[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

Carbonyl Reactions. II. Kinetics of the Formation of the Cyanohydrin of Propionaldehyde in Methanol

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The kinetics of formation of the cyanohydrin of propionaldehyde were studied in methanol at 25°. Measurements were conducted in acetate buffers to ascertain the influence of ionic strength and buffer composition on the rate constants. The following results were obtained: (1) the reaction of propionaldehyde with HCN follows a second-order rate equation; (2) the kinetic salt effect is small; (3) the reaction goes to completion in the buffered media used; (4) a pronounced general catalytic effect exists in methanol solutions. The molar catalytic constants were calculated by a modification of the usual procedure. The mechanism previously proposed for cyanohydrin formation is supported by the present investigation.

Introduction

Recently, Svirbely and Roth[2] studied the kinetics of formation of the cyanohydrins of propionaldehyde, acetaldehyde and acetone in water at 25° under various acetate buffer conditions. Evidence was obtained that the rate constants for the propionaldehyde reaction only increased with increasing buffer concentration, indicating that the reaction was subject to general catalysis. The increase in the rate constants was not large but it appeared to be outside experimental error.

Inasmuch as the detection of general catalysis is important in elucidating the mechanism of the reaction it was deemed worthwhile to establish the fact more conclusively by studying the kinetics of formation of the cyanohydrin of propionaldehyde in another solvent. Methanol was selected as the new solvent, since it had been shown[3] and later verified[4] that methanol has a higher acid level than water and, consequently, it might play a more observable role in the reaction. Accordingly, the kinetics of the formation of the cyanohydrin of propionaldehyde have been studied at 25° in methanol under various conditions of ionic strength and buffer composition.

Materials and Apparatus

Salts.—Mallinckrodt Analytical Reagent grade of potassium thiocyanate, silver nitrate and sodium nitrate and Eimer and Amend Test Purity grade of sodium acetate were dried in an oven at 120°. Mallinckrodt C.P. sodium chloride was purified using standard procedures. The purified salt was used as a primary standard and also as an inert electrolyte.

Standard Solutions.—Solutions of potassium thiocyanate and silver nitrate were prepared. The thiocyanate solutions were standardized with sodium chloride using the Volhard procedure. Silver nitrate solutions were standardized against potassium thiocyanate solutions.

Propionaldehyde.—Matheson Technical Grade propionaldehyde was treated as before.[2]

Methyl Alcohol.—Commercial Solvents Technical Grade methanol was purified according to a method in the literature.[5]

Acetic Acid.—J. T. Baker Reagent Grade acid was treated according to a procedure in the literature.[6]

Hydrogen Cyanide.—The method of Slotta[7] was used to prepare this substance in the anhydrous state. The gas was allowed to pass into anhydrous methanol. To facilitate solution, the alcohol was cooled in an acetone–Dry Ice mixture.

Nitrogen.—Southern Oxygen Co. nitrogen was used to provide the inert atmosphere in the reaction flask. The gas was freed first from residual oxygen and then dried using standard procedures.

Apparatus.—The reactions were carried out in the apparatus already described.[2] The constant temperature bath was maintained at 24.99 ± 0.02°.

Acetate Buffers.—For each series of runs at a constant buffer ratio, a standard concentrated buffer solution of anhydrous acetic acid and sodium acetate in methanol was prepared. Its concentration was chosen so that 20-, 10- and 5-ml. samples when withdrawn and diluted to 50% would contain the desired concentrations of sodium acetate and acetic acid. The required amounts of both compounds were weighed and placed in a volumetric flask. The solution was made up to the mark with methanol as the solvent.

Experimental Procedure and Data

Prior to the preparation of solutions for a run, all glass apparatus was carefully cleaned and dried. An atmosphere of nitrogen was maintained in the reaction flask at all times.

In general, sodium nitrate was used as the neutral salt to maintain the ionic strength. In some runs, however, sodium chloride was used.

In preparing a reaction mixture at an ionic strength of 0.200, the following procedure was used: (1) when initial concentrations of aldehyde were desired, a weighed amount of freshly distilled propionaldehyde was placed into a 100-ml. volumetric flask which already contained a weighed amount of sodium nitrate, methanol and the desired volume of buffer solution. The volumetric flask was then filled to the mark with methanol and placed in the thermostat. The amount of sodium nitrate in the volumetric flask was such that the total salt concentration was 0.200 *N*; (2) fifty ml. of the stock hydrogen cyanide solution in methanol was pipetted into the reaction flask which contained sufficient sodium nitrate to give a 0.200 *N* solution. The reaction flask was placed in the thermostat; (3) after the hydrogen cyanide and propionaldehyde solutions had come to temperature equilibrium, 50 ml. of the aldehyde solution was pipetted into the reaction flask which was then shaken vigorously; (4) from here on the experimental procedure was the same as before.[2]

In preparing a reaction mixture at an ionic strength less than 0.200, step (2) above was duplicated except that the amount of sodium nitrate necessary in 100 ml. of the reaction mixture was added to the reaction flask. In this case no inert salt was added to the aldehyde solution prepared as in step (1).

Evidence that the reaction between propionaldehyde and hydrogen cyanide in methanol goes virtually to completion was obtained as in the previous work.[2] Furthermore, in those experiments where the cyanide was initially in excess, a qualitative test with freshly prepared 2,4-dinitrophenylhydrazine[8] proved the absence of aldehyde at the end of the run.

In calculating the rate constants, the graphical method based on the second-order rate equation, namely

$$kt = \frac{2.303}{a-b} \log \frac{b(a-x)}{a(b-x)} \tag{1}$$

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[1] Abstracted in part from the Ph.D. thesis of F. H. Brock.

[2] W. J. Svirbely and J. F. Roth, THIS JOURNAL, **75**, 3106 (1953).

[3] J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).

[4] W. C. Woodland, R. B. Carlin and J. C. Warner, *ibid.*, **75**, 5835 (1953)

[5] N. Bjerrum and L. Zechmeister, *Ber.*, **56**, 894 (1923).

[6] K. J. P. Orton, G. Edwards and H. J. King, *J. Chem. Soc.*, **99**, 1178 (1911).

[7] K. H. Slotta, *Ber.*, **67B**, 1028 (1934).

[8] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 97.

where a and b are the initial concentrations and $(a - x)$ and $(b - x)$ are the existing concentrations at any time, t, was used. For the calculations, existing hydrogen cyanide concentrations were experimentally determined as before[2] while existing aldehyde concentrations were calculated since the data show that the reaction occurs on the mole for mole basis. The data for a typical run are shown in Table I.

TABLE I

Buffer composition, 0.01314 N HOAc, 0.00657 N NaOAc; $\mu = 0.200$; final concn. of HCN, $(a - b) = 0.0605$ N; slope of $\log \frac{a - x}{b - x}$ *vs.* $t = 0.00328$; $k = 0.125$ liter/mole min.

t (min.)	HCN (exp.) $(a - x)$, moles/l.	Aldehyde (calcd.) $(b - x)$, moles/l.
10.15	0.1015	0.0410
20.10	.0974	.0370
29.98	.0936	.0332
40.08	.0899	.0295
49.75	.0867	.0264

In Table II are listed the k values for several experiments in which the initial HCN/propionaldehyde ratio was varied from 0.56 to 1.7. The rate constants are in fair agreement with one another, showing a true second-order reaction. Generally, however, the hydrogen cyanide was initially in excess of the aldehyde.

TABLE II

Initial aldehyde, moles/l.	Initial HCN, moles/l.	Ionic strength	$\frac{OAc^-}{HOAc}$	k, l./mole min.
0.0803	0.1165	0.05	0.224	0.086
.2094	.1167	.05	.224	.088
.0572	.0988	.200	.500	.100
.1460	.0601	.200	.500	.092
.0474	.0879	.200	.500	.100

The effect of ionic strength at a constant buffer ratio and of buffer composition at a constant ionic strength on the rate constants are summarized by the data listed in Tables III and IV, respectively. Two or three runs were made under each set of conditions. The reproducibility of the data are indicated in the tables.

TABLE III

INFLUENCE OF IONIC STRENGTH ON THE RATE CONSTANTS AT $OAc^-/HOAc$ EQUAL TO 0.224

Buffer compn. NaOAc, N	HOAc, N	Neutral salt	Ionic strength	k, l./mole min.
0.01315	0.0588	$NaNO_3$	0.050	0.088 ± A.D.M. 0.001
.01315	.0588	NaCl	.050	.087 ± A.D.M. .001
.01318	.0590	$NaNO_3$	.100	.090 ± A.D.M. .001
.01318	.0590	$NaNO_3$	.200	.080 ± A.D.M. .000
.01317	.0588	NaCl	.200	.079 ± A.D.M. .001

Discussion

Influence of Ionic Strength.—Reference to Table III shows that the salt effect on the kinetics of formation of the cyanohydrin of propionaldehyde in methanol is small but not negligible.

Influence of Buffer Concentrations.—In order to suppress the salt effect, all runs at the various buffer ratios were carried out at a constant ionic strength of 0.2. Reference to Table IV shows that the rate constants in every group of experiments run at a constant buffer ratio in methanol increased markedly with increasing concentration of the buffer components, thus indicating general catalysis. Similar behavior, but not as marked, had been observed[2] for the same reaction in water.

TABLE IV

EFFECT OF BUFFER COMPOSITION ON THE RATE CONSTANT AT A CONSTANT IONIC STRENGTH[a] OF 0.200

HOAc, N	NaOAc, N	$\frac{OAc^-}{HOAc}$	k, l./mole min.	k, calcd. by eq. 7
0.671	0.1500[b]	0.224	0.087 ± 0.000	1.50
.0590	.01317	.224	.079 ± .001	.171
.01652	.03370	.224	.073 ± .001	.078
.00826	.00185	.224	.061 ± .000	.060
.01312	.00459	.350	.095 ± 0.002	.096
.00655	.00229	.350	.077 ± .002	.074
.00328	.00115	.350	.061 ± .003	.063
.01314	.00657	.500	.128 ± 0.002	.127
.00657	.00328	.500	.097 ± .004	.095
.00325	.00164	.500	.072 ± .001	.079
.00131	.000657	.500	.068 ± .002	.069
.01310	.01310	1.00	.226 ± 0.001	.230
.00655	.00655	1.00	.169 ± .003	.166
.00328	.00328	1.00	.135 ± .003	.134
.00659	.01318	2.00	.319 ± 0.000	.309
.00330	.00659	2.00	.241 ± .01	.245
.00165	.00330	2.00	.205 ± .000	.212

[a] $NaNO_3$ was used as the inert electrolyte in all runs.
[b] Ionic strength was 0.150.

In the case of general catalysis, the molar rate constant, k, can be expressed in terms of the molar catalytic constants, k_i, and the concentrations of the various catalytic species[9] by equations 2 and 3, namely

$$k = \Sigma k_i C_i \tag{2}$$

$$k = k_0 + k_{H^+}(H^+) + k_{RO^-}(RO^-) + k_{HA}(HA) + k_{A^-}(A^-) \tag{3}$$

Equation 3 is usually rearranged to give

$$k = k_0 + k_{H^+}(H^+) + k_{RO^-}(RO^-) + (HA)\left[k_{HA} + k_{A^-}\frac{(A^-)}{(HA)}\right] \tag{4}$$

In accordance with equation 4, the usual procedure is to plot k *vs.* (HA) at a constant buffer ratio of $(A^-)/(HA)$. Such a plot should be linear for each ratio value and the slope and intercept of such a plot will be equal to $[k_{HA} + k_{A^-}(A^-)/(HA)]$ and $[k_0 + k_{H^+}(H^+) + k_{RO^-}(RO^-)]$, respectively. If one now plots the slopes of these lines against their corresponding ratio values the result should be a straight line whose slope will be k_{A^-} and intercept will be k_{HA}. From such a plot, we calculate k_{OAc^-} and k_{HOAc} to be 9.4 and 0, respectively.

However, it is also possible to start with equation 3 and obtain other relations which can be used for evaluating the catalytic constants. Rearrange equation 3 to give

$$k = [k_0 + k_{HA}(HA)] + \frac{(A^-)}{(HA)}\left[k_{RO^-}\frac{K_{ROH}}{K_{HA}} + k_{A^-}(HA)\right] + k_{H^+}K_{HA}\frac{(HA)}{(A^-)} \tag{5}$$

At constant (HA), equation 5 becomes

$$k = k_1 + k_2 x + k_3\, 1/x \tag{6}$$

in which $x = (A^-)/(HA)$. The application of equation 6 is possible only when the last term in the equation is small relative to the rest of the terms. If such is the case, then in accordance with equation 6, one can plot k against $(A^-)/(HA)$ at con-

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(9) (a) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, Oxford, England, 1941, p. 60; (b) "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 174.

stant HA. Such a plot should be linear and the slope and intercept will be equal to $[k_{\mathrm{RO}^-}K_{\mathrm{ROH}}/K_{\mathrm{HA}} + k_{\mathrm{A}^-}(\mathrm{HA})]$ and $[k_0 + k_{\mathrm{HA}}(\mathrm{HA})]$, respectively. Such plots of our data are shown in Fig. 1. If one now plots the slopes of the lines of Fig. 1 against their corresponding (HA) values, the result should be a straight line whose slope and intercept will be k_{A^-} and $k_{\mathrm{RO}^-}(K_{\mathrm{ROH}}/K_{\mathrm{HA}})$, respectively. Our calculated results for k_{OAc^-} and $k_{\mathrm{CH_3O}^-}$ using the above procedure are 9.8 and 0.86×10^6, respectively. In making these calculations, the autoprotolytic constant of methanol and the dissociation constant of acetic acid in methanol were taken[10] to be 0.2×10^{-16} and 0.22×10^{-9}, respectively. The intercept of each plot of Fig. 1 is defined by $[k_0 + k_{\mathrm{HA}}(\mathrm{HA})]$. In accordance with this definition, a plot of the intercepts of Fig. 1 against the corresponding (HA) values should permit us to evaluate k_0 and k_{HA} from the intercept and slope of the resulting line. Actually in our case, as reference to Fig. 1 will show, only one intercept was obtained. Therefore, it follows that k_{HOAc} and k_0 are 0 and 0.024, respectively.

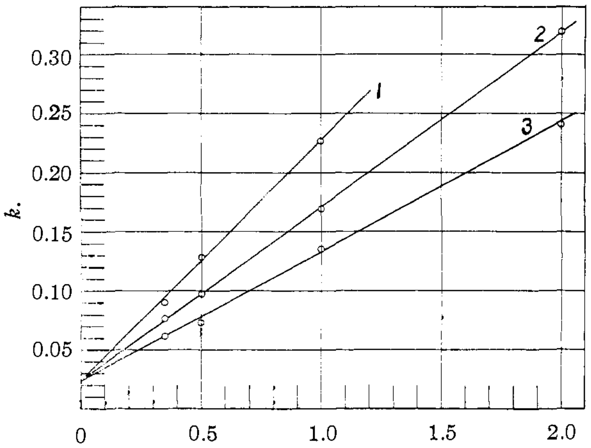

Fig. 1.—Rate constant *versus* buffer ratio at constant acid concentration in methanol. HOAc values are 0.0131, 0.00657, and 0.00328 for curves 1, 2 and 3, respectively.

On substituting the calculated catalytic constants into equation 5 one obtains

$$k = 0.024 + 9.8(\mathrm{OAc}^-) + 0.078\,\frac{(\mathrm{OAc}^-)}{(\mathrm{HOAc})} \qquad (7)$$

The last column in Table IV shows that equation 7 reproduces the experimental data very well except in the two most concentrated acetic acid solutions.

It is possible to rearrange equation 7 to yield

$$k = 0.024 + 9.8\,(\mathrm{OAc}^-) + \frac{0.078K_{\mathrm{HOAc}}}{(\mathrm{H}^+)} \qquad (8)$$

On the basis of equation 8 one concludes that the reaction is catalyzed by the acetate ion but retarded by the hydrogen ion. Since $(\mathrm{H}^+) = K_{\mathrm{HOAc}}[(\mathrm{HOAc})/(\mathrm{OAc}^-)]$, then at equal acetate ion concentrations but at different $(\mathrm{OAc}^-)/(\mathrm{HOAc})$ values, the rate constant should be smaller in the more acidic solutions. This is borne out by the data in Table IV.

It is also possible to rearrange equation 8 and obtain

$$k = 0.024 + 9.8(\mathrm{OAc}) + 0.078\,\frac{K_{\mathrm{HOAc}}}{K_{\mathrm{CH_3OH}}}\,(\mathrm{CH_3O}^-) \qquad (9)$$

On the basis of equation 9 one concludes that the rate constant not only depends on the concentration of the acetate ion but also on concentration of the methoxy ion.

If one plots k *vs.* $(\mathrm{A}^-/\mathrm{HA})$ at constant (HA) for the propionaldehyde reaction in *water*, interpolating the data given in reference 2, then Fig. 2 is obtained. From this plot, in accordance with the procedure already described, one obtains the empirical relation

$$k = -0.03 + 0.7(\mathrm{OAc}^-) + 1.33\,\frac{K_{\mathrm{HOAc}}}{K_{\mathrm{W}}}\,(\mathrm{OH}^-) \qquad (10)$$

Equation 10 reproduces quite well all of the data given in Table VI, reference 2, for the propionaldehyde reaction. It is apparent that the results in both water and methanol lead to the same conclusion concerning the propionaldehyde reaction in regard to catalysis by the acetate ion and by the basic ion furnished by the solvent.

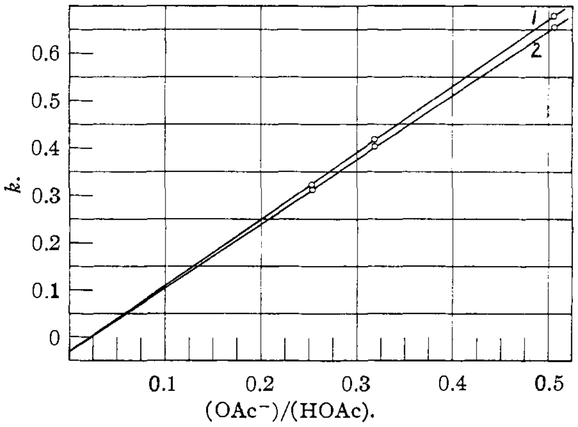

Fig. 2.—Rate constant *versus* buffer ratio at constant acid concentration in water. HOAc values are 0.1010 and 0.0202 for curves 1 and 2, respectively. Data interpolated from data given in ref. 2.

Mechanism.—The mechanism postulated in the earlier paper[2] for carbonyl addition reactions becomes for cyanohydrin formation

$$>\mathrm{C{=}O} + \mathrm{HA} \underset{}{\overset{K_1}{\underset{\text{fast}}{\rightleftarrows}}} >\mathrm{C{=}O}\text{- - -}\mathrm{HA} \qquad (11a)$$

$$>\mathrm{C{=}O}\text{ - - - }\mathrm{HA} + \mathrm{CN}^- \xrightarrow[k_2]{\text{slow}} >\mathrm{C(CN)(OH)} + \mathrm{A}^- \qquad (11b)$$

in which HA is any acid present, including the solvent. Since the second step is rate-determining, the rate will be given by

$$\begin{aligned} \text{rate} &= k_2(\mathrm{AO}\text{ - - }\mathrm{HA})(\mathrm{CN}^-) \qquad (12) \\ &= k_2K_1\,\frac{K_{\mathrm{HCN}}}{K_{\mathrm{HA}}}\,(\mathrm{AO})(\mathrm{HCN})(\mathrm{A}^-) \end{aligned}$$

Equation 12 indicates general base catalysis.

Equation 12 may be rearranged to give

$$\text{rate} = k_2K_1\,\frac{K_{\mathrm{HCN}}}{(\mathrm{H}^+)}\,(\mathrm{AO})(\mathrm{HCN})(\mathrm{HA}) \qquad (13)$$

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[10] N. Bjerrum, A. Unmack and L. Zechmeister, *Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd.*, **5**, No. 11 (1925).

In solutions of essentially constant acidity, a condition which is attained when the reaction is carried out in solutions with a fixed buffer ratio, equation 13 could be considered to indicate general acid catalysis. However, our results in both water and methanol indicate that the molar catalytic constant for acetic acid is zero. Therefore, one must conclude that the reaction is subject to general base catalysis only.

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Kinetics of the Catalytic Rearrangement of Tetrathionate

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The catalytic effect of thiosulfate on the rearrangement of tetrathionate in tri- and pentathionate, has been investigated kinetically. The rate of disappearance of tetrathionate has been determined by titration with the cyanide method. The initial rate was extrapolated graphically and found to be proportional to the initial concentration of tetrathionate and thiosulfate. An equation has been derived based on the assumption that the rearrangement is due to the reaction between a molecule of tetrathionate and one of thiosulfate giving one molecule of pentathionate and one of sulfite. The latter, whose concentration is always very small, may in turn react (specific rate k_2) with the tetrathionate in excess giving trithionate and thiosulfate, or with the pentathionate formed in the mean time going back to tetrathionate and thiosulfate (specific rate k_{-1}). The experimental values are found to fit the equation. Moreover the ratio k_{-1}/k_2 given by the equation closely agrees with that obtained from the values of k_{-1} and k_2 found in literature. The influence of different electrolytes at constant ionic strength is shown, and the strong catalysis of polyvalent positive ions is pointed out.

Higher polythionates in neutral solution decompose under the action of thiosulfate ions according to the equations

$$2S_4O_6^{--} \longrightarrow S_3O_6^{--} + S_5O_6^{--} \qquad (1)$$

$$S_5O_6^{--} \longrightarrow S_4O_6^{--} + S \qquad (2)$$

$$S_6O_6^{--} \longrightarrow S_5O_6^{--} + S \qquad (3)$$

Catalysis of thiosulfate ions has been known for a long time and studied by several workers. A complete bibliography on the argument may be found in papers of Foss[2a] and Goehring.[2b]

The most studied of these reactions is the tetrathionate rearrangement. The reaction occurs according to equation (1) only initially because when the concentration of pentathionate becomes high, other side reactions take place, sulfur separates, and concentration of pentathionate is no longer equal to that of trithionate. This paper deals only with the first part of the reaction, that is up to the point where tri- and pentathionate cease to be formed in equimolecular amounts. Though several authors have put forward hypotheses about the probable mechanism and the literature reports approximate values of velocity, no kinetic work has been done as yet, so that no unambiguous mechanism can be suggested.

We have, therefore, studied kinetically this reaction with the purpose of deciding between the proposed mechanisms.

Some authors[3–6] have suggested that thiosulfate catalysis is due to the dissociation of thiosulfate, according to

$$S_2O_3^{--} \longrightarrow SO_3^{--} + S \qquad (4)$$

followed by

$$S_4O_6^{--} + S \longrightarrow S_5O_6^{--} \qquad (5)$$

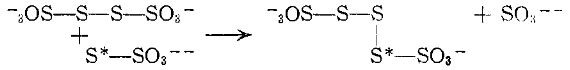
$$S_4O_6^{--} + SO_3^{--} \longrightarrow S_3O_6^{--} + S_2O_3^{--} \qquad (6)$$

However this point of view has been criticized by Foss[7–9] and by Goehring, Helbing and Appel,[10] who suggested that rearrangement of tetrathionate is due to the reactions

$$S_4O_6^{--} + S_2O_3^{--} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} S_5O_6^{--} + SO_3^{--} \qquad (7)$$

$$S_4O_6^{--} + SO_3^{--} \xrightarrow{k_2} S_3O_6^{--} + S_2O_3^{--} \qquad (8)$$

This interpretation is more consistent with the chemical behavior of polythionates. According to this hypothesis the first step is the nucleophilic attack on the chain of sulfur atoms of tetrathionate by a thiosulfate ion, with displacement of sulfite according to the scheme



$$\begin{matrix} {}^-{}_3OS{-}S{-}S{-}SO_3^- \\ + \\ S^*{-}SO_3^{--} \end{matrix} \longrightarrow \begin{matrix} {}^-{}_3OS{-}S{-}S \\ | \\ S^*{-}SO_3^- \end{matrix} + SO_3^{--}$$

This view seems very likely since Foss' hypothesis concerning the exchange of thiosulfuric groups between thiosulfate ion and polythionates has been experimentally confirmed[11] by exchange experiments with isotopically labeled thiosulfate and polythionates.

Our reasoning is therefore based on reactions (7) and (8): one molecule of tetrathionate reacts with one molecule of thiosulfate, with specific rate k_1, giving one molecule of pentathionate and one molecule of sulfite. The latter may now react either with tetrathionate in excess giving thiosulfate and trithionate according to (8) with specific rate k_2, or with the pentathionate formed simultaneously, giv-

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(2) (a) O. Foss, *Kgl. Norske Videnskabers Selskab. Skrifter*, 1945 NR 2 (1947). (b) M. Goehring, *Fortschr. Chem. Forsch.*, **2**, 444 (1952).

(3) A. Kurtenacker, *Z. anorg. Chem.*, **148**, 225 (1925).

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(6) F. Foerster and K. Centner, *ibid.*, **157**, 45 (1926).

(7) See reference 2a, p. 117.

(8) O. Foss, *Acta Chem. Scand.*, **3**, 1385 (1949).

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(10) M. Goehring, W. Helbing and I. Appel, *Z. anorg. Chem.*, **254**, 185 (1947).

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