up of dipoles to high aggregates. These results are confirmed by conductance measurements.[7] The minimum occurs at 1×10^{-5} N, with the conductance slowly rising as the concentration is increased. The behavior of salts in benzene is exceedingly complex and no quantitative theory can be proposed as yet, but it seems certain that at the concentrations of our solubility measurements the effect of simple ions is negligible.

An adequate explanation of the observed solubility increase must await the accumulation of more data. Addition of other salts increases the dielectric constant,[8] but since the effect is small and the solubility changes observed in this work are too large to be ascribed to a dielectric constant effect, it seems likely that association is the primary factor. This appears to be supported by the fact that the solubility of the iodide increases more rapidly at first upon addition of the nitrate than with the picrate. Association, according to the work of Kraus and Fuoss, is higher when symmetrical ions are involved and the difference in the

(7) Luder, P. B. Kraus, C. A. Kraus and Fuoss. THIS JOURNAL, 58, 255 (1936).

(8) C. A. Kraus, Trans. Electrochem. Soc., 66, 201 (1934).

two solubility curves may be in line with corresponding differences in the conductance curves for symmetrical and unsymmetrical salts.

IV. Summary

The solubility of tetrabutylammonium iodide in benzene in the presence of tetrabutylammonium picrate and nitrate has been measured and found to increase rapidly with the concentration of added salt. These measurements are the first in a series of investigations of the solubility effect in solvents of low dielectric constants in an attempt to secure more information about the complex behavior of electrolytes in such solvents. A discussion of the nature of the problem and of proposed research has been given.

The Hydrolysis of Methyl Acetate in a Non-Aqueous Solvent[1]

BY HAROLD B. FRIEDMAN AND GLENN V. ELMORE

Introduction

In 1883, Ostwald[2] first studied the velocity of the hydrolysis of methyl acetate: $CH_3COOCH_3 + H_2O \rightleftarrows CH_3COOH + CH_3OH$. This reaction is stoichiometrically second order but due to the relative constancy of the water concentration the velocity follows a first order course. Ostwald ignored the reverse reaction, which was small during the period in which he made his measurements.

Griffith and Lewis[3] determined the velocity of the hydrolysis in the presence of hydrochloric and trichloroacetic acids and with varying initial concentrations of the ester. Schreiner[4] compiled the earlier data on the analogous reaction of ethyl

(1) Constructed from a thesis presented to the department of Chemistry. Georgia School of Technology, June. 1940. by Glenn V. Elmore in partial fulfillment of the requirements of the degree of Master of Science in Chemistry.

(2) Ostwald, J. prakt. Chem., 28, 449 (1883).

(3) Griffith and Lewis, J. Chem. Soc., 109, 67 (1916).

(4) Schreiner, Z. anorg. Chem., 116, 102 (1921).

acetate catalyzed by hydrochloric acid. Harned and Pfanstiel[5] calculated the velocity constant for the ethyl acetate hydrolysis in aqueous solution, in which they ignored neither the reverse reaction nor the slight change in the water during the reaction.

More recently, Harned and Samaras,[6] using varying amounts of organic solvents, studied the hydrolysis of ethyl orthoformate with acetic acid–sodium acetate buffers. Other work involving hydrolysis in low dielectrics includes that of Tommila and Hinshelwood,[7] who studied the hydrolysis in aqueous acetone of a large number of substituted esters, in order to determine the effect of the substituents. Poethke[8] was able to detect only a slight hydrolysis of ethyl acetate in aqueous solution using no catalyst.

(5) Harned and Pfanstiel, THIS JOURNAL. 44. 2193 (1922).

(6) Harned and Samaras, ibid., 54, 1 (1932).

(7) Tommila and Hinshelwood, J. Chem. Soc., 1801 (1938).

(8) Poethke. Ber., 68B, 1031 (1935).

Purpose.—The purpose of this investigation was to find the velocity constant of the hydrolysis of methyl acetate when the concentration of water was reduced so much that 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: Approximately 10 N sulfuric acid was standardized by titrating a known weight of the acid with standard sodium hydroxide, using methyl red as indicator.

Sodium Hydroxide.—The sodium hydroxide solution was standardized each day by titrating it against a known weight of potassium acid phthalate from the U. S. Bureau of Standards, using phenolphthalein as indicator.

Water.—Recently boiled distilled water was used throughout.

Acetone.—Commercial acetone was refluxed for two hours over magnesium and distilled. The fraction used had a boiling point range of 55.35–55.40° at a pressure of 743 mm. The boiling point of pure acetone corrected for this pressure is 55.4°.

Methyl Acetate.—The methyl acetate used had a boiling point range of 56.30–56.40° at a pressure of 743 mm. The boiling point of methyl acetate corrected for this pressure is 56.4°.

Procedure.—A quantity of methyl acetate was weighed into a glass-stoppered 100-cc. volumetric flask, placed in a constant temperature bath at 25±0.01°, 5 cc. of 9.421 N sulfuric acid added, and diluted 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 distilled water and a measured quantity of the standard sodium hydroxide—almost enough to neutralize the acid in the sample. This sample was then titrated to the end-point of phenolphthalein with sodium hydroxide.

The equilibrium constant measurements were made by preparing the samples as before except that a quantity of water was weighed into the volumetric flask with the methyl acetate. With excess of water, the increase in hydrogen ion activity caused equilibrium to be reached after two days.

Method of Calculation.—To calculate K, the equilibrium constant, the concentrations of the reactants at equilibrium in the samples containing excess of water were substituted in the equation

$$K = x^2/(a - x)(b - x) \qquad (1)$$

where a is the original concentration of the methyl acetate in moles per liter, b is the original concentration of water in moles 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 second order and including the velocity of the reverse reaction, the rate equation would be

$$dx/dt = k(a - x)(b - x) - k'x^2 \qquad (2)$$

where a and b are the same as defined for K, x is the concentration of acetic acid formed in time t, in moles per liter, k is the velocity constant for the hydrolysis and k' the velocity constant for the reverse reaction. Dividing by k

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

But $k'/k = 1/K = K'$ where K' is the reciprocal of the equilibrium constant. By substitution

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

Upon integration this equation becomes

$$k = \frac{2.3026}{t\sqrt{(a - b)^2 + 4K'ab}} \log$$
$$\left\{ \left[\frac{-2(1 - K')x + a + b + \sqrt{(a - b)^2 + 4K'ab}}{2(1 - K')x - a - b + \sqrt{(a - b)^2 + 4K'ab}} \right] \right.$$
$$\left. \left[\frac{-a - b + \sqrt{(a - b)^2 + 4K'ab}}{a + b + \sqrt{(a - b)^2 + 4K'ab}} \right] \right\} \qquad (3)$$

which is of the same form as the equation used by Harned and Pfanstiel. To determine whether under the conditions it would be permissible to ignore the reverse reaction, yet retain the second order form

$$k = \frac{2.3026}{t(a - b)} \log \frac{(a - x)(b)}{(b - x)(a)} \qquad (4)$$

was used.

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

$$dx/dt = k (a - x) - k'x^2$$

which upon integration becomes

$$k = \frac{2.3026}{t \sqrt{1 + 4K'a}} \cdot$$
$$\log \left\{ \left[\frac{2K'x + 1 + \sqrt{1 + 4K'a}}{-2K'x - 1 + \sqrt{1 + 4K'a}} \right] \right.$$
$$\left. \left[\frac{-1 + \sqrt{1 + 4K'a}}{1 + \sqrt{1 + 4K'a}} \right] \right\} \qquad (5)$$

Data and Results.—All measurements were made at 25 ± 0.01°; a is original concentration of methyl acetate in moles/liter, b is original concentration of water in moles/liter, x is concentration of acetic acid at any time in moles/liter, and K equilibrium constant of the hydrolysis.

TABLE I

To Calculate K (Equation (1))

x	a	b	K
0.8180	1.2504	13.3187	0.1238
0.7173	1.2588	8.3507	.1244

Av. 0.1241

$K' = 1/K = 1/0.124 = 8.06$

TABLE II

Calculation of k According to Equations 3, 4 and 5

a	t. hr.	x (moles/ liter)	k (eq. 3)	k (eq. 4)	k (eq. 5)
1.994	1	0.1049	0.0250	0.0259	0.0550
	2	.2132	.0276	.0280	.0610
	3	.2960	.0279	.0259	.0636
	4	.3524	.0270	.0239	.0652
2.511	1	.1379	.0262	.0246	.0571
	2	.2611	.0264	.0262	.0600
	3	.3589	.0276	.0255	.0632
	4	.4177	.0262	.0225	.0649
2.766	1	.1521	.0266	.0258	.0576
	2	.2824	.0271	.0257	.0591
	3	.3863	.0275	.0248	.0625
	4	.4550	.0268	.0277	.0660
3.167	1	.1741	.0268	.0262	.0582
	2	.3236	.0277	.0259	.0605
	3	.4300	.0274	.0243	.0624
	4	.4947	.0260	.0217	.0638
3.437	1	.1745	.0247	.0236	.0527
	2	.3421	.0271	.0256	.0545
	3	.4553	.0270	.0237	.0609
	4	.5286	.0252	.0214	.0646
3.895	1	.2197	.0280	.0268	.0603
	2	.3980	.0287	.0269	.0626
	3	.5247	.0290	.0247	.0675
	4	.5856	.0267	.0213	.0695

TABLE III

Other Values of k from Equation 3 Only

a	1st hour	2d hour	3d hour	4th hour
2.271	0.0248	0.0277	0.0279	0.0286
2.327	.0266	.0271	.0274	.0267
2.539	.0279	.0271	.0270	.0265
2.548	.0254	.0285	.0285	.0276
2.755	.0278	.0282	.0274	.0257
2.780	.0265	.0287	.0292	.0272
3.006	.0277	.0275	.0269	.0270
3.119	.0295	.0281	.0281	.0277
3.242	.0259	.0269	.0271	.0260
3.276	.0284	.0278	.0274	.0270
3.390	.0294	.0288	.0283	.0269
3.551	.0252	.0271	.0261	.0263
3.635	.0290	.0285	.0285	.0257
3.824	.0271	...	.0290	.0281
4.670	.0260	...	.0291	.0264
6.311	.0263	...	.0278	.0240
7.493	.0252	.0294	.0298	.0218

Analysis of Data.—Table I shows the data from which the equilibrium constant, K, was calculated.

In Table II we have selected at random 6 of our runs, extending over a range of concentrations, and calculated the results using all three equations, nos. 3, 4, and 5, while the remaining runs, listed for completeness in Table III, have been calculated by equation 3 only.

It is seen that the velocity constant, calculated from the second order form (eq. 3), is reasonably 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 unity.

The lowering of the ionization of sulfuric acid when the water concentration is decreased beyond a certain value is suggested by the decrease in the velocity constant in the last two samples in Table III during the fourth hour. These samples had the largest original concentrations 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 at one time because of the charring effect upon the acetone on standing in contact with the sulfuric acid.

k, calculated from equation 4, ignoring the reverse reaction, exhibited as the reaction proceeded, a greater difference from the k calculated when the reverse reaction was considered. We have not calculated all of our many constants by equations 4 and 5, but enough to show their lack of constancy.

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

Summary

The classical calculations of the velocity constant in the hydrolysis of methyl acetate have been made upon the assumption of a first order 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 second order; but heretofore this 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 second order course of the reaction under these conditions.
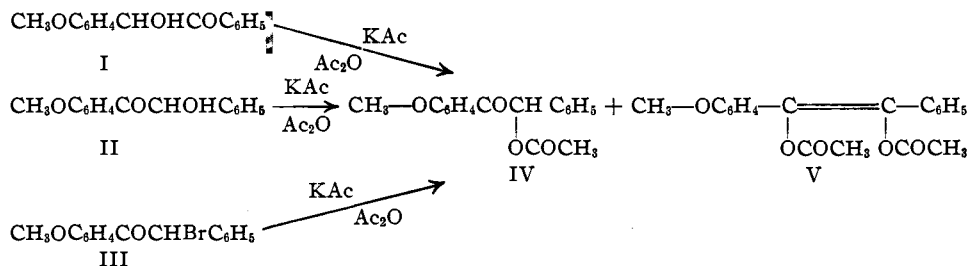
NOTES

Interconversion of Mixed Benzoins

BY R. P. BARNES AND V. J. TULANE

In view of the ease with which it has been found possible to prepare diacetates of ene-diols from benzoin and non-enolic α-bromo ketones,[1,2] we made pure anisbenzoin (I), benzanisoin (II) and anisoyl phenyl bromo-methane (III), and acetylated[1] each of these compounds. In each instance there was obtained a mixture of the monoacetate (IV) and the diacetate (V). The anisbenzoin melted sharply at 89°, the benzanisoin

modification contains a completely conjugated system, and since the CH_3O- group possesses a strong tendency toward electron release,[3,4] its mesomeric effect will give rise to a condition of electronic strain in the attached aromatic nucleus with the result that the para-carbon atom will be negatively charged and the two intermediate carbon atoms (α and β) charged positively and negatively, respectively. Thus there is created a seat for a proton on the β-carbon from the anisyl group

$$CH_3OC_6H_4CHOHCOC_6H_5 \quad \xrightarrow[Ac_2O]{KAc}$$

I

$$CH_3OC_6H_4COCHOHC_6H_5 \xrightarrow[Ac_2O]{KAc} CH_3-OC_6H_4COCH\ C_6H_5 + CH_3-OC_6H_4-C=\!\!=\!\!=\!\!C-C_6H_5$$

II

$$\overset{|}{OCOCH_3} \qquad \overset{|}{OCOCH_3}\ \overset{|}{OCOCH_3}$$

IV   V

$$CH_3OC_6H_4COCHBrC_6H_5 \xrightarrow[Ac_2O]{KAc}$$

III

at 106°. Since the mono-acetate was the same in each instance and since it hydrolyzed to benzanisoin, it is reasonable to conclude that it resulted by way of a partial hydrolysis of the diacetate.
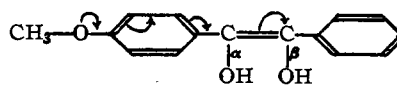
When an alcoholic solution of the diacetate was boiled for a few minutes with a few cubic centimeters of concd. hydrochloric acid an odor of ethyl acetate was produced and on cooling, the 106°-melting benzoin separated out. Thus the diacetate upon hydrolysis goes by way of the unstable ene-diol to the more stable high-melting benzanisoin in acid solution.

In this case of the ene-diol of anisbenzoin or benzanisoin there is obviously a directing influence. We believe that this influence can be explained in terms of the CH_3O- group. This ene-diolic

This molecule combines with a proton at the β-carbon

with subsequent ejection of a proton from the α-hydroxyl and regeneration of the stable benzanisoin

This mechanism lends support to the view that benzanisoin must be the stabler isomer (lower
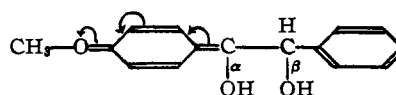
(1) R. P. Barnes and Victor J. Tulane. THIS JOURNAL, 62, 894 (1940).

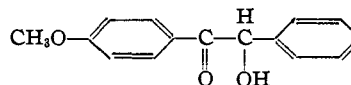(2) R. P. Barnes, Charles I. Pierce and Chappelle C. Cochrane, ibid., 62, 1084 (1940).

(3) R. Robinson and co-workers, J. Chem. Soc., 401 (1926).

(4) C. K. and E. H. Ingold. ibid., 1310 (1926).