

THE REACTION VELOCITIES OF THE HYDROLYSIS OF  
METHYL ACETATE WITH A NON-AQUEOUS SOLVENT

A THESIS

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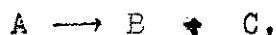
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## INTRODUCTION

The mechanism of a reaction, that is the manner in which the molecules interact, may be studied by observing the rate of reaction and how this reaction rate changes as the reaction proceeds. Guldberg and Waage, when they formulated the law of mass action in 1867, were able to explain the rate of reaction as a function of concentration. Van't Hoff, generally credited with the law of mass action, was the first to bring the subject under comprehensive treatment. This law states that the rate with which a given reaction takes place is proportional to the concentrations of the reacting substances if the temperature and pressure remain constant.

If, for example, a single compound A reacts to form two new substances, B and C,



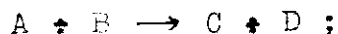
the velocity with which A decomposes will depend upon the instantaneous concentration of A, and the reaction is called unimolecular. Since A is consumed as time progresses, the rate gradually decreases. If x represents the amount of A which decomposes in time t and a is the initial concentration of A, then the amount present at time t will be  $a - x$ ; and the rate of decomposition of A will be proportional to  $a - x$ . Expressing this mathematically,

$$\frac{dx}{dt} = k (a - x)$$

where  $k$  is a constant, known as the velocity constant of the reaction.  $k$  may be calculated from the integration of the above equation, which becomes,

$$k = \frac{2.3026}{t} \log \frac{a}{a - x},$$

A given reaction may be bimolecular if



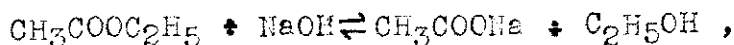
and the rate of decomposition is proportional to the concentration of both  $A$  and of  $B$  or

$$\frac{dx}{dt} = k (a - x)(b - x),$$

where  $a$  and  $b$  represent the initial concentrations of  $A$  and  $B$ . Upon integration this becomes

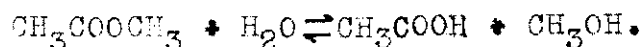
$$k = \frac{2.3026}{t (a - b)} \log \frac{(a - x)(b)}{(b - x)(a)} .$$

Most inorganic reactions proceed at a very rapid rate, almost instantaneously; and, therefore, the rate may not conveniently be studied. Organic reactions, on the other hand, are slower and lend themselves very well to a study of their velocities. In 1885, Reicher (1) studied the velocity of saponification of ethyl acetate by sodium hydroxide,



and found the reaction to be bimolecular. He also observed the effect of different bases on the rate of saponification. Warder (2) in 1881 and Arrhenius (3) in 1887 also studied the saponification rate of .02 molar ethyl acetate in .02 molar alkali and found the reaction to be bimolecular. The saponification of methyl acetate in a sodium hydroxide solution was examined by Gooch and Terry (4) in 1929. They obtained very accurate results by using refined methods including an ingenious method of pipetting. They calculated the velocity constant of the reaction and found it to be bimolecular.

In 1883, Ostwald (5) first studied the velocity of the hydrolysis of methyl acetate in a water solution by titrating, with sodium hydroxide, the acetic acid formed,



This reaction, it can be seen, should be bimolecular. However, since the methyl acetate was dissolved in a large amount of water, the concentration of water changed only infinitesimally and could be considered constant. Thus in the equation for the bimolecular reaction,

$$\frac{dx}{dt} = k (a - x)(b - x),$$

(b - x) was constant and the equation then became

$$\frac{dx}{dt} = k' (a - x),$$

which is the monomolecular form. Ostwald (loc.cit.) ignored

the reverse reaction which was small during the period in which he made his measurements. In 1922, Harned and Pfanstiel (6) calculated the velocity constant for the hydrolysis of methyl acetate in aqueous solution in which they ignored neither the reverse reaction nor the slight change in the concentration of water during the reaction. Harned and Samaras (7), in 1932, then studied the hydrolysis of ethyl ortho-formate using varying amounts of organic solvents (in no instance did the concentration of organic solvent exceed 3.32 mols per 1000 grams of solution). They found that the velocity constants calculated from the monomolecular formula were the same as those calculated from the bimolecular formula. Tommila and Hinshelwood (8) in 1938 also studied the hydrolysis of various esters when acetone was added to the reaction as a solvent. They used 400 cc of acetone per liter of solution and found the velocity constants for the hydrolysis of benzyl acetate, phenyl acetate, and ethyl and methyl benzoates, nitrobenzoates and para-aminobenzoates and found the reactions to be bimolecular. Poethke (9) in 1935 was able to detect a slight hydrolysis of ethyl acetate in aqueous solution using no catalyst; but, when ethyl acetate was made 0.5 normal in water, no hydrolysis was detected after 34 days.



## PURPOSE

It was the purpose of our investigations to find the velocity constant of the hydrolysis of methyl acetate when the concentration of water was reduced until it changed materially during the course of the reaction. This was accomplished by using acetone as a solvent instead of water.

## PREPARATION OF MATERIALS

Sulfuric Acid: Concentrated C.P. sulfuric acid was diluted with recently boiled distilled water to approximately 10 normal. This acid was standardized by weighing a portion from a weight burette and titrating it with standardized sodium hydroxide solution, using methyl red as indicator. Also the weight of one cc of sulfuric acid was determined by weighing, in a weight burette, a known number of cc. From these data, the weight of hydrogen sulfate, and the weight of water per 5 cc of the acid were found. The normality, also, was determined from these data. The acid was 9.421 normal and contained 2.3099 grams of hydrogen sulfate and 4.0135 grams of water per 5 cc of acid solution.

Sodium Hydroxide: The sodium hydroxide solution used to

standardize the sulfuric acid was made by dissolving C.P. sodium hydroxide in recently boiled distilled water and standardizing with potassium acid phthalate from the U. S. Bureau of Standards, using phenolphthalein as indicator. The sodium hydroxide used to standardize the sulfuric acid was 0.1728 normal.

The sodium hydroxide used in titrating the acetic acid formed in the reaction was made approximately .05 normal and standardized every day in the same manner as mentioned.

Water: All water used was recently boiled distilled water.

Acetone: The acetone was prepared from a commercial grade of acetone by reflexing it for two hours over magnesium and then distilling it. The fraction used had a boiling point range of  $55.35^{\circ} - 55.40^{\circ}$  at a pressure of 743 mm. of mercury. From the International Critical Tables, acetone has a boiling point of  $56.10^{\circ} \text{C}$  at 760 mm. pressure. Using the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta H p}{RT^2},$$

where  $\Delta H$  is the heat of vaporization,  $p$  is the pressure,  $T$  is the temperature of the boiling point on the Kelvin scale, and  $R$  is the gas constant in the same units as  $\Delta H$ . From the International Critical Tables,

$$\Delta H = 521 \text{ joules per gm} = 7232 \text{ cal / mol for acetone.}$$

By substitution,

$$dT = \frac{(17)(1.9885)(329.2)^2}{(760)(7232)} = 0.67 .$$

Therefore the correct boiling point at 743 mm pressure is

$$56.10 - .67 = 55.43^{\circ}\text{C}.$$

The observed range was 55.35 - 55.40.

Methyl Acetate: The methyl acetate used was C.P. grade with a boiling point range of 55.80 - 56.40°C at 743 mm of pressure. From the International Critical Tables, the boiling point at 760 mm of pressure is 57.1°C. The heat of vaporization at 57.1° from the International Critical Tables is 410.6 joules / gm or 7287 cal / mol. Using the Clapeyron equation again ,

$$dT = \frac{(17)(1.9885)(330.2)^2}{(760) 7287} = 0.67 .$$

Therefore the boiling point at 743 mm pressure is

$$57.1 - .7 = 56.4^{\circ}\text{C} .$$

The observed range was 55.80 - 56.40°C.

## PROCEDURE

The procedure was to weigh a quantity of methyl acetate into a glass stoppered 100 cc volumetric flask, add 5 cc of 9.421 normal  $H_2SO_4$  and dilute to 100 cc with anhydrous acetone. A 5 cc portion was pipetted from the sample, immediately after mixing and at definite time intervals thereafter, into a beaker containing 50 cc of recently distilled water and a measured quantity of standardized sodium hydroxide--almost enough to neutralize the acid in the sample. This was then titrated to the end point of phenolphthalein with the standardized sodium hydroxide. Care had to be taken to obtain the correct end point because of the reappearance of the color of phenolphthalein in the sample on standing for a short time. The 100 cc volumetric flask containing the sample was immersed in a constant temperature bath at  $25^\circ \pm 0.1^\circ C$ . during the entire run.

To insure that exactly 5 cc of acid were added to each sample, 100 cc of the sulfuric acid were diluted with anhydrous acetone to 500 cc in a 500 cc volumetric flask and 25 cc of this solution added to the sample from a burette.

To obtain the equilibrium constant  $K$ , a 5 cc sample was taken from the hydrolysis two days after the hydrolysis was started. It was found, however, that, after two days, the concentration of water used had diminished, due to the hydrolysis until the catalytic action of the sulfuric acid

was inhibited by decrease in ionization (10), (11). Therefore, it was not practical to obtain the equilibrium point by this method. The equilibrium constant, then, was obtained by preparing the samples as before except that a quantity of water was weighed into the volumetric flask with the methyl acetate. With the excess of water, the reaction proceeded to equilibrium, after two days, and the equilibrium constant was found.

## METHOD OF CALCULATIONS

To calculate  $K$ , the equilibrium constant, the concentrations of the reactants at equilibrium in the samples containing the excess of water were substituted in the equation ,

$$K = \frac{x^2}{(a - x)(b - x)} ,$$

where  $a$  is the original concentration of methyl acetate in mols per liter,  $b$  is the original concentration of water in mols per liter and  $x$  is the concentration of acetic acid present at equilibrium.

From the amount of sodium hydroxide required to titrate at different times, from the original amount of methyl acetate present, from the original amount of water present, and from the equilibrium constant, the velocity constants were calculated. Assuming the reaction to be bimolecular and including the velocity of the reverse reaction, the equation of the rate would be

$$\frac{dx}{dt} = k (a - x)(b - x) - k'x^2 ,$$

where  $a$  and  $b$  are the same as defined for  $K$ ,  $x$  is the concen-

tration of acetic acid formed in time  $t$  in mols per liter,  $k$  is the velocity constant for the hydrolysis, and  $k'$  the velocity constant for the reverse reaction. Dividing the above equation by  $k$ ,

$$\frac{dx}{dt k} = (a - x)(b - x) - \frac{k'}{k} x^2.$$

But

$$\frac{k'}{k} = \frac{1}{K} = K',$$

where  $K'$  is the reciprocal of the equilibrium constant. By substitution,

$$\frac{dx}{dt k} = (a - x)(b - x) - K' x^2.$$

Upon integration this equation becomes

$$k = \frac{2.3026}{t \sqrt{(a-b)^2 + 4K'ab}} \log \left\{ \frac{\sqrt{2(1-K')x + a + b} + \sqrt{(a-b)^2 + 4K'ab}}{2(1-K')x - a - b + \sqrt{(a-b)^2 + 4K'ab}} \right\}.$$

$$\left. \begin{array}{l} \frac{-a-b + \sqrt{(a-b)^2 + 4K'ab}}{+a+b + \sqrt{(a-b)^2 + 4K'ab}} \end{array} \right\}.$$

Assuming the reaction to be bimolecular but ignoring the velocity of the reverse reaction the equation of the rate is, as was shown before,

$$\frac{dx}{dt} = k(a - x)(b - x).$$

Upon integration this becomes

$$k = \frac{2.3026}{t(a-b)} \log \frac{(a-x)(b)}{(b-x)(a)}$$

Assuming the reaction to be monomolecular, that is, independent of the concentration of water, the equation is

$$\frac{dx}{dt} = k(a-x) - k'x^2,$$

which upon integration becomes

$$k = \frac{2.3026}{2\sqrt{1+4K'a}} \log \left\{ \frac{+2K'x+1+\sqrt{1+4K'a}}{-2K'x-1+\sqrt{1+4K'a}} \left[ \frac{-1+\sqrt{1+4K'a}}{+1+\sqrt{1+4K'a}} \right] \right\}$$



## DATA AND RESULTS

Table No. 1  
To Calculate K

- x = Concentration of acetic acid in mols / liter.  
 a = Original concentration of methyl acetate in mols / liter.  
 b = Original concentration of water in mols per liter.  
 K = Equilibrium constant of the hydrolysis.

<u>x</u>	<u>a</u>	<u>b</u>	<u>K</u>
.8180	1.2504	13.3187	.1238
.7173	1.2588	8.3507	.1244

K (correct to 3 figures) = .124

$$K' = \frac{1}{K} = \frac{1}{.124} = 8.06$$

Table No. 2

Calculation of k as bimolecular and considering the velocity of the reverse reaction.

$$K' = 8.06, \quad b = 2.2272 \text{ mol / liter}$$

<u>Sample</u>	<u>a</u>	<u>t(in hrs.)</u>	<u>x(mols / liter)</u>	<u>k</u>
1	1.994	1	.1049	.0250
		2	.2132	.0276
		3	.2960	.0279
		4	.3524	.0270
2	2.271	1	.1178	.0248
		2	.2401	.0277
		3	.3306	.0279

<u>Sample</u>	<u>a</u>	<u>t(in hrs.)</u>	<u>x(mols / liter</u>	<u>k</u>
		4	.4051	.0286
3	2.3265	1	.1287	.0266
		2	.2413	.0271
		3	.3331	.0274
		4	.3959	.0267
4	2.511	1	.1379	.0262
		2	.2611	.0264
		3	.3589	.0276
		4	.4177	.0262
5	2.539	1	.1484	.0279
		2	.2625	.0271
		3	.3567	.0270
		4	.4246	.0265
6	2.548	1	.1347	.0254
		2	.2732	.0285
		3	.3696	.0285
		4	.4336	.0276
7	2.755	1	.1575	.0278
		2	.2873	.0282
		3	.3838	.0274
		4	.4431	.0257
8	2.766	1	.1521	.0266
		2	.2824	.0271
		3	.3863	.0275
		4	.4550	.0268

<u>Sample</u>	<u>a</u>	<u>t(in hrs.)</u>	<u>x(mols / liter)</u>	<u>k</u>
9	2.780	1	.1524	.0265
		2	.2963	.0287
		3	.4036	.0292
		4	.4602	.0272
10	3.006	1	.1713	.0277
		2	.3076	.0275
		3	.4074	.0269
		4	.4873	.0270
11	3.1185	1	.1881	.0295
		2	.3252	.0281
		3	.4342	.0281
		4	.5075	.0277
12	3.167	1	.1741	.0268
		2	.3236	.0277
		3	.4300	.0274
		4	.4947	.0260
13	3.242	1	.1723	.0259
		2	.3231	.0269
		3	.4357	.0271
		4	.5046	.0260
14	3.276	1	.1814	.0284
		2	.3346	.0278
		3	.4422	.0274
		4	.5194	.0270

<u>Sample</u>	<u>a</u>	<u>t(in hrs.)</u>	<u>x(mols / liter)</u>	<u>k</u>
15	3.390	1	.2017	.0294
		2	.3538	.0288
		3	.4643	.0283
		4	.5314	.0269
16	3.437	1	.1745	.0247
		2	.3421	.0271
		3	.4553	.0270
		4	.5286	.0252
17	3.551	1	.1837	.0252
		2	.3523	.0271
		3	.4790	.0261
		4	.5439	.0263
18	3.635	1	.2131	.0290
		2	.3727	.0285
		3	.4924	.0285
		4	.5595	.0257
19	3.824	1	.2104	.0271
		3	.5172	.0290
		4	.5916	.0281
20	3.895	1	.2197	.0280
		2	.3980	.0287
		3	.5247	.0290
		4	.5856	.0267
21	4.670	1	.2449	.0260
		3	.6031	.0291
		4	.6617	.0264

<u>Sample</u>	<u>a</u>	<u>t(in hrs.)</u>	<u>x(mols / liter)</u>	<u>k</u>
22	6.311	1	.3252	.0263
		3	.7254	.0278
		4	.7713	.0240
23	7.493	1	.3642	.0252
		2	.6787	.0294
		3	.7938	.0298
		4	.8260	.0218

Table No. 3

Calculation of  $k$  as bimolecular ignoring velocity of reverse reaction.

<u>Sample</u>	<u>a</u>	<u>t(in hrs.)</u>	<u>x</u>	<u>k (ignor- ing reverse reaction)</u>	<u>k (from Table 2)</u>
8	2.766	1	.1521	.0258	.0266
		2	.2824	.0257	.0271
		3	.3863	.0243	.0275
		4	.4550	.0227	.0268

Table No. 4

Calculation of  $k$  as monomolecular.

<u>Sample</u>	<u>a</u>	<u>t(in hrs.)</u>	<u>x</u>	<u>k (monomolecular)</u>	<u>k (from Table 2)</u>
12	3.167	1	.1741	.05816	.0259
		2	.3236	.06045	.0269
		3	.4300	.06237	.0271
		4	.4947	.06382	.0260

## ANALYSIS OF DATA

It is seen that the velocity constant, calculated from the bimolecular form, is fairly constant in spite of the exaggeration of errors made by the equation. The lower value for the first hour may be caused by a slight error in determining the amount of water originally present,  $b$  which error is exaggerated in the first hour because the number whose logarithm is obtained is close to one.

The fact of lowering of ionization of the sulfuric acid when the water concentration is decreased beyond a certain value is substantiated by the decrease in the velocity constant in Table 2, samples 22 and 23, during the fourth hour. These samples had the largest original concentration of methyl acetate and therefore, after four hours, had the least water present. Any slight decrease in ionization of the sulfuric acid in the other cases was compensated by the formation of the acetic acid.

The differences in  $k$  in some samples may be due to a slight difference in the original sulfuric acid concentration. A large quantity of sulfuric acid in acetone solution could not be prepared because of the charring effect on standing, of the sulfuric acid upon the acetone.

$k$ , calculated from the equation ignoring the reverse reaction exhibited as the reaction proceeded, a greater difference from the  $k$  calculated when the reverse reaction was not ignored.

Calculated from the monomolecular equation, k exhibited a constant increase in the values as the reaction proceeded. Thus the reaction proved to be a bimolecular one.

## SUMMARY

The classical calculations of the velocity constant in the hydrolysis of methyl acetate have been made upon the assumption of a monomolecular reaction. This was due to the dual role played by the water present, a role of both solvent and reactant. It has been assumed that, if the reaction were carried out with a solvent other than water, the reaction would be bimolecular; but heretofore it has never been actually demonstrated. By using acetone as a solvent and having present only enough water to react with the methyl acetate, we were able to demonstrate the bimolecular course of the reaction under these conditions.



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