and material balances are given in Table III. Note that again the pH of the solution decreases.

Equilibrium Established before Analysis. All of the mole ratio vs. $S_2O_3^{2-}$ ion curves indicate that the reaction expressed by eq 5 is quantitative. Little or no curvature is observed around the point where the slope goes to zero, and a quantitative yield of $S_2O_3^{2-}$ ion is produced over the entire concentration range studied.

It has been noted, however, that when the pH dips below about 6, generally after the HSO_3^-/HS^- mole ratio has been exceeded and excess HSO_3^- ion is added, a finely divided, white precipitate identified as elemental sulfur by infrared measurements forms and will not redissolve on standing. In most of the reaction mixtures, the same precipitate occurs during the HCl addition, but it redissolves in 30 min or less. For that reason, the reaction mixtures were allowed to stand tightly stoppered for at least 1 h before analysis.

To ensure that 1 h is sufficient, solutions have been analyzed after standing 1 h and after longer than 1 h. One solution that measured 1.14 mmol of $S_2O_3^{2-}$ after 1 h measured 1.11 mmol of $S_2O_3^{2-}$ after 3 h, while another showed 13.92 mmol after 1 h and 13.73 mmol after 18 h. Those solutions as well as the uniformity of the curves imply that the reaction does indeed go to completion prior to analysis.

Acknowledgment. The laboratory assistance of Mr. H. K. Bedillion, who collected the analytical data, is appreciated.

Registry No. HS^-, 15035-72-0; HSO_3^-, 15181-46-1.

References and Notes

(1) H. Stamm and M. Goehring, *Z. Anorg. Allg. Chem.*, **242**, 413 (1939).
(2) R. Barbieri and R. Majorca, *Ric. Sci. Suppl.*, **30**, 2337 (1960).
(3) M. B. Neiman, E. S. Torsueva, A. I. Fedoseeva, and P. S. Shantarovich, *Dokl. Akad. Nauk SSSR*, **86**, 317 (1952).
(4) V. F. Foerster and R. Vogel, *Z. Anorg. Allg. Chem.* **155**, 161 (1926).
(5) V. F. Foerster and E. Th. Mommsen, *Ber.*, **57**, 258 (1924).
(6) A. Kurtenacker, *Z. Anal. Chem.*, **64**, 56 (1924).
(7) D. N. Fogg. and N. T. Wilkinson, *J. Appl. Chem.*, **2**, 357 (1952).