[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

INHIBITION IN THE DECOMPOSITION OF ORGANIC ACIDS BY SULFURIC ACID

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The most outstanding group of negative catalytic reactions in homogeneous solution to which Taylor's theory of negative catalysis appears to apply is probably that which deals with the decomposition of organic acids by sulfuric acid. The results of the first intensive study of inhibition in these reactions were published by Bredig and Lichty in 1906. Within the past few years, principally through the efforts of Professor Walton and his students at Wisconsin, several other reactions of this type have been investigated. There are now data available for the effect of inhibitors on the velocity of decomposition of six organic acids in sulfuric acid. In addition to the well-known investigation of Bredig and Lichty[2] on the decomposition of oxalic acid, studies have been made of the reaction of sulfuric acid with formic,[3] malic,[4] *o*-benzoylbenzoic,[5] triphenylacetic[6] and citric[7] acids. In addition, the influence of inhibitors on the temperature coefficient of the malic acid[8] reaction and the effect of sulfur trioxide on the decomposition of oxalic acid[9] have been measured. In view of the increasing interest in inhibited reactions in general, the data covering the decomposition of organic acids in sulfuric acid have been deemed sufficient to warrant an analysis of the experimental results, together with a discussion of the application, of Taylor's theory[10] of negative catalysis.

The decompositions mentioned above all follow the unimolecular reaction law in spite of the fact that sulfuric acid would seem to be one of the reactants. This may be due to the large excess of sulfuric acid always employed, since under such conditions the change in its concentration in a single experiment would be negligible. On the other hand, the reaction may be a true unimolecular decomposition if we consider that the reaction whose velocity is actually measured is the decomposition of a sulfuric acid–organic acid complex. The velocity constants obtained are not,

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[1] National Research Fellow in Chemistry.

[2] Bredig and Lichty, *Z. Elektrochem.*, **12**, 459 (1906); Lichty, *J. Phys. Chem.*, 11, 225 (1907).

[3] Schierz, THIS JOURNAL, **45**, 447 (1923).

[4] Whitford, *ibid.*, **47**, 953 (1925).

[5] Gleason and Dougherty, *ibid.*, **51**, 310 (1929).

[6] Dittmar, *J. Phys. Chem.*, **33**, 533 (1929).

[7] Wiig, THIS JOURNAL, **52**, 4729 (1930).

[8] Dittmar, *ibid.*, **52**, 2746 (1930).

[9] Wiig, *ibid.*, **52**, 4737 (1930).

[10] Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

however, always constant but often decrease considerably. As the reaction being studied always produces water or other inhibitors, a falling velocity constant is to be expected. The magnitude of the decrease in the velocity constant depends on the extent to which the substance formed inhibits. Thus, in the decomposition of oxalic acid[2] in 100% sulfuric acid at 25°, $k \times 10^3$ decreases from 21.5 to 11.9 during a single experiment. This is in agreement with the observation that water is an extremely powerful inhibitor of the reaction. In contrast with this, water is a comparatively weak inhibitor for the condensation of *o*-benzoylbenzoic acid and, as might be predicted, the water formed during the reaction does not cause a measurable decrease in the velocity constant. Furthermore, where a reaction displays sensitiveness to the small quantity of water formed during the experiment, this sensitiveness vanishes in the more dilute sulfuric acid solutions used.

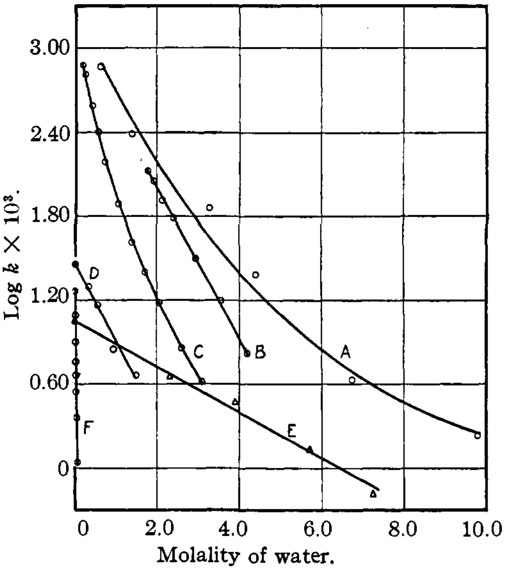

Fig. 1.—Effect of water on the reaction rates of (A) formic, (B) triphenylacetic, (C) citric, (D) malic, (E) *o*-benzoylbenzoic and (F) oxalic acids. A, C, F at 25°; B at 12°; D at 30°; E at 75°.

Inhibition by Water.—The effect of water on the velocity of decomposition of the six acids investigated has been determined over wide concentrations and at temperatures varying from 12 to 98°. In Fig. 1 there is presented one curve for each acid showing the influence of water on the reaction velocity at 25° or as near thereto as the data permit. The values used in plotting the curves are those given in the original papers except in the case of formic and *o*-benzoylbenzoic acids. For the former the velocity constants of Schierz[3] were multiplied by 2.303 to obtain the ordinary velocity constant, but, for the latter acid, velocity constants are given at only one concentration of sulfuric acid. Fortunately, Gleason and Dougherty[5] have presented their experimental data in the form of a curve showing the percentage of *o*-benzoylbenzoic acid decomposed at four hours as a function of the sulfuric acid concentration. By substituting in the usual equation for a unimolecular reaction $a = 1$, $t = 240$ and $x =$ the fraction of *o*-benzoylbenzoic acid condensed, we obtain one value of the velocity constant for each concentration of sulfuric acid. In view of the small inhibiting effect of water in this reaction, one value is sufficiently accurate for purposes of comparison.

From the figure it may be seen that in all six cases the effect of water is an exponential function of the concentration. Gleason and Dougherty[5] concluded that for *o*-benzoylbenzoic acid the retarding action of added water is in direct proportion to the amount added, and that it would appear that the *o*-benzoylbenzoic acid condensation differs fundamentally from reactions of the oxalic acid type. However, the curve for *o*-benzoylbenzoic acid in Fig. 1 indicates that the velocity constant is a logarithmic function of the added water and consequently this decomposition is similar to the others. Although these reactions are all of the same type, they differ in sensitivity to inhibition by water. The influence of water, as measured by the slope of the curves, is greatest in the decomposition of oxalic acid and least for *o*-benzoylbenzoic acid. At small concentrations of water the relative effect is nearly the same for the other four acids. The strength of the acids, as measured by the ordinary acid dissociation constants, decreases in the order oxalic, citric, malic, *o*-benzoylbenzoic, formic, triphenylacetic. Thus it may be seen that there is apparently no relationship between the strength of the acid undergoing decomposition and the retarding action of water. However, there may be some question as to whether it is justifiable to carry over into sulfuric acid, for purposes of comparison, dissociation constants that were determined with water as the solvent.[11]

Inhibition by Sulfur Trioxide.—The influence of sulfur trioxide on the rate of decomposition has been studied for only three of the six acids under consideration. For a number of years there was an apparent inconsistency in the results obtained with this substance. Bredig and Lichty[2] found qualitatively that 1% SO_3 accelerated the decomposition of oxalic acid to such an extent that it could not be measured by the method they employed. Whitford,[4] working with malic acid, found 1% SO_3 to have no effect while 12.5% decreased the reaction rate. Recently the effect of sulfur trioxide has been determined in the case of citric[7] and oxalic[9] acids and now the results appear entirely concordant. Figure 2 shows graphically the experimental results that have been obtained.

It will readily be seen that the three curves conform in shape to a curve with a maximum. The position of the maximum and the slopes of the curve on either side of the maximum depend wholly on the relative inhibiting powers of water and of sulfur trioxide. The relative retarding effects may be summarized as in Table I.

Since there exists in sulfuric acid the equilibrium $H_2SO_4 \rightleftharpoons H_2O + SO_3$ and since the ratio of the relative inhibiting powers of water and of sulfur trioxide may have any value whatever, the maximum reaction ve-

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[11] Kolthoff, *Rec. trav. chim.*, **49**, 413 (1930).

Table I

Influence of H_2O and of SO_3 on the Reaction Rate

Acid	Relative inhibiting power Water	 Sulfur trioxide
Oxalic	Very, very strong	Very weak
Malic	Strong	Weak
Citric	Strong	Very strong

locity may occur anywhere within a concentration range determined by the equilibrium. It may be predicted that when formic, triphenylacetic and *o*-benzoylbenzoic acids are studied over sufficiently great concentrations of water and of sulfur trioxide in sulfuric acid, a maximum analogous to those in Fig. 2 will be found in each case.

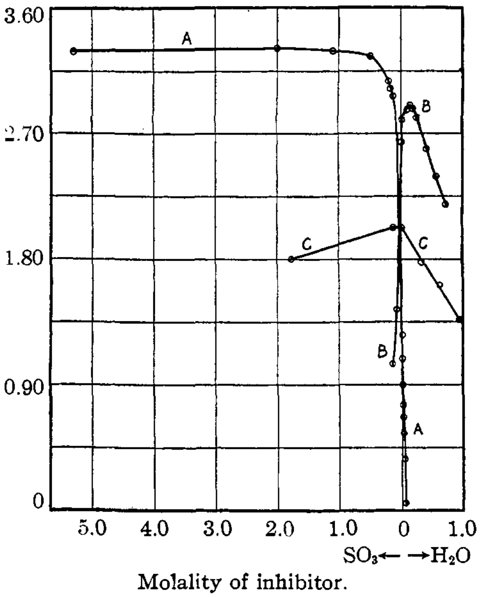

Fig. 2.—Effect of sulfur trioxide and of water on the reaction rates of (A) oxalic, (B) citric and (C) malic acids. A, B at 25°; C at 40°.

Relative Rates of Decomposition.—Attempts have been made to find some relationship between the velocity of decomposition of the organic acids and their strength. For the acids studied up to 1925 Whitford[4] gives the following table, where the velocity constant is for the reaction in 0.562 molality of water at 50°.

Table II

Relation of Acidity to Reaction Velocity

Acid	Dissociation constant	Velocity constant
Oxalic	3.8×10^{-2}	0.515
Malic	4.0×10^{-4}	158.5
Formic	2.1×10^{-4}	Reaction immeasurably fast

Dittmar[6] added triphenylacetic acid to this list since he found that it decomposes more rapidly than formic acid and is the weakest acid of the four. Also, Dittmar points out that the reaction velocities increase in the order of decreasing heats of activation as calculated from temperature coefficients by means of the Arrhenius equation. An inspection of the curves in Figs. 1 and 2 shows that such comparisons no longer hold when all the data now available are considered. The decomposition velocities vary so greatly with the concentration of water and of sulfur trioxide that the organic acids might be arranged in several orders of increasing reaction rates.

The original comparison of Whitford was based on Kendall's rule[12] that the tendency toward molecular compound formation between sulfuric acid and an organic acid varies with the acidity of the second acid. The decomposition of the organic acids which have been investigated is supposed to proceed by way of an unstable sulfuric acid–organic acid complex, so that Kendall's rule should apply here *provided* the mere tendency toward compound formation can be assumed to govern the velocity of reaction. We have just seen, however, that reaction velocity comparisons cannot be made (unless an extrapolated value for each acid in the total absence of inhibitors can be obtained). Furthermore, Kendall's rule is at the best qualitative. For example, Hoogewerf and van Dorp[13] isolated an addition compound of sulfuric acid with mesaconic acid ($K_A \times 10^4 = 8$), whereas Kendall and Carpenter[12] obtained no indication by the freezing point method of similar compound formation between sulfuric acid and α-chlorocrotonic acid ($K_A \times 10^4 = 7.2$). The structure of the organic acid, the presence of various groupings, steric hindrance, etc., may play a not inconsiderable role in molecular compound formation. In addition, as already mentioned, acid dissociation constants determined in water solution may not furnish a proper basis of comparison when the medium is sulfuric acid. It is not surprising, therefore, to find that there is no apparent relation between velocity of decomposition and the ordinary acid dissociation constant of the organic acids. Furthermore, no such relationship would be expected since the rate of decomposition of the organic acid-sulfuric acid complex would depend on its instability rather than the rate or extent of its formation.

The Effect of Miscellaneous Inhibitors.—The retarding influence of numerous substances other than water and sulfur trioxide has been studied. Whitford[4] and Dittmar[6] found, in agreement with Kendall's rule for compound formation, that sodium and potassium sulfates were stronger inhibitors than water for the decomposition of malic and triphenylacetic acids. However, in the case of oxalic acid, Bredig and Lichty[2] found that water was a slightly better inhibitor than potassium sulfate. Dittmar's data covering the effect of a large number of inhibitors on the velocity of decomposition of malic and triphenylacetic acids show analogous differences very convincingly. For example, ethyl alcohol is a better inhibitor than crotonic acid in the decomposition of triphenylacetic acid but the reverse is true in the case of malic acid. A similar relationship holds for the following pairs of inhibitors: phenol–*p*-cresol, ethyl alcohol–*o*-toluic acid, coumarin–*o*-toluic acid, benzophenone–*o*-toluic acid.

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[12] Kendall and Carpenter, This Journal, **36,** 2506 (1914).

[13] Hoogewerf and van Dorp, *Rec. trav. chim.*, **18,** 211 (1899).

These results are not unexpected when we recall the wide variation in the relative effects of water and of sulfur trioxide on the decomposition of oxalic, malic and citric acids. If the action of an inhibitor depended solely on compound formation with sulfuric acid, then the same relative effects on the velocity of decomposition of the organic acids by sulfuric acid should be obtained. Since the experimental results show such marked differences in inhibiting power, it must be concluded that it is not sufficient to consider only the tendency toward compound formation with sulfuric acid in seeking for a mechanism of inhibition. In this connection Dittmar[8] points out that although phosphoric acid is an inhibitor for the decomposition of malic and triphenylacetic acids, no molecular compound of phosphoric and sulfuric acids has been shown to exist. On the other hand, Walton and Kepfer[14] have found, from solubility measurements, that phosphoric acid forms a molecular complex with malic acid. Dittmar concludes, therefore, that inhibition may be more satisfactorily explained by compound formation between malic acid and the inhibitor.

The Effect of Temperature.—Determinations of temperature coefficients have been made for the six organic acids whose decompositions have been studied but many of the values vary so much that they are not of much use for purposes of comparison. The chance for error is so large in these sulfuric acid systems that only by making careful measurements at a large number of sulfuric acid concentrations at two or more temperatures can dependable values of the temperature coefficient be obtained. In this way the experimental errors may be averaged, but in much of the data given in the literature this has not been taken into consideration. However, it may be stated that, in general, the addition of an inhibitor increases the temperature coefficient, and increase in concentration of the inhibitor increases the temperature coefficient. Where there are exceptions to these statements, and there are several, more data are usually needed before a definite decision may be made.

Dittmar[8] has determined the temperature coefficients for the decomposition of malic acid by sulfuric acid in the presence of a large number of inhibitors and finds that, in general, the temperature coefficient is greater than that for 100% sulfuric acid. Also, in the majority of the experiments the temperature coefficients increase with increase in inhibitor concentration. This last generalization holds very well for citric acid[7] also, where the data for the effect of water are sufficiently complete so that the trend of the temperature coefficient may be seen. The results are thus in general agreement with Dhar's[15] statement that a negative catalyst increases the temperature coefficient of a reaction. In the event

[14] Walton and Kepfer, *J. Phys. Chem.*, **34**, 543 (1930).

[15] Dhar, *ibid.*, **28**, 951 (1924).

that these reactions follow a chain mechanism, the agreement with Dahr's rule may be only fortuitous, since at present the temperature coefficient of a chain reaction has no theoretical significance.

Mechanisms

Of the Decomposition.—It is rather generally agreed that the decomposition of oxalic, formic, malic, triphenylacetic, *o*-benzoylbenzoic and citric acids is brought about by the formation of an unstable sulfuric acid–organic acid complex (oxonium compound) which subsequently breaks up into the reaction products and sulfuric acid. The process may be represented by the equations

$$\text{Organic Acid} + H_2SO_4 \rightleftharpoons \text{Organic Acid}\cdot H_2SO_4 \qquad (1)$$

$$\text{Organic Acid}\cdot H_2SO_4 \longrightarrow \text{Products of decomposition} + H_2SO_4 \qquad (2)$$

The experimentally determined velocity would be that of the second reaction, which is dependent on the concentration of the molecular complex. Thus, it is evident that these reactions are not to be considered as simple dehydrations. This is convincingly shown by the fact that the decomposition of triphenylacetic acid by sulfuric acid involves no water at all, the products being triphenylcarbinol and carbon monoxide.

There is also the possibility that the formation of the simple organic acid–sulfuric acid complex is not in itself sufficient for decomposition, especially in view of the fact that evidence for the existence of these compounds has been obtained in the case of oxalic, citric and malic acids from solubility data. It may be that addition of another molecule of sulfuric acid at a second point in the organic acid (which is possible since the acids all contain two or more oxygen atoms) is required to produce sufficient strain to cause a rupture of the atomic linkages. This process would also give a unimolecular reaction. The effect of inhibitors would be the same in the two cases. However, this mechanism really has nothing to recommend it as being better than the simpler one given first. Moreover, the data which indicate compound formation of oxalic,[16] malic[8] and citric[16] acids with sulfuric acid have been obtained in aqueous solutions where it is quite possible that these molecular compounds are also combined with water, a possibility of which the method employed can give no evidence.

Of Inhibition.—The retardation of the velocity of decomposition of organic acids in sulfuric acid by the addition of a third substance may best be explained by what has come to be known as Taylor's theory[10] of negative catalysis. The Titoff concept, according to which a negative catalyst acts by suppression of a positive catalyst, certainly does not hold for these reactions, especially when one considers the positions of the maxima in the curves for citric, malic and oxalic acids in Fig. 2. Like-

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[16] Knox and Richards, *J. Chem. Soc.*, **115**, 508 (1919).

wise, as pointed out by Christiansen[17] for the decomposition of oxalic acid in sulfuric acid, the chain reaction theory does not appear to be applicable to these inhibited decompositions, though there is no direct experimental evidence on which to base such a conclusion. That chain reactions may occur in solution is shown by the work of Bäckström[18] and of Alyea and Bäckström[19] on the oxidation of sodium sulfite solutions. The reaction between mercuric chloride and the oxalate ion in aqueous solution also appears to be a chain reaction.[20] It is not impossible, therefore, that the decomposition of organic acids in sulfuric acid may be chain reactions.

Deactivation by mere collision of the inhibitor with organic acid–sulfuric acid complexes which have acquired sufficient energy to undergo reaction also seems to be out of the question. In this case inhibition would depend only on the number of free molecules of the negative catalyst. At a given concentration of inhibitor, then, approximately the same relative decrease in the velocity of decomposition should be observed for all the acids whereas the actual effects vary greatly. This difficulty might be obviated by assuming a specific deactivating effect for each molecular complex, but then we really approach momentary compound formation instead of mere physical impact.

The mechanism of negative catalysis proposed by Taylor[10] is the direct opposite of that for positive catalysis in homogeneous reactions in solution where the reaction proceeds more readily by way of the intermediate compound. In negative catalysis the intermediate compound diverts one or more of the reactants from the main reaction, thus decreasing the active concentration of the reactants and slowing down the reaction velocity. According to the theory the function of inhibitors must be, in the present case, to bring about a decrease in the concentration of the unstable critical complex–organic acid$\cdot H_2SO_4$. The concentration of the unstable complex is determined by the equilibrium represented in Equation 1. Consequently, its concentration may be reduced by a decrease in the concentration of (1) H_2SO_4, through the formation of H_2SO_4·Inhibitor, and (2) the organic acid, through the formation of Organic Acid·Inhibitor. A third possibility is that the active concentration of the complex, Organic Acid$\cdot H_2SO_4$, may also be lowered by reaction of the addition compound itself with the inhibitor. It is evident then that inhibition may be brought about by any one, or various combinations, of the above three possibilities. However, by a consideration of the experimental data some of these mechanisms would seem to be eliminated.

[17] Christiansen, *J. Phys. Chem.*, **28**, 145 (1924); *Trans. Faraday Soc.*, **24**, 596 (1928).

[18] Bäckström, THIS JOURNAL, **49**, 1460 (1927).

[19] Alyea and Bäckström, *ibid.*, **51**, 90 (1929).

[20] Roseveare and Olson, *ibid.*, **51**, 1716 (1929); Roseveare, *ibid.*, **52**, 2612 (1930).

(a) **Inhibition Due only to H_2SO_4 + Inhibitor $\rightleftharpoons$ H_2SO_4·Inhibitor.**—That this possibility must be discarded has already been shown by the discussion in the section dealing with the effects of miscellaneous inhibitors. In case of inhibition by sulfur trioxide, for example, if compound formation with sulfuric acid were the only factor, then the effects with oxalic, malic and citric acids should be similar. Experimentally it is found that for the decomposition of citric acid sulfur trioxide is a very strong inhibitor, in the malic acid reaction a fair inhibitor, and for the oxalic acid decomposition an extremely weak inhibitor only after the concentration exceeds 14% SO_3.

(b) **Inhibition Due only to Organic Acid + Inhibitor $\rightleftharpoons$ Organic Acid·Inhibitor.**—The same sort of argument that was used to eliminate the preceding mechanism would appear to apply here. Kendall's rule for compound formation seems to work fairly well for hydrates of the acids but the inhibiting effect of water does not vary with the strength of the organic acid, as has previously been indicated. Similarly the very diverse effects of sulfur trioxide on the oxalic, malic and citric acid reactions seem to preclude the possibility that compound formation between the inhibitor and the organic acid determines completely the retarding action. Furthermore, Dittmar[8] found that *o*-toluic acid is a better inhibitor for the malic acid reaction than phosphoric acid, which has been shown to form a compound with malic acid, whereas compound formation between malic and *o*-toluic acids is scarcely to be expected since they are of nearly the same acid strength ($K_A \times 10^4$ is 4.0 and 1.25, respectively). While it would seem that compound formation between the organic acid and the inhibitor cannot be the only factor governing inhibition, still it must be admitted that there are weaknesses inherent in the reasons just advanced. Part of the argument depends on the use of the ordinary dissociation constants of the acids but the comparisons are made for sulfuric acid as the solvent, instead of water. Again, the effect of an inhibitor, *o*-toluic acid for example, in 100% sulfuric acid might be to change the $H_2SO_4 \rightleftharpoons H_2O + SO_3$ equilibrium (by combination with either of the products). Then inhibition by *o*-toluic acid might be due to compound formation between water (or sulfur trioxide) and malic acid rather than between *o*-toluic and malic acids as we have supposed. However, the mechanism being discussed would seem to be eliminated definitely by the consideration, in the next section, of the extremely small concentrations of negative catalysts necessary for inhibition to manifest itself.

(c) **Inhibition Due to Reaction of the Inhibitor with the Organic Acid·Sulfuric Acid Complex.**—This postulate is so flexible that no experimental evidence may be adduced against it. If it be assumed that reaction of the negative catalyst with the fugitive complex is highly specific, then this mechanism must be in agreement with the observed effects for all the negative catalysts. Since the acid properties of the two acids in the oxonium addition compound are very probably altered, the assumption of specific inhibitor effects is reasonable.

There are several experimental facts that would seem to be in accord with this mechanism. The concentration of the critical complex must, of course, be very small, so that inhibition by very minute amounts of negative catalysts should be possible. Such inhibition is indicated in the case of oxalic and citric acids. It will be recalled that for citric acid[7] the maximum reaction velocity at 25° occurs at 0.14 molality of water (0.25%). The decrease in the velocity of decomposition at concentrations of water less than 0.14 molality was attributed to the presence of sulfur trioxide formed as a result of the reaction $H_2SO_4 \rightleftharpoons H_2O + SO_3$. The concentration of sulfur trioxide in 99.75% sulfuric acid must be vanishingly small since calculations[9] indicate that its concentration in 100% sulfuric acid is at the most of the order of 3×10^{-4} molality. An entirely analogous explanation holds for the finding of the maximum reaction velocity for oxalic acid[9] at a molality of sulfur trioxide of about 2.0. If inhibition is due to compound formation with the sulfuric acid or the organic acid, or even both, it is difficult to see how a concentration of inhibitor of the order of 10^{-4} molality can influence the concentration of the organic acid·sulfuric acid complex simply by diverting an extremely minute amount of sulfuric acid or organic acid from the main reaction. Even in higher concentrations of water, say 3.0 molality, the concentration of *free* water, resulting from the equilibrium $H_2SO_4 + H_2O \rightleftharpoons H_2SO_4 \cdot H_2O$, must be small, so that inhibition by reaction of this free water with the fugitive complex would not be sufficient to bring the reaction to a full stop.

We may, of course, have all three inhibiting mechanisms operative at the same time, especially in the more concentrated inhibitor solutions. It would appear from the foregoing discussion, however, that the negative catalytic action must be due principally to reaction of the inhibitor with the intermediate compound through which the decomposition proceeds. The only weakness in this mechanism is that its great flexibility makes it very difficult to devise experimental tests.

In view of the present lack of any positive evidence for the existence of reaction chains in the decomposition of organic acids in sulfuric acid, it would seem that Taylor's theory of negative catalysis offers the only satisfactory explanation for the effect of inhibitors on these reactions. It is well to bear in mind, however, that no definite decision with respect to the applicability of the chain reaction theory can be made until more data are available.

In conclusion, the author wishes to acknowledge his indebtedness to Professor Hugh S. Taylor for valuable suggestions and criticisms.

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