

g. of solvent). Each value corresponds to the average velocity constant at 50% decomposition in from three to seven experiments.

TABLE I
EFFECT OF WATER ON THE REACTION VELOCITY AT 35°

Water, %	Molality of water	$k \times 10^3$
0	0	87.5
0.04	0.022	90.3
.07	.039	86.1
.15	.084	75.8
.22	.122	72.1
.32	.178	65.2
.68	.380	45.1

TABLE II
EFFECT OF SULFUR TRIOXIDE ON THE REACTION VELOCITY AT 35°

Sulfur trioxide, %	Molality of sulfur trioxide	$k \times 10^3$
0.13	0.016	86.4
.61	.078	35.2
1.32	.167	25.1
3.57	.460	19.8
7.05	.950	18.2

The data are shown graphically in Fig. 1. These curves for the reaction rate at various concentrations of inhibitor show that after a certain minimum amount of water is present, additional amounts of water have a marked inhibitory effect, the relative effect diminishing with increasing amounts of water. The curves show a maximum at molalities of water 0.024 and 0.030 for 35 and 45°, respectively. The position of the maximum and the slope on either side is dependent upon the relative inhibiting powers of water and sulfur trioxide.

The Effect of Temperature on the Reaction Rate.—The velocity constants obtained by Whitford⁴ and by Dittmar⁷ in 100% sulfuric acid at 20, 30, 40 and 50° did not agree, but temperature coefficients calculated from each set of data were concordant. The discrepancy was apparently due to a slight error in concentration, as the temperature coefficients calculated at 100% sulfuric acid are on the steepest part of the curve. The velocity constants found in this investigation agreed with those obtained by Dittmar.⁷

Since the maximum of the curve shifts with temperature, temperature coefficients have little

(7) Dittmar, THIS JOURNAL., 52, 4737 (1930).

TABLE III
EFFECT OF WATER ON THE REACTION VELOCITY AT 45°

Water, %	Molality of water	$k \times 10^3$
0	0	328.4
0.02	0.011	335.0
.04	.022	338.2
.07	.039	337.4
.15	.084	321.3
.22	.122	280.0
.32	.178	254.3
.68	.380	155.3

TABLE IV
EFFECT OF SULFUR TRIOXIDE ON THE REACTION VELOCITY AT 45°

Sulfur trioxide, %	Molality of sulfur trioxide	$k \times 10^3$
0.09	0.011	305.8
.31	.039	257.9
.61	.078	123.9
1.51	.192	93.0
3.57	.460	76.9
7.05	.950	57.3

meaning unless taken at the same distance from the maximum. The temperature coefficient 35–45° for 100% sulfuric acid found in this investigation was 3.75, which is of the same order as those found by the other investigators.^{4,7}

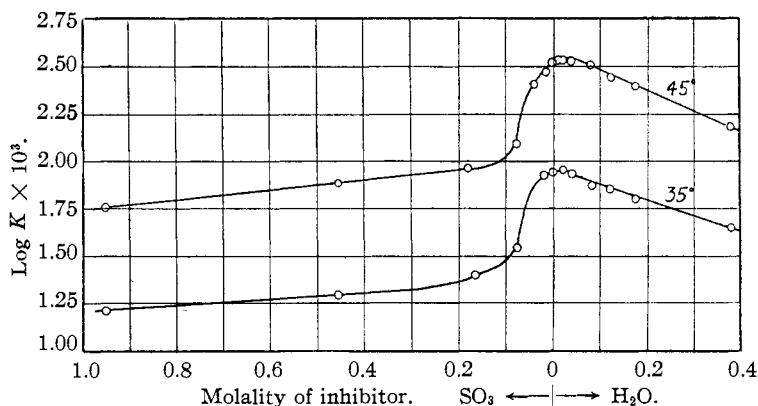


Fig. 1.—Effect of sulfur trioxide and of water on the reaction rate.

Discussion

The decomposition of malic acid seems to be best explained by Taylor's theory of negative catalysis, as is the decomposition of the several acids previously studied.² The decomposition occurs through the formation of a malic acid—sulfuric acid complex, this disintegrating to give the decomposition products of malic acid and to regenerate the sulfuric acid.

The inhibition by water and by sulfur trioxide appears to be brought about through the formation of a compound between the inhibitor and

the sulfuric acid-malic acid complex. The inhibitor thus decreases the concentration of the complex and thereby slows down the reaction.

The explanation for the maximum appears to be the same as for the other acids mentioned;² *i. e.*, there exists an equilibrium, $\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{H}_2\text{O}$. As water is removed the velocity of decomposition is accelerated until a point is reached where the inhibiting effect of the increased concentration of sulfur trioxide more than offsets the accelerating effect due to the removal of water. The maximum in the velocity of decomposition of malic acid came at a molality of water of 0.024 and 0.030 at 35 and 45°, respectively, as compared to citric acid which exhibits a maximum at molalities of water of 0.10, 0.14, 0.20 at 15, 25 and 35°, respectively.⁴ The position of the maximum and the slope of the curve on either side of the maximum in both cases are evidence for the correctness of Wiig's explanation. In each case sulfur trioxide is a stronger inhibitor than water (as evidenced by the steeper slope of the curve in the sulfur trioxide region); hence, the maximum appears at a small concentration of water. The relative effect is not so pronounced in the case of malic acid as in citric acid, so that the maximum falls nearer to zero concentration of water. One would expect from this theory, if sulfur trioxide and water should have the

same inhibiting power in the decomposition of some compound, the curve for the velocity of decomposition would be symmetrical and exhibit a maximum at 100% H_2SO_4 .

The sharp flattening out of the curve after a concentration of about 2% sulfur trioxide has been reached is interesting. More than enough sulfur trioxide is then present to form a molecular compound with all of the malic acid or malic acid-sulfuric acid complex present; hence, the velocity measured from this point on may be that of the disintegration of this new complex.

The author wishes gratefully to express his appreciation to Dr. Edwin O. Wiig, under whose direction this work has been done, for his sincere and friendly interest in the completion of it.

Summary

The decomposition of malic acid by sulfuric acid has been found to proceed in the same manner as formic, oxalic and citric acids.

A maximum in the rate of decomposition has been found, the rate increasing up to a certain point as water was removed, then decreasing. The location of this maximum, which has been overlooked in a previous investigation, brings malic acid into agreement with the theory for inhibition in the decomposition of these acids.

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The Equilibrium in the Reaction $\text{Cl}_2 + \text{Br}_2 = 2\text{BrCl}$

BY HAROLD G. VESPER AND G. K. ROLLEFSON

The existence of bromine chloride has been a subject of dispute for many years. Early investigators¹ recorded the formation of a yellow or red-brown liquid when chlorine was passed into bromine in a freezing mixture, or bromine into liquid chlorine, and assumed the liquid to contain bromine chloride. That this was other than a solution of bromine and chlorine was questioned² on the basis of the small heat developed in the process, and from studies of the freezing point- and boiling point-composition curves. However, Andrews and Carlton³ noted a marked contraction

in volume upon mixing liquid bromine and liquid chlorine, and workers⁴ in the field of organic chemistry have for some time reported that mixtures of bromine and chlorine in addition reactions give bromochloro products, as if the substance adding were bromine chloride.

Physicochemical evidence for the formation of the compound BrCl on mixing Br_2 and Cl_2 in carbon tetrachloride solution was furnished by Barratt and Stein⁵ and by Gillam and Morton.⁶ It was found that the absorption of light by the mixtures, in the visible region, was markedly less

(1) (a) Balard, *Ann. chim. phys.*, [2] **32**, 337 (1826); (b) Schönbein, *J. prakt. Chem.*, [1] **88**, 483 (1863); (c) Bornemann, *Ann.*, **189**, 184 (1877); (d) Thomas and Dupois, *Compt. rend.*, **143**, 282 (1906).

(2) (a) Berthelot, *Compt. rend.*, **94**, 1619 (1882); (b) Lebeau, *ibid.*, **143**, 589 (1906); (c) Karsten, *Z. anorg. Chem.*, **53**, 365 (1907).

(3) Andrews and Carlton, *THIS JOURNAL*, **29**, 688 (1907).

(4) (a) Simpson, *Proc. Roy. Soc. (London)*, **A27**, 118, 424 (1879); (b) James, *J. Chem. Soc.*, **43**, 37 (1883); (c) Delépine and Ville, *Compt. rend.*, **170**, 1390 (1920); (d) Hanson and James, *J. Chem. Soc.*, 1955, 2979 (1928).

(5) Barratt and Stein, *Proc. Roy. Soc. (London)*, **A122**, 582 (1929).

(6) Gillam and Morton, *ibid.*, **A124**, 604 (1929).