

sion constant of the polymer. For a typical value of R of 0.1 cm. and taking $t_D \approx \tau$, we find for the Dow PST. in tetralin with $\bar{M}_w = 1.5 \times 10^6$ a value of D of 4×10^{-7} cm.²/sec. This compares, in order of magnitude at least, with a diffusion constant of 1.06×10^{-7} cm.²/sec. reported²³ for a PST. fraction in toluene with a $\bar{M}_{w,w}$ of 1.1×10^6 .²⁴ Such a diffusion process is caused not by the presence of an initial concentration gradient but by a

(23) H. A. Stuart, ref. 21, p. 474.

(24) The M dependence of τ (since $\nu \approx 1/D$) is not inconsistent with the above.

gradient in chemical potential of the polymer in the drop.

Acknowledgments.—We are grateful to Dr. E. Fatt and his associates at the California Research Center for allowing us to study their pendant drop apparatus. Finally we wish to thank Prof. K. J. Mysels for many valuable suggestions and clarifying discussions in connection with the experimental work as well as for his interest in this problem.

LOS ANGELES, CAL.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Displacement Reactions at the Sulfur Atom. I. An Interpretation of the Decomposition of Acidified Thiosulfate

BY ROBERT EARL DAVIS¹

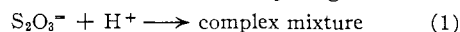
RECEIVED JANUARY 30, 1958

The kinetic results of La Mer and co-workers on the decomposition of acidified sodium thiosulfate in dilute aqueous solution have been interpreted on a mechanistic basis. The initial rate of production of sulfur is given by the rate $k(\text{Na}_2\text{S}_2\text{O}_3)^{3/2}(\text{HCl})^{1/2}$. This rate expression has been explained using a series of nucleophilic displacement reactions at the sulfur atom. The proposed reactions fit the experimental data and the rate laws are derived. The production of various polythionic acids and hydrogen sulfide during the decomposition has been explained.

Introduction

The decomposition of acidified sodium thiosulfate solutions has received intensive study²⁻¹² and has been important in the development of the physical chemistry of colloidal solutions.⁶⁻¹⁰ The products of the reaction have been determined^{4-6,12} and various kinetic investigations have been made,^{4-6,8,11,12} but the results have remained essentially unexplained and difficult to interpret on a mechanistic basis.¹¹ Any proposed mechanism must be able to explain the products of the reaction, and the results of the kinetic studies: the reaction order and the effect of salts upon the rate.

Products.—The products of reaction 1 are sulfur dioxide, colloidal sulfur, S_8 , S_6 , various polythionic acids of the formula $\text{H}_2\text{S}_x\text{O}_6$ and hydrogen sulfide.



The nature of the products has been determined by Bassett and Durrant⁵ and confirmed by other workers. Several forms of sulfur are produced in the reaction; much of the sulfur occurs as S_8 and some as insoluble sulfur which is a polymeric form having long sulfur chains. Hexatomic sulfur, S_6 , is produced in small yield from the decomposition of concentrated solutions of sodium thiosulfate and

hydrochloric acid in the cold.^{13,14} This form has been characterized by molecular weight determinations, by its greater reactivity,¹⁴ by its ultraviolet spectrum^{14,15} and by X-ray diffraction patterns.¹⁶ The production of the polythionic acids can be increased by the addition of varying amounts of arsenic trioxide^{17,18} to the reaction mixture. The presence of hydrogen sulfide formed during the reaction escaped the attention of many of the early workers but has been detected in small amounts.^{5,19} The yield of hydrogen sulfide has always been low; this would be expected because sulfur dioxide and hydrogen sulfide react in water, producing among other products sulfur.^{18,20} The results of the radiochemical study of reaction 1 demonstrate that the two sulfur atoms of thiosulfate are not equivalent²¹ and that during the preparation of thiosulfate and during the decomposition in acid the sulfur atoms maintain their identities and individualities.

(13) A. H. W. Aten, *Z. physik. Chem.*, **88**, 321 (1914).

(14) P. D. Bartlett and G. Meguerian, *THIS JOURNAL*, **78**, 3710 (1956).

(15) R. E. Whitfield, Thesis, Harvard University.

(16) C. Frondel and R. E. Whitfield, *Acta Cryst.*, **3**, 242 (1950).

(17) A. Kurtenacker and K. Matejka, *Z. anorg. Chem.*, **229**, 19 (1936).

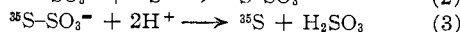
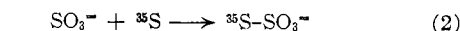
(18) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1946, pp. 387-399.

(19) J. Janickis, *Z. anorg. Chem.*, **234**, 193 (1937).

(20) The reaction of hydrogen sulfide with sulfur dioxide in water produces a solution known as Wackenroder's Solution. Historically, the polythionic acids were first observed in this reaction mixture. Numerous investigations on this reaction have been made since 1850; however, the chemistry is much in doubt and the mechanism of the reaction is not known. The same solution can be prepared by the hydrolysis of sulfur chlorides in water. Wackenroder's Solution will cold vulcanize gum rubber.

(21) H. H. Voge and W. F. Libby, *THIS JOURNAL*, **59**, 2474 (1937); E. B. Andersen, *Z. physik. Chem.*, **B32**, 237 (1936).

- (1) National Institutes of Health Predoctoral Fellow, 1957-1958.
- (2) H. Landolt, *Ber.*, **16B**, 2958 (1883).
- (3) G. Foussereau, *Ann. chim. phys.*, [6] **15**, 533 (1888).
- (4) J. Scheffer and F. Böhm, *Z. anorg. Chem.*, **183**, 151 (1929).
- (5) H. Bassett and R. G. Durrant, *J. Chem. Soc.*, 1401 (1927).
- (6) C. K. Jablczynski and Z. Warszawska-Rytel, *Bull. soc. chim. France*, [4] **39**, 409 (1926).
- (7) G. Oster, *J. Colloid Sci.*, **2**, 291 (1947).
- (8) E. M. Zaiser and V. K. La Mer, *ibid.*, **3**, 571-598 (1948).
- (9) V. K. La Mer and A. S. Kenyon, *ibid.*, **2**, 257 (1947).
- (10) I. Johnson and V. K. La Mer, *THIS JOURNAL*, **69**, 1184 (1947).
- (11) R. H. Dinegar, R. H. Smellie and V. K. La Mer, *ibid.*, **73**, 2050 (1951).
- (12) F. Prakke and E. Stiasny, *Rec. trav. chim.*, **52**, 615 (1933).



Kinetics.—The most recent and reliable kinetic investigation of the reaction has been that of La Mer and co-workers.⁸⁻¹¹ The decomposition was studied spectrophotometrically in dilute aqueous solution^{8,11} at constant ionic strength. Measurements were made at 400 μ , and the time of appearance of discrete sulfur particles was determined when the Tyndall beam appeared. The amount of sulfur produced at the time of Tyndall beam appearance was estimated to be of the order of 3.9×10^{-7} molar (based on S_8). The results were found to be expressed in terms of the rate of sulfur appearance as

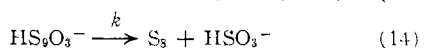
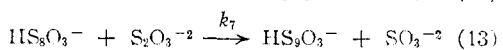
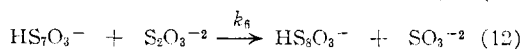
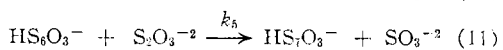
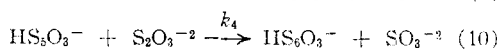
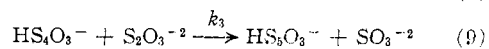
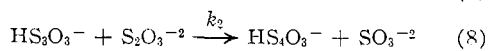
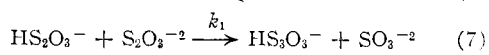
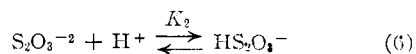
$$\text{rate} = k'(\text{Na}_2\text{S}_2\text{O}_3)^{3/2}(\text{HCl})^{1/2} \quad (4)$$

Such a rate expression was difficult for the investigators to interpret.¹¹ The reaction was followed further by titration^{8,11} and the rate of production of sulfur dioxide was found to obey the relationship

$$\text{rate} = k''(\text{Na}_2\text{S}_2\text{O}_3)^2(\text{HCl})^1 \quad (5)$$

The addition of salts demonstrated a positive salt effect.

Interpretation. Production of Sulfur.—The reaction scheme which can explain the experimental data is based upon the steps



Derivation of Rate Equation.—The feature of equations 6-14 is that a series of bimolecular reactions produce the precursor (HS_9O_3^-) of sulfur. This precursor then reacts by a unimolecular reaction. The nature of the intermediates will be considered in the following discussion.

Stage I.—The extent of reaction when the first turbidity of sulfur appears is only 0.01%. The initial concentrations of thiosulfate and hydrogen ion are about 10^{-3} molar and the concentration of sulfur produced is of the order of 10^{-7} molar based on S_8 .^{8,11} Thus (HS_2O_3^-) and ($\text{S}_2\text{O}_3^{2-}$) are constant. This fact allows the complete solution of the rate equations derived from the reaction scheme. Let $x = (\text{HS}_9\text{O}_3^-)$, $B = (\text{HS}_8\text{O}_3^-)$, $C = (\text{HS}_7\text{O}_3^-)$. . . $G = (\text{HS}_3\text{O}_3^-)$, $S = (\text{S}_2\text{O}_3^{2-})$ and $T = (\text{HS}_2\text{O}_3^-)$, S and T constant, then

$$\frac{dS_8}{dt} = kx \quad (15)$$

$$\frac{dx}{dt} = k_7BS - kx \quad (16)$$

$$\frac{dB}{dt} = k_6CS - k_7BS \quad (17)$$

$$\frac{dC}{dt} = k_5DS - k_6CS \quad (18)$$

$$\frac{dD}{dt} = k_4ES - k_5DS \quad (19)$$

$$\frac{dE}{dt} = k_3FS - k_4ES \quad (20)$$

$$\frac{dF}{dt} = k_2GS - k_3FS \quad (21)$$

$$\frac{dG}{dt} = k_1TS - k_2GS \quad (22)$$

Several methods can be used to solve the system of equations 15 to 22. One treatment would consider the system as a sequence of first-order processes because S , the thiosulfate concentration, and T , the bithiosulfate concentration, are constant during the initial stage of the reaction. However, equation 22 is a linear first-order differential equation in G (T and S constant) which can be integrated from $t = 0$ to t and evaluated using the boundary conditions that $G = 0$ at $t = 0$. The result can be expressed as

$$k_2GS = k_1TS(1 - e^{-k_2St}) \quad (23)$$

This solution is then put into equation 21 which is another linear first-order differential equation in F . Integration and evaluation with the appropriate boundary conditions give

$$k_3FS = k_1TS(1 - e^{-k_3St}) + k_1TS \frac{k_3}{k_3 - k_2} [e^{-k_2St} - e^{-k_3St}] \quad (24)$$

Substitution of equation 24 into 20 and integration gives

$$k_4ES = k_1TS(1 - e^{-k_4St}) + k_1TSk_4 \left[\frac{e^{-k_3St}}{k_4 - k_3} - \frac{e^{-k_2St}}{k_4 - k_2} \right] + k_1TS \frac{k_3k_4}{k_3 - k_2} \left[\frac{e^{-k_2St}}{k_4 - k_3} - \frac{e^{-k_1St}}{k_4 - k_3} + \frac{e^{-k_1St}}{k_4 - k_2} - \frac{e^{-k_2St}}{k_4 - k_2} \right] \quad (25)$$

The form of the equations can be seen to be

$$k_jZS = k_1TS(1 - e^{-k_jSt}) + k_1TSf(k_2, k_3, \dots, k_1, e^{-k_jSt})$$

This operation is repeated until an expression for k_7BS is obtained in terms of k_1TS and k_j ($j = 2, \dots, 7$). Equation 16 is then solved for x in the same manner and kx introduced into equation 15

$$\frac{dS_8}{dt} = k_1TS(1 - e^{-k_7St}) + k_1TSf(k_7, S, t) \quad (26)$$

where $f(k_7, S, t)$ is a composite function like the terms of equation 25. Integration of (26) with the boundary conditions that $S_8 = 0$ at $t = 0$ gives

$$S_8 = k_1TS \left[t + \frac{e^{-kt} - 1}{k} \right] + k_1TSF(k_7, S, t) \quad (27)$$

where the function F is a complex summation of terms. La Mer¹¹ obtained the first term of equation 27 by considering only one bimolecular reaction followed by a unimolecular decomposition. The data were then treated by plotting the concentration of sulfur *versus*

$$\left[t + \frac{e^{-kt} - 1}{k} \right]$$

The resultant linear plot had a slope of k_1TS and an intercept, which in their figure (*cf.* Fig. 3)¹¹ is not identically zero, but very close to zero. The inter-

cept represents the second term of equation 27, which is now seen to be small. No assumptions have been made in the derivation concerning the values of the various rate constants. However, many of the rate constants ought to be nearly equal because of the similarity of the chemical intermediates. If $k_2 = k_3 = k_4$ the complex terms of equation 25 are zero, leaving only the first term. Expressing the concentrations of bithiosulfate (T) and the thiosulfate ions (S) in terms of the initial concentrations of sodium thiosulfate and acid, the following equations are needed

$$K_2 = \frac{(H^+)(S_2O_3^{2-})}{(HS_2O_3^-)} = \frac{[(H^+)_0 - (HS_2O_3^-)][(S_2O_3^{2-})_0 - (HS_2O_3^-)]}{[HS_2O_3^-]} \quad (28)$$

where $(H^+)_0$ is the initial acid concentration, $(S_2O_3^{2-})_0$ the initial thiosulfate concentration, and K_2 is the second ionization constant of thiosulfuric acid. Neglecting terms in $(HS_2O_3^-)^2$

$$HS_2O_3^- = \frac{(H^+)_0(S_2O_3^{2-})_0}{K_2 + (H^+)_0 + (S_2O_3^{2-})_0} \quad (29)$$

and

$$(S_2O_3^{2-}) = (S_2O_3^{2-})_0 - (HS_2O_3^-) \quad (30)$$

Substituting (29) and (30) into (27) gives

$$S_8 = k_1 \frac{(H^+)_0(S_2O_3^{2-})_0^2 [K_2 + (S_2O_3^{2-})_0]}{[K_2 + (H^+)_0 + (S_2O_3^{2-})_0]^2} \left[t + \frac{e^{-kt} - 1}{k} + F(k_1, (S_2O_3^{2-})_0, t) \right] \quad (31)$$

Further approximation of (31) can be obtained by expanding the exponential, e^{-kt} , into the first three terms of a power series (in Stage I of the reaction both k and t are small). The first term of (31) becomes

$$S_8 = \frac{k}{2} \frac{(H^+)_0(S_2O_3^{2-})_0^2 [K_2 + (S_2O_3^{2-})_0]}{[K_2 + (H^+)_0 + (S_2O_3^{2-})_0]^2} t^2 \quad (32)$$

(32) can be transformed into

$$\frac{1}{t} = \frac{k^{1/2}(H^+)_0^{1/2} [K_2 + (S_2O_3^{2-})_0]^{1/2}}{(2S_8)^{1/2} [K_2 + (H^+)_0 + (S_2O_3^{2-})_0]} \quad (33)$$

Expanding $[K_2 + (S_2O_3^{2-})_0]^{1/2}$ in power series and neglecting terms above the square gives

$$\frac{1}{t} \propto (H^+)_0^{1/2} (S_2O_3^{2-})_0^n \quad n > 1 \quad (34)$$

As the amount of sulfur produced at the time of Tyndall beam appearance is constant,¹¹ $1/t$ is proportional to the rate. The higher terms of (31) become of the form

$$\frac{1}{t} \propto (H^+)^{1/2} (k_m S + k_n S^2 + k_q S^3 + \dots) \quad (35)$$

where the constants k_m, k_n, k_q are functions of the rate constants k_2, \dots, k_7 . The individual rate constants of these intermediate reactions are not known; however, they would probably be of the same order of magnitude. Therefore, only the first few terms of (35) would be important. An estimation of the values of k_2, \dots, k_7 and the convergence of the series could bound n within the range $\sim 2 > n > 1$. The form of the rate expression during the initial part of the decomposition was found experimentally^{8,11} to be

$$\text{rate} \propto (H^+)^{1/2} (S_2O_3^{2-})^{3/2}$$

compared to the predicted (equation 34)

$$\text{rate} \propto (H^+)^{1/2} (S_2O_3^{2-})^n \quad 2 > n > 1$$

Thus the suggested reactions 6 to 14 do predict the rate equation for the *initial* production of sulfur.

Stage II.—When the extent of reaction proceeds further, S and T can no longer be considered constant. An analytic solution to the system of competitive, bimolecular reactions cannot be obtained in closed form. However, the steady-state approximation can be made: $dG/dt = G' = 0 = F' = E' = D' = C' = B' = 0$, then $k_1 TS = k_2 GS = k_7 BS$. Then

$$\frac{dx}{dt} = k_1 TS - kx$$

$$\frac{dS_8}{dt} = kx$$

This pair of equations can be solved in closed form by introduction of dimensionless parameters, K and τ , and the results expressed in terms of K, τ and the exponential integral

$$Ei(x) = \int_{-\infty}^x \frac{e^{\xi}}{\xi} d\xi$$

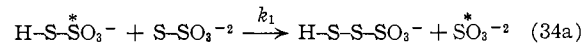
However, in the present discussion only the order of the rate expression is required. As the time becomes large, e^{-kt} terms become small and the rate reduces to $k_1 TS$. This result also can be obtained from the steady-state treatment assuming $dx/dt = 0$ in the pair of preceding equations. Expressing T and S in terms of the initial concentrations, the rate of production of sulfur (which is proportional to the production of sulfur dioxide) becomes

$$\text{rate} \propto (H)(S_2O_3^{2-})^2$$

which was found experimentally.

Discussion

Having analyzed the kinetic situation and fitted the series of reactions to the observed rate data, the nature of the intermediates and chemistry involved should be considered. The equations explain the positive salt effect, indicative that ionic species of the same charge type are reacting, and the observed dependence upon the acid concentration is explained in terms of a bimolecular reaction between bithiosulfate and thiosulfate. The thiosulfate can be visualized as undergoing a nucleophilic reaction displacing sulfite ion which then forms sulfur dioxide upon protonation. The system of equations 6 to 14 can be complicated further by including all the various protonated forms. The sulfite and thiosulfate groups have been observed to undergo displacement reactions with one another²²⁻²⁵ and several reactions have been studied kinetically using radiosulfur. Equation 7 can be described in terms of the displacement reaction



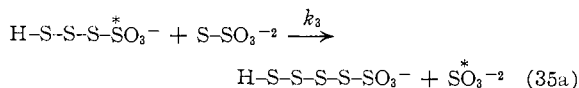
and the following reactions displacing the $-SO_3^-$ group on the end of the sulfur chain. The polysulfur intermediates

(22) D. P. Ames and J. E. Willard, *THIS JOURNAL*, **75**, 3267 (1953); **73**, 164 (1951).

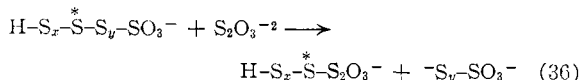
(23) J. A. Christiansen and W. Drost-Hansen, *Nature*, **164**, 759 (1949).

(24) A. Fava, *Gazz. chim. ital.*, **83**, 87 (1953).

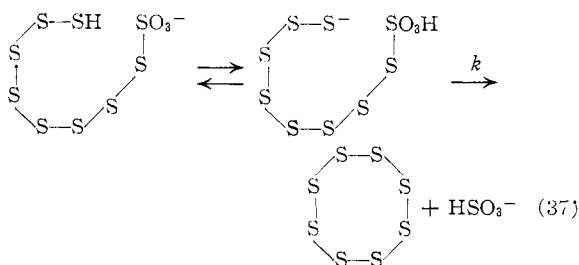
(25) A. Fava and G. Pajaro, *THIS JOURNAL*, **78**, 5203 (1956).



would resemble the hydrogen polysulfides (polysulfanes) in many respects and would be expected to have a weakly acidic hydrogen (H-S-S_x-). There is no *a priori* reason to exclude the attack of the thiosulfate in the middle of a sulfur chain; no doubt such reactions do occur

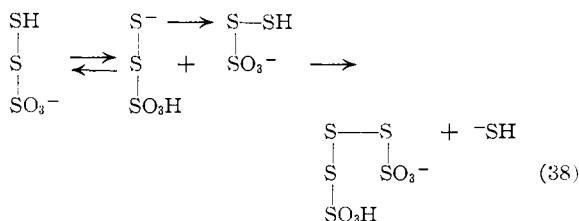


The formation of the S₈ ring in a unimolecular reaction could be formulated as



The precursor of S₆ would be HS₇O₃⁻ which then would undergo an internal displacement forming the S₆ ring. The yield of S₆ would be predicted to be low because of the instability of the S₆ ring compared to the S₈ ring^{14,26}; thus, the frequency factor of HS₇O₃⁻ forming S₆ would be lower than the chance of producing longer sulfur chains by displacement reactions with thiosulfate. The longer sulfur chains of insoluble sulfur would be built up by further displacement reactions. The true nature of these chains and the nature of termination are not known. The formation of macro rings or/and chains of H-S-S_x-S-SO₃H (x large) are possibilities but the current experimental data give no indication of the character of these materials.

The formation of the polythionic acids can also be explained using thiophilic, nucleophilic displacement reactions. The sulfo-polysulfane²⁷ intermediates could produce the polythionates by using the sulfide sulfur as the displacement reagent. Thus the production of pentathionate could be formulated



Fragmentation of the sulfur chains by attack in the middle of the sulfur chains forming polysulfides and polythionates are likely reactions also. The species of (38) could be in various stages of protonation. Hydrogen sulfide is never produced in

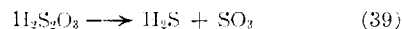
(26) L. Pauling, *Proc. Nat. Acad. Sci.*, **35**, 495 (1949).

(27) Compounds of the type H-S_x-SO₃H have been recently reported and some reactions discussed. In many cases the reactions are explicable on the thesis of nucleophilic displacement reactions at the sulfur atom (M. Schmidt, *Z. anorg. Chem.*, **289**, 158 (1957)).

yields equivalent to that of the polythionic acids; however, hydrogen sulfide and the polysulfanes react with sulfur dioxide producing sulfur and other products.²⁰ Addition of arsenic trioxide increases the yield of the polythionic acids.^{17,18} Arsenic (III) would shift the equilibria of reactions like (38) by removing the hydrogen sulfide as arsenic sulfide. In dilute aqueous solution La Mer^{8,11} estimated that sulfur is the main product of the reaction with only small amounts of polythionate formation. Under controlled conditions, using arsenic trioxide, rather good yields of the polythionic acids can be obtained.^{17,18}

The Decomposition in Concentrated Solutions.—

The kinetic results were obtained in dilute aqueous solution of the order of 10⁻³ molar in the reactants. The effect of large amounts of acid has been measured by many investigators. If cold, concentrated hydrochloric acid is used in large excess, there is an immediate precipitation of sodium chloride, and the solution remains clear and colorless for eight hours.¹⁹ Bassett and Durrant⁵ obtained minima in their curves of sulfur appearance time *versus* the concentration of hydrochloric acid added. The minima occur in the region of one molar acid. The facts can be described by the effects of hydrogen ion upon the equilibrium 6 and the various other reactions which produce decomposition. Thiosulfuric acid in very strong hydrochloric acid appears to be somewhat stable¹⁹ and much less stable in phosphoric acid.⁵ Foss²⁸ predicted that pure thiosulfuric acid should decompose into hydrogen sulfide and sulfur trioxide



Recently, Schmidt²⁹ has prepared solutions of thiosulfuric acid by the decomposition of sodium thiosulfate with HCl in ether at -78°. A dietherate of thiosulfuric acid was obtained which decomposed at -5° by reaction 39. Likewise, the reaction of hydrogen sulfide and sulfur trioxide in ether at low temperatures produced thiosulfuric acid. Reaction of the polysulfanes (H₂S_x) with sulfur trioxide in ether at -78° was found to produce either the polysulfane monosulfonic acids, H-S_x-SO₃H, or the polythionic acids, HSO₃-S_x-SO₃H. The polysulfane monosulfonic acids have been inferred to be present in the decomposition analyzed in this report.

The stepwise build up of a sulfur chain by displacement reactions is consistent with the kinetic results of a series of reactions in which a sulfur chain is degraded atom by atom. The reactions of triarylphosphines,^{14,30} cyanide ion,³¹ sulfide and sulfite³² with sulfur have been studied kinetically in homogeneous solution. In each case the sulfur ring is opened and then degraded by the thiophilic reagent one atom of sulfur at a time. The suggested mechanism of formation of the polythionates is consistent with the radiochemical data of Brodskii

(28) O. Foss, *Tids. Kjem. Bergvesen. Met.*, **6**, 3 (1946).

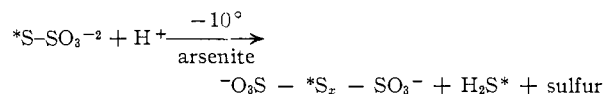
(29) M. Schmidt, *Z. anorg. Chem.*, **289**, 141, 158, 175 (1957).

(30) P. D. Bartlett, E. Cox and R. E. Davis, unpublished data.

(31) P. D. Bartlett and R. E. Davis, *THIS JOURNAL*, **80**, 2513 (1958).

(32) R. E. Davis, unpublished data.

and Eremenko.³³ It was found that the decomposition of $^*SSO_3^{-2}$ in the presence of acid and sodium arsenite gave $^-O_3S-^*S_x-SO_3^-$. The general over-all decomposition was found to be



Estimation of the Rate Constants.—The values reported for the dissociation constants of thiosulfuric acid have been near 0.45 (K_1) and in the range 0.01 to 0.062 for the second dissociation (K_2) in dilute solutions.¹¹ The previous investigators¹¹ used the value of 0.01 for K_2 and calculated the rate constants to be $k = 0.14 \pm 0.02 \text{ min.}^{-1}$ and $k_1 = 0.31 \text{ l. mole}^{-1} \text{ min.}^{-1}$ during the initial stages of the reaction and as $0.29 \text{ l. mole}^{-1} \text{ min.}^{-1}$ from the titrametric data from the latter stages of the reac-

(33) A. I. Brodskii and R. K. Eremenko, *J. Gen. Chem. (U.S.S.R.)*, **24**, 1137 (1954); **25**, 1189 (1955).

tion based upon the gram atom of sulfur. The values of the rate constants are dependent upon the value of K_2 but the values calculated are correct within the order of magnitude of the data. A reasonable assumption can be made concerning the other bimolecular reactions. These reactions are probably somewhat faster than k_1 and probably $k_3 \sim k_4 \sim k_5 \sim \dots$ because of the very similar nature of the intermediates. Assuming $k_3 = k_4 = k_5 \dots$ makes many of the higher terms of (26) and (27) zero, thus simplifying the expression and increasing the importance of the first term. The rates of formation of the various polythionates as equation 38 cannot be obtained from the data but in dilute solution these reactions are much slower and the sulfur is the main product of the decomposition.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, UNIVERSITY OF LUCKNOW]

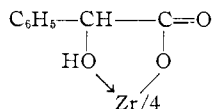
Organic Compounds of Zirconium. V. Studies of Zirconium Mandelates

By R. N. KAPOOR AND R. C. MEHROTRA

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The reaction of zirconyl chloride with mandelic acid in aqueous solution yields mainly zirconium monomandelate which dissolves in one equivalent of alkali. The tetramandelate is formed only in the presence of higher concentrations of hydrochloric acid. The reaction between zirconium isopropoxide and mandelic acid in benzene shows that the carboxyl group is more reactive than the hydroxyl group in replacing isopropyl alcohol; the latter becomes active only when a sufficient concentration of carboxyl groups is not available. The following new compounds of zirconium have been isolated: $Zr(C_6H_5O_3)(OPr-iso)_2$, $Zr(C_6H_5O_3)(C_6H_7O_3)(OPr-iso)$, $Zr(C_6H_7O_3)_2(OPr-iso)_2$ and $Zr(C_6H_5O_3)(C_6H_7O_3)(OBu)$.

The preparation of zirconium alkoxides^{1,2} and tricarboxylates³ has been reported recently. The alkoxides and tricarboxylates are immediately hydrolyzed by water, and even the zirconium salts of the strong acids are appreciably hydrolyzed in solution.⁴ Therefore, the precipitation of pure zirconium tetramandelate from solutions of zirconyl chloride in concentrated hydrochloric acid⁵ is noteworthy in view of the weakly acidic nature of mandelic acid (dissociation constant at $25^\circ = 4.29 \times 10^{-4}$). To explain this, Feigl⁶ postulated the formation of a chelate type structure



This structure explains the solubility of the tetramandelate in dilute alkaline solution as due to the enhanced acidity of the weakly acidic hydroxyl group through coordination.

Hahn and Weber,⁷ in a conductometric titration

(1) D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, 2027, 4204, 5020 (1952); 1634 (1953).

(2) R. C. Mehrotra, *THIS JOURNAL*, **76**, 2266 (1954).

(3) R. N. Kapoor and R. C. Mehrotra, *Chem. & Ind.*, 68 (1958).

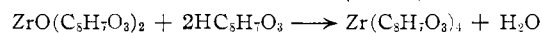
(4) B. A. J. Lister and L. A. Donald, *J. Chem. Soc.*, 4315 (1952).

(5) C. A. Kumins, *Anal. Chem.*, **19**, 376 (1947).

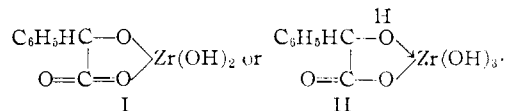
(6) F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, pp. 213-215.

(7) R. B. Hahn and L. Weber, *THIS JOURNAL*, **77**, 4777 (1955).

of zirconyl chloride solution with sodium mandelate, observed a sharp maximum when the ratio of mandelate to zirconium was 2.3:1. To explain their observations, they assumed that the following reactions occur in solution



However, it has been reported recently^{8,9} that zirconium monomandelate preferably is precipitated when zirconyl chloride is treated with mandelic acid or sodium mandelate solution. The monomandelate could have either structure



The easy hydrolysis of the alkoxy oxygen-zirconium linkage suggests that II is probably correct. Furthermore, in the titration of zirconium monomandelate with sodium hydroxide (Fig. 1), we found that that monomandelate dissolves when about 1 mole of alkali has been added; this can be explained by the neutralization of the hydroxyl hydrogen atom which has been made more acidic (dissociation con-

(8) R. B. Hahn and E. S. Baginski, *Anal. Chim. Acta*, **14**, 45 (1956).

(9) R. N. Kapoor and R. C. Mehrotra, *J. Sci. industr. Res.*, **1CB**, 300, 304 (1957).