served by Bridgman[15] in researches utilizing high pressures. He has been led to the conclusion that no simple "law of force" can adequately represent the repulsive force between atoms.

BERKELEY, CALIFORNIA RECEIVED OCTOBER 30, 1950

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[15] P. W. Bridgman, *Rev. Mod. Phys.*, **7**, 1 (1935).

[JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, COLUMBIA UNIVERSITY, AND TRINITY COLLEGE]

Kinetics of the Acid Decomposition of Sodium Thiosulfate in Dilute Solutions

BY ROBERT H. DINEGAR,[1a] ROBERT H. SMELLIE[1b] AND VICTOR K. LA MER

The kinetics of the acid decomposition of sodium thiosulfate in dilute solution has been reinvestigated spectrophotometrically at constant ionic strength. Measurements made at $\lambda = 4000$ Å. show that the time of formation of discrete particles of colloidal sulfur after mixing of reagents depends approximately on $(H^+)_0{}^{1/2}$ and $(S_2O_3^{=})_0{}^{>1}$. The resultant data have been analyzed in conjunction with the facts that the decomposition shows a positive primary salt effect and that thiosulfuric acid is not completely dissociated with respect to its second ionization. By assumption of a bimolecular mechanism between $HS_2O_3^-$ and $S_2O_3^{=}$ with an intermediate complex whose first order specific rate constant (k_2) is comparable to the bimolecular specific rate constant (k_1) kinetic equations have been derived that express the experimental results reasonably well. The values of k_1 and k_2 calculated are 0.31 and 0.14, respectively. Iodine and acid–base titrations during the course of the reaction show that although sulfite ion is produced in significant amounts in the early stages of the decomposition the production of polythionates is insignificant in dilute solutions.

Sulfur hydrosols[2] prepared from dilute sodium thiosulfate and strong acids arise from the molecularly dispersed sulfur produced by a reaction whose velocity is given approximately by $k(Na_2S_2O_3)^{1/2}(HCl)^{1/2}$. Such a rate equation is difficult to interpret mechanistically. Simultaneously a side reaction, producing pentathionic acid instead of sulfur, has been stated to occur in appreciable amounts according to the stoichiometric equation

$$6H^+ + 5S_2O_3^{=} \longrightarrow 2S_5O_6^{=} + 3H_2O \qquad (1)$$

The present investigation of this system has given results that are interpretable in terms of a bimolecular reaction between $HS_2O_3^-$ and $S_2O_3^{=}$ and shows that this reaction proceeds without the complication of an appreciable amount of the side reaction (1) in the early stages.

Experimental.—C.P. sodium thiosulfate recrystallized from ethanol–water solutions was standardized against resublimed I_2 in KI for which C.P. KIO_3 was the primary standard. A 1% starch solution was the indicator in all cases.

The HCl solutions were made up by dilution of the concentrated acid and standardized against standard NaOH for which potassium acid phthalate was the primary standard. Phenolphthalein was the indicator.

The KCl used for adjusting ionic strengths was the C.P. salt, dried for 24 hours in an oven at 110°, and then weighed out. The concentration of the resulting solution was restandardized according to the Mohr method for soluble chlorides using standard $AgNO_3$, with K_2CrO_4 as the indicator.

Solutions of various concentrations of acid and thiosulfate and enough KCl to ensure equality of ionic strengths throughout all runs were mixed as rapidly as possible and the resulting solutions examined by means of a Beckman spectrophotometer (model DU) for the first appearance of turbidity signifying the formation of discrete particles of supercooled liquid sulfur. The wave length used was 4000 Å., the lowest value to which sulfur is transparent. The temperature was 25 ± 0.02° and the cell length was 10 cm. The time of appearance of the Tyndall beam as a function of the concentration of reagents is shown in Table III and plotted graphically in Fig. 1 where the product $[(H^+)_0(t)]$ is plotted *versus* $(H^+)_0$. Figure 2 shows the variation of the slopes of Fig. 1 as a function of the thiosulfate concentration. These figures represent only empirical relationships facilitating the correlation of data between initial concentration of reagents and the time of appearance of the Tyndall beam.

Derivation of Rate Equations.—Any interpretation of the data must begin with the consideration of two important observations. The first is that actual measurements show that the hydrogen ion activity measured immediately upon mixing of reagents is significantly smaller than that calculated on the basis of the concentration of acid added and the known activity coefficient. This indicates that some species is either present initially or produced extremely rapidly which results in the immediate removal of some of the hydrogen ion. Since no significant amount of $S_2O_3^{=}$ is decomposed, no significant quantity of sulfite ion can exist in these early stages. The loss in hydrogen ion activity is due then to the formation of $H_2S_2O_3$ and $HS_2O_3^-$. Previous investigators[3,4] report the value of the first dissociation constant (K_1) to be of the order of 0.45 and the second (K_2) equal to 0.01 for dilute solutions and 0.062 for moderately concentrated sodium thiosulfate solutions. These values show that $H_2S_2O_3$ is a strong acid only with respect to the first dissociation and that the second equilibrium must be considered in any rate equation derived. By designating the initial concentrations of reagents added (H^+ and $S_2O_3^{=}$) with zero subscripts the expression for the second equilibrium constant is

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

Neglecting $(HS_2O_3^-)^2$ and simplifying gives, for the amount of bithiosulfate ion

$$(HS_2O_3^-) = \frac{(H^+)_0(S_2O_3^{=})_0}{K_2 + (H^+)_0 + (S_2O_3^{=})_0} \qquad (3)$$

and since

$$(S_2O_3^{=}) = (S_2O_3^{=})_0 - (HS_2O_3^-)$$

the amount of free thiosulfate ion as a function of initial reactants is

$$(S_2O_3^{=})_0 - \frac{(H^+)_0(S_2O_3^{=})_0}{K_2 + (H^+)_0 - (S_2O_3^{=})_0} \qquad (4)$$

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[2] E. M. Zaiser and V. K. La Mer, *J. Colloid Sci.*, **3**, 571 (1948).

[3] K. Jellinek, *Z. physik. Chem.*, **76**, 257 (1911).

[4] I. Kolthoff, *Rec. trav. chim.*, **43**, 216 (1924).

The second consideration is that two possible bimolecular mechanisms may occur since the reaction has a positive Brönsted primary salt effect (1). The first is $HS_2O_3^- + HS_2O_3^-$ for which the rate equation is

$$d(S)/dt = k(HS_2O_3^-)^2$$

This law becomes identical with the one proposed by Taube[5] for higher acidities if $d(S)/dt = d(S_2O_3^=)/dt$ or

$$\frac{d(S)}{dt} = k\left\{\frac{(H^+)_0\,(S_2O_3^=)_0}{K_2 + (H^+)_0\,(S_2O_3^=)_0}\right\}^2$$

This predicts that the rate of production of sulfur for specified values of $(H^+)_0$ and $(S_2O_3^=)_0$ will be the same if the concentrations are interchanged. Experimentally this is incorrect. $(H^+)_0 = 0.002$ M and $(S_2O_3^=)_0 = 0.003$ M do not give the same rate as $(H^+)_0 = 0.003$ M and $(S_2O_3^=)_0 = 0.002$ M. This mechanism must, accordingly, be discarded, for dilute solutions.

The remaining bimolecular mechanism is reaction between a bithiosulfate and thiosulfate ion

$$HS_2O_3^- + S_2O_3^= \xrightarrow{k_1} [HS_2O_3 \cdot S_2O_3]^= \qquad (5)$$

which then decomposes unimolecularly to sulfur, bisulfite and sulfite

$$[HS_2O_3 \cdot S_2O_3]^= \xrightarrow{k_2} S_2 + HSO_3^- + SO_3^= \qquad (6)$$

Let k_1 and k_2 denote the specific rate constants for the reactions (5) and (6). If $k_2 >>> k_1$, the over-all rate is controlled by the rate of reaction (5). Analysis of the data shows, however, that this is not the case, nor is $k_1 >>> k_2$, but that both specific rate constants are comparable in magnitude. The complete rate expression for the production of sulfur must then be handled as a problem of consecutive reactions.

let x = concentration of $[HS_2O_3 \cdot S_2O_3]^=$

$$\frac{dx}{dt} = k_1\,(HS_2O_3^-)\,(S_2O_3^=) - k_2(x) \qquad (7)$$

which, when integrated with respect to time with the condition $x = 0$ at $t = 0$, gives

$$k_2t = \ln \frac{k_1(HS_2O_3^-)(S_2O_3^=)}{k_1(HS_2O_3^-)(S_2O_3^=) - k_2(x)}$$

$$\therefore\ k_2(x) = k_1(HS_2O_3^-)(S_2O_3^=)(1 - \exp(-k_2t)) \qquad (8)$$

The assumption of first order decomposition of the intermediate complex gives, for the rate of appearance of sulfur

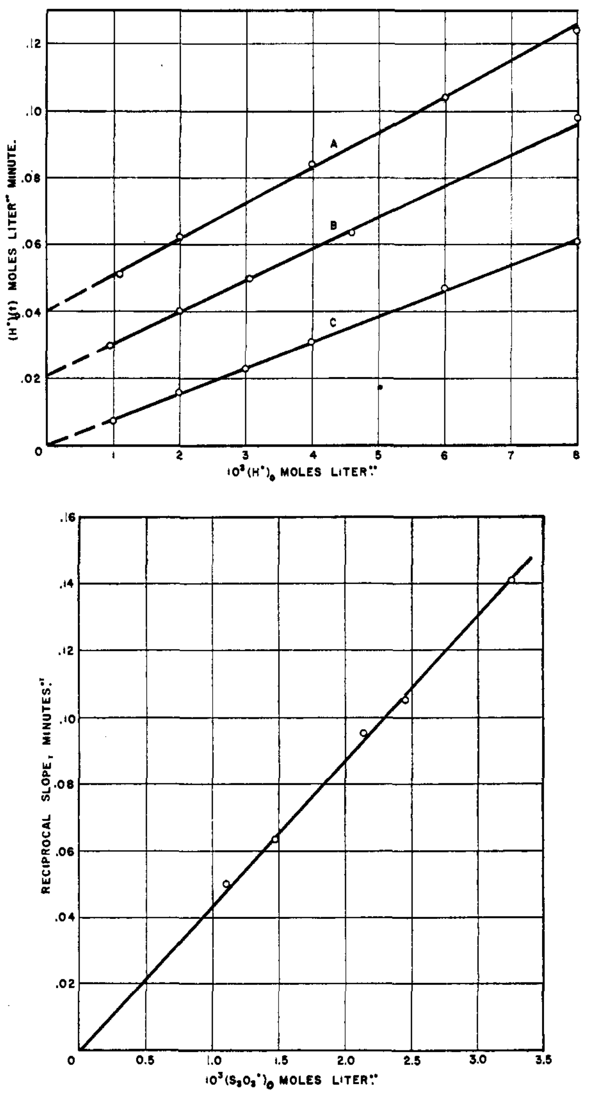
$$d(S)/dt = k_1(HS_2O_3^-)(S_2O_3^=)(1 - \exp(-k_2t)) \qquad (9)$$

This expression for S may now be integrated with respect to t since the change of $(HS_2O_3^-)$ and $(S_2O_3^=)$ over the time interval is small. With the boundary condition (S) = 0 at $t = 0$, equation (9) becomes

$$(S) = k_1(HS_2O_3^-)(S_2O_3^=)\left[t + \left(\frac{\exp(-k_2t) - 1}{k_2}\right)\right] \qquad (10)$$

The concentrations of $(HS_2O_3^-)$ and $(S_2O_3^=)$ in terms of initial concentrations of reactants are given by equation (3). Substitution of these values in equation (10) above gives

$$(S) = k_1\frac{(H^+)_0(S_2O_3^=)_0^2[K_2 + (S_2O_3^=)_0]}{[K_2 + (H^+)_0 + (S_2O_3^=)]^2}\left[t + \left(\frac{\exp.(-k_2t) - 1}{k_2}\right)\right] \qquad (11)$$



Figs. 1 and 2.—Time of appearance of Tyndall beam as a function of initial concentration of hydrogen ion: $(H^+)_0(t)$ *versus* $(H^+)_0$; $\mu = 0.0155$.

Curve	$10^3 M Na_2S_2O_3$	Plotting increment in ordinate
A	2.14	+0.008
B	2.48	− .002
C	3.21	− .015

A normal criterion for the validity of a derived rate equation is the constancy of the specific rate constant under varying initial conditions. Since (S) at the condensation point has been shown to be a constant[6] independent of initial conditions, we may choose as our criterion of validity $(S)/(k_1)$ and call it F, a kinetic factor. The unknown k_2 may be evaluated by solving simultaneous equations. k_2 was found to have a value 0.14 ± 0.02 for 10 arbitrarily chosen runs. Using this value of k_2 and $K_2 = 0.01$ gives the results shown in Table III for the factor F. Reasonable constancy results.

The specific rate constant k_1 may be evaluated in the following manner. Equation (10) gives the concentration of sulfur as a function of time after mixing of reagents. This value has also been

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[5] Taube, THIS JOURNAL, 65, 526 (1943).

[6] E. M. Zaiser and V. K. La Mer, *J. Colloid Sci.*, 3, 571 (1948).

measured experimentally. Plotting (S) *versus* $\left[t + \left(\frac{\exp(-k_2t) - 1}{k_2}\right)\right]$ should give a straight line with a slope of $k_1(HS_2O_3^-)(S_2O_3^=)$ and intercept equal to zero. The result is shown in Fig. 3 for $(H^+)_0 = (S_2O_3^=)_0 = 0.002$ *M*. The calculated value of k_1 is 0.31. Since $F = (S)/k_1$, the concentration of sulfur at the condensation point (Tyndall beam appearance) is 3.1×10^{-6} g. at. S/l.

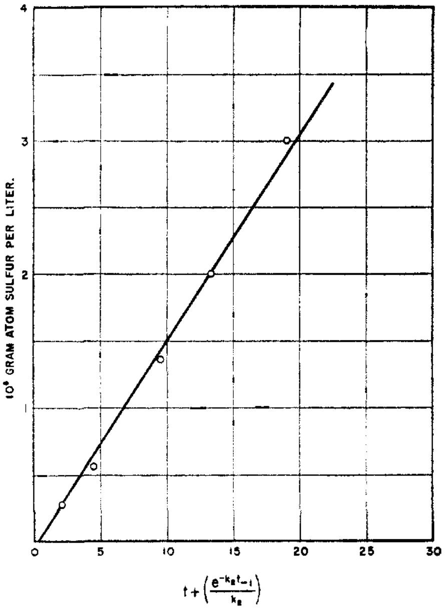

Fig. 3.—Variation of the reciprocal slopes of Fig. 1 as a function of initial concentration of $Na_2S_2O_3$.

General Considerations.—Further application of equation (11) shows that an *approximate* solution of the quantity $1/t$ is, for small values of $(H^+)_0$ and $(S_2O_3^=)_0$, dependent upon $(H^+)_0^{1/2}$ and $(S_2O_3^=)_0^{>1}$ as found empirically by Zaiser and La Mer. *I.e.*, by expanding exp (k_2t) into three terms $\left(1 - k_2t + \frac{k^2{}_2t^2}{2}\right)$

$$(S) = \frac{k_1'(H^+)_0(S_2O_3^-)_0^2[K_2 + (S_2O_3^-)_0]}{[K_2 + (H^+)_0 + (S_2O_3^-)_0]^2}\,(t^2)$$

or

$$\frac{1}{t} = k_1''(H^+)_0^{1/2}\,[K_2 + (S_2O_3^-)_0]^{1/2}/K_2 + (H^+)_0 + (S_2O_3^-)_0$$

Expanding $(K_2 + (S_2O_3^=)_0]^{1/2}$ in a power series in $(S_2O_3^=)_0$ and discarding powers above the square gives

$$\frac{1}{t} = \frac{k_1''(H^+)_0^{1/2}\,[K_2^{1/2}(S_2O_3^-)_0 + {}^1/_2K_2(S_2O_3^-)_0^2]}{K_2 + (H^+)_0 + (S_2O_3^-)_0}$$

or approximately

$$1/t \propto (H^+)_0^{1/2}\,(S_2O_3^-)_0^{>1}$$

Decomposition Products.—The heterogeneous deposition of sulfur, formed by the chemical reaction on the nuclei produced at the phase transition begins with the appearance of the Tyndall beam. Many investigators[2] have reported the simultaneous production of various polythionates, the most likely of which is pentathionate formed by reaction 1. Since the amount of sulfite and pentathionate present at any time may be determined by titration[2] the extent of each of the two reactions

$$H^+ + S_2O_3^= \longrightarrow HSO_3^- + S \qquad (12)$$
$$6H^+ + 5S_2O_3^= \longrightarrow 2S_5O_6^= + 3H_2O \qquad (1)$$

may be evaluated separately.

Sols prepared in the prescribed manner,[2] were titrated potentiometrically with *ca.* 0.02 *N* NaOH. In this manner, potential breaks due to the two dissociations of H_2SO_3 were obtained. These curves are plotted in Fig. 4, where the *p*H of the solution is seen as a function of the number of cc.'s of added base. The time is the number of hours (at 25°) after mixing of reagents.

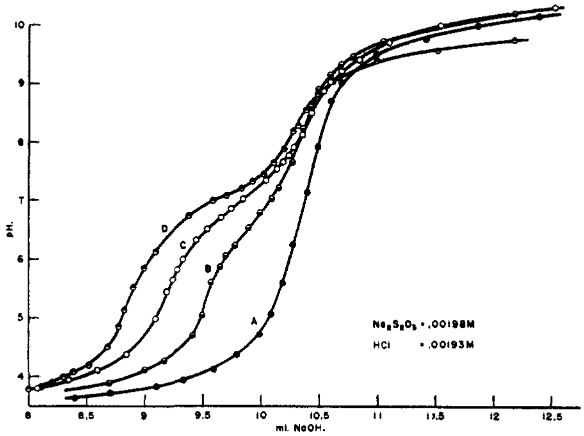

Fig. 4.—Sulfur concentrations as a function of $t + \frac{\exp(-k_2t) - 1}{k_2}$ during the homogeneous reaction: $HCl = Na_2S_2O_3 = 0.00200$ *M* (data of Zaiser and La Mer).

The titers corresponding to the complete dissociation of HSO_3^- show constancy to within experimental error with that at zero time. Although this does not give any indication as to the magnitude of sulfite formed, this constancy of H^+ indicates no appreciable formation of polythionate since this would remove H^+ as H_2O as the reaction proceeds.

Two other methods give the value of the sulfite produced and again show the absence of appreciable amounts of polythionate.

When an acid is weak, its dissociation on the acid side of the end-point may be neglected and, from equilibrium considerations, the relationship

$$pH = pK\text{ acid} + \log C\text{ salt}/C\text{ acid}$$

holds. When the acid is half neutralized, *p*H = *pK* acid. For HSO_3^-, $K_2 = 6.24 \times 10^{-8}$ at 25°[7] and *p*H = 7.2, at this point.

Twice the difference between the titer at *p*H 7.2 and the second end-point gives the moles of sulfite in the solution. Table I shows this as a function of time.

The third method is that described by Zaiser and La Mer using simultaneous iodine and base titrations.[2] Calculation of our data using the latest value of $K_{HSO_3^-}$ as 6.2×10^{-8}, gives the moles of polythionate and sulfite formed as shown in Table II.

(7) Tartar and Garretson, THIS JOURNAL, 63, 808 (1941)

TABLE I

$S_2O_3^{=}$ = 0.00198 *M*; H^+ = 0.00193 *M*

Time	10^5 moles sulfite liter $^{-1}$
0	0
4	4.8
8	9.4
12	12.6
16	15.1
20	16.8
24	19.3

TABLE II

$S_2O_3^{=}$ = 0.00205; H^+ = 0.00201 *M*; *T* = 25°

Time, hr.	10^5 moles sulfite liter $^{-1}$	10^5 moles polythionate liter $^{-1}$	10^5 moles $S_2O_3^{=}$ liter $^{-1}$ decomp.
0	0	0	0
4	5.8	0.08	6.0
8	11.0	.24	11.6
12	14.8	.32	15.6
16	17.9	.44	19.0
20	20.1	.52	21.6
24	22.0	.72	23.8

If the data of ref. 2 are recalculated using the latest value of $K_{HSO_3^-}$ we find substantial agreement as shown below.

0.00200 *M* = $S_2O_3^{=}$; 0.00200 *M* = H^+

0	0	0	0
4	5.7	0.05	5.8
8	10.2	.24	10.8
12	13.4	.48	14.6
16	16.3	.84	18.4
20	18.7	.92	21.0
24	20.8	.96	23.2

These data show that only reaction (12) proceeds to an appreciable extent in the first few hours after mixing and that even over a long period of time reaction (1) is considerably the less important of the two.

The rate equation for the production of sulfur (equation 9) may be applied to the disappearance of $S_2O_3^{=}$ as given in Table II in the following manner

$$d(S)/dt = k_1(HS_2O_3^-)(S_2O_3^=)\ (1 - e^{-k_2t})$$

Since the length of time of reaction is now large, equation 9 may not be integrated assuming ($HS_2O_3^-$) and ($S_2O_3^{=}$) constant as before. The amounts of ($HS_2O_3^-$), ($S_2O_3^{=}$) and (H^+) at any time, *t*, always stand, however, in the relation

$$\frac{(H^+)_t(S_2O_3^=)_t}{(HS_2O_3^-)_t} = K_2 = 0.01$$

∴ equation 9 becomes

$$\frac{d(S)}{dt} = k_1\,\frac{(H^+)_t(S_2O_3^=)_t^{\,2}}{0.01}\,(1 - \exp(-k_2t)) \quad (13)$$

Assuming only reaction (12) to occur one mole of sulfur and one mole of sulfite are produced for every mole of $S_2O_3^{=}$ decomposed. In addition, one mole of H^+ is used up for every mole of sulfite formed (giving HSO_3^-).

Designating the original concentrations as zero subscripts for the special case where equal initial concentration of reagents were used $(H^+)_0$ = ($S_2O_3^{=}$) = *a* and $(H^+)_t = (S_2O_3^=)_t = a - y$ where *y* is the amount of sulfur formed or the amount of $S_2O_3^{=}$ reacted.

$$\therefore \frac{dy}{dt} = \frac{k_1(a - y)^3}{0.01}\,(1 - \exp(-k_2t)) \quad (14)$$

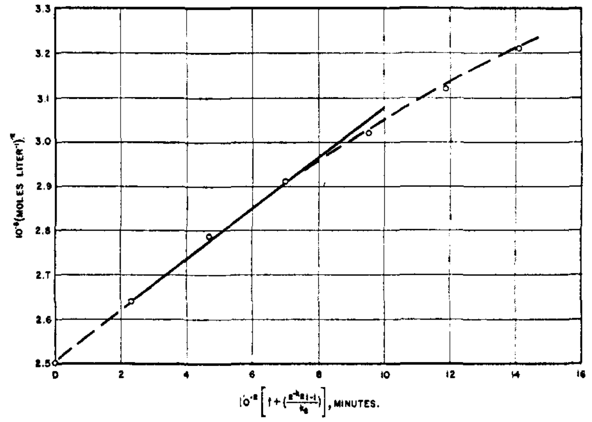

Fig. 5.—Acid–base titration curve of dilute solution acid decomposition of sodium thiosulfate: hours after mixing of reagents are, curve A, 0; curve B, 6.5; curve C, 15.5; curve D, 24.

which gives, upon integration with the condition (S) = 0 when *t* = 0

$$\frac{1}{(a - y)^2} = \frac{2k_1}{0.01}\left[\,t + \left(\frac{\exp(-k_2t) - 1}{k_2}\right)\right] + \frac{1}{a^2} \quad (15)$$

TABLE III

TIME OF APPEARANCE OF COLLOIDAL SULFUR AND *F* FACTOR AS A FUNCTION OF INITIAL CONCENTRATION OF REAGENTS

$10^3(H^+)_0M$	*t*, min.	10^4KCl *M*	$10^2\mu$	10^6 *F*
	$Na_2S_2O_3$ = 1.07 × 10^{-3} *M*			
1.1	138	11	1.53	1.2
3.0	64	9	1.52	1.1
4.0	53	8	1.52	1.0
6.0	43	6	1.52	1.2
8.0	36	4	1.52	0.8
10.0	33	2	1.52	0.8
	$Na_2S_2O_3$ = 1.485 × 10^{-3} *M*			
1.14	60	10	1.55	0.8
2.0	50	9	1.55	1.2
4.0	32.5	7	1.55	1.2
6.1	27	5	1.55	1.0
8.0	24	3	1.55	0.9
10.0	22.5	1	1.55	0.9
	$Na_2S_2O_3$ = 2.14 × 10^{-3} *M*			
1.1	39	8	1.55	1.1
2.0	27	7	1.54	1.1
4.0	19	5	1.54	1.1
6.0	16	3	1.54	1.0
8.0	14.5	1	1.54	0.9
10.0	15	0	1.64	1.0
	$Na_2S_2O_3$ = 2.48 × 10^{-3} *M*			
0.95	33	6.5	1.49	1.1
2.00	21	6	1.55	1.1
3.08	16.5	5	1.55	0.9
4.60	14	3	1.50	1.0
8.00	12.5	0	1.55	1.0
	$Na_2S_2O_3$ = 3.21 × 10^{-3} *M*			
1.0	23	5	1.56	1.1
2.0	15.5	4	1.56	1.1
3.0	12.5	3	1.56	1.0
4.0	11.5	2	1.56	1.1
6.0	10.75	0	1.56	1.1
8.0	9.5	0	1.76	1.0

For large values of the time (*i.e.*, greater than about an hour) equation (15) reduces to

$$\frac{1}{(a-y)^2} = \frac{2k_1}{0.01}\left[t - \frac{1}{k_2}\right] + \frac{1}{a^2} \qquad (16)$$

This equation predicts a linear dependence of $1/(a-y)^2$ on $[t - (1/k_2)]$ with a slope equal to $2k_1/0.01$ and intercept equal to $1/a^2$. The results of plotting (using $k_2 = 0.14$ as previously) the data of section 2 of Table II are shown in Fig. 5. The value of k_1 so calculated is 0.29, in good agreement with the previous value of 0.31. The intercept is $1/a^2$. Deviation occurring at times greater than 16–20 hours is probably due to the side reaction (1), which produces polythionate, becoming important.

NEW YORK, N. Y. RECEIVED SEPTEMBER 22, 1950

[CONTRIBUTION FROM THE APPLIED PHYSICS LABORATORY, THE JOHNS HOPKINS UNIVERSITY]

The Kinetics of Hexose Formation from Trioses in Alkaline Solution[1]

BY WALTER G. BERL AND CHARLES E. FEAZEL

The kinetics of the formation of D,L-sorbose and D,L-fructose by the condensation of D,L-glyceraldehyde in sodium hydroxide solution have been investigated, using a colorimetric method, based on the anthrone–sulfuric acid reagent, for the quantitative estimation of the hexoses. The reaction was found to follow first-order kinetics at a given concentration of alkali. The effects of variables such as sodium hydroxide concentration, temperature and the initial concentration of glyceraldehyde have been investigated. An increase in rate on the addition of dihydroxyacetone to the reaction was observed, confirming the work of earlier investigators.

The products of the reaction were subjected to paper partition chromatography to demonstrate the virtual absence of triose at the end of the reaction. It is suggested that a branched-chain hexose may be formed as a by-product in the condensation.

The production of hexoses from D,L-glyceraldehyde in alkaline solution was first studied by Emil Fischer[2a] who obtained a mixture of sugars later identified as D,L-fructose and D,L-sorbose by Schmitz.[2b] This work was repeated by Fischer and Baer, using D-glyceraldehyde as a starting material and barium hydroxide solution as the medium.[3] The use of optically active material allowed them to follow the course of the reaction polarimetrically, and to show that the addition of dihydroxyacetone greatly increased the rate of reaction. The interpretation of these data was that in the condensation of glyceraldehyde, the primary step is the conversion of glyceraldehyde to dihydroxyacetone, followed by reaction between the two to form the ketohexoses. The yields of D-fructose and D-sorbose were estimated to be 50 and 44%, respectively, by precipitation and separation of the phenylosazones.

Meyerhof and Schulz[4] studied the condensation of glyceraldehyde with dihydroxyacetone in trisodium phosphate solution and regarded it as coming to a triose–hexose equilibrium containing about 92% hexose.

We have investigated the kinetics of the condensation of D,L-glyceraldehyde in dilute sodium hydroxide solution, using as an analytical tool the anthrone–sulfuric acid colorimetric test for hexoses.[5–9]

Experimental

Materials.—Crystalline D,L-glyceraldehyde (m.p. 142–144°) from Concord Laboratories, and crystalline dihydroxyacetone (m.p. 75–80°) from Bios Laboratories, were used. Anthrone was prepared by the method of "Organic Syntheses,"[10] and dissolved in C.P. concentrated sulfuric acid to give a 0.2% solution. This reagent is unstable and must be used within a few days of its preparation. It also gives better results if allowed to stand at room temperature for at least eight hours before use.

Apparatus.—The kinetic determinations were made in a constant temperature bath, the temperature of which was controlled to within ±0.1°. A Klett–Summerson test-tube photoelectric colorimeter equipped with a Baird Associates 6275 Å. filter[9] was used for the colorimetry. The *p*H was measured with a Leeds and Northrup *p*H meter.

Use of the Anthrone Reagent.—The applicability of Beer's law to the hexose–anthrone color has been demonstrated,[9] and was checked in our work with standard solutions of D-glucose, D-fructose and L-sorbose. The anthrone reagent used in the kinetic work was standardized before each experiment with a solution of D-glucose. In order to convert the colorimeter readings to fructose and sorbose concentration, it was necessary to apply an empirical correction factor, due to the fact that while fructose was found to give the same color intensity as glucose for equal concentrations, the intensity of the sorbose–anthrone color was 76% of the glucose–anthrone color, for the same concentrations. Therefore, assuming that fructose and sorbose were formed in equal amounts during the course of the reaction, the fructose–sorbose equivalent of the colorimeter reading was equal to the glucose equivalent multiplied by 1.13. The presence of glyceraldehyde did not interfere appreciably with the intensity at 6275 Å. of the hexose–anthrone color and could be neglected.

Experimental Procedure.—In carrying out the runs, weighed samples of D,L-glyceraldehyde were dissolved in 80–90 ml. of water in a 100-ml. volumetric flask, which was then immersed in the constant temperature bath. Then a measured volume of 0.1000 *N* carbonate-free sodium hydroxide solution (also at reaction temperature) was added and the contents of the flask diluted to 100.0 ml. A 1.0 ml. sample was removed and diluted to an appropriate volume in a volumetric flask. This latter volume was chosen so that 1.0 ml. of the contents would have a triose content of 40–50 γ. From this flask two 2.0 ml. aliquots were pipetted into Klett–Summerson test-tubes. To each

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