

REACTION RATES AND INDICATOR ACIDITIES

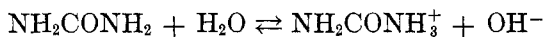
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Since the general adoption of the Arrhenius theory the usual quantitative measure of acidity has been hydrogen-ion concentration or sometimes hydrogen-ion activity. It is a measure which is based entirely upon the behavior of dilute aqueous solutions. So long as chemists generally were content to restrict their theoretical investigations to these solutions it was a moderately successful one, but it leads to inextricable confusion when it is extended to non-aqueous solutions or to concentrated aqueous ones. There is therefore an almost irresistible tendency to set up a measure of acidity which shall be capable of this extension without confusion or ambiguity, and some difference of opinion about the procedure to be adopted (4). The criterion of acidity in terms of a measurement with a basic indicator, which was suggested by Hammett and Deyrup (18), is unambiguous, historically reasonable, and measurable. But the real justification for its adoption, as for the adoption of any definition, must lie in its utility. It is therefore extremely important that this criterion of acidity makes it possible to predict from an indicator measurement the rate at which sucrose is hydrolyzed in 4 molar hydrochloric acid or the rate of the Beckmann rearrangement of acetophenone oxime in 95 per cent sulfuric acid, and that this correlation promises to lead to a clearer insight into the nature and mechanism of these and similar reactions.

The problem of a measure of acidity is most easily stated in terms of an extremely weak base such as urea. In water this reacts to a minute extent according to the reaction



the equilibrium constant being not far from 10^{-14} . If formic or sulfuric acid is added, more of the base NH_2CONH_2 is converted to the cation $\text{NH}_2\text{CONH}_3^+$. This process of converting a base B to the corresponding cation BH^+ is so important as to deserve a name of its own, and it will be referred to in this article as the salt formation or the ionization of the base. In particular the ratio of the concentrations of cation and base $C_{\text{BH}^+}/C_{\text{B}}$ will be called the ionization ratio of the base. In sufficiently dilute solu-

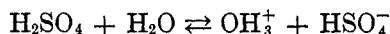
tions there is direct proportionality between the ionization ratio and the hydrogen-ion concentration, the equation

$$C_{\text{H}^+} = K \frac{C_{\text{BH}^+}}{C_{\text{B}}} \quad (1)$$

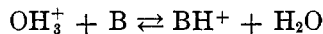
being a simple and direct consequence of the mass law.

As the concentration of the acid increases, however, deviations from this simple law appear and rapidly increase in magnitude. Eventually a point is reached beyond which the conductivity of a sulfuric acid–water mixture decreases, but the tendency toward salt formation with a weak base does not. Consequently pure formic or sulfuric acids are very slightly ionized, but they are nevertheless capable of converting such weak bases as urea practically completely to the cation (19, 20). Now it has seemed to many people, following the lead of Hantzsch (23), that the extent of salt formation or ionization of a weak base is so closely related to the original and fundamental concepts of acidity upon which the ionization theory grafted the idea of hydrogen-ion concentration that the salt formation criterion should be accepted when the two disagree. On this basis pure formic or sulfuric acids are said to be more acidic than the highly ionized dilute aqueous solutions because the pure acids react more completely with weak bases.

The explanation of the divergent behavior of conductivity and salt formation in the sulfuric acid–water solutions is to be found in a hypothesis, also due to Hantzsch (23), according to which sulfuric acid does not dissociate into ions when it is dissolved in water, but rather reacts with the base, water,



to form an oxonium ion, OH_3^+ , which bears the same relation to water that ammonium ion does to ammonia. There is indeed strong evidence from a variety of sources that the substance conventionally referred to as hydrogen ion in dilute aqueous solutions is really oxonium ion. This has been reviewed elsewhere (16). The conductivity due to a reaction of this sort must obviously reach a maximum somewhere in the neighborhood of an equimolar mixture of acid and water. On the other hand, the very fact that the reaction occurs demonstrates that hydrogen ions are less firmly bound, are more available for reaction with weak bases, in H_2SO_4 than they are in OH_3^+ . The first effect of increasing the proportion of H_2SO_4 in a sulfuric acid–water mixture is to increase the concentration of OH_3^+ . By mass action this increases the tendency toward salt formation of weak bases by the reaction



With further increase in the proportion of acid, a point is reached beyond which the concentration of OH_3^+ decreases rather than increases, but it decreases only by virtue of an increase in the concentration of free, unreacted H_2SO_4 . Since the H_2SO_4 carries less firmly bound hydrogen ion, it has, mole for mole, a greater tendency for salt formation with weak bases than does OH_3^+ . The ionization ratio of a weak base continues therefore to increase with increasing acid concentration, although the concentration of OH_3^+ decreases.

To give these qualitative ideas a quantitative meaning some method of determining the extent of ionization of weak bases is required, and the simplest and most obvious method is to use bases which have the properties of an indicator. For a simple basic indicator is merely a monoacid base whose ionization or salt formation process is accompanied by a change in light absorption in the visible region. From this change the ionization ratio can be determined by the methods of colorimetry. If a given indicator is measurably ionized in two solutions,¹ the relative extent of that ionization in the two solutions is a measure of their relative acidities in terms of the salt formation criterion. The range of acidity accessible to investigation by any one indicator is of course limited; at too low acidities the concentration of the ion BH^+ cannot be detected or measured, at too high acidities the same thing is true of the base B. If, however, the ranges of two indicators overlap, the relative strengths of the two indicator bases can be determined by determining their degrees of ionization in some solution whose acidity lies within the overlapping portion of the ranges. With this knowledge it becomes possible to compare by indicator measurements the relative acidities of two solutions, one of which is measurable only by the first indicator, the other only by the second. If the second indicator range overlaps the range of a third, the relative strengths of the first and third indicators may be obtained even though they cannot be directly compared. A still further range of acidities is thereby opened to investigation, and a fourth and more indicators may of course be added in the same way.

In mathematical language these ideas take the following form: the criterion of the strength of a base B is the quantity (18)

$$\text{p}K' = - \log \frac{a_{\text{H}^+} a_{\text{B}}}{a_{\text{BH}^+}} \quad (2)$$

where the a 's are activities. (This is really the logarithmic acidity constant of the acid BH^+ (3).) The measure of acidity is the acidity function H_0 .

¹ It is of course necessary that the amount of indicator be so small that its addition does not appreciably change the acidity of the solution.

defined by the equation (18)

$$H_0 = \text{p}K' - \log C_{\text{BH}^+}/C_{\text{B}} \quad (3)$$

It is determined experimentally by the colorimetric measurement of the ionization ratio $C_{\text{BH}^+}/C_{\text{B}}$, the value of $\text{p}K'_\text{B}$ being determined by comparison with other indicator bases. The whole series of indicators is standardized in such a way that the acidity function H_0 becomes equal to the ordinary pH in dilute aqueous solutions.

It should be emphasized that the value of H_0 is exactly the measure of acidity that would be obtained if one forgot all about hydrogen-ion activities, about activity coefficients, and about the salt error of indicators, and set about in the simplest way possible to determine the pH of a solution by using basic indicators.² It would be quite justified therefore to call the H_0 value the "pH by a basic indicator." It must be realized, however, that it would not in general be equal to the electrometric pH even within the limited range in which an electrometric pH measurement has any meaning. It would also differ from the quantity which might be called the "pH by an acid indicator," for which the symbol H_- has been proposed (18), but it must certainly be a better measure of the behavior of the solution toward weak uncharged bases than either electrometric pH or H_- .

The justification for this apparently naive procedure is best given in terms of another expression for H_0 which may easily be shown to be equivalent to equation 3:

$$H_0 = - \log a_{\text{H}^+}f_{\text{B}}/f_{\text{BH}^+} \quad (4)$$

Here a_{H^+} is the activity of hydrogen ion, and the f 's are the activity coefficients of the base B and the cation BH^+ . It is clear from this equation that the value of H_0 will be independent of the particular base used for the measurement only if the ratio $f_{\text{B}}/f_{\text{BH}^+}$ has the same value for all bases in any given medium. Unfortunately this is not exactly true (5, 15, 17); it is perhaps not even approximately true in extreme cases. It has, however, been possible to show that the requirement is fulfilled to a satisfactory precision for mixtures of the four strong acids, sulfuric, perchloric, hydrochloric, and nitric, with water, and for anhydrous formic acid (18, 21). Within this range of media, which turns out to be an interesting and practically important one, the value of H_0 has a general meaning and usefulness which is independent of the particular base used for the measurement.

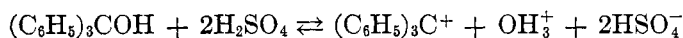
² Of course the simplicity must not extend to a neglect of the chemical and electrical nature of the indicators. They must be simple basic indicators in the sense that their color change is actually a measure of the extent of conversion of a neutral base B to an ion BH^+ . There are ways of making certain of this (see reference 18, p. 2723).

Table 1 lists the indicators which have been studied in this way, together with the pK' constants obtained in various media (18, 21). It will be noted that only the first two are commonly recognized as indicators, and that even these are not among the most familiar ones; further that four of them depend for their basic properties upon an oxygen atom instead of upon a nitrogen atom. The unfamiliarity depends partly of course upon the fact that these indicators are designed for the investigation of a higher range of acidities than is the case with those used in dilute aqueous solutions, but even more upon the requirement that they be simple monoacid bases. The indicators used in aqueous solutions are in fact poorly suited

TABLE 1
Basic strength of indicators (18, 21)

INDICATOR	HCl- H ₂ O	HNO ₃ - H ₂ O	H ₂ SO ₄ - H ₂ O	HClO ₄ - H ₂ O	HCOOH
Aminoazobenzene.....	+2.80				
Benzeneazodiphenylamine.....	+1.52				
<i>p</i> -Nitroaniline.....	+1.11	[+1.11]	[+1.11]	[+1.11]	
<i>o</i> -Nitroaniline.....	-0.17	-0.20	-0.13	-0.19	[-0.17]
<i>p</i> -Chloro- <i>o</i> -nitroaniline.....	-0.91	-0.97	-0.85	-0.91	-0.94
<i>p</i> -Nitrodiphenylamine.....			-2.38		-2.51
2,4-Dichloro-6-nitroaniline.....			-3.22	-3.18	-3.31
<i>p</i> -Nitroazobenzene.....			-3.35	-3.35	-3.29
2,6-Dinitro-4-methylaniline.....			-4.32		
2,4-Dinitroaniline.....			-4.38	-4.43	
<i>N,N</i> -Dimethyl-2,4,6-trinitroaniline.....			-4.69		
Benzalacetophenone.....			-5.61		
β -Benzoylnaphthalene.....			-5.92		
<i>p</i> -Benzoyldiphenyl.....			-6.19		
6-Bromo-2,4-dinitroaniline.....			-6.59		
Anthraquinone.....			-8.15		
2,4,6-Trinitroaniline.....			-9.29		

to the investigation of changing media. They commonly contain sulfonic acid groups which increase their water-solubility, but greatly complicate the interpretation of salt and medium effects. Their brilliance of color is frequently associated with a triphenylcarbinol structure, and triphenylcarbinol is known to react with acids according to equations such as



The formation of water in the ionization makes the ionization ratio specifically dependent upon the activity of water, and therefore no unique measure of acidity. There is finally some indication that they have been selected to give as close an approximation over as wide a range as possible

to the electrometric pH, and this can only result from very specialized and complex compensations of opposing effects (2).

The range of base strength covered by this list of indicators is very wide, the strongest base involved, aminoazobenzene, which has an indicator range about the same as that of methyl orange, is 10^{12} stronger than the weakest one, trinitroaniline, which is not completely ionized in pure sulfuric acid.

It may be easily shown that a failure of the fundamental requirement that the ratio f_B/f_{BH^+} be the same for all bases in a given medium would lead necessarily to differences in the pK' values obtained for a single base in different media. The agreement between the values for these five media, which is probably as good as the colorimetric method permits, demonstrates therefore the satisfaction of the requirement in this range.

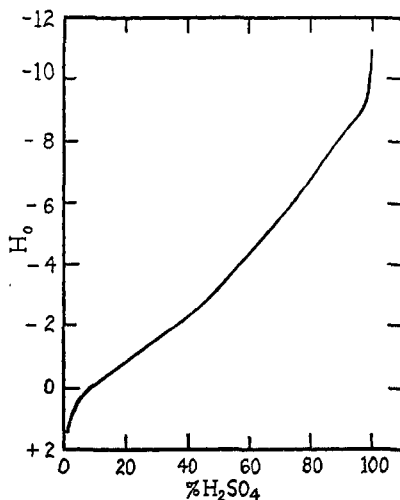


FIG. 1. Acidity function of $H_2SO_4 - H_2O$ solutions

Figure 1 shows the variation of H_0 with percentage composition of sulfuric acid-water mixtures (18, 21). It clearly exhibits the continuous increase in acidity with increasing acid concentration, which was previously mentioned. The very great acidity of pure sulfuric acid is shown by the large negative value of H_0 , nearly -11 , obtained. It seems probable that fuming sulfuric acid is even more acidic than this.

Figure 2 shows the variation of H_0 with molality for five acids in moderately concentrated aqueous solution (21). The behavior of the transition acid, trichloroacetic acid, differs strongly from that of the four strong ones.

The crucial test of this whole system is to be found in its usefulness and especially in its ability to predict reaction rates and to assist in the inter-

pretation of reaction mechanisms. The problem of reaction rates in highly acid solutions may be approached in very much the same simple fashion that was used in setting up the scale of acidity. In a dilute aqueous solution the rate of an acid-catalyzed reaction is frequently, although as Brønsted has shown (6), not always, proportional to the concentration of hydrogen ion. The velocity constant k_v is then given by $k_v = k_0 c_{H^+}$, where k_0 is a proportionality constant. This may be put in a form very suitable for a test of its applicability by taking logarithms

$$\log k_v = -\text{pH} + \log k_0$$

If the equation holds, a plot of $\log k_v$ against pH is a straight line whose slope is -1 .

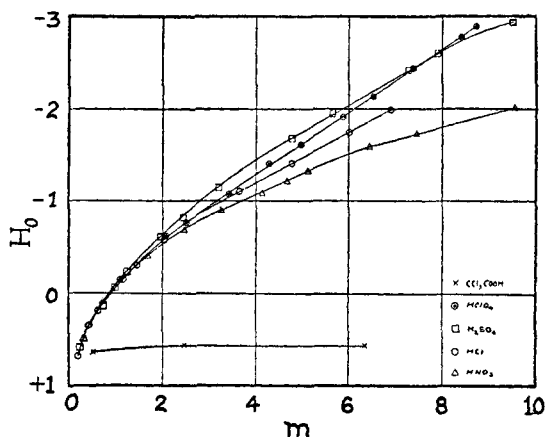


FIG. 2. Acidity functions of moderately concentrated aqueous acids

Since the acid catalysis may be supposed to depend upon the addition of hydrogen ion to a very weak base, sucrose, ethyl acetate, or the like, that is, upon a process which is very similar to the ionization of a simple basic indicator, it seems natural to look for a similar correlation between k_v and H_0 in more concentrated acid solutions. Figure 3 shows such a test for that veritable classic of reaction velocity experiments, the sucrose hydrolysis (22). There is perfect agreement for the four strong acids at concentrations extending far beyond the region of dilute solutions. Within that region it has of course been long recognized and amply demonstrated that the reaction rate is proportional to the concentration of hydrogen ion; but all kinds of attempts to correlate the rate with some sophisticated measure of acidity in more concentrated acid solutions have failed. By contrast there is here demonstrated a direct proportionality between reac-

tion rate and the measure of hydrogen-ion concentration or activity obtained by an almost naive use of basic indicators without consideration of salt or medium effects.

Figure 4 shows a similar successful correlation for the hydrochloric acid-catalyzed hydrolysis of ethyl acetate and for the nitric acid-catalyzed hydrolysis of cyanamide (22).

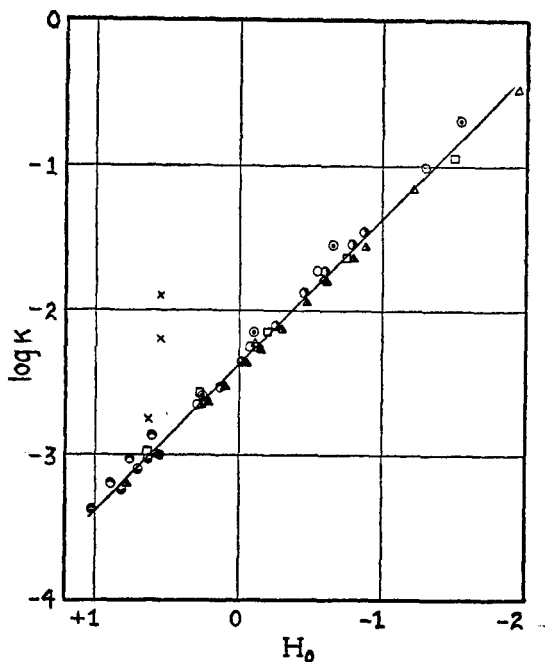


FIG. 3. Relation between H_0 and velocity constant for hydrolysis of sucrose. \odot , 0.5–4 M $HClO_4$; \square , 0.25–3.77 M H_2SO_4 ; \circ , 0.5–4 M HCl ; \triangle , 0.5–6.95 M HNO_3 ; \times , 0.5–4 M CCl_3COOH , all from data of Hantzsch and Weissberger. \bullet , 0.23–3.08 M HCl ; \blacktriangle , 0.19–3.08 M HNO_3 , data of Armstrong and Wheeler and of Worley. \ominus , 0.1 N HCl + 0.3 M KCl ; $\omin�$, 0.1 N HCl + 0.1.3 M $BaCl_2$, data of Kautz and Robinson.

There are, however, acid-catalyzed reactions, for instance the hydrolysis of hydrocyanic acid or the rearrangement of acetylchloroaminobenzene, which exhibit no parallelism whatsoever between reaction rate and indicator acidity. And even in the sucrose case the rate of the hydrolysis by the transition acid, trichloroacetic, deviates widely from the theoretical line with which the values for the strong acids agree so closely. Whatever the reason for these differences, and much more experimental information will be necessary if any assurance on this question is to be obtained, they represent very definitely a classification of reactions occurring in concentrated

acid solutions into those that do and those that do not exhibit a parallelism between reaction rate and acidity function. The difference must depend upon some fundamental contrast in mechanism, and its recognition cannot but assist in the further interpretation and understanding of the catalytic process.

The sucrose and ester hydrolyses are typical cases of acid catalysis. But the same relation between reaction rate and acidity function holds for some reactions of an apparently quite different sort which take place at much higher acid concentrations.

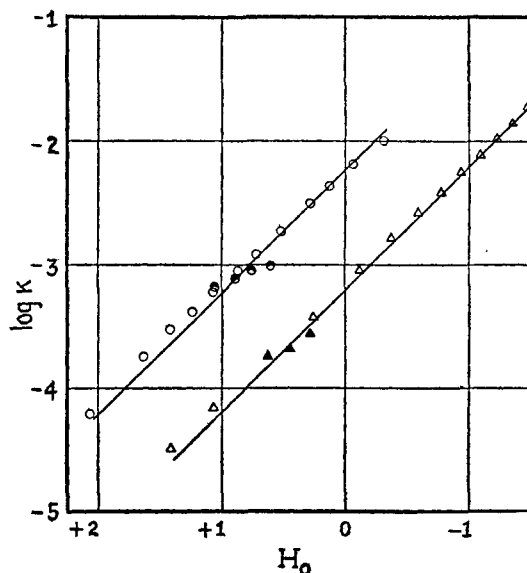


FIG. 4. Relation between H_0 and velocity constants for hydrolysis of ethyl acetate and for hydrolysis of cyanamide. Ethyl acetate hydrolysis: \circ , 0.01-1.50 M HCl; \bullet , 0.1 N HCl + 0-3 M KCl. Cyanamide hydrolysis: Δ , 0.05-5.0 M HNO₃; \blacktriangle , 0.25 N HNO₃ + 0-2.7 M KNO₃.

Thus curve A in figure 5 shows an excellent agreement between the reaction rate data of Lobry de Bruyn and Sluiter (7, 18) for the Beckmann rearrangement of acetophenone oxime and the acidity functions of the sulfuric acid-water mixtures of concentrations from 93.6 to 98.7 per cent in which the reaction was carried out. The fundamental similarity of this reaction to an acid catalysis in dilute aqueous solution which is suggested by this result is of especial interest, because sulfuric acid-water mixtures of proper concentration have recently been shown to be excellent preparative reagents for this reaction (24).

Curve B in the same figure shows similar agreement with the acidity

function for the data of DeRight (10) on the rate of decomposition of formic acid into carbon monoxide and water. The marked inhibition by small amounts of water of the rate of this and similar reactions in concentrated sulfuric acid has long been a matter of interest. The present result shows that it may be treated quantitatively as the inhibition by a base of an acid-catalyzed reaction; that it is the same sort of thing as the inhibition by sodium hydroxide of the hydrochloric acid-catalyzed hydrolysis of sucrose or ethyl acetate.

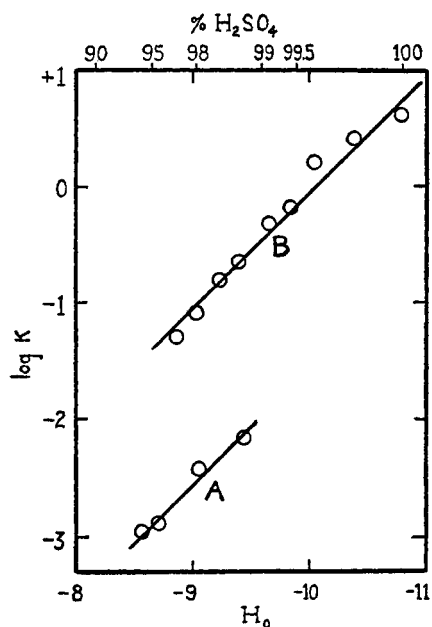


FIG. 5. Relation between H_0 and velocity constants for (A) Beckmann rearrangements of acetophenone oxime, (B) formic acid decomposition

The reaction rate data of Wiig (27) on the decomposition of citric acid offers a somewhat more complicated picture (figure 6). Over a large part of the range studied, there is agreement with a straight line of slope -2 , but at very high acidities deviations appear and the actual curve goes through a maximum. In the region of the straight line, the reaction is clearly analogous to one in dilute aqueous solution whose rate is proportional to the square rather than to the first power of the hydrogen-ion concentration, certainly a conceivable situation. And the phenomenon of a maximum at a particular acidity, on both sides of which the rate drops off, is not infrequently found among acid-catalyzed reactions in dilute aqueous

solutions (8, 9). In both aqueous and sulfuric acid media detailed explanations for the appearance of the maximum can easily be found. Thus citric acid is very probably a polyacid base which can form several ions of differing charge by the addition of different numbers of hydrogen ions. To account for the maximum it is only necessary to suppose that some particular ion is more reactive than the product which is formed from it by the addition of further hydrogen ion. To make this picture more than a mere speculation will, however, require further information on the state of citric acid in solution in sulfuric acid.

The decompositions of formic and citric acids are typical of a number of decomposition reactions which take place in concentrated sulfuric acid

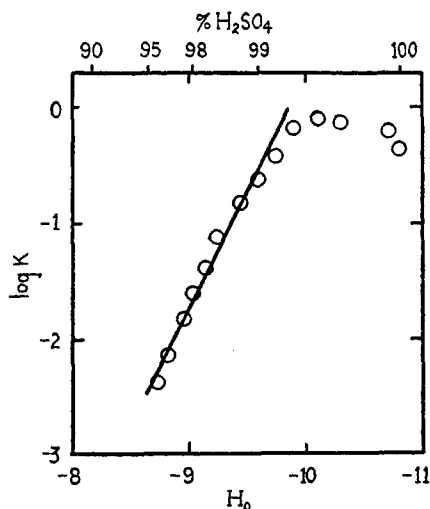
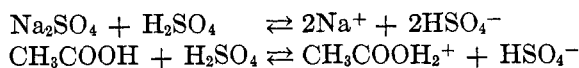
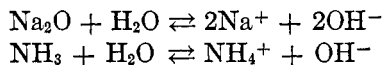


FIG. 6. Relation between H_0 and velocity constant for the citric acid decomposition

and are inhibited by water, and represent the most accurately and reliably measured cases. The decomposition rates of oxalic (1, 25, 28), malic (26, 13, 11), and triphenylacetic (12) acids are likewise in at least qualitative agreement with the idea that the reactions are acid-catalyzed rather than water-inhibited. This interpretation is, moreover, strongly supported by the behavior of the many other inhibitors which have been studied. Almost all of these are substances which are bases in the solvent sulfuric acid, as a result of reactions like the following,



reactions which are the exact analogues of the reactions of sodium oxide and of ammonia with water.



Furthermore the data of Whitford (26) and of Dittmar (12) on the decomposition of malic and of triphenylacetic acids show that, in nearly every case, the inhibiting effect is the same per mole of bisulfate ion with these other inhibitors as it is with water.³ Now bisulfate ion plays the same part in sulfuric acid as hydroxyl ion does in water, and its concentration bears the same inverse relation to the acidity function in sulfuric acid that the concentration of hydroxyl ion does to the pH in water. The exact analogue in aqueous solutions of these reactions would therefore be a reaction which takes place in an alkaline medium at a rate which increases with decreasing pH. An example of this situation may be found in the polymerization of cyanamide in strongly alkaline solutions. Buchanan and Barsky (8) found that under these conditions the rate increases with decreasing alkalinity, and that it may therefore be said to be acid-catalyzed in spite of the high alkalinity of the medium. This reaction also exhibits a maximum at a particular pH and thus shows a close, although a purely formal, similarity to the decomposition of citric acid in sulfuric acid.

This group of acid decompositions represents only part of a much larger classification of reactions in which a molecule of water is split out from one or more molecules of reactants and in which sulfuric acid, concentrated hydrochloric acid, zinc chloride, or the like are commonly used as condensing agents. This includes such familiar reactions as nitration, the preparation of ethers and ethylene derivatives from alcohols, and many nuclear condensations, both intra- and inter-molecular, of which the anthraquinone synthesis from benzoylbenzoic acid and reactions used in the preparation of triphenylmethane dyes are important examples. It has been rather generally supposed that the function of the condensing agent is really that of a dehydrating agent, which by combination with the water formed in the reaction is able somehow to accelerate it. The reasoning back of this idea is not particularly sound, but the best evidence that the explanation is an entirely unsatisfactory one is the frequency with which it has been reported with a note of surprise that the much more efficient dehydrating agent phosphorus pentoxide has been found to be quite useless as a condensing agent in a reaction in which sulfuric acid is very effective.

On the other hand, the hypothesis that the reactions are acid-catalyzed,

³ This fact was obscured in the papers referred to because the molar concentrations of the inorganic bisulfates were calculated in terms of neutral sulfates.

that the function of the condensing agent is to provide a medium of sufficiently high acidity, agrees with all of the rather qualitative information available.⁴ It predicts that phosphorus pentoxide should not be an effective condensing agent, and it further predicts that other condensing agents are to be sought among strongly acidic media. Upon the success of the latter prediction must depend the ultimate judgment as to its validity.

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⁴ The quantitative relation between rate and acidity function previously noted (18) in the case of the anthraquinone synthesis from benzoylbenzoic acid was based upon an error in figure 1 of the article by Gleason and Dougherty (14). Professor Dougherty has kindly informed me that the ordinates given in that figure should be increased by 10 to obtain the true values. With these corrected values an approximate relation is obtained, which is perhaps as good as is to be expected in view of the difference in the temperatures at which the rate and the indicator measurements were made, and because the large concentrations of benzoylbenzoic acid, itself a base, make the acidity of the reaction mixture differ from that of the sulfuric acid-water mixture in which it was dissolved. Further experimental data which avoids these difficulties is obviously needed.