illustrations, which find a place in the "five possible types" under discussion.

It seems to the writer therefore that the accepted classification of Roozeboom for the "five possible types" of solid solution formation between two components is not all inclusive, and that at least a "sixth type" must be added, to include those cases in which there is incomplete miscibility, with an equilibrium between a pure component (or compound) and a solid solution.

Summary

1. Solubility measurements are given for the system Na_2SO_4–$NaBrO_3$–H_2O at 10, 25, 30, 37.5, 45 and 52°. The two salts form no double compounds in this temperature range; but a solid solution is formed between anhydrous Na_2SO_4 and $NaBrO_3$, the composition of the solid extending from about 2% as a lower limit to about 10% $NaBrO_3$ at 37.5°, and to about 19% $NaBrO_3$ at 52°.

2. The binary system Na_2SO_4–$NaBrO_3$ therefore shows the existence of a single solid solution, at the temperatures studied, in equilibrium, not with a conjugate solid solution, but with the pure solid components. This type of solid solution formation is shown not to be impossible, and is added as a "sixth type" to the "five possible types" of Roozeboom.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

The Kinetics of the Alkaline Hydrolysis of Ethyl Carbonate and of Potassium Ethyl Carbonate

BY NEVILLE F. MILLER AND LEE O. CASE

Introduction

As a result of his studies of the rate of saponification of ethyl carbonate, Skrabal[1] concluded that the secondary reaction—the decomposition of the monoethyl carbonate—is immeasurably fast. He therefore assumed a reaction mechanism which represented the saponification of ethyl carbonate as essentially a simple second order process.

Later, however, in a series of equilibrium and kinetic investigations of the monoalkyl carbonates, Faurholt[2] showed that the decomposition of ethyl potassium carbonate proceeds with measurable speed in alkaline solution. He showed that Skrabal had erred in using the methyl orange end-point for titration of his solutions. At this acidity, ethyl potassium carbonate decomposes almost instantly. By the use of the phenolphthalein end-point in the presence of excess barium chloride the residual potassium hydroxide may be titrated without decomposition of the ethyl potassium carbonate or the barium carbonate formed. Faurholt showed also that the secondary reaction is not a true saponification, since its velocity is independent of hydroxyl ion concentration but is dependent upon alcohol concentration.

From a study of the measurements of Faurholt (which were carried out at 0° and were concerned chiefly with the monomethyl carbonate), it appears probable that the reaction mechanism governing the alkaline hydrolysis of ethyl carbonate at ordinary temperatures is essentially that of two consecutive reactions, one of the second order followed by one of the first order. Until now this has not been verified.

The results of the present investigation strongly support this hypothesis. Special interest attaches to the general mechanism indicated, since so far as can be determined it has not heretofore received detailed treatment.

The velocity constants of both reactions were measured by two distinct methods and for different concentrations at a temperature of 25°. By means of additional measurements at 35° the temperature coefficients for both reactions were determined. Since a small amount of alcohol was necessary to keep ethyl carbonate in solution, the velocity constant for the second reaction was also measured in the absence of alcohol in order to determine the effect of this factor.

Relations Involved.—Omitting ionic considerations, the following abbreviated mechanism is proposed for the sake of convenience of mathematical treatment:[3]

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[1] A. Skrabal, *Monatsh.*, **38**, 305–318 (1917).

[2] Faurholt, *Z. physik. Chem.*, **126**, 211–226 (1927).

[3] The last two equations are intended as schematic only, being mathematically equivalent to the more detailed mechanism indicated by the extensive work of Faurholt.

$$\begin{array}{llll} R_2CO_3 + KOH \xrightarrow{k_1} KRCO_3 + ROH & & & \text{slow} \\ (a-x) \quad (b-x-y) \quad (x-y) & & & \\ KRCO_3 + HOH \xrightarrow{k_2} KHCO_3 + ROH & & & \text{slow} \\ (x-y) \qquad\qquad\qquad 0 & & & \\ KHCO_3 + KOH \longrightarrow K_2CO_3 + HOH & & & \text{fast} \\ 0 \qquad\qquad\qquad\quad y & & & \end{array}$$

In terms of the instantaneous concentrations indicated below the formulas in the equations above, the differential equations governing the first two (controlling) reactions, are

$$dx/dt = k_1\,(a - x)\,(b - x - y) \qquad (1)$$

$$dy/dt = k_2\,(x - y) \qquad (2)$$

where a and b represent the initial concentrations of ethyl carbonate and potassium hydroxide, respectively.

Since no solution was found for this pair of differential equations, graphical methods were necessary. For this purpose the following equations, obtained directly from eqs. (1) and (2) were employed

$$\frac{d(x + y)}{dt} = k_1(a - x)\,(b - x - y) + k_2(x - y) \qquad (3)$$

$$\log_{10}\frac{a}{(a - x)} = \frac{k_1}{2.3}\int^{t}(b - x - y)\,dt \qquad (4)$$

There is also the identity

$$b - (b - x - y) = x + y \qquad (5)$$

Since the calculation of k_1 is greatly simplified if an approximate value of k_2 is known, the latter was measured first.

Materials Used.—The potassium ethyl carbonate was synthesized by the method used by Skrabal,[1] care being taken to remove moisture from the apparatus and all reagents. Analysis for potassium indicated the product to be 99.4% potassium ethyl carbonate.

The ethyl carbonate used was an Eastman Kodak Company product.

Determination of k_2. First Method.—In this method, mixtures of potassium ethyl carbonate with varying amounts of potassium hydroxide were allowed to titrate themselves as a "clock reaction" to disappearance of the color of phenolphthalein. Since, as previously indicated, the potassium hydroxide is not directly involved in the decomposition of potassium ethyl carbonate, the (rapid) reaction by which it disappears was employed as an "indicator" for the extent of the primary reaction.

Varying known amounts of standard 0.1 N potassium hydroxide were introduced into a series of flasks containing 6.7 cc. of pure ethyl alcohol, 2 drops of 1% phenolphthalein solution and 20 cc. of barium chloride solution (containing 27.5 g. per liter). Boiled distilled water was added to bring the total volume of each solution to 200 cc. The flasks were then corked and suspended in the thermostat.

Samples of exactly 0.1400 g. of potassium ethyl carbonate were weighed out quickly. A flask was removed from the thermostat, given a whirl so that its contents were in motion, and the ester salt brushed in, the time of adding the salt being taken as the starting point of the reaction. The flask was suspended again in the thermostat and the time required for the disappearance of the pink color was noted. A stop watch was used for the smaller titrations. The constant k_2 was found by substituting in the usual expression for first order reactions.

Table I summarizes the results of twenty-eight determinations of k_2 (natural logarithms, time in minutes) in which the initial concentration of potassium hydroxide was varied in 1 cc. steps from 1 through 10 cc. The presence of 3.3% alcohol changed k_2 very slightly.

TABLE I

DETERMINATION OF k_2. FIRST METHOD

Init. alc. concn., %	Temp., °C.	Mean value of k_2	Av. dev. of individuals from means	Max. variation from mean
3.3	25.1 ± 0.1	0.0544	±0.0006	0.0016
3.3	35.0 ± 0.1	.1788	± .0012	.0024
None	25.2 ± 0.1	.0556	± .0006	.0015

Initial concentration of $KEtCO_3$ = 0.00546 mole/liter.

Determination of k_1. First Method.—As one means of following this reaction the quantity $(b-x-y)$ representing the instantaneous concentration of potassium hydroxide was determined by a phenolphthalein titration of the reaction mixture in the presence of barium chloride.

Although ethyl carbonate is but slightly soluble in water, its alcoholic solutions may be largely diluted with water without causing the ester to separate from solution. The presence of alcohol however made necessary the procedure indicated below in order to obviate errors due to the temperature rise which occurs when alcohol is diluted with water.

The required amount of tenth normal potassium hydroxide was measured into a series of flasks. To each was added barium chloride solution containing 27.5 g. per liter, 15 cc. with the larger, 7 cc. with the smaller, concentration of potassium hydroxide used. The volume of solution in each flask was brought to exactly 75 cc. by dilution with boiled, distilled water, two drops of phenolphthalein solution were added and after corking, the flasks were suspended in the thermostat. An alcoholic solution of ethyl carbonate was prepared by weighing the required amount into a small volumetric flask and diluting with absolute alcohol. Sixty cc. of boiled, distilled water, cooled three degrees below the reacting temperature, was poured into a small beaker. To the water in the beaker 5 cc. of the alcoholic solution was added from a pipet, stirring meanwhile with a thermometer. A flask containing the alkaline solution was removed from the thermostat and when the ester solution was at the reacting temperature, it was poured into the flask, and the beaker rinsed with 10 cc. of water. The flask now contained 150 cc. of reacting mixture. The time of addition of the ethyl carbonate solution to the alkali was taken as the starting point of the reaction. The flask, which was again suspended in the thermostat, was removed and its contents titrated at the proper time, the half time of titration being taken as "t," the time of stopping the reaction. The standard hydrochloric acid solution used for the titrations was 0.1 N in the case of the higher, 0.05 N in the case of the lower alkali concentration used.

Values of k_1 were determined from these measurements as follows: the values of $(b - x - y)$ were plotted against t and a smooth curve drawn. Values of $(b - x - y)$ read from this curve were graphically differentiated and graphically integrated against t. From corresponding values of $(b - x - y)$, $\int_0^t (b - x - y)\mathrm{d}t$ and of $\mathrm{d}(x + y)/\mathrm{d}t$, it was then possible to determine by trial what value of k_1 would give values of x and y consistent with eqs. (3), (4) and (5).

The results obtained by this method appear in Table II. Data are given for two sets of initial concentration values at 25° and at two temperatures for the same concentrations. It should be noted that in each series the value of k_2 used for the calculation of k_1 was that which gave no trend to the values of k_1. For the measurements at 35° this value (0.179) was identical with the previous experimental value; for the measurements at 25°, however, it was 0.051 instead of 0.0536, the value calculated for 25° from the results of the previous work.

Figure 1 shows the variation in concentration of the reactants (with time) for the experiments at 35°.

Determination of k_2. Second Method. The following method, which makes possible independent determinations of both constants, depends upon the fact that the intermediate ester decomposes instantly in solutions acid to methyl orange. If the reaction mixture is titrated to the methyl orange end-point, the same titration is always obtained because not only is all residual potassium hydroxide titrated (which equals $b - x - y$) but also all the intermediate ester present (equal to $x - y$) and all the barium carbonate which has been formed, which equals

TABLE II

DETERMINATION OF k_1. FIRST METHOD

	$a = 0.00282$; $b = 0.00667$ Temp., 35.0 ± 0.1°			$a = 0.00282$; $b = 0.00667$ Temp., 25.0 ± 0.1°			$a = 0.00564$; $b = 0.01207$ Temp., 25.0 ± 0.1°		
t, min.	Av.[a] $b-x-y$ mole/l. × 10^3	$\int_{t=0}^{t=t}(b-x-y)\mathrm{d}t$	$\frac{\mathrm{d}(x+y)}{\mathrm{d}t}$ × 10^6	Av.[a] $b-x-y$ mole/l. × 10^3	$\int_{t=0}^{t=t}(b-x-y)\mathrm{d}t$	$\frac{\mathrm{d}(x+y)}{\mathrm{d}t}$ × 10^6	Av.[a] $b-x-y$ mole/l. × 10^3	$\int_{t=0}^{t=t}(b-x-y)\mathrm{d}t$	$\frac{\mathrm{d}(x+y)}{\mathrm{d}t}$ × 10^6
0	6.67	0		6.67	0		12.07	0	
5	6.04	0.0318	131.0						
10	5.38	.0604	122.7	6.10	0.0640	56.0	10.05	0.1100	180.0
15	4.80	.0858	101.0						
20	4.36	.1086	81.0	5.57	.1220	53.2	8.40	.2022	141.0
30	3.70	.1486	55.0	5.05	.1746	47.0	7.20	.2799	111.0
40	3.23	.1829	40.0						
50	2.87	.2133	30.5	4.22	.2664	35.9			
60	2.63	.2407	23.0	3.90	.3069	31.5	4.80	.4560	58.5
90	2.12	.3103	13.1	3.16	.4113	20.6	3.53	.5781	32.0
120	1.82	.3679	9.1	2.70[b]	.4977	12.5	2.86[c]	.6726	19.0
	Av. k_1 = 5.51; av. dev. = ±0.06 max. dev. = +0.11			Av. k_1 = 2.66; av. dev. = ±0.03 max. dev. = −0.06			Av. k_1 = 2.76; av. dev. = ±0.06 max. dev. = +0.21		

[a] Of at least two titrations. [b] Data to seven hours omitted to save space. [c] Data to three and one-half hours omitted to save space.

$2y$ in terms of standard acid. The sum of these is "b," the initial concentration of alkali.

If, however, the barium carbonate is filtered off, $2y$ is thus removed from the titration, which now measures $(b - x - y) + (x - y)$ or $(b - 2y)$.

The reaction mixtures of ethyl carbonate and potassium hydroxide were made exactly as before but at the proper time a flask was withdrawn from the thermostat and its contents filtered rapidly (with suction) into excess standard hydrochloric acid contained in the suction flask. The filter consisted of a large glass filter funnel containing two filter papers sealed against the bottom with collodion. The half time of filtration (and of neutralization by the standard acid) was taken as the time of stopping the reaction. After bubbling a rapid stream of air through the solution for several minutes, to free it from carbon dioxide, the excess acid was titrated with standard carbonate-free potassium hydroxide using methyl orange indicator.

From these titrations and the initial concentration of alkali, values of y were calculated. By graphical differentiation of the curve of y against t, corresponding values of dy/dt were obtained.

Values of x corresponding to these values of y were also required and these were obtained from the values of $(b - x - y)$ from a previous experiment for the same temperature and initial concentrations of ethyl carbonate and alkali (Table II). Finally, values of $x - y$ obtained by subtraction were substituted with the corresponding values of dy/dt in eq. (2), thus effecting calculations of k_2.

TABLE III

DETERMINATION OF k_1 AND k_2. SECOND METHOD

$a = 0.00564$; $b = 0.01207$

t, min.	Av.[a] y mole/l. × 10^3	dy/dt × 10^6	$b-x-y$ from curve of Table II × 10^3	x from curve × 10^3	dx/dt × 10^6
10	0.40	60.5	10.05	1.62	110.7
15	.72	69.0	9.21	2.12	87.5
20	1.09	72.5	8.45	2.53	70.9
25	1.44	69.6	7.80	2.86	58.0
30	1.78	65.5	7.20	3.12	48.1
40	2.37	54.5	6.25	3.52	34.5
50	2.87	44.8	5.42	3.80	25.2
60	3.27	35.5	4.80	4.01	19.8
75	3.76	25.8	4.03	4.26	14.6
90	4.08	18.6	3.55	4.46	11.1
120	4.50	11.0	2.85	4.72	7.0
150	4.76	7.4	2.40	4.89	4.8
180	4.93	4.5	2.12	5.02	3.4

Av. k_2 = 0.0498; av. dev. = ±0.0006. Av. k_1 = 2.64; av. dev. = ±0.05

[a] Average of at least two titrations.

Determination of k_1. Second Method.—From the values of x obtained as just described, corresponding values of dx/dt were calculated by graphical differentiation. Substitution in eq. (1) now gave the required values of k_1.

Temperature Coefficients, 25.0 to 35.0°.—Calculated from average values of the constants at both temperatures, the coefficients for the ten-degree interval are 2.06 for k_1 and 3.46 for k_2.

By the use of Arrhenius' equation the value of k_2 in 3.3% alcohol solution is calculated to be 0.00069 (common logarithms) at 0.0°. Faurholt found for this temperature 0.00097 and 0.00080 for 0.0 and 9.0% alcohol, respectively.

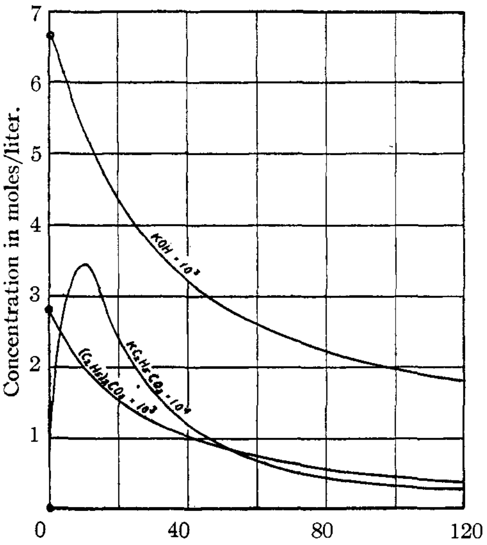

Fig. 1.—Saponification of ethyl carbonate with potassium hydroxide: $a = 0.00282$; $b = 0.00667$ mole/liter; temp., = 35.0 ± 1°.

Discussion

A discrepancy of 8% exists between the average values of k_2 found by the two methods. The higher value of the constant as determined by the first method may be due to the impossibility of completely purifying the potassium ethyl carbonate used from its hydrolysis products. It may be assumed that the value 0.051 which gave no trend to computed values of k_1 is within ±4% of the true value.

In only two cases did k_1 vary from the average value by more than 3%.

A noteworthy point about this reaction mechanism is that the curve of $(b - x - y)$ against t

has a point of inflection and its first derived curve has a maximum when $k_2/k_1 > (a + b)$, but these points disappear when $k_2/k_1 < (a + b)$ (see Fig. 2). Thus under the former condition, the rate of decomposition of the reactant increases to a maximum and subsequently decreases as in the case of an autocatalytic reaction.

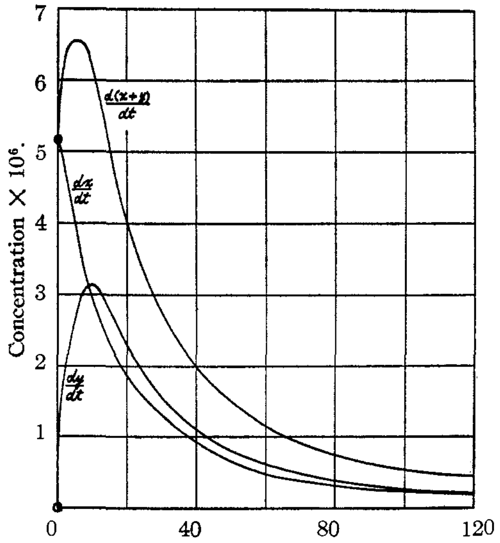

Fig. 2.—First derived curves of Fig. 1.

A further interesting point may be noted by reference to the following equation obtained by division of equation (2) by equation (1)

$$\frac{dy}{dx} = \frac{k_2}{k_1} \frac{(x - y)}{(a - x)(b - x - y)} \tag{6}$$

It is readily shown that $y = f(x)$ has a point of inflection and approaches asymptotically the line $y = x$ (see Fig. 3). Hence for the longer time periods $(dy/dx) \cong 1$ and $y \cong x$, whence from equation (6)

$$y = x - \frac{k_1}{k_2}(a - x)(b - 2x)$$

In the present instance this relation was found to hold within 5% after one and one-half to two hours.

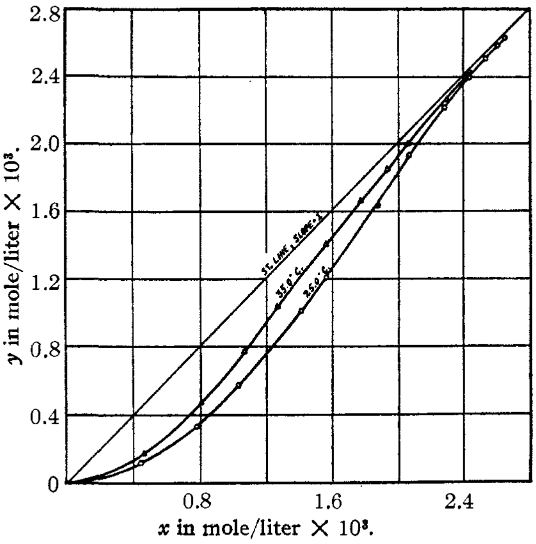

Fig. 3.—Variation of the concentration of potassium ethyl carbonate with that of ethyl carbonate.

Summary

1. The rate of the reaction between ethyl carbonate and potassium hydroxide has been measured at different initial concentrations and for two different temperatures.

2. The results confirm the hypothesis, based on the work of Faurholt, that the mechanism consists of a reaction of the second order followed by one of the first order.

3. The constants for the two consecutive reactions have each been determined by two methods which were found to be in satisfactory agreement.

4. The temperature coefficient has been computed for each reaction.

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