Due to the large amount of sulfuric acid present compared with the amount of water liberated, the concentration of sulfuric acid is not altered appreciably during the reaction; hence, the reaction would appear to be one of the first order.

The author desires to take this opportunity of expressing his appreciation to Professor J. H. Walton, at whose suggestion this research was undertaken and under whose direction it was carried out, for his kind interest and guidance during its progress.

Summary

1. The velocity of decomposition of formic acid by sulfuric acid has been measured for the following concentrations of sulfuric acid: 98.9%, 97.6%, 94.5%, 91.8%, 89.2%, 88.9%, 85%, at temperature intervals of 10° from 15° to 45°.

2. The reaction was found to be one of the first order.

3. The reaction is probably one of dehydration.

4. Copper, silver, potassium, sodium and mercurous sulfates added separately to the sulfuric acid retard the reaction but slightly.

5. Acetone and acetic acid act as inert diluents, not decreasing the dehydrating power of sulfuric acid.

6. Hydrochloric acid increases the velocity of the reaction markedly, probably acting as a catalytic agent.

7. The temperature coefficients of the reaction have been given and an irregularity in them pointed out for 91.8% sulfuric acid.

Madison, Wisconsin

[Contribution from the Laboratories of General Chemistry of the University of Wisconsin]

THE CATALYTIC DECOMPOSITION OF FORMIC ACID IN ACETIC ANHYDRIDE[1]

By Ernest R. Schierz

Received August 21, 1922

Introduction

The dehydration of formic acid by sulfuric acid with the concomitant formation of carbon monoxide[2] suggested the use of another dehydrating agent. Formic acid is soluble in acetic anhydride and under certain conditions decomposes, yielding carbon monoxide copiously. It is possible

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[1] The work included in this paper is from the thesis presented by Ernest R. Schierz in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. This investigation was conducted under the supervision of Professor J. H. Walton.

[2] This Journal, **45**, 447 (1923).

to look at this reaction as one of pure dehydration in which formic acid undergoes decomposition according to the equation,

$$HCOOH \longrightarrow H_2O + CO \qquad (1)$$

On the other hand, evidence exists to show that the formation of carbon monoxide is due to the decomposition of a mixed anhydride which results from the interaction of formic acid and acetic anhydride.

This mixed anhydride was first described by Béhal,[3] who formed it by dissolving formic acid in acetic anhydride, a method which had previously been used by Autenreith[4] in the preparation of *iso*valeric-acetic anhydride Béhal described the formic-acetic anhydride as a liquid with an odor similar to that of acetic anhydride, boiling at about 29° at a pressure of 18 mm. On being treated with sodium acetate, quinoline, pyridine and dimethyl aniline, carbon monoxide was evolved with the concomitant formation of acetic acid. With primary, secondary and tertiary alcohols, formic acid esters of the alcohol and acetic acid were formed without even traces of acetic acid esters. Béhal states that the acid with the lower number of carbon atoms is the only one which is esterified. Severin[5] found that this generalization does not apply to all mixed anhydrides. With ammonia in ethereal solution formamide was formed. Other investigators have since described mixed anhydrides, but no further work on formic-acetic anhydride appears in the literature.

The object of this investigation was to study (1) the mechanism of the evolution of carbon monoxide from formic acid in acetic anhydride solution, (2) the influence of impurities on the reaction.

Experimental Part

Preparation and Purification of Materials.—The formic acid used in this investigation was the same as that prepared for the study of catalytic decomposition of formic acid by sulfuric acid.[2]

Acetic anhydride obtained from a commercial source and labeled "Acetic anhydride 93%," was redistilled. The fraction distilling at 136–140° at 748 mm. was taken for this investigation.

The pyridine was purified by the method of Wilcox.[6] The fraction distilling at 113.6–114.2° was preserved for this investigation.

The alkaloids were the purest obtainable and were in each case recrystallized several times from appropriate solvents and dried in a vacuum at 35–40° over phosphorus pentoxide. The nicotine was redistilled, the portion distilling 246.4–246.8° being taken for this work.

Apparatus.—The velocity of decomposition of formic acid in acetic anhydride solution was determined by measuring the rate of evolution of carbon monoxide. The apparatus used was the same as that described in the study of the catalytic decomposition of formic acid by sulfuric acid.[2] The method of procedure was the same; where modifications were necessary, mention will be made in the appropriate section.

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[3] Béhal, *Compt. rend.*, **128**, 1460 (1899).

[4] Autenreith, *Ber.*, **20**, 3189 (1887).

[5] Severin, *Bull. soc. chim.*, [3] **25**, 500 (1901).

[6] Wilcox, *J. Phys. Chem.*, **14**, 584 (1910).

Preliminary Experiments

Several unsuccessful attempts were made to prepare the mixed anhydride by the method of Béhal. According to this author it can be isolated from the other product of reaction by fractional distillation at reduced pressure. At a pressure of 18 mm. the boiling points of formic acid,[7] acetic acid,[7] acetic anhydride,[8] and the mixed anhydride lie within a range of 40° and the boiling point of acetic acid is within 5° of that of the mixed anhydride. The most probable impurity in the mixed anhydride was acetic acid. Because of the difficulty in preparing the mixed anhydride, it was decided to use an equimolecular mixture of acetic anhydride and formic acid.

That such a mixture is not very stable at room temperature over long periods is shown by the following observations. About 50 cc. of this mixture in a 100cc. volumetric flask provided with a rubber stopper, after standing undisturbed for about 2 weeks, suddenly exploded, shattering the flask. This was evidently due to the formation of carbon monoxide, for when a lighted splinter was held near the mouth of a flask or bottle containing this solution the characteristic blue flame of carbon monoxide appeared. The other product of decomposition is acetic acid.

$$OC(CH_3)—O—CHO \longrightarrow CH_3COOH + CO \qquad (2)$$

A number of experiments were carried out to find types of substances which would catalyze this reaction. These experiments were of a qualitative nature only, and were performed by adding to 1 cc. of an equimolecular mixture of formic acid and acetic anhydride a drop or two of the substance to be tested. Conc. sulfuric, hydrochloric, nitric and hydrofluoric acids caused a very vigorous evolution of carbon monoxide. Sirupy phosphoric acid caused an evolution of the monoxide at a moderate rate, while solid oxalic acid produced only a very slow evolution of gas. Conc. acetic acid was without effect.

In the case of nitric acid the reaction proceeded vigorously at the beginning, then more slowly; suddenly a puff of dense brown fumes appeared and immediately the reaction ceased—the solution was blue. Morgan[9] found that when nitric acid was added to the reaction between formic and sulfuric acids a very violent reaction occurred with the formation of a blue color in solution.

The decomposition of the mixed anhydride by the tertiary bases quinoline, pyridine and dimethyl aniline as shown by Béhal suggested the possibility of similar action by other nitrogen bases. It was observed that all of the bases which brought about the evolution of carbon monoxide contained tertiary nitrogen. Primary and secondary nitrogen bases did not act

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[7] Schmidt, *Z. physik. Chem.*, **7**, 442 (1893).

[8] Kahlbaum, *Ber.*, **16**, 2481 (1883).

[9] Morgan *J. Chem. Soc.*, **109**, 274 (1916).

similarly. Tertiary nitrogen compounds of a less basic character did not cause the liberation of carbon monoxide.

With nicotine, brucine and strychnine the action was very vigorous; with pyridine, picoline, lutidine, collidine, tri-*iso*propyl amine, diethyl aniline, dimethyl aniline and cocaine the evolution of gas was moderately rapid. Morphine acted slowly, and with papaverine, quinine and quinoline, the action was very slow. The following compounds caused no perceptible evolution of carbon monoxide: piperidine, pyrrole, *o*-toluidine, aniline, ethyl aniline, caffeine, theobromine, hippuric acid, saccharin, indigo, isatin, magenta, amyl nitrite, aconitine, formamide and methyl cyanide.

The results of these experiments show: (1) that the substances which bring about decomposition are all tertiary nitrogen compounds; (2) that all such substances possess marked basic properties.

Caffeine, an amphoteric tertiary nitrogen compound, does not cause the evolution of carbon monoxide. These facts suggest that this decomposition of the mixed anhydride might be useful to detect the presence of tertiary nitrogen of a basic character in a compound. Tetramethyl-ammonium hydroxide causes a slight decomposition of the mixed anhydride. This compound is decomposed readily into methyl alcohol and trimethyl amine[10] and it may have been the latter which was effective on the mixed anhydride.

In an attempt to study the reaction in the absence of a large excess of acetic anhydride, several qualitative experiments were conducted with various organic solvents. About 0.5 cc. of an equimolecular mixture of formic acid and acetic anhydride was added to 1–2 cc. of the solvent to be tested; then a drop of pyridine was introduced. The evolution of carbon monoxide was very vigorous in toluene, carbon tetrachloride, nitrobenzene, and benzaldehyde, only moderately so in benzene and acetone, slow in amyl acetate and in ethyl, amyl, and *iso*butyl alcohols, and imperceptible in ether and carbon disulfide.

Following this preliminary work with solvents, quantitative experiments were conducted with toluene as the solvent. The toluene used for this study was the U. S. P. quality purified by the method of Haller and Michel by boiling it with anhydrous aluminum chloride under a reflux condenser for 1 hour. The toluene was then distilled, the portion distilling 109–109.7° (corr.) being taken for this investigation. To 10 cc. of the toluene so prepared was added 0.26 cc. of an equimolecular mixture of acetic anhydride and formic acid. This constituted the reaction mixture. By means of the capsule, 0.5 cc. of pyridine was introduced into the reaction flask.

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[10] Hofmann, *Ber.*, **14**, 494 (1881).

[11] Haller and Michel, *Bull. soc. chim.*, [3] **15**, 1063 (1896).

In all the experiments in toluene it was observed that the amount of gas evolved was not equivalent to the amount of formic acid added. This is due to the solubility of carbon monoxide in toluene.[12] For this reason also the values of the velocity constant calculated for the first order of reaction decrease with increasing values of *t* (time).

These difficulties could probably be overcome by saturating the toluene with carbon monoxide before adding the mixed anhydride. This was not done.

The well-known effect of sulfuric acid on formic acid in aqueous solution suggested the study of its effect on the formic acid in acetic anhydride solution. In these experiments the formic acid was dissolved in the acetic anhydride, placed in the reaction flask and the sulfuric acid introduced by means of the capsule. The amount of sulfuric acid necessary was too small for an accurate measurement; consequently, an attempt was made to prepare a solution of sulfuric acid in acetic anhydride. Ten cc. of pure sulfuric acid was diluted to 100 cc. with acetic anhydride. Of this solution 0.1 cc. was used as catalyst. It was not possible to obtain concordant results because the catalyst solution underwent a change upon standing, decreasing in effectiveness. Further, the reaction did not go to completion, probably due to the fact that the sulfuric acid reacted with the acetic anhydride,[13] forming a compound which was not a catalyst for the reaction. When 1.0 cc. of sulfuric acid was added to the mixture after the reaction had apparently ceased, the reaction proceeded to completion almost instantaneously. This experiment showed that the sulfuric acid was a catalyst for the reaction, but due to side reactions it was made ineffective. In view of this disturbing factor the study of the effect of sulfuric acid as a catalyst was not continued. An examination of the literature showed that hydrochloric and hydrofluoric acids[14] and nitric acid[15] also reacted with acetic anhydride, so further work along this line was discontinued.

Catalysis of Reaction by Various Nitrogen Bases

Completeness of the Reaction.—In the preliminary experiments it was noticed that there was a marked difference in the catalytic effect of the various organic bases on the decomposition of formic acid in acetic anhydride solution. Those bases usually characterized as strong showed a marked activity, while certain weak bases showed a corresponding lack of activity. In order to study the relative activity of these bases, it was first of all necessary to determine whether or not the decomposition of formic acid in acetic anhydride solution was quantitative. To study this point the following experiments were carried out.

[12] Just, *Z. physik. Chem.*, **37**, 361 (1901).

[13] Stillich, *Ber.*, **38**, 1246 (1905).

[14] Colson, *Bull. soc. chim.*, [3] **17**, 59 (1897); *Ann. chim. phys.*, [7] **12**, 225 (1897).

[15] Pictet and Genequand, *Ber.*, **35**, 2526 (1902).

A solution of formic acid in acetic anhydride was prepared containing 7.9595 g. of formic acid (d., 1.217) in 100 cc. of solution at 25°. Assuming complete decomposition, 100 cc. of this solution would evolve 3870 cc. of carbon monoxide measured under standard conditions. A measured amount of this solution was dissolved in 25 cc. of acetic anhydride and decomposed with about 0.5 cc. of pyridine.

Analyses. Subs., 0.944 cc.: Calc. as CO: 44.51 cc. Found: 44.98, 45.08 cc. (25°, 740.6 mm.; v. p., H_2O 23.6 mm.).

Order of Reaction and Method of Procedure.—The completeness of the reaction being established, the next point to be developed was a method of procedure. By means of several preliminary experiments it was found that the velocity of evolution of carbon monoxide was not appreciably affected by the order in which the reactants were mixed. Hence the method used in these determinations was essentially as follows.

A measured volume (25 cc.) of acetic anhydride added to a definite amount of base constituted the reaction mixture. This was transferred to the reaction flask. The formic acid (0.07 cc.) was introduced into the mixture by means of the capsule. Since some of the bases decompose the formic acid in acetic anhydride solution very slowly at 25°, all determinations were conducted at 50°.

In Table I, which shows data for a typical run, t is the time in minutes, x the amount of substance decomposed (the volume of carbon monoxide formed since $t = 0$), and a is the amount of substance present at $t = 0$ (or the volume of carbon monoxide evolved from $t = 0$ to the end of reaction).

The value of the velocity constant 0.4343 K was determined from the equation

$$0.4343\ K = \frac{1}{t} \log \frac{a}{a - x} \tag{3}$$

It will be observed that the values of 0.4343 K are constant, indicating that Equation 3 is applicable and that the reaction is one of the first order.

TABLE I

THE CATALYTIC DECOMPOSITION OF FORMIC ACID IN ACETIC ANHYDRIDE BY NITROGEN BASES

Strychnine 0.30 Moles/liter Temp. 50°

t	CO evolved Observed	Vol. from $t=0$	x	0.4343 K
0	5.0	...	...	....
1	9.4	4.4	6.0	0.0570
2	13.18	8.18	11.15	0.0555
4	19.3	14.3	19.3	0.0531
6	24.09	19.09	26.03	0.0533
8	27.8	22.8	31.11	0.0528
11	31.9	26.9	36.73	0.0524
14	34.67	29.67	40.5	0.0515
Final	41.62	36.62	50.0	....
			Av.	0.0537

The values of K show a slight decrease with increasing values of t; the variation from the average does not exceed 5%.

Relation Between Concentration of the Catalyst and Speed of the Reaction.—The bases selected for the quantitative study of their effect on the decomposition of formic acid in acetic anhydride solution were strychnine, brucine, nicotine, cocaine, pyridine, morphine, quinine and papaverine. The decomposition by means of quinoline proceeded so slowly that no measurements were made. The results of these experiments with various concentrations of base are shown in Table II. In order to conserve space the data are given in a condensed form in which $K_s = 0.4343 K \times 10^3$.

TABLE II

THE CATALYTIC DECOMPOSITION OF FORMIC ACID IN ACETIC ANHYDRIDE BY NITROGEN BASES

Catalyst	Conc. mole/liter	K_s	Catalyst	Conc. mole/liter	K_s	Acetic anhydride "B" K_s
Brucine	0.041	61.7	Strychnine	0.030	52.9	111.0
	0.0206	28.5		0.026	..	77.9
	0.0129	19.9		0.015	25.0	52.0
	0.0103	13.8		0.013	19.8	..
				0.0075	..	22.6
				0.0065	..	15.5
Nicotine	0.2	45.8		0.0109	..	27.9
	0.113	30.0		0.0044	..	10.0
	0.067	13.5		0.0019	..	1.91
	0.05	8.28				
	0.034	6.03	Morphine	0.139	14.2	30.2
				0.105	10.4	19.5
Cocaine	0.119	24.1		0.070	5.96	12.6
	0.060	10.8		0.035	..	5.84
	0.030	4.63				
	0.0175	2.61	Pyridine	0.281	28.4	28.1
				0.246	..	24.8
Quinine	0.139	9.24		0.210	21.2	..
	0.094	6.34		0.202	..	20.4
	0.070	4.66		0.152	..	15.1
	0.035	2.10		0.140	15.0	..
				0.070	..	7.65
				0.035	..	4.46
Papaverine	0.139	4.07				
	0.070	2.30				

The results summarized in Table II, except those for morphine, are shown graphically in Fig. 1.

It will be observed that for the concentrations of the base used above a certain minimum, the velocity of evolution of carbon monoxide is directly proportional to the amount added. The uncatalyzed reaction at 50° proceeds very slowly. In 24 hours, less than 2 cc. of gas is evolved. This reaction, therefore, does not interfere with the measurement of the catalyzed reaction, and its effect cannot be observed on the curves. If the effect were measurable, the curves would cross the axis of ordinates at a positive value. An examination of the extrapolated curves near the origin shows that this is not the case. The curve for cocaine exhibits a change in direction near the origin that suggests that only *after* the addition of a certain minimum concentration of catalyst does the rate of reaction become proportional to the amount of base added. It will be observed that the curve for pyridine passes through the origin. The curves for the other catalysts, especially the weaker bases, cross the axis of abscissas. This retarding of the action of the catalyst is probably due to the acetic acid formed in the reaction. The catalytic action of pyridine is not affected by acetic acid. This will be discussed in another section of this paper.

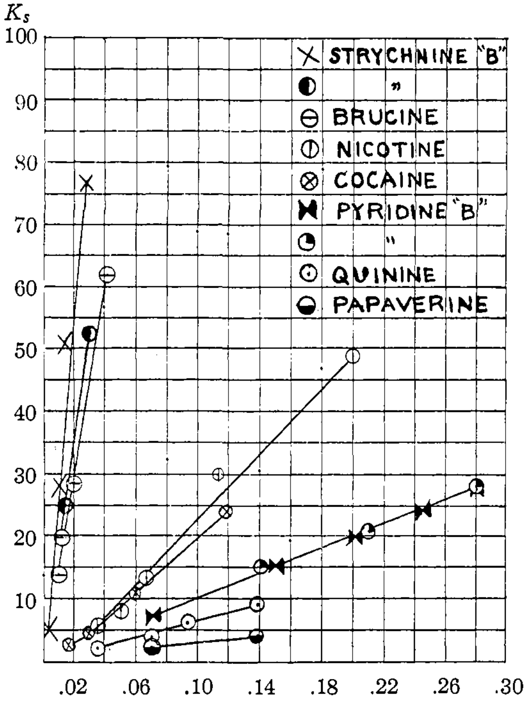

Fig. 1.

Fig. 1 shows quantitatively that the strong base, brucine, causes a more rapid evolution of carbon monoxide than does a weak one (such as papaverine). Not only is the decomposition more rapid for equivalent concentration of base, but the increase in velocity due to addition of equal mole fractions of base is also greater with strong bases.

Veley[16] has determined the "affinity values" of alkaloids. These may be taken as a measure of basicity, although the author states that he believes it would be prudent to

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[16] Veley, *J. Chem. Soc.*, **95**, 766 (1909).

keep basicity and affinity values distinct from one another. Colson[17] also prepared a classification of bases into weak and strong, according to the magnitude of the sum of their heats of solution and neutralization.

Arnall[18] has determined the strength of nitrogen bases by measuring the hydrolysis of their hydrochlorides. However, the common alkaloids such as strychnine, brucine, cocaine and morphine were too strongly basic to be measured by this method.

A comparison of the order of basicity as determined by these investigators and others[19] shows that there exists no simple relation between the basicity of the bases and their influence on the reaction.

Bredig[20] found that in the catalytic formation of carbon dioxide from camphocarboxylic acid by organic bases no simple relation was evident between the "affinity constants" of the bases in water and the velocity of formation of the carbon dioxide in organic solvents, such as acetophenone, *o*-nitrotoluene and *m*-xylene. It must be borne in mind that the measurements of basicity are made in aqueous solution, while in this investigation water has been excluded. The effect of acetic anhydride on some of the bases containing hydroxyl groups may also exert an influence on their action.[21]

In order to determine whether any simple relation exists between the conductance of the bases in acetic anhydride solution and their activity as catalysts, the specific conductance of 0.05 *M* solutions in acetic anhydride was determined. The measurements in Table III were made in a conductivity cell of the Washburn type[22] which is especially designed for solutions of low conductivity.

TABLE III

SPECIFIC CONDUCTANCE OF SOME NITROGEN BASES IN ACETIC ANHYDRIDE AT 50°

0.05 *M*

Substance	$K \times 10^4$	K_s (from Fig. 1)	Substance	$K \times 10^4$	K_s (from Fig. 1)
Acetic anhydride..	0.169	..	Strychnine........	11.48	91.0
Pyridine.........	4.003	6.0	Nicotine..........	19.3	10.0
Brucine..........	9.35	75.0	Cocaine...........	116.7	8.5
Quinine..........	10.56	3.0			

It will be observed that the increasing order of specific conductances does not coincide with the order of activity of these bases in the reaction being studied. In the study of conductance in non-aqueous solution the results have often been at variance with those obtained in aqueous solution, so that it has not been possible to arrive at any generalizations. The solvent as well as the solute have a very specific effect on the con-

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[17] Colson, *Bull. soc. chim.*, [3] **4**, 625 (1890).

[18] Arnall, *J. Chem. Soc.*, **117**, 835 (1920).

[19] Constam and White, *Am. Chem. J.*, **29**, 36 (1903). Goldschmidt and Salcher, *Z. physik. Chem.*, **29**, 89 (1899). Lunden, *J. chim. phys.*, **5**, 574 (1907). Nasini and Pezzalato, *Z. physik. Chem.*, **12**, 501 (1893). Mauz, Phys. Chem. Untersuchungen d. Alkaloide *Dissertation*, Tübingen, **1904**. Wood, *J. Chem. Soc.*, **83**, 568 (1903); **89**, 1831, 1839 (1906).

[20] Bredig, *Z. Elektrochem.*, **24**, 285 (1918).

[21] Wright, *J. Chem. Soc.*, **27**, 1032 (1874); **28**, 25, 312, 702 (1875); **29**, 170, 655 (1876); **40**, 615 (1881).

[22] Washburn, THIS JOURNAL, **38**, 2448 (1916).

ductance. The same solvent may cause dissociation in some cases and association in others.

The Effect of Acetic Acid on the Catalysis of the Reaction by Bases

Acetic acid is usually present in small amounts in acetic anhydride; it is formed simultaneously with the mixed anhydride, and is one of the products of the decomposition of the latter; hence, it was necessary to determine its effect on the rate of the reaction.

A series of determinations was made with acetic anhydride prepared in this Laboratory by the action of acetyl chloride on fused sodium acetate.[23] The portion boiling between 136.4° and 136.8° at 740 mm. was used. This will be referred to as acetic anhydride B. The bases used were strychnine, morphine and pyridine. The results are collected in Table II, under column marked Acetic Anhydride "B."

A comparison of the two sets of data shows that for the same concentration of strychnine and morphine, respectively, the velocity constant in the anhydride B is about 100% greater than in the other anhydride. In the case of pyridine, however, the constants are identical in the two anhydrides. This anomalous behavior of pyridine will be discussed more extensively in another section of this paper. Acetic anhydride B, boiling between much narrower limits than the other acetic anhydride, would undoubtedly be less contaminated with acetic acid.

In order to determine the effect of different concentrations of acetic acid on the decomposition of formic acid in acetic anhydride solution by brucine and pyridine, the following series of experiments was performed. The reaction mixtures consisted of a definite amount of base dissolved in mixtures of acetic acid and acetic anhydride. The results are shown in Table IV.

TABLE IV

EFFECT OF ACETIC ACID ON THE CATALYTIC DECOMPOSITION OF THE MIXED ANHYDRIDE BY BRUCINE

c^a	Acetic acid Cc.	K_s	c^a	Acetic acid Cc.	K_s
0.0206	0.25	21.0	0.0206	1.50	11.1
0.0206	0.50	18.1	0.0206	2.0	8.41

[a] Moles of catalyst per liter of reaction mixture. Temp. 50°

An examination of Table V shows that increasing amounts of acetic acid progressively decrease the catalytic action of brucine. On the catalytic action of pyridine no effect is produced. This corresponds with the action of pyridine in the two acetic anhydrides mentioned in the preceding section.

The addition of small amounts of acetic acid produces a measurable effect on the velocity constant, especially when the acetic anhydride is

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[23] Gerhardt, *Ann.*, **87**, 149 (1853).

practically pure. The effect of the 0.1 g. of acetic acid liberated in the reaction when 0.07 cc. of formic acid is used is probably not so marked because it is not all present at the beginning of the reaction. The constants decrease somewhat as the reaction proceeds; this is especially noticeable near the end of the reaction. This decrease is undoubtedly due to the formation of the acetic acid which, it has been shown, has an inhibitory effect on the catalysis of the reaction.

In view of the marked effect of acetic acid, the possibility is suggested of using this reaction for determining the amount of acetic acid in acetic anhydride. Acetic anhydride is used extensively in the cellulose ester industry and in synthetic organic preparations (such as that of aspirin). There is at present no satisfactory method for determining the amount of acetic acid in acetic anhydride, obviously an important determination. The details of a method for analyzing this substance based on the reaction investigated will be the subject of further examination.

The Catalytic Effect of Mixture of Two Bases on the Reaction

When two substances which individually accelerate a reaction are allowed to act simultaneously, the total velocity may be equal to the sum of the separate velocities or it may be greater or less than this sum as in the case of promoter action. Brode[24] found that the oxidation of hydriodic acid by hydrogen peroxide was accelerated by the following inorganic substances: ferrous sulfate, copper sulfate, and zinc sulfate, sulfuric, molybdic and tungstic acids; and that mixtures of certain of these catalysts showed promoter action. Bohnson[25] found that copper sulfate accelerated the ferric sulfate catalysis of hydrogen peroxide to a very marked degree, giving a velocity constant about 250% greater than the sum of the separate velocities.

In order to ascertain whether a mixture of bases showed promoter action in this reaction, experiments were carried out using mixtures of brucine and cocaine and brucine and quinine. It was found that the velocity due to the mixture approximated the sum of the velocities of each taken separately, giving no evidence of promoter action.

The Action of Nitrogen Bases on Anhydrous Oxalic Acid in Acetic Anhydride Solution

From qualitative experiments, it was found that tertiary nitrogen bases caused a decomposition of a solution of oxalic acid in acetic anhydride with the evolution of carbon monoxide and carbon dioxide. Due to the solubility of carbon dioxide in acetic anhydride[26] equal volumes of carbon mon-

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[24] Brode, *Z. physik. Chem.*, **37**, 257 (1901).

[25] Bohnson, *J. Phys. Chem.*, **25**, 49 (1921).

[26] Ref. 12, p. 342.

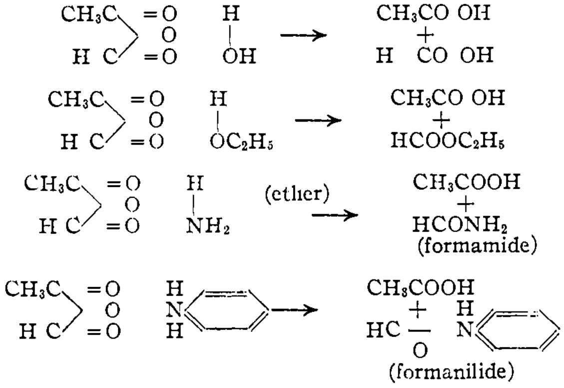
oxide and carbon dioxide were not evolved. This reaction will be subjected to further investigation.

Conclusion

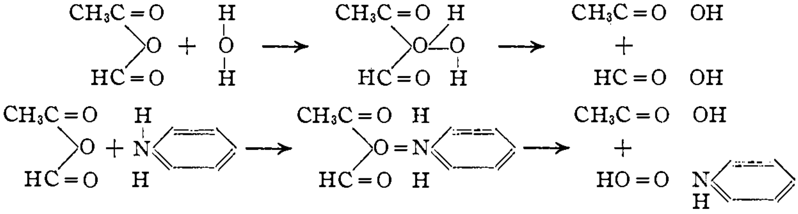
A Possible Mechanism of the Reaction.—In preparing the mixed anhydride Béhal[3] found that the yield increased with increase in acetic anhydride until an equimolecular solution was obtained. Increase in acetic anhydride beyond that ratio did not cause an increase in yield of the mixed anhydride. He determined the composition of the mixture after the reaction had occurred by determining (1) the amount of formic acid by reduction of iodic acid, (2) the total acidity by titration with barium hydroxide, (3) the amount of mixed anhydride by measuring the amount of carbon monoxide evolved when the mixture was treated with quinoline. Assuming complete decomposition of formic-acetic anhydride by quinoline, he found that the yield was 68.9%. The author gives numerical data for the amount of mixed anhydride only.

In this investigation, it was found that in the presence of an excess of acetic anhydride the amount of carbon monoxide evolved was equivalent to the amount of formic acid added, that is, the yield of mixed anhydride measured by the amount of carbon monoxide evolved was always 100%. This may be due to either of two reasons: (1) the formation of the mixed anhydride is the result of a complete reaction; (2) the formation of the mixed anhydride is an equilibrium reaction, but the reaction goes to completion because of the removal of the mixed anhydride by decomposition in the presence of the nitrogen bases.

The following equations illustrate some of the reactions described by Béhal, by structural formulas,

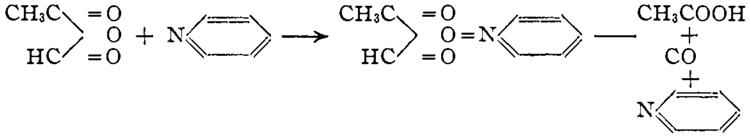


To explain the mechanism of the above reactions, the formation of an intermediate compound may be assumed,



In each case, the unstable compound decomposes to form more stable compounds. It will be observed that the acetyl group of the anhydride combines with a hydrogen atom of the second reactant to form acetic acid.

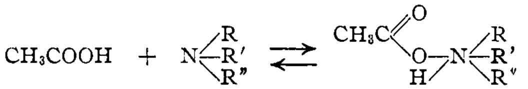
In the case of a tertiary nitrogen base there is no such available hydrogen atom on the nitrogen, and the hydrogen of the formyl group unites with the acetyl group, leaving carbon monoxide.



The reactions with the other bases can be formulated similarly. These equations explain the formation of the carbon monoxide, but do not explain the fact that the catalytic decomposition of the mixed anhydride is not affected by acetic acid.

The bases brucine[27] morphine[28] and quinine[29] form well-defined crystalline acetates. A pyridine acetate has been described by Gardner[30] but it is a very unstable compound. Pyridine is so weakly basic that it can be extracted from acetic acid solutions by ether.[31]

In the reaction mixture the acetic acid formed during the reaction must be in equilibrium with the nitrogen base. The stronger the base, the more complete the reaction.



The addition of acetic acid would tend to shift the equilibrium in the direction of the formation of acetate. In the case of pyridine, which is such a weak base, the acetate in solution would probably be dissociated to a great extent, thus leaving the free pyridine to react. This explains the fact that acetic acid has no effect on the catalysis by pyridine.

The author desires to take this opportunity for expressing publicly his appreciation to Professor J. H. Walton, at whose suggestion this re-

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[27] Shentone, *J. Chem. Soc.*, **39**, 454 (1881).

[28] Merck, *Ann.*, **24**, 48 (1837).

[29] Regnault, *ibid.*, **26**, 38 (1838).

[30] Gardner, *Ber.*, **23**, 1592 (1890).

[31] Dennstedt and Zimmermann, *ibid.*, **19**, 75 (1886).

search was undertaken and under whose direction it was carried out, for his kindly interest and guidance during its progress.

Summary

1. Sulfuric, nitric, hydrochloric, hydrofluoric, phosphoric and oxalic acids cause a catalytic decomposition of formic acid in acetic anhydride solution. Due to side reactions between the catalysts and acetic anhydride, no quantitative measurements were possible.

2. Tertiary nitrogen bases cause a catalytic decomposition of formic acid in acetic anhydride solution. The velocity of decomposition corresponds in a general way to the basicity of the compound. Very weakly basic compounds, such as caffeine, do not cause decomposition.

3. The decomposition by pyridine proceeded with various velocities in the solvents, benzene, toluene, acetone, carbon tetrachloride and nitrobenzene, ethyl, amyl, and *iso*butyl alcohols, amyl acetate and benzaldehyde. Of these, toluene was used for quantitative experiments, but due to the solubility of carbon monoxide in this solvent, satisfactory results with it could not be obtained.

4. The velocities of the catalytic decompostion of formic acid in acetic anhydride solution with the liberation of carbon monoxide, by brucine, strychnine, pyridine, quinine, morphine, nicotine, cocaine and papaverine, were measured at 50°.

5. The reaction is one of the first order.

6. The velocity of decomposition increases with increase in concentration of catalyst. For pyridine, it is a linear function; for the other bases, it is approximately linear.

7. Acetic acid has an inhibitory effect on the catalysis by brucine, strychnine and morphine, but not on the catalysis by pyridine.

8. The inhibitory action of acetic acid may be used as a quantitative method for determining acetic acid in acetic anhydride.

9. The joint effect of quinine and brucine, and cocaine and brucine, was the sum of the separate effects of each catalyst. No promoter action was discovered.

10. A possible mechanism for the reaction has been suggested postulating the formation of an intermediate compound.

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