THE KINETICS OF THE REACTION OF ISOPROPYL BENZOATE WITH HYDROXIDE ION IN ISOPROPYL ALCOHOL SOLUTION[1]

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In a study of the reaction of potassium iso, propoxide with haloforms[2] it was necessary to dry isopropyl alcohol and to establish its dryness. Since in our hands the methods of Fischer[3] and of Henle[4] for the determination of small amounts of water in alcohol proved unsatisfactory, we have modified the method worked out by Smith for the drying and determination of the water content of ethyl alcohol.[5] Smith used an excess of sodium or potassium ethoxide and diethyl succinate and for analytical purposes determined the decrease in base concentration between zero and "infinite" time, the infinite titer being determined by extrapolation. We hoped by a kinetic study to learn somewhat more about our system than Smith did about his, and to this end we used a monofunctional ester-isopropyl benzoate (if the only purpose were drying, the less volatile phthalate would probably have been a better choice[6]) that should also obviate the possibility of a competing Claisen condensation.

In this procedure a mobile equilibrium is established between water and hydroxide ions.

$$RO^- + H_2O \rightleftharpoons ROH + OH^- \qquad (1)$$

The nucleophilic alkoxide and hydroxide ions then attack the carbonyl carbon atoms of the ester much more rapidly than at any other position. Since attack by an alkoxide ion simply regenerates the reactants, only attack by hydroxide ion is detectable (without isotopic labelling). Here a molecule of the carboxylic acid is produced and neutralized

$$OH^- + R'CO_2R \longrightarrow R'CO_2H + RO^- \qquad (2)$$
$$R'CO_2H + RO^- \longrightarrow R'CO_2^- + ROH \qquad (3)$$
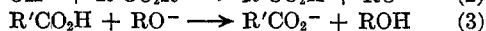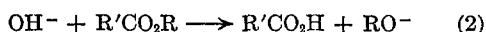
The net result of eqs. 1, 2 and 3 is to remove one molecule of water at the expense of one ester molecule and one alkoxide ion. Thus so long as any appreciable amount of water remains, the concentration of strong base in the alcohol solution falls relatively rapidly. When the water is removed, only such slow reactions as S_N2 and E2 attack[7] on the alkyl portion of the ester may occur.[8]

By waiting until the falling base concentration approached a constant value, we could have determined the water content by a method like that of Smith. However, by studying the reaction kinetics we found it possible to devise an alternate method that did not require us to wait until the reaction was almost complete. We were also able to determine the specific rate constant for the reaction of hydroxide ion with the ester, a type of datum that does not appear to have been directly determined previously.[9]

Results and Discussion

The rate-controlling step of the reaction is represented by eq. 2. Therefore for periods of time of less than a day (at 50°) where the reaction that occurs in absence of water may be neglected, we may write

$$-\frac{dB}{dt} = k[OH^-]E \qquad (4)$$

where E is the concentration of ester and B is the total strong base concentration ($[OH^-] + [RO^-]$). The equilibrium constant for eq. 1 may be expressed by eq. (5) if the large and constant concentration of the solvent is included in K.

$$K = \frac{[OH^-]}{[RO^-][H_2O]} \qquad (5)$$

From this relation the hydroxide ion concentration may be expressed

$$[OH^-] = \frac{1 + K(W + B) - \sqrt{[1 + K(W - B)]^2 + 4KB(1 + KW)}}{2K} \qquad (6)$$

where W is the total concentration of water in its two forms ($[H_2O] + [OH^-]$). Substitution of eq. 6 into 4, rearrangement and integration leads to

$$\int_{B_0}^{B} \frac{2K\,dB}{(E_0 - B_0 + B)[\sqrt{[1 + K(W_0 - B_0)]^2 + 4KB(1 + KW)} - 1 - K(W_0 - B_0) - 2KB]} = kt \qquad (7)$$

The reaction with known initial concentrations of isopropyl benzoate, water and potassium isopropoxide in isopropyl alcohol at 50° was followed by determining the strong base concentration at various times. Since K has been determined[10] as 1.2 at about 27° and since it would not be expected to be much different at 50°, we have used this figure to evaluate the integral in eq. 7 by the trapezoidal rule using a high-speed computer. The definite integrals thus evaluated were then plotted against time as shown for one run in Fig. 1. From the slopes of such lines, values of k of 8.46, 8.28, 8.48 and 8.48 (all $\times 10^{-3}$ l. mole^{-1} sec.$^{-1}$) were obtained in the presence of initial water concentrations of 0.110, 0.250, 0.260 and 0.610 M. Initial ester concentrations of 0.608 M and initial base concentrations of about 0.1 M were used and all runs were followed to at least 65% completion.

The k values obtained are the actual k's for the bimolecular attack of hydroxide ion on the ester, unlike the ordinary second-order rate constants for alkaline ester hydrolysis in an alcohol-containing solvent mixture. These latter rate constants should be multiplied by $(1 + KW)/KW$ to ob-

(1) Supported in part by the Office of Naval Research.

(2) J. Hine and K. Tanabe, *J. Am. Chem. Soc.*, **79**, 2654 (1957); **80**, 3002 (1958).

(3) K. Fischer, *Angew. Chem.*, **48**, 395 (1935).

(4) H. Henle, *Ber.*, **53**, 719 (1920).

(5) E. L. Smith, *J. Chem. Soc.*, 1284, 1288 (1927). *Cf.* also J. Koskikallio, *Suomen Kemistilehti*, **30B**, 108 (1957).

(6) *Cf.* R. H. Manske, *J. Am. Chem. Soc.*, **53**, 1106 (1931).

(7) For the meaning of the terms S_N2 and E2, see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, chaps. 5 and 7.

(8) *Cf.* J. F. Bunnett, M. M. Robison and F. C. Pennington, *J. Am. Chem. Soc.*, **72**, 2378 (1950).

(9) *Cf.* E. Tommila, A. Koivisto, J. Lyyra, K. Antell and S. Heimo, *Ann. Acad. Sci. Fennicae*, **47A**, 1 (1952).

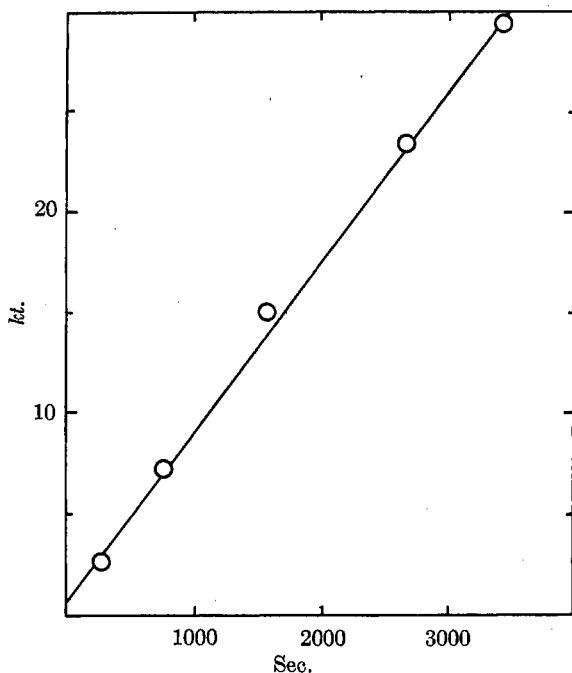(10) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

Fig. 1.—Plot of the left side of eq. 7 vs. time.

tain the true k in the common cases where $W \gg B$. This is possible, of course, only when K has been determined.[11]

It may be seen that when the concentrations of water and potassium isopropoxide are relatively small the approximations $B = [RO^-]$ and $W = [H_2O]$ are justified, so that eq. 4 leads to a simple third-order equation

$$-\frac{dB}{dt} = kKEWB \tag{8}$$

When ester is present in sufficient amounts that its concentration does not change greatly during the period of measurement, eq. 8 may be treated as a second-order rate equation and integrated to give

$$kKEt = \frac{2.303}{B_0 - W_0} \log \frac{W_0 B}{B_0(W_0 - B_0 + B)} \tag{9}$$

Thus from any point the initial water content, W_0, may be calculated (most conveniently by successive approximations). We have found it possible to calculate water concentrations with an average deviation that approaches 0.001 M at concentrations below 0.01 M and approaches about 3% at concentrations above 0.1 M. The most reliable points taken under our conditions, using an excess of base over water, should be those between about 1 and 5 hours after most of the water has reacted but before the side reaction has become important. It might be noted that from eq. 9 the concentration of water remaining in the presence of 0.5 M ester and 0.1 M base after one day at 50° should be less than one *molecule* per liter, so that essentially all of the water present in alcohol dried in this manner is that introduced while fractionally distilling the material from the flask in which it was dried into a new container, etc. With suitable

(11) For two estimates of K's see E. F. Caldin and G. Long, *J. Chem. Soc.*, 3737 (1954), and J. Kaskikallio, *Suomen Kemistilehti*, **30B**, 111 (1957).

precautions alcohols less than 0.001 M in water has been obtained.

Under suitable conditions (the principal requirement being that the alcohol be sufficiently weakly acidic) it should be possible to determine K by choosing that value which in eq. 7 gives the most nearly constant values of k. However, under many conditions eq. 7 is well approximated by an integrated form of eq. 8, from which only the product kK may be obtained.

Experimental

Reagents.—Reagent grade isopropyl alcohol was used. The final drying procedure adopted consisted of dissolving a considerable excess (over the amount of water present) of potassium in several liters of the alcohol and then adding a somewhat larger molar quantity of redistilled reagent isopropyl benzoate. After refluxing for several hours the material was fractionally distilled. All operations were carried out under dry nitrogen. In one run the white solid that precipitated during the period of reflux was isolated and shown to be potassium benzoate.

Kinetic Runs.—In a typical run, 50 ml. of potassium isopropoxide solution in isopropyl alcohol was pipetted into a 100-ml. low-actinic volumetric flask in a 50° constant temperature bath and 0.25 ml. of water added by use of a "tuberculin" syringe. At zero time, 5 ml. of isopropyl benzoate (at 50°) was added by pipet and at recorded intervals 10-ml. samples were pipetted from the reaction flask into an excess of distilled water and titrated to the phenolphthalein end-point with standard perchloric acid. Preliminary tests show that ester hydrolysis was negligible during the sample-taking period. When points were taken, a slow stream of dry nitrogen was directed at the top of the reaction flask to prevent entry of moisture from the air.

ELECTRIC MOMENTS FROM EXTRAPOLATED MIXED SOLVENT DATA. III. BENZENE-INSOLUBLE COMPOUNDS[1,2]

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Using a method of extrapolating data from mixed benzene–dioxane solvent environment to a condition of hypothetical benzene solution, results were reported in a previous paper[3] for certain compounds exhibiting different degrees of association and benzene solubility. In this paper results are given for substances whose moments cannot be determined from direct measurements in benzene solution because of insolubility. In addition, for comparative purposes, data for the slightly soluble compound p-nitroaniline are also reported. Moments for these substances derived from dioxane solution have been reported by other workers, but these may generally be expected to be too high because of abnormal solute–solvent interaction.

Experimental

Preparation and Purification of Compounds.—Benzene and dioxane solvents were purified as indicated earlier.[3]

p-**Aminobenzoic acid**, an Eastman Kodak Co. product, was recrystallized once from 20% ethanol, and then again from 10% ethanol; m.p. 187–188°.

p-**Nitrobenzamide** was prepared from p-nitrobenzoic

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(2) This work was supported by a Frederick Gardner Cottrell grant from Research Corporation, New York, N. Y.

(3) G. K. Estok and S. P. Sood, THIS JOURNAL, **61**, 1445 (1957).