

of the type of malachite green gave normal orientation.

The maximum orientation obtainable in the

several cases is calculated and compared with the observed values.

BERKELEY, CALIF.

RECEIVED NOVEMBER 10 1942

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, CORNELL UNIVERSITY]

## Disappearance of Thiosulfate in Solutions of Maleic Acid; Catalysis of *cis-trans* Isomerization

BY HENRY TAUBE

Tanatar<sup>1</sup> observed that, when a solution of sodium thiosulfate is added to a solution of maleic acid, fumaric acid forms and the thiosulfate disappears. The complete reaction products are not known, although Tanatar<sup>2</sup> did identify the compound  $\text{EtCO}_2\cdot\text{CHSH}\cdot\text{CHSO}_3\text{H}\cdot\text{CO}_2\text{Et}$  in an alcoholic extract of the reaction mixture. Sulfur is not observed as a product even when moderate amounts of mineral acid are added. The catalysis of the maleic-fumaric change by thiosulfate has been<sup>3</sup> attributed to the separation of finely divided sulfur even though Tanatar<sup>1</sup> proved that no transformation takes place if the thiosulfate is decomposed by a mineral acid before adding the maleic acid, and that certain other reactions producing sulfur (which presumably is in a finely divided state at some stage of the reaction) do not induce the transformation. Finely dispersed sulfur does catalyze<sup>3</sup> the transformation but only at higher temperatures where hydrolysis or other reactions of sulfur become possible, and in fact appear to be involved.

In the present work the rate of disappearance of thiosulfate in solutions of maleic acid and the rate of formation of fumaric in such solutions are studied as a function of concentration variables. The interpretation of the data leads to some conclusions about the mechanisms of the reactions.

**Method.**—In an experiment, the initial and final concentrations of thiosulfate, the amount of fumaric acid produced and the reaction time were measured.

Reaction mixtures were made up by adding known volumes of thiosulfate to known volumes of solution containing the other constituents. The reaction was quenched a short measured interval of time after mixing to measure the "initial" concentration of thiosulfate. To quench the mixture, the concentration of acid was decreased to low values by the addition of sodium hydroxide, or of potassium biphosphate solution if no other buffering agent was present.

Since some sulfite is usually produced in the reaction, the method of Kurtenacker<sup>4</sup> for the analysis of mixtures of sulfite and thiosulfate was used. The method depends on the fact that in a solution which is only slightly acid, formaldehyde reacts rapidly with sulfite, yielding a product which does not reduce iodine in the ordinary titration of thiosulfate with that reagent.

In analyzing for fumaric acid, one sample was quenched at "zero" time by adding iodine solution; another was quenched in a similar fashion at the end of the reaction interval. Both samples were then made up to the same volume and a solution of potassium fumarate sufficient to supersaturate both solutions with fumaric acid was then added. Excess sulfuric acid was added to both and the solutions were allowed to settle in a constant temperature bath for about forty-eight hours. The fumaric acid was filtered off, washed with saturated fumaric acid solution and titrated with standard sodium hydroxide. The difference in titer was a measure of the fumaric acid produced in the reaction. Blank tests proved that the reactions:  $\text{I}_2 + \text{S}_2\text{O}_8^{2-}$ ,  $\text{I}_2 + \text{sulfite}$ , sulfite + maleic acid and the presence of  $\text{I}^-$  or  $\text{S}_4\text{O}_6^{2-}$  did not induce a measurable transformation of maleic to fumaric acid in the experiments.

**Materials.**—Maleic acid was prepared by dissolving *c. p.* maleic anhydride in water, and a solution of potassium maleate was prepared by neutralizing a maleic acid solution with potassium hydroxide. The other chemicals were *c. p.* quality used without further purification.

**Conditions and Definitions.**—All experiments were carried out at a temperature of 25.3° and an ionic strength of *ca.* 0.61. The ionic strength was maintained by adding potassium chloride. In many experiments the desired ( $\text{H}^+$ ) could not be attained with maleic acid. For such experiments (beginning at about experiment 17 in Table II and experiment 18 in Table III) hydrochloric acid was added to fix ( $\text{H}^+$ ) at the tabulated values. The units used throughout are: time, *t*, in minutes, concentration in moles per liter.

Certain abbreviations are adopted for convenience. T represents total thiosulfate;  $\text{H}_2\text{M}$ ,  $\text{HM}^-$ ,  $\text{M}^{2-}$  represent maleic acid and its ions;  $\text{H}_2\text{F}$  represents fumaric acid.

Where ( $\text{H}^+$ ) was fixed by a buffer solution, the composition required was calculated by using the following values of  $K_{\text{diss}}$  for maleic, phosphoric and oxalic acid, respectively:  $1.78 \times 10^{-2}$ ,  $1.43 \times 10^{-2}$ ,  $7.9 \times 10^{-2}$ . The value of  $K_{\text{diss}}$  for maleic acid at 25° and  $\mu = 0.61$  was estimated

(1) Tanatar, *J. Russ. Phys.-Chem. Soc.*, **43**, 1742-1746 (1911).

(2) Tanatar, *ibid.*, **44**, 1320-1324 (1912).

(3) Freundlich and Schikorr, *Kolloid-Beihfte*, **22**, 1 (1926).

(4) Kurtenacker, *Z. anal. Chem.*, **64**, 56 (1924).

from the known<sup>5</sup> value at 25° and low ionic strength by assuming that  $\log K$  for maleic acid varies with (KCl) in the same way that  $\log K$  for  $H_2C_2O_4$  does.<sup>6</sup> The value for phosphoric acid was estimated from the known value at 18°<sup>7</sup> and  $\mu = 0.61$  and the temperature coefficient.<sup>8</sup>

### Results and Discussion

Table I presents the results of experiments on the decomposition of thiosulfate in acid solutions without added maleic acid.

TABLE I

THE DECOMPOSITION OF THIOSULFATE IN ACID SOLUTIONS WITHOUT MALEIC ACID ( $\mu = 0.62$ )

No.	(T <sub>0</sub> ) × 10 <sup>3</sup>	(T) × 10 <sup>3</sup>	(HCl) added	k' <sub>d</sub>	(H <sup>+</sup> ) × 10 <sup>2</sup>	k <sub>d</sub>
1	24.35	20.55	0.600	2.60	57.8	3.01
2	24.44	21.43	.300	2.06	28.0	2.86
3	23.28	19.85	.300	2.14	28.0	2.97
	23.28	12.97	.300	2.03	27.6	2.83
	23.28	8.02	.300	2.14	27.0	3.00
	23.28	5.57	.300	2.10	26.6	2.97
4	3.16	2.72	.300	2.02	29.7	2.75
5	24.56	21.81	.100	1.06	8.46	2.70
6	24.54	22.79	.060	0.71	4.80	2.94
7	24.55	22.77	.040	.46	3.07	3.17

Mean 2.92

8 24.29 20.99 .247 2.14 28.3<sup>a</sup> 2.97

<sup>a</sup> In Expt. 8 ( $H_2C_2O_4$ ) added = 0.253 M.

$k'_d$  is defined by the relation  $-d(T)/dt = k'_d(T)^2$ . The results of experiments 2, 3 and 4 show that the reaction is 2nd order with respect to thiosulfate. The variation with (H<sup>+</sup>) is explained if it is assumed that the reacting species is  $HS_2O_3^-$ , and that the dissociation constant for  $HS_2O_3^-$  is 0.05.<sup>9</sup>  $k_d \left[ = k'_d \left( \frac{(H^+) + K}{(H^+)} \right)^2 \right]$  was calculated on this basis. While a reaction  $(2H^+ + 2S_2O_3^{2-} \rightarrow)$  would give kinetically the same variation with (H<sup>+</sup>), such an interpretation seems less likely. If this were an acid catalyzed reaction, it would be expected that  $H_2C_2O_4$  (and other acids) would increase the rate at constant (H<sup>+</sup>). Comparison of experiments 2, 3 and 8 shows that  $H_2C_2O_4$  has no appreciable effect.

Prakke and Stiasny<sup>10</sup> have reported complete analyses of the reaction products. No attempt

(5) Ostwald, *Z. physik. Chem.*, **3**, 369 (1889). These values are based on measurement of conductivity and are given for various values of maleic acid concentration. At 0.031 M maleic acid ( $\mu = 0.015$ )  $K_{diss} = 1.30 \times 10^{-2}$ .

(6) Dawson, *J. Chem. Soc.*, 1889 (1929), gives values of  $K_{H_2C_2O_4}$  at various concentrations of KCl. For (KCl) = 0 and  $\mu = ca. 0.01$ ,  $K_{diss} = 5.7 \times 10^{-2}$ .

(7) Lugg, *THIS JOURNAL*, **53**, 2554-2560 (1931). The ratio of  $K_{diss}$  at (KCl) = 0.61 M to  $K_{diss}$  at  $\mu = 0$  at 18° = 1.95.

(8) Nims, *ibid.*, **56**, 1110 (1934).

(9) Kolthoff (*Rec. trav. chim.*, **43**, 219 (1924)) reports a value for  $K_{HS_2O_3^-}$  of 0.057 at 15° and lower ionic strength.

(10) Prakke and Stiasny, *ibid.*, **52**, 615 (1933).

was made in the present work to repeat the analysis, except to check their observation that at high acid the main products are sulfur dioxide and sulfur. Under the conditions of experiment 2, *ca.* 88% of the decomposed thiosulfate yielded these products. If sulfur dioxide is removed by passing air through the solution, as in experiment 3,  $k_d$  is shown to be independent of the accumulation of other products; in a similar experiment without removal of sulfur dioxide,  $k_d$  decreases by 10 to 12% after 50% decomposition. In all experiments except 3, sulfur dioxide was not removed, but values of  $k_d$  for small decomposition were measured.

Table II contains the data used as basis for discussing the rate of disappearance of thiosulfate in a solution of maleic acid. In most cases,  $(H_2M)_0 \gg (T_0)$ . In calculating the decrease in  $(H_2M)$  it was assumed that each mole of thiosulfate uses one of maleic acid; the decrease in maleic acid due to formation of fumaric acid was also taken into account.

TABLE II

THE RATE OF DISAPPEARANCE OF THIOSULFATE IN SOLUTIONS OF MALEIC ACID  
 $\mu = 0.61$ , temp. = 25.3°

No.	(H <sup>+</sup> ) × 10 <sup>2</sup>	(H <sub>2</sub> M)	(T <sub>0</sub> ) × 10 <sup>3</sup>	(T) × 10 <sup>3</sup>	k' <sub>1</sub>	k <sub>1</sub>	k <sub>2</sub>
1	0.35	0.0485	3.401	2.852	0.159	0.159	..
2	.35	.118	3.357	1.963	.202	.202	..
3	.70	.0680	3.321	2.466	.218	.215	0.08
4	.70	.220	3.275	2.134	.327	.327	.08
5	1.36	.0482	3.293	2.379	.260	.242	.29
6	1.36	.118	3.279	2.080	.320	.313	.29
7	1.36	.168	3.089	1.811	.364	.358	.29
8	1.36	.158	24.80	16.13	.393	.356	.29
9	1.36	.0482	3.293	2.379	.260	.242	.29
10	1.36	.118	3.279	2.080	.320	.313	.29
11	1.36	.198	3.260	1.878	.397	.394	.29
12	1.36	.396	3.171	1.553	.520	.520	.29
13	2.2	.0683	3.190	2.120	.352	.328	.60
14	2.2	.198	3.133	1.804	.464	.457	.60
15	3.3	.0683	3.176	2.065	.420	.382	1.00
16	3.3	.198	3.124	1.878	.513	.503	1.00
17	5.0	.0690	3.190	2.270	.493	.440	1.44
18	5.0	.199	3.230	2.143	.586	.570	1.44
19	10.0	.0692	3.188	2.172	.617	.516	2.45
20	10.0	.199	3.134	2.124	.650	.617	2.45
21	15.0	.059	3.312	2.179	.710	.547	3.10
22	15.0	.199	3.249	2.154	.686	.640	3.10
23	30.0	.0493	3.330	2.219	.825	.560	4.60
24	30.0	.199	3.222	2.203	.635	.575	4.60
25	30.0	.195	24.31	16.19	1.037	.580	4.60
26	30.0	.192	38.53	26.66	1.276	.550	4.60
27	50.0	.0493	3.338	2.255	0.795	.475	5.22
28	50.0	.1995	3.289	2.349	.563	.486	5.22

$k'_1$  is defined by the equation:  $-d(T)/dt = k'_1(T)(H_2M)$ , and was calculated from the integrated form

$$k'_1 = \frac{2.3}{(H_2M)_t} \log \frac{(T_0)}{(T)}$$

where

$$\overline{(\text{H}_2\text{M})} = \frac{(\text{H}_2\text{M})_0 + (\text{H}_2\text{M})_t}{2}$$

Experiments 7 and 8 of Table II show that at low  $(\text{H}^+)$ ,  $k_1'$  is nearly independent of  $(\text{T}_0)$ , *i. e.*, the reaction in this region is nearly first order with respect to thiosulfate. Comparison of the  $k_1'$  values for experiments 24, 25 and 26 of Table II shows that as  $(\text{H}^+)$  increases a reaction of higher order with respect to thiosulfate becomes significant.  $k_1$  and  $k_2$  (not necessarily constants) are defined by the equation

$$-d(\text{T})/dt = k_1(\text{H}_2\text{M})(\text{T}) + k_2(\text{T})^2$$

and were calculated from the experimental results applying a method of successive approximations to the integrated form

$$\frac{2.30}{k_1(\overline{\text{H}_2\text{M}})} \left[ \log \frac{(\text{T}_0)}{(\text{T})} + \log \frac{k_1(\overline{\text{H}_2\text{M}}) + k_2(\text{T})}{k_1(\overline{\text{H}_2\text{M}}) + k_2(\text{T}_0)} \right] = t$$

The constancy of the values of  $k_1$  and  $k_2$  for the fairly wide range of maleic acid and thiosulfate studied at  $0.30 M \text{H}^+$  shows that at constant high  $(\text{H}^+)$ , the rate law expresses the variation of rate with maleic acid and thiosulfate concentrations.

$k_2$  must decrease rapidly with  $(\text{H}^+)$  to explain the results in the region of low  $(\text{H}^+)$ . A com-

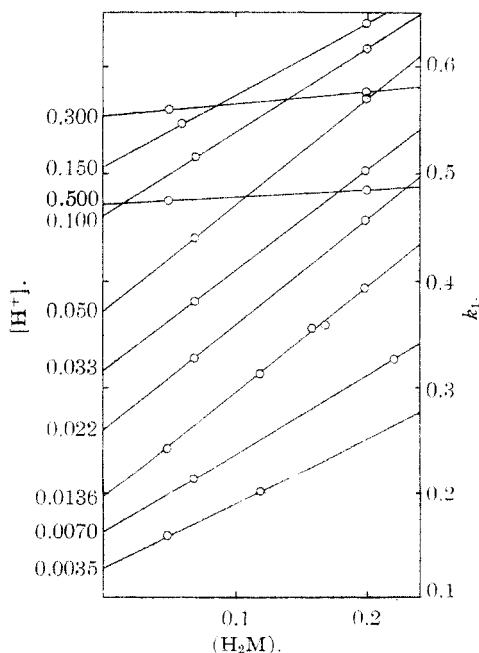
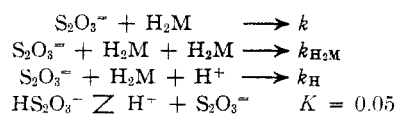


Fig. 1.—The variation of the maleic acid dependent rate of disappearance of thiosulfate with the concentration of maleic acid for various values of hydrogen ion concentration. The point for  $(\text{H}_2\text{M}) = 0.396 M$  at  $(\text{H}^+) = 0.0136$  (Expt. 12, Table II) would lie well below the extrapolated line this for concentration of hydrogen ion.

plete experimental investigation to measure  $k_2$  at lower  $(\text{H}^+)$  was not attempted. It was assumed that  $k_2$  decreases with  $(\text{H}^+)$  in the same manner that  $k_1'$  does; this is equivalent to assuming that the reaction is 2nd order with respect to  $\text{HS}_2\text{O}_3^-$ . The coefficient  $\left[ = k_2 \left( \frac{(\text{H}^+) + K}{(\text{H}^+)} \right)^2 \right]$  calculated for such a rate law from the experimental value for  $k_2$  at  $0.30 M \text{H}^+$  is 6.26. It is perhaps significant that this is *ca.* twice the value of  $k_1$ , the rate constant for the decomposition of thiosulfate in mineral acid.

It will be shown that the main observations on the rate law corresponding to  $k_1$  can be interpreted by the rate determining steps<sup>11</sup>



The rate of disappearance of thiosulfate by these paths =  $(\text{S}_2\text{O}_3^{2-})(\text{H}_2\text{M}) [k + k_{\text{H}_2\text{M}} (\text{H}_2\text{M}) + k_{\text{H}^+} (\text{H}^+)]$ . Since  $(\text{S}_2\text{O}_3^{2-}) = \frac{K}{(\text{H}^+) + K} (\text{T})$ ,

$$\therefore k_1 = \frac{K}{(\text{H}^+) + K} [k + k_{\text{H}_2\text{M}} (\text{H}_2\text{M}) + k_{\text{H}^+} (\text{H}^+)]$$

In Figure 1  $k_1$  is plotted against  $(\text{H}_2\text{M})$  at various values of  $(\text{H}^+)$ . The results for  $(\text{H}^+) = 0.0136 M$  show that at low values  $k_1$  varies linearly with  $(\text{H}_2\text{M})$ . Straight lines were drawn through the pairs of points at other concentrations of  $(\text{H}^+)$ . The theoretical rate law requires that the intercepts at  $(\text{H}_2\text{M}) = 0$  be given by  $\frac{K}{\text{H}^+ + K} [k + k_{\text{H}^+} (\text{H}^+)]$ . In Fig. 2, the intercepts multiplied by  $[(\text{H}^+) + K]/K$  are plotted against  $(\text{H}^+)$ . The slope of the straight line obtained gives for  $k_{\text{H}^+}$  a value of 14 and the intercept at  $(\text{H}^+) = 0$  gives for  $k$  the value 0.095. The points at  $(\text{H}^+) = 0.3 M$  and  $0.5 M$  are not included; the former would lie very near the line but the latter well below it—5.2 instead of 7.9.

$k_{\text{H}_2\text{M}}$  can be obtained by multiplying the slopes of the lines in Fig. 1 by  $[(\text{H}^+) + K]/K$ . The values thus obtained are plotted in Fig. 3 against  $(\text{H}^+)$ . The plot shows that  $k_{\text{H}_2\text{M}}$  increases with  $(\text{H}^+)$  and probably reaches a limit. The irregularities are due to magnification of error; for example, an error of 1% in measuring  $k_1'$  at high  $(\text{H}_2\text{M})$  in  $0.300 M \text{H}^+$  would alter  $k_{\text{H}_2\text{M}}$  by about

(11) The rate studies do not allow one to distinguish reactions involving:  $\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{M} \rightarrow$  from:  $\text{HS}_2\text{O}_3^- + \text{HM}^- \rightarrow$  or  $\text{HS}_2\text{O}_3 + \text{M}^- \rightarrow$ . The corresponding rate constants are related by simple functions of the acid dissociation constants.

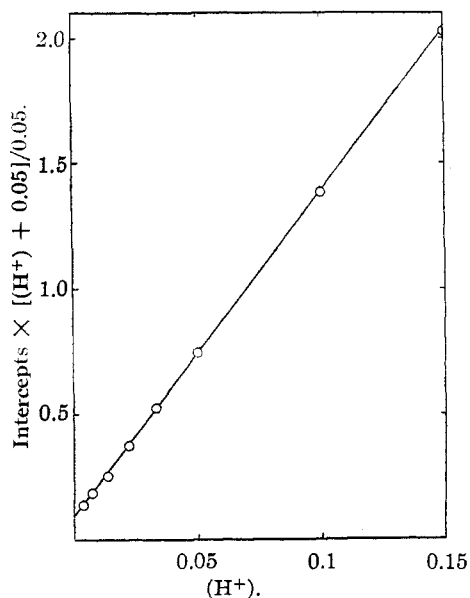


Fig. 2.—The variation of the maleic acid independent part of  $k_1$  with  $(H^+)$ . The ordinates are the intercepts on the vertical axis of Fig. 1 multiplied by  $[(H^+) + K]/K$ . 100%; this effect operates to a smaller extent at lower values of  $(H^+)$ .

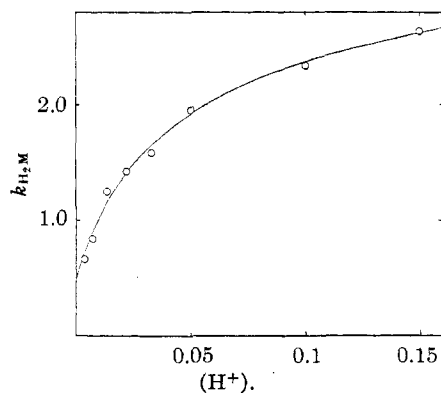


Fig. 3.—The variation of the coefficient of the maleic acid dependent part of  $k_1$  with  $(H^+)$ . The ordinates are the slopes of the lines in Fig. 1 multiplied by  $[(H^+) + K]/K$ .

The variation of  $k_{H_2M}$  represented in Fig. 3 cannot be explained by an additional path involving  $HS_2O_3^-$  or  $H^+ + S_2O_3^{2-}$ ; if such were the case, the increase in  $k_{H_2M}$  (Fig. 3) would be linear with  $(H^+)$ . Nor can the leveling off be due to the formation of thiosulfuric acid; attempts to fit the data with varying values of  $K_{HS_2O_3}$  and  $K_{HS_2O_3^-}$  proved futile. A possible interpretation is that the results at high  $(H^+)$  represent the true value of  $k_{H_2M}$ ; at low values of  $(H^+)$  where  $MH^-$  becomes high,  $k_{H_2M}$  is decreased by some intervention of  $HM^-$  (e. g., formation of a complex:  $HM^- \cdot H_2M$ ).

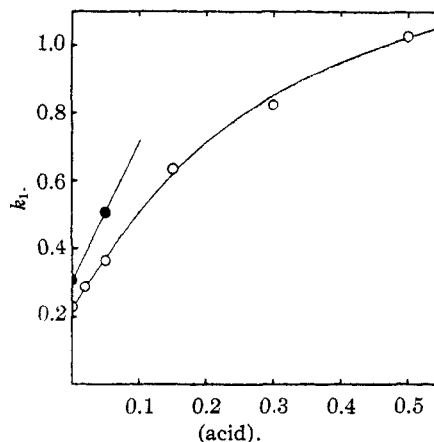


Fig. 4.—The variation of  $k_1$  with concentration of  $H_2C_2O_4$  at  $0.025 M H^+$  and of  $H_3PO_4$  at  $0.0143 M H^+$ .  $(H_2M) = 0.196 M$ . The values for  $H_2C_2O_4$  and  $H_3PO_4$  are distinguished by the symbols:  $\bullet$ ,  $\circ$ , respectively.

Experiments with other moderately strong acids show that the reaction is catalyzed by acids in general. Figure 4 shows the effect of increasing concentration of phosphoric acid and the effect of oxalic acid on the reaction. Similar to the effect of maleic acid, phosphoric acid gives a linear increase at low values but becomes relatively less effective at higher concentration. The effect of oxalic acid at higher concentrations could not be studied since a solid phase (presumably  $KH_3(C_2O_4)_2 \cdot 2H_2O$ ) separates.

The catalytic coefficients of the acids  $H_3O^+$ , oxalic acid, phosphoric acid and  $H_2M$  are 14, 6.00, 3.6 and *ca.* 2.6, respectively. The value cited for  $H_2M$  is the maximum value in Fig. 3. The observed order is expected from the Brönsted rule. The catalysis by  $H^+$  cannot be separated, by a kinetic analysis such as was carried out, from a possible contribution by a reaction of  $HS_2O_3^-$ , and the coefficient may include such a term. Also, the coefficients for phosphoric acid and oxalic acid contain the contributions due to the ions  $H_2PO_4^-$  and  $HC_2O_4^-$ ; however, these are probably quite small due to the lower dissociation constants.

A possible explanation of the fact that  $k_2$  is *ca.* twice  $k'_d$  at the same  $(H^+)$ , is that the maleic acid molecules attacked by the products resulting from the reaction  $2HS_2O_3^- \rightarrow$  are able to react with two additional molecules of thiosulfate. That the products in question do react with maleic acid seems certain since sulfur which is produced by this reaction in the absence of maleic acid is not observed. Small quantities of sulfur

dioxide are produced, the amount depending on the concentrations of maleic acid, thiosulfate, and of acid. Experiments were carried out in which sulfite was added initially. This operation did not affect the rate of disappearance of thiosulfate (or the production of fumaric acid); it was observed however that if the initial concentration of sulfite was high, the reaction did not produce additional quantities. This indicates that rather complex changes, some of them reversible, follow the rate determining steps.

In Table III, the results obtained in a study of the maleic-fumaric acid transformation which accompanies the disappearance of thiosulfate are presented.

The rate constant  $k'_f$  is defined by the relation

$$d(\text{H}_2\text{F})/dt = k'_f(\overline{\text{H}_2\text{M}})(\text{T})$$

Since

$$-d(\text{T})/dt = k_1(\text{T})(\text{H}_2\text{M}) + k_2(\text{T})^2$$

it follows that

$$k'_f = \frac{\Delta(\text{H}_2\text{F})k_2}{2.3(\overline{\text{H}_2\text{M}}) \log \frac{k_1(\overline{\text{H}_2\text{M}}) + k_2(\text{T}_0)}{k_1(\overline{\text{H}_2\text{M}}) + k_2(\text{T})}}$$

This equation was used in calculating  $k'_f$  where  $k_2$  was appreciable (above 0.022  $M$   $\text{H}^+$ ). For the experiments at lower values of  $(\text{H}^+)$ , the simplified form:  $k'_f = [(\Delta(\text{H}_2\text{F})/\Delta(\text{T}))k_1]$  was used. The values of  $k_1$  and  $k_2$  were obtained from Fig. 1.

Experiments 5-9 cover a fairly wide range of  $(\text{H}_2\text{M})$  and  $(\text{T})$  at constant  $(\text{H}^+)$ . In this region of low  $(\text{H}^+)$  where the second order path for the disappearance of  $\text{T}$  is negligible, it is observed that the assumed rate law expresses the data.<sup>12</sup> Catalysis of the transformation thus probably results from a direct interaction of  $\text{S}_2\text{O}_3^{2-}$  with  $\text{H}_2\text{M}$ . The exact mechanism of such interaction cannot be established by the rate law, nor can it be decided whether the addition of thiosulfate by maleic acid and the transformation of maleic to fumaric acid involve the same intermediate complex. Primary decomposition of the thiosulfate and catalysis by the resulting intermediates would, however, appear to be excluded for this concentration region.

A simple picture for the catalysis of the *cis-trans* change by  $\text{S}_2\text{O}_3^{2-}$  is the following. It is assumed that  $\text{S}_2\text{O}_3^{2-}$  can attach itself, with inversion

of configuration about the carbon atom, to one end of the double bond, yielding a complex which now has a single bond connecting the carbon atoms, about which rotation can take place. If spontaneous loss of the thiosulfate ion does not produce inversion, fumaric acid will be formed as the product on dissociation of the ion. The dissociation is energetically possible since the dissociated state maleic acid + thiosulfate ion has a higher potential energy than fumaric acid + thiosulfate ion.

At higher  $(\text{H}^+)$ , *e. g.*, 0.3  $M$ , expts. 19-22, where the  $(\text{H}_2\text{M})$  independent term for the disappearance of thiosulfate becomes important, the values of  $k'_f$  vary in a way to suggest that this reaction can induce the transformation. Presumably the interaction:  $2\text{HS}_2\text{O}_3^- \rightarrow$  produces an intermediate (or intermediates) which adds to maleic acid (to explain the non-appearance of  $\text{S}$ ) and which also catalyzes the *cis-trans* reaction.

The values of  $k_f (= k'_f[(\text{H}^+) + K]/K)$  are calculated on the assumption that  $\text{S}_2\text{O}_3^{2-}$  is the catalytic species. It is observed that there is an increase with  $(\text{H}^+)$ . Part of this can be attributed to the contribution by the  $\text{H}_2\text{M}$  independent path for thiosulfate disappearance. It is unlikely however that this will account for the sharp increase at low  $(\text{H}^+)$ . It is possible that this phenomenon is related to the similar one discussed for the variation of  $k_{\text{H}_2\text{M}}$  with  $(\text{H}^+)$ .

The addition of phosphoric acid and oxalic acid does not catalyze the *cis-trans* isomerization by  $\text{S}_2\text{O}_3^{2-}$  as is shown by the results of experiments 10-12 and 16, Table III.

It has already been mentioned that sulfur dioxide does not affect the catalysis. Some experiments also were done in which thiosulfate was allowed to decompose partially in mineral acid before adding the maleic acid. The rate of disappearance and the *cis-trans* catalysis was not affected by the sulfur and other products which had appeared.

Skraup<sup>13</sup> observed that when  $\text{H}_2\text{S} + \text{SO}_2$  react in a solution of maleic acid, fumaric acid forms. Since thiosulfate forms under some conditions when the  $\text{H}_2\text{S}$  and  $\text{SO}_2$  react in aqueous solution, experiments were undertaken to determine whether  $\text{S}_2\text{O}_3^{2-}$  is the cause of the catalysis. Accordingly a solution of sodium bisulfite was added to a maleic acid-maleate ion solution containing  $\text{H}_2\text{S}$ . The initial concentrations were: 0.02  $M$

(12) A rate law similar in form, except for the variation with  $\text{H}^+$ , was observed by Nozaki and Ogg [THIS JOURNAL, **63**, 2584 (1941)] for catalysis of the *cis-trans* change by  $\text{CNS}^-$ . This paper includes a discussion of mechanisms.

(13) Skraup, *Monatsh.*, **12**, 718 (1891).

TABLE III

THE PRODUCTION OF FUMARIC ACID BY THIOSULFATE IN SOLUTIONS OF MALEIC ACID

No.	(H <sup>+</sup> ) × 10 <sup>2</sup>	( $\overline{H_2M}$ )	(T <sub>0</sub> ) × 10 <sup>3</sup>	(T) × 10 <sup>3</sup>	Δ(H <sub>2</sub> S) × 10 <sup>3</sup>	k <sub>f</sub>	k <sub>t</sub>
1 <sup>a</sup>	...	....	25.04	21.85	19.2	0.54	0.54
2	0.35	0.105	24.91	17.75	24.6	.67	.72
3	.70	.0262	3.465	2.046	5.64	.75	.83
4	.70	.086	3.383	1.358	6.40	.70	
5	1.36	.045	3.147	1.317	6.60	.84	
6	1.36	.0715	3.151	0.895	6.40	.76	
7	1.36	.168	3.090	0.850	4.72	.76	
8	1.36	.150	24.80	10.96	29.3	.73	.97
9	1.36	.400	24.43	9.80	20.5	.73	
10 <sup>b</sup>	1.43	.0283	3.485	0.654	3.15	.71	
11 <sup>b</sup>	1.43	.0284	3.455	0.565	2.90	.83	1.01
12 <sup>b</sup>	1.43	.0276	3.455	0.565	2.41	.83	
13	2.2	.099	3.420	1.450	4.07	.76	
14	2.2	.30	24.39	11.14	20.7	.85	1.21
15	2.2	.30	3.460	0.41	5.17	.96	
16 <sup>c</sup>	2.5	.0285	3.460	1.11	4.17	.82	1.23
17	4.8	.188	24.73	13.79	13.2	.86	1.7
18	9.8	.188	24.96	11.84	11.9	.76	2.3
19	28	.088	24.70	7.05	8.0	.58	3.7
20	28	.189	24.31	7.00	7.0	.31	2.1
21	28	.285	28.25	4.40	7.6	.27	1.8
22	28	.180	38.53	9.90	11.3	.42	2.8
23	48	.188	24.46	5.31	5.0	.23	2.4

<sup>a</sup> 0.3 M HM<sup>-</sup>, 0.1 M M<sup>-</sup>. <sup>b</sup> (H<sub>3</sub>PO<sub>4</sub>) was 0.15, 0.30, 0.50 M in Exps. 10, 11, 12, respectively. <sup>c</sup> (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) = 0.05 M.

NaHSO<sub>3</sub>, 0.01 M NaHS, 0.22 M H<sub>2</sub>M, and HM<sup>-</sup> to make (H<sup>+</sup>) = 0.0136 M. Twenty seconds after mixing the solution was quenched and analyzed as before for thiosulfate. It was shown by adding metal ions that the time interval allowed was sufficient for the consumption of the H<sub>2</sub>S. A similar solution was allowed to stand for some time and again analyzed for S<sub>2</sub>O<sub>3</sub><sup>=</sup>. The results showed that reducing material analyzing for S<sub>2</sub>O<sub>3</sub><sup>=</sup> amounted to 10.4 × 10<sup>-3</sup> immediately after mixing and fell to 7.4 × 10<sup>-3</sup> M after twenty-five minutes. Analysis for fumaric acid showed that immediately after mixing *ca.* 3.6 × 10<sup>-3</sup> M is produced; after twenty-five minutes, 4.8 × 10<sup>-3</sup> additional appears; if the decrease in titer

were due to S<sub>2</sub>O<sub>3</sub><sup>=</sup>, *ca.* 5.4 × 10<sup>-3</sup> M additional would be expected. However, k<sub>f</sub> calculated from the results is 0.064 while a value of 0.44 would be expected for the conditions if all the reducing material were S<sub>2</sub>O<sub>3</sub><sup>=</sup>. These results indicate that a catalyst other than S<sub>2</sub>O<sub>3</sub><sup>=</sup> operates during the reaction of H<sub>2</sub>S + SO<sub>2</sub>, that S<sub>2</sub>O<sub>3</sub><sup>=</sup> may account for the continuing slow catalysis, and that a reducing material in addition to S<sub>2</sub>O<sub>3</sub><sup>=</sup> is produced by the reaction under the experimental conditions. These results were checked by other experiments.

### Summary

Data on the rate of disappearance of thiosulfate in solutions of maleic acid are presented and analyzed. At low acid a term varying with the product of thiosulfate and maleic acid concentrations is predominant; the reaction by this path is subject to catalysis by various acids, including maleic acid. At high acid, a term second order with respect to thiosulfate and independent of maleic acid is also important; the coefficient of this term is about twice the coefficient of the similar rate law which describes the decomposition of thiosulfate in acid solutions without added maleic acid.

Two paths are also observed for the formation of fumaric acid in solutions containing maleic acid and thiosulfate. At low acid, the rate of formation is proportional to the product of thiosulfate and maleic acid concentration; at high acid another path, which may be related to the maleic acid independent path for the disappearance of thiosulfate, also contributes.

Experiments on the catalysis of fumaric acid formation by the reaction of H<sub>2</sub>S + SO<sub>2</sub> are described.

ITHACA, NEW YORK

RECEIVED OCTOBER 14, 1942