

CLXXX.—*Hydrolysis of Acetic Anhydride.*

By KENNEDY JOSEPH PREVITÉ ORTON and MARIAN JONES, B.Sc.  
(Research Student of the University of Wales).

SEVERAL chemists have investigated the reaction of acetic anhydride with water. Menschutkin and Vasilieff (*J. Russ. Phys. Chem. Soc.*, 1889, **21**, 192) studied the change in a homogeneous mixture of acetic acid, anhydride, and water, and showed that the reaction is by no means very rapid. Benrath (*Zeitsch. physikal. Chem.*, 1909, **67**, 501), using molecular proportions of the same three substances, tried to follow the hydrolysis by determining the density. Lumière and Barbier (*Bull. Soc. chim.*, 1906, [iii], **35**, 625), with the aid of Menschutkin and Vasilieff's method, investigated the

hydrolysis in 5 and 10 per cent. aqueous solutions of acetic anhydride. Using similar and more dilute aqueous solutions, Rivett and Sidgwick (Trans., 1910, **97**, 733, 1677) followed the hydrolysis by measuring the electric conductivity; their results, which will be discussed further, in general confirm and extend Lumière and Barbier's.

The genesis of our experiments lay in a study of the formation of nitroamines when anilines are treated with nitric acid and acetic anhydride; for this purpose it was necessary to know how rapidly acetic anhydride reacts with water in a medium of glacial acetic acid containing only a fractional percentage of water. The method of estimating acetic anhydride in acetic acid or aqueous acetic acid media, which was discovered by Edwards and Orton (Trans., 1911, **99**, 1181), provided a means of studying the hydrolysis of acetic anhydride in various media, and under the influence of catalysts.

### I.—The Effect of the Medium.

As media, glacial acetic acid, various aqueous acetic acids, water, aqueous acetone, and acetic anhydride have been used.

Table I shows the effect of the solvent on the rate of hydrolysis. (The composition of the acetic acids is stated by volume.)

TABLE I.

Medium.	Temperature.	Concentration of acetic anhydride.	Velocity-coefficient or velocity-factor.
Glacial acetic acid .....	16°	0·0804 ( $[H_2O]=0\cdot18$ )	$k_{II}=0\cdot00042$
97 per cent. acetic acid ...	15	0·081	$k_I=0\cdot0006$
95   "           "    ...	16	0·0782	$k_I=0\cdot001$
90   "           "    ...	16	0·0815	$k_I=0\cdot0028$
80   "           "    ...	16	0·0813	$k_I=0\cdot0056$
50   "           "    ...	15	0·083	$k_I=0\cdot016$
Water .....	15	0·473	$k_I=0\cdot074$
	0	0·495	$k_I=0\cdot028$
95 per cent. aqueous acetone	15	0·087	6 per cent. hydro- lysed in 118 hours
50   "           "    ...	15	0·088	$k_I=0\cdot006$
Acetic anhydride .....	15	$[Ac_2O]=10\cdot3$ $[H_2O]=1\cdot8$	$k_{II}=0\cdot000071$

Obviously, if the hydrolysis of the anhydride is represented by the equation,  $Ac_2O + H_2O = 2CH_3\cdot CO_2H$ , the velocity-coefficient,  $k_{II}$ , should be given by the equation of the second order. Except in the case of glacial acetic acid and in the last experiment, when the anhydride and water are used alone, the water is in such large excess, and hence of approximately unchanging concentration, that the constant, the velocity factor,  $k_I (=k_{II}[H_2O])$ , is given by the equation of the first order.

With regard to the media other than water, it is to be noted that acetone provides an environment less favourable to the reaction than acetic acid. In a 50 per cent. aqueous acetone medium the rate is only something more than  $\frac{1}{3}$  of a similar aqueous acetic acid medium. In the experiments with an acetic anhydride medium, saturated solutions of water, containing 2.7 grams of water to 100 grams of anhydride, were used. The very small values of the velocity-coefficient show that pure acetic anhydride is a curiously unfavourable medium for its own reaction with water. For aqueous acetic acid media, the speed of hydrolysis is nearly proportional to the concentration of the water; the increase in  $k_1$  is somewhat more rapid than the increase in the proportion of water.

*Hydrolysis in Aqueous Solution.*—As is shown in table II, our results in aqueous solution are in agreement with Lumière and Barbier's and Rivett and Sidgwick's.

TABLE II.

Lumière and Barbier.		Rivett and Sidgwick.			Orton and Jones.	
$A.$	$k_1^{15^\circ}.$	$A.$	$k_1^{25^\circ}.$	$k_1^{15^\circ}.$	$A.$	$k_1^{15^\circ}.$
0.491	0.0735	0.487	0.1383	0.074	0.486	0.074
		0.265	0.1484	0.0793	0.269	0.084
		0.058	0.1561	0.0835		

The velocity factor,  $k_1$ , has been calculated from the equation  $k_1 = \frac{1}{t} \log_e \frac{A}{A-x}$ , where  $t$  is in minutes,  $A$  the original concentration of the anhydride in moles per litre, and  $x$  the amount changed in time,  $t$ . Lumière and Barbier had not deduced a constant from their measurements, which were made at  $0^\circ$  and  $15^\circ$ . Rivett and Sidgwick worked at  $25^\circ$ , using a wide range of concentrations, only the higher of which are suitable for our method of analysis. The values of  $k_1$  given in the table are not Rivett and Sidgwick's, but those calculated from their numbers by use of the above equation. By taking the ratio,  $k_1^{25^\circ}/k_1^{15^\circ} = 1.87$ , from ours and one of Rivett and Sidgwick's measurements, we have reduced these authors' other values to  $15^\circ$ . Further, by determining  $k_1$  also at  $0^\circ$ , it has been shown that the value of the velocity factor has the normal relation to temperature.

II The most striking fact is that the values of the velocity factor are not independent of the initial concentration of the anhydride, but are larger for the lower concentrations. This relation is given by both Lumière and Barbier's, Rivett and Sidgwick's, and our measurements. Rivett and Sidgwick suggested that this might be partly due to the effect of changing viscosity on their method of measurement, but this peculiarity is not found in the hydrolysis of

other anhydrides. Since, however, the relation is still more marked in our values, on which viscosity can have no influence, the value of the velocity factor must actually depend on the initial concentration. It should be noted, however, that the value of  $k_1$  for the lower concentrations continuously falls. We find that measurements made in 50 per cent. acetic acid show the same phenomenon:  $A = 0.0813$ ,  $k_1^{15} = 0.0057$ ;  $A = 0.1625$ ,  $k_1^{15} = 0.0047$ .

Burke and Donnan (Trans., 1904, **85**, 555) have observed the same phenomenon in the reaction of silver nitrate and alkyl iodides, except that the value of  $k$  increases, not decreases, with the initial concentration, and they have shown that it is represented by the exponential law,  $k = Kc^n$ . By plotting  $\log k$  for a series of values of  $c$  (0.1169—0.3947) against  $\log c$  from Rivett and Sidgwick's measurements, a straight line is obtained; hence the relation of  $k$  to  $c$  is expressed by the same law, but the sign of  $n$  is negative, since  $k$  decreases with concentration.

On the addition of alkalis, hydroxides, carbonates, or hydrogen carbonates, the hydrolysis becomes too fast for measurement. In the presence of acetic acid, Rivett and Sidgwick found a fall in the value of  $k_1$ . We have confirmed this fact.

	[Ac <sub>2</sub> O].	[CH <sub>3</sub> ·CO <sub>2</sub> H].	[H <sub>2</sub> SO <sub>4</sub> ].	$k_1^{15}$ .
Rivett and Sidgwick .....	0.283 *	—	—	0.079
	0.283	0.828	—	0.0709
Orton and Jones .....	0.269	—	—	0.084
	0.286	1.0	—	0.07
	0.266	—	0.005 <i>N</i>	0.09
	0.530	—	0.266 <i>N</i>	0.11

\* Obtained from mean of experiments 21 and 22.

Replacing the acetic acid by an isohydric solution of sulphuric acid, however, produces a rise in the value of  $k_1$ .

Sulphuric acid is obviously much less effective than alkalis. With sodium acetate the acceleration is so considerable that the measurements can only be conveniently made at 0°.

In conclusion, it may be said that although hydrogen ions do accelerate hydrolysis in aqueous solution, hydroxyl ions are far more effective, a relation which has been observed in the hydrolysis of esters, and so forth.

## II.—The Effect of Catalysts.

The effect of acids, sodium acetate, and ferric chloride in acetic acid and aqueous acetic acids has been studied.

Acids are the most powerful catalysts of the hydrolysis. This effect is most obvious in media containing but little water, and

diminishes as the proportion of the water is increased; it is least obvious in pure water.

TABLE III.

Medium.	Con- centration of $H_2SO_4$ .	Con- centration of $Ac_2O$ .	Tem- perature.	Speed of hydrolysis.
Glacial acetic acid ... ..	—	0.0804	16°	12 per cent. in 24 hrs. $k_{II}=0.00042$
	0.002M	0.077	16	52 per cent. in 10 mins.
97 per cent. acetic acid ...	—	0.081	16	$k_I=0.0006$
	0.0041M	0.081	16	$k_I=0.0172$
95     "     "     " ...	—	0.0782	16	$k_I=0.001$
	0.004M	0.0813	16	$k_I=0.0075$
90     "     "     " ...	—	0.0815	16	$k_I=0.0028$
	0.0166M	0.0807	16	$k_I=0.016$
	0.1M	0.091	15	$k_I=0.076$
80     "     "     " ...	—	0.0813	16	$k_I=0.0056$
	0.0166M	0.085	15	$k_I=0.0084$
50     "     "     " ...	—	0.083	15	$k_I=0.016$
	0.034M	0.0835	15	$k_I=0.03$

The acceleration by acids in acetic anhydride or acetone as media is not so great as in glacial acetic acid; thus the hydrolysis has proceeded to the extent of 30 per cent. in nine hours in acetic anhydride, whilst in the presence of a trace of sulphuric acid ( $M/794$ ), 50 per cent. is hydrolysed in four hours. In 95 per cent. acetone, where the hydrolysis is scarcely perceptible, in the presence of the relatively high concentration (0.05M) of hydrochloric acid, the value of the  $k_I$  is only 0.0011.

*Effect of Concentration and Nature of the Acid.*—Hydrochloric acid cannot be easily compared with sulphuric acid in glacial acetic acid, owing to the low solubility of the former. In 95 per cent. acetic acid molecular, not equivalent, quantities are found to be equally effective; thus,  $k_I = 0.0075$  for concentrations of  $M/240$  of each acid at 15°. As the medium is further diluted, neither molecular not equivalent quantities of the acids have an equal effect, but when a medium of 50 per cent. acetic acid is reached, equivalent quantities show the same accelerating effect. Experiments with hydrobromic and perchloric acids demonstrate a similar relation to sulphuric acid.

This relation indicates that we are dealing with the non-ionised acid as effective catalyst in media of 90 per cent. and upwards, and in media of 50 per cent. and below with ionised acids. Measurements of equilibria between hydrochloric acid and chloroamines in various aqueous acetic acid media (Orton and Jones, *Trans.*, 1909, **95**, 1456) lead to identical conclusions. For 90 per cent. and upwards the equilibrium was  $NCl + HCl \rightleftharpoons :NH + Cl_2$ , and for 65 per cent. and below:  $:NCl + H^+ + Cl^- \rightleftharpoons :NH + Cl_2$ .

It is not easy to determine the relation between the concentration of the catalyst and the increase of the speed, owing to the limitations imposed by the methods of measurement. In 90 per cent. acetic acid, with sulphuric acid as catalyst, it has, however, been shown that the relation is linear.

TABLE IV.

[Ac <sub>2</sub> O].	[H <sub>2</sub> SO <sub>4</sub> ].	$k_I^{15^\circ}$ .	$k_I^{15^\circ}/[H_2SO_4]$ .
0.0815	—	0.0028	—
0.0795	0.0166 <i>M</i>	0.0106	0.66
0.0815	0.033 <i>M</i>	0.0196	0.594
0.0823	0.05 <i>M</i>	0.035	0.7
0.091	0.1 <i>M</i>	0.076	0.76

### III.—Nitric Acid as Catalyst.

Nitric acid occupies a quite exceptional position. In 50 per cent. acetic acid its catalytic effect on the hydrolysis is identical with that of other acids, but with larger proportions of acetic acid in the medium its relative effectiveness steadily falls, as table V shows, until in glacial acetic acid, when such an acid as sulphuric has greatest influence, that of nitric acid reaches a minimum. Variation of the concentration of nitric acid is shown in the case of 90 per cent. acetic acid medium. It is obviously not linear, as in the case of sulphuric acid.

TABLE V.

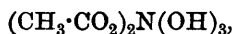
Medium.	Catalyst.	Ac <sub>2</sub> O.	Temperature.	$k_I$ .
50 per cent. acetic acid ...	—	0.083	15°	0.016
	0.034 <i>M</i> -H <sub>2</sub> SO <sub>4</sub>	0.084	15	0.021
	0.07 <i>M</i> -HCl	0.083	15	0.022
	0.071 <i>M</i> -HNO <sub>3</sub>	0.087	15	0.022
	—	0.0813	15	0.0057
80     "     "     ...	0.0165 <i>M</i> -H <sub>2</sub> SO <sub>4</sub>	0.0804	15	0.0084
	0.033 <i>M</i> -HCl	0.086	15	0.0139
	0.033 <i>M</i> -HNO <sub>3</sub>	0.078	15	0.011
	—	0.0815	15	0.0026
	0.033 <i>M</i> -HCl	0.081	15	0.023
90     "     "     ...	0.0165 <i>M</i> -HNO <sub>3</sub>	0.083	15	0.0065
	0.033 <i>M</i> -HNO <sub>3</sub>	0.0805	15	0.008
	0.066 <i>M</i> -HNO <sub>3</sub>	0.079	15	0.012
	—	0.078	15	0.001
	0.0041 <i>M</i> -HCl	0.083	15	0.007
95     "     "     ...	0.0166 <i>M</i> -HNO <sub>3</sub>	0.0857	15	0.0044
	—	0.0804	15	12 per cent. in 24 hours
	0.002 <i>M</i> -H <sub>2</sub> SO <sub>4</sub>	0.077	15	50 per cent. in 10 minutes
	0.05 <i>M</i> -HNO <sub>3</sub>	0.088	15	32 per cent. in 24 hours
	Glacial acetic acid .....	—	—	—

The great difference between nitric and other acids is not to be attributed to the disappearance of the latter. Solutions of nitric

acid in glacial acetic acid have been shown to be quite stable (Orton and Gray, *Analyst*, 1912, **37**, 303), and although in the presence of acetic anhydride there is a slow reduction and disappearance owing to nitration (of the acetic acid or anhydride), it cannot account for its apparent inactivity as a catalyst of hydrolysis; only a few per cent. of the acid is lost in a week.

In solutions where acids are ionised, nitric acid behaves as other acids; the abnormality appears when the acid is not ionised. This singularity is not confined to the hydrolysis of acetic anhydride; whilst a mixture of acetic acid, nitric acid, and acetic anhydride yields nitroaminobenzenes with aniline (Orton, *Trans.*, 1902, **81**, 806), a similar mixture, in which nitric acid is replaced by other acids, is a powerful acetylating agent for anilines, the acid acting as a positive catalyst (Smith and Orton, *Trans.*, 1908, **93**, 1242; 1909, **95**, 1060).

The most obvious suggestion, perhaps, is that the nitric acid combines with the acetic anhydride to form one of the compounds,



or acetyl nitrate,  $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{NO}_2$ , described by Pictet and Genequand (*Ber.*, 1902, **35**, 2526) and Pictet and Khotinsky (*Ber.*, 1907, **40**, 1163), and hence cannot exert its catalytic effect. Such a suggestion necessitates, in the first place, that these compounds are not much more rapidly hydrolysed than acetic anhydride, and in the second place that they react with the dichloroaniline (in the presence of sodium acetate), forming the acetanilide. But on the supposition that the formation of one or other of these compounds is the cause of the inactivity of nitric acid, certain other properties (such as the hydrolysis into acetic anhydride and nitric acid) must also be attributed to them for the following reasons: The addition of a trace of sulphuric acid to a system containing nitric acid produces its usual powerful effect. Diluting such a system with an equal volume of water leads to the same rate of hydrolysis as is observed when nitric acid is added to acetic anhydride in 50 per cent. acetic acid, that is, the usual acid catalysis. Only further investigation can decide between the various possibilities, and determine the condition which differentiates nitric from other acids.

### *Discussion of Results.*

The results recorded in this paper bring the hydrolysis of acetic anhydride into line with its reactions with hydroxy-compounds and bases, and with the similar hydrolysis of esters, amides, etc. That this would be found to be the case was suggested in the *Annual Reports* (1910, 64) in the discussion of Rivett and Sidgwick's results.

These authors, mainly through the limitations imposed by their method, had been lead to the conclusion that the mechanism of the hydrolysis of acetic anhydride was quite different from that of the hydrolysis of amides and esters (*loc. cit.*, p. 1684). Although acetic anhydride reacts rapidly with most hydroxy- and amino-compounds, the acetylation is greatly accelerated by strong acids, both in the case of hydroxy-compounds (Franchimont, Skraup, and others), and in the case of weak bases (Smith and Orton, *loc. cit.*). A similar relation was therefore to be expected in the reaction with water. In the light of the recent researches of Lapworth, Goldschmidt, and others, mainly on esterification, the following equations may represent the mechanism of the hydrolysis:

- (i)  $\text{Ac}_2\text{O} + \text{H}_2\text{O} = 2\text{AcOH}$ ;
- (ii)  $\text{Ac}_2\text{O} + \text{H}_2\text{O} + \text{H}' = 2\text{AcOH} + \text{H}'$ ;
- (iii)  $\text{Ac}_2\text{O} + \text{H}_2\text{O} + \text{HX} = 2\text{AcOH} + \text{HX}$ ;
- (iv)  $\text{Ac}_2\text{O} + \text{H}_2\text{O} + \text{OH}' = 2\text{AcOH} + \text{OH}'$ .

The third substance,  $\text{H}'$ ,  $\text{HX}$ , or  $\text{OH}'$ , may be supposed to exert its influence by forming a reacting ionic or non-ionised complex with one or other of the reagents. Any one of the four forms of the hydrolysis may predominate according to the conditions, medium; etc.

In aqueous solution the choice lies between (i), (ii), and (iv). Strong acids have a feeble, whilst bases and even such a slightly hydrolysed salt as sodium acetate have a powerful, catalytic effect. These relations suggest that in aqueous solution hydroxyl ions play the predominant part. In that case traces of acids by decreasing the concentration of the hydroxyl ion should have a great retarding influence. It is true that acetic acid does slightly retard the hydrolysis, but we have not found any such effect with sulphuric. Hence, although hydroxyl ions are powerful catalysts, it may be concluded that in pure water the hydrolysis mainly follows equation (i) and is non-catalytic.

In relatively anhydrous media, reaction (iii) obviously predominates. Molecular quantities of acids are equally effective, and the speed is a linear function of the concentration of the acid.

In media such as 50 per cent. acetic acid or acetone, the catalytic effect is now due to the hydrogen ions (equation ii), for equivalent quantities of acids are of equal influence; but probably here in the absence of strong acids the reaction is also following equation (i).

In media with less than 50 per cent. of water, the catalytic effect of acids follows both equations (ii) and (iii).



## EXPERIMENTAL.

*The Estimation of Acetic Anhydride.*—In order to follow the hydrolysis of acetic anhydride in these experiments, the method of estimating the anhydride devised by Edwards and Orton (*loc. cit.*) has been used. The general procedure is the same as previously described, but for our particular purposes, for example, the estimation of acetic anhydride in aqueous solution, it has been necessary to make some slight modifications. Our procedure is as follows:

The solution of the anhydride which does not contain more than 0.2 gram, is added to a solution of 2:4-dichloroaniline (at least two to three times the quantity equivalent to the anhydride) in so much glacial acetic acid that the final mixture is not below 90 per cent. acetic acid (by volume). Direct trials have shown that the combination of aniline and anhydride is complete in fifteen minutes in 90 per cent. acetic acid, but to a somewhat less extent in 80 per cent. Gentle warming above the water-bath for a short time may be resorted to, and is without any danger of reaction between the acetic acid medium and the aniline.

The anilide is extracted by diluting the mixture to 20 per cent. acetic acid, and shaking with three successive volumes of chloroform. The three volumes of chloroform are shaken vigorously with the solution for three, five, and seven minutes respectively. For every 100 c.c. of diluted solution the three volumes of chloroform are 10, 7, and 3 c.c. It has been found that the first extraction, which contains the larger proportion of the anilide, needs particular care in separating if loss of anilide is to be avoided; the final volume of chloroform only contains 0.92 per cent. of the anilide. The aniline is extracted from the chloroform solution by shaking once for two minutes with 90 c.c. of a 10 per cent. solution of hydrochloric acid for each gram of aniline used. The chloroform solution of the anilide is then mixed with an equal volume of glacial acetic acid and treated with excess of bleaching powder solution to form the chloroamine,  $C_6H_3Cl_2 \cdot NClAc$ , such a volume of water being added that the acetic acid aqueous layer is finally 20 per cent. acetic acid (compare Edwards and Orton, *loc. cit.*). After thorough shaking the chloroform is withdrawn, washed with water (containing a little bleaching powder), and evaporated at  $30^\circ$  under slightly diminished pressure in a current of dust-free dry air, which is not drawn from the laboratory, but from the open. This precaution is of importance, as it has been found that the accidental occurrence of reducing gases (hydrogen sulphide and sulphur dioxide) in the laboratory air will often give misleading results by reducing the chloroamine.

The errors in a determination of this type will obviously all be on the negative side, but with practice and scrupulous avoidance of contact of the chloroamine with reducing materials, the error is less than 0.5 per cent.\*

In the experiments when aqueous acetone was used as the medium, the aniline was dissolved as before in acetic acid. It was found that acetone retards the interaction of the aniline and anhydride.

When acids were present as catalysts of the hydrolysis, anhydrous sodium acetate at least equivalent to the acid is added to the solution of the aniline before introducing the solution of the anhydride.

*Method of carrying out Velocity-measurements.*—The acetic acid used was the special material supplied by Kahlbaum and free from reducing substances (Orton, Edwards, and King, Trans., 1911, 99, 1178). The acetic anhydride was prepared from Kahlbaum's "free from homologues," as described in the following paper.

Our usual procedure in carrying out a measurement is as follows: About 150 c.c. of the medium is brought to the experimental temperature in the bath. When a catalyst is used the requisite quantity dissolved in about 30 c.c. of the medium is placed in the bath. The weighed quantity of the anhydride is placed in a stoppered measuring flask about half filled with the medium; the solution of the catalyst is then added, and the volume made up with the medium (2—5 c.c.) to 100—150 c.c.

At intervals from four to six portions of 10—20 c.c. were with-

\* The following numbers were obtained in testing various stages of the process :

1. Given weights of the chloroamine were dissolved in chloroform, treated with bleaching powder solution, and then the chloroform evaporated.

Chloroamine used.	Chloroamine found.	Loss.
0.1888	0.1882	0.0006 = 0.3 per cent.
0.2048	0.2046	0.0002 = 0.1 „

2. Given weights of anilide were put through the entire process and estimated as chloroamine.

Anilide used.	Anilide found.	Error.
0.1718	0.1722	+ 0.2 per cent.
0.1698	0.1703	+ 0.5 „
0.1418	0.1419	
0.2322	0.2321	

3. Given weights of acetic anhydride were treated with aniline and so forth, and estimated as chloroamine.

Anhydride used.	Aniline used.	Anhydride found.	Error.
0.5061	3.0	0.5046	- 0.3 per cent.
0.1828	1.2	0.1820	- 0.6 „
0.1564	1.0	0.1560	- 0.2 „
			5 x 2

drawn and added to the dichloroaniline (and sodium acetate in the case of an acid catalyst) in 10—40 c.c. of acetic acid, that is, such quantity that the medium is 90 per cent. acetic acid. These mixtures were in all cases kept for an hour, but it was often convenient to let them remain overnight. The completion of the analysis of such a series by the method described in the foregoing occupies about four hours.

In the experiments in which a mixture of acetic anhydride and water was used, the anhydride (about 5.59 grams, that is, 5 c.c.) was placed in a weighed flask and brought to the temperature of the bath. A very accurately measured volume of water (about 0.17 c.c.) was then added. At intervals about 0.4 gram was withdrawn and added to the aniline (2 grams) and acetic acid, which had been previously weighed. The increase of weight gives the exact quantity of the mixture withdrawn. When an acid catalyst was used, the acid was dissolved in the water.

In all, something more than three hundred measurements of this kind have been made in the course of this inquiry. No measurement has been accepted unless a coincident duplicate has been obtained.

The following table shows the numbers obtained in typical experiments.

TABLE VI.

Medium: 97 per cent. acetic acid. Temperature 15°.

Thiosulphate = 0.992*N*/10. Exp. 130.

Time (minutes).	C.c. of thiosulphate.	Weight of $\text{Ac}_2\text{O}$ in 20 c.c.	Percentage changed.	$k_1$ .
0	—	0.1681	0.0	—
160	31.0	0.1570	4.5	0.00059
360	26.5	0.1341	21.2	0.000618
480	24.6	0.1242	26.1	0.00062
595	23.3	0.118	29.8	0.00059
765	20.75	0.105	37.5	0.00061

Medium: 97 per cent. acetic acid. Temperature 16°.

$\text{H}_2\text{SO}_4 = M/240$ . Thiosulphate = 1.047*N*/10. Exp. 105.

Time (minutes).	C.c. of thiosulphate.	Weight of $\text{Ac}_2\text{O}$ in 20 c.c.	Percentage changed.	$k_1$ .
0	—	0.1652	0.0	—
21	20.5	0.1095	33.7	0.0178
33	17.2	0.0918	44.4	0.0178
40	15.4	0.0822	50.2	0.0174
60	10.8	0.0577	65.1	0.0175
72	9.1	0.0486	70.6	0.0168

Medium: 95 per cent. acetic acid. Temperature 16°.

Thiosulphate = 1.23*N*/10. Exp. 125.

Time (minutes)	C.c. of thiosulphate.	Weight of $\text{Ac}_2\text{O}$ in 20 c.c.	Percentage changed.	$k_t$ .
0	—	0.1657	0.0	—
60	24.8	0.1558	5.8	0.001
210	24.0	0.1505	9.2	0.00102
285	22.75	0.1424	23.6	0.00093
360	20.4	0.1280	31.4	0.00103
465	18.2	0.1142	38.7	0.00105
540	16.7	0.105	44.0	0.00104

Medium: 95 per cent. acetic acid. Temperature 16°.

$\text{HNO}_3 = N/60$ . Thiosulphate = 1.047*N*/10. Exp. 109.

0	—	0.1748	0.0	—
60	27.9	0.149	14.8	0.00266
130	22.8	0.1218	30.3	0.00277
195	18.9	0.1010	42.2	0.0028
270	15.3	0.0844	51.7	0.0027
375	12.25	0.0654	62.6	0.0026
439	10.5	0.0561	67.9	0.0026

Medium: 50 per cent. acetic acid. Temperature 15°.

Thiosulphate = 1.002*N*/10. Exp. 142.

0	—	0.1695	0.0	—
20.7	23.6	0.1206	29.0	0.0168
31	19.8	0.1012	40.3	0.0166
42.7	16.14	0.0844	50.2	0.0163
50	14.3	0.073	56.9	0.0168
70	10.8	0.0542	68.0	0.0162

### Summary.

(1) The hydrolysis of acetic anhydride in glacial acetic acid is a slow reaction of the second order ( $k_{11}^{16^\circ} = 0.00042$ ). As the acetic acid is diluted, the speed of the hydrolysis increases approximately proportional to the water.

In aqueous acetone, acetic anhydride hydrolyses more slowly than in the corresponding concentrations of acetic acid.

The hydrolysis in solutions of water in acetic anhydride is slower than in acetic acid, thus  $k_{11}^{15^\circ} = 0.000071$ .

(2) In aqueous solutions Lumière and Barbier's and Rivett and Sidgwick's results are confirmed. The value of the velocity factor varies with the initial concentration of the anhydride;  $\log k$  is a linear function of  $\log c$  for concentrations above 0.115.

The relation of the velocity factor to the temperature is normal.

(3) Acids are very powerful catalysts of the hydrolysis in anhydrous media, but only feeble catalysts in water. Molecular quantities are equally effective in aqueous acetic acid of 90 per

cent. acetic acid and above, but equivalent quantities for 50 per cent. acetic acid and below. The value of the velocity factor is a linear function of the concentration of the acid.

Alkalis and hydrolysed salts are powerful catalysts of the hydrolysis in aqueous solutions.

(4) Nitric acid is unique in its effect. In 50 per cent. acetic acid its effectiveness is equivalent to that of other acids, but as the proportion of the acetic acid in the medium increases, the effectiveness of nitric acid diminishes until in glacial acetic acid it is relatively infinitesimal.

The investigation of the hydrolysis of acid anhydrides and of acylation is being continued.

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UNIVERSITY COLLEGE OF NORTH WALES,  
BANGOR.

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