

## The Reaction Rate of the Alkaline Hydrolysis of Ethyl Acetate

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The reaction rate of the alkaline hydrolysis of ethyl acetate was studied by means of a continuous measurement of the electric conductivity change. The second-order rate constant decreased as the reaction proceeded. The decrease was evident when the initial concentrations of the ester and the base were close together. The initial rate constant at 25°C was measured as 0.1120 l./mol./sec. and the activation energy was 11.56 kcal./mol., values agreed well with those of previous studies. From the standpoint of the electronic theory of organic chemistry, Day and Ingold proposed a sequential reaction mechanism passing through an addition complex. The results of the approximate calculations to the pseudo-first-order reaction and the analog-computation of the exact models coincided with the experimental results. The difference in the activation energies of the forward and reverse reaction rates was calculated from the experimental data. At lower temperatures this reverse reaction rate was small, and the overall reaction rate was approximated as a pure second-order reaction. Other probable reasons for the rate constant decrease were also discussed.

The reaction rate of the alkaline hydrolysis of ethyl acetate has been well established to be a second-order reaction, and the mechanism has been discussed in detail.<sup>1)</sup>

For the study of the performance of a flow-type stirred tank reactor, we carried out the hydrolysis reaction in it and analyzed the flow pattern in the reactor from the yield of the reaction. However, during the experiments, we found that the hydrolysis reaction could not satisfactorily be expressed as a second-order reaction. It was necessary to analyze the reaction rate more carefully. Therefore, we measured and analyzed the rate of the hydrolysis of ethyl acetate continuously. We will discuss the mechanism of the reaction kinetically.

### Experimental

**Apparatus.**—The reaction was carried out in a batch-type reactor, and the electric conductivity of the reacting solution was measured with the time. The main apparatus is shown in Fig. 1. A 2-l. polyethylene beaker was used as the reaction vessel instead of a glass one, because in the case of a glass vessel some alkaline ions dissolved from the wall and so disturbed the exact measurement of the reaction rate.

During the reaction hydroxide ions are consumed and acetate ions are produced. This change in ion concentration results in a conductivity change in the solution, and by the measurement of this conductivity we could ascertain the degree of saponification.

The electrode used is shown in Fig. 2; it is set horizontally near the turbine so that the reactant flows thoroughly in it. The electrical circuits of the measuring system is shown in Fig. 3. A 0.8 V. a. c. current of

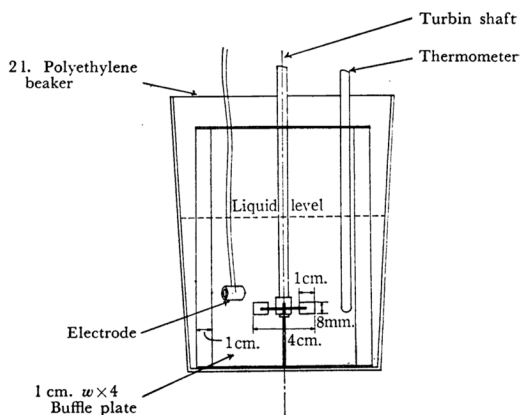


Fig. 1. The Experimental apparatus.

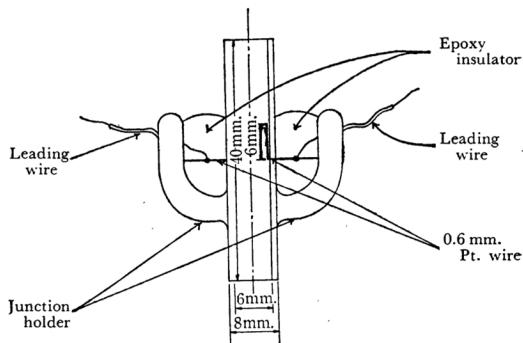


Fig. 2. The electrode.

1000 c/s is added at the electrode + a 5-ohm resistor in series. The voltage between the two sides of the resistor is amplified, converted into d. c., and recorded

1) M. L. Bender, *Chem. Revs.*, **60**, 53 (1960).

on a recording ammeter. Generally, the input-output characteristics of a diode are not linear, so the relation between the output current and the  $\text{OH}^-/\text{CH}_3\text{COO}^-$  ratio must be calibrated.<sup>2)</sup> However, the negative feeding-back of the converted d. c. current to the intermediate part of the amplifier (the 15 kilohm resistor and 10 microfarad condenser circuit of Fig. 3) forms a linear relationship between the current and the concentration ratio, as is shown in Fig. 4. By comparing the line in Fig. 4. with the conductivity of the reacting solution, in which the total concentration of  $\text{OH}^-$  and  $\text{CH}_3\text{COO}^-$  was about 0.02 N, we can calculate the degree of hydrolysis with the time.

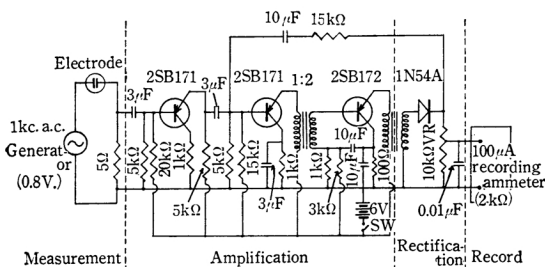


Fig. 3. The electric circuit for the electro-conductivity measurement.

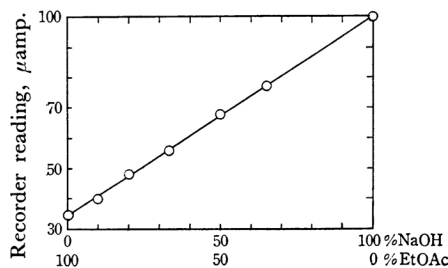


Fig. 4. The relationships between the ammeter reading and the reaction proceeding.

- Total concentration of  $\text{Na}^+ = 0.0200$  mol./l.
- The ammeter was set  $100 \mu\text{amp.}$  for 100% NaOH

**Procedure.**—A sodium hydroxide solution was prepared by dissolving sodium hydroxide (made by the Wako Pure Chemicals Co., Ltd., G. R. grade) in ion-exchange water with a relative resistance of more than  $2 \times 10^6$  ohm-cm. The concentration was checked by an automatic titrator using a 0.1 N standard hydrochloric acid solution. Ethyl acetate (made by the Osaka Organic Chemicals Co., Ltd., G. R. grade) was used without any special processing; it yet gave a mean equilibrium conversion of 97%, which agrees with the theoretical equilibrium conversion.

To start the reaction, 994 ml. of a 0.02 N sodium hydroxide solution was poured into a beaker dipped in a water bath, and then vigorously stirred for more than 30 min., after which a definite volume of ethyl acetate was added to the solution under the stirring. The tem-

perature of the mixture was kept constant during the reaction within a range of  $\pm 0.1^\circ\text{C}$ .

Ethyl acetate dissolved into water within 10 sec., so the mixing time of the ester was negligible in comparison with the reacting time. During the reaction the conductivity of the solution was recorded continuously, and the degree of conversion was calculated. A small portion of the solution was sampled during the reaction and was acidified to stop the reaction rapidly; by the backtitration of the acid, the remaining hydroxide ions in the reacting system were determined. The concentration of hydroxide ions, as determined by this titration agreed well with that calculated from the conductivity measurements of the solution.

## Results

Some results are shown in Fig. 5, where the concentration change is plotted as  $(c_B - x_0)/(c_{A_0} - x)$  against the reaction time. The circled points in Fig. 5 stand for the experimental values, while the straight line in the figure shows the theoretical relation derived from the second order rate equation.

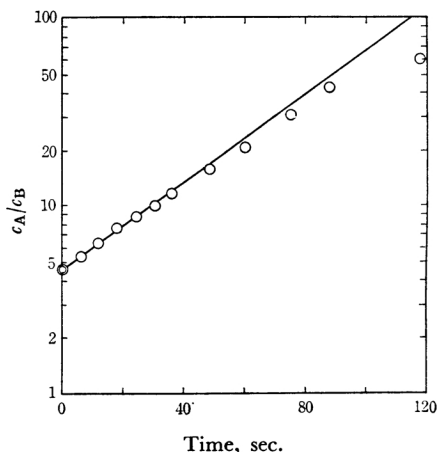


Fig. 5. Semi-logarithmic plot of experimental results.

Exptl. No.	R-27	$c_{A_0}$	0.09897 N
Temp.	$40.7^\circ\text{C}$	$c_{B_0}$	0.02104 N
$k_1$ obsd.	0.337 l./mol. sec.		

If the reaction is expressed as that of a complete second-order reaction, all the experimental values must be on the line. However the points obtained from the experiments deviate downwards from the linear relation. The deviation of the rate from the second-order rate equation becomes more remarkable as the initial concentrations of base and ester draw closer to each other.

Previous works on this kinetics did not analyze the rate in detail; usually only the mean initial rate constant has been obtained. The deviation from the second-order rate equation has never been analyzed in detail kinetically. Indeed, no such deviation has even been actually observed in the initial rate of the hydrolysis.

2) D. G. Flom and P. J. Elving, *Anal. Chem.*, **25**, 541 (1953).

We measured the initial rate constant by the addition of different amounts of the ester, and observed the rate constant independent of the concentration of the ester. These results coincided with those of previous works on the second-order rate equation. They are shown in Fig. 6, along with the inverse of the absolute temperature,  $1/T$ . The calculated activation energy of 11.56 kcal./mol. agrees well with those obtained in previous works; the rate constant at 25°C, 0.1125 l/N-sec., also agrees with them.<sup>3-6)</sup>

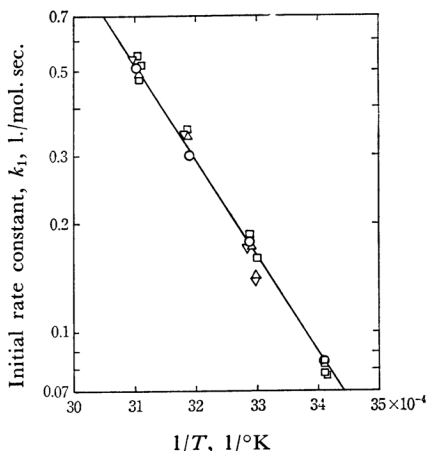
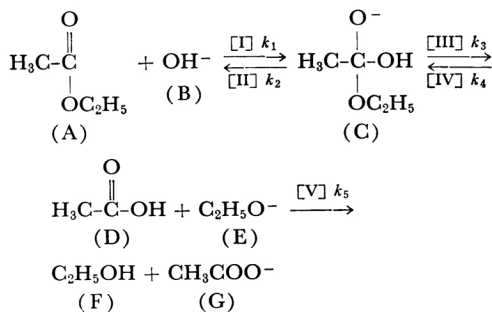


Fig. 6. The Arrhenius plots of the initial rate constants.

- $c_{A_0}$  about 0.02 mol./l.
  - $c_{A_0}$  about 0.05 mol./l.
  - △  $c_{A_0}$  about 0.10 mol./l.
  - ▽  $c_{A_0}$  about 0.25 mol./l.
- $E = 11.56$  kcal./mol.

### Analysis and Discussion

The mechanism of the basic hydrolysis of ester has been discussed hitherto, and it is well known that the mechanism may be expressed by the following reaction scheme:



This mechanism of the basic hydrolysis of esters was proposed by Day and Ingold.<sup>7)</sup> and since analyzed by Bender,<sup>8)</sup> Swarts,<sup>9)</sup> and many other investigators.<sup>1)</sup> However, these studies were mainly from the viewpoint of organic chemistry; no detailed kinetic analysis of the hydrolysis of ethyl acetate has ever been made. Usually the reaction has been considered to be a second-order form, but, according to the above mechanism, the second-order rate equation is applicable only when the concentration of the addition complex C is very small and when the reverse reaction rate is negligible in comparison with the forward reaction rate.

In general, the total reaction path may be expressed by the following mathematical equations:

$$\frac{dc_A}{d\theta} = \frac{dc_B}{d\theta} = -k_1c_Ac_B + k_2c_C \quad (1)$$

$$\frac{dc_C}{d\theta} = k_1c_Ac_B - (k_2 + k_3)c_C + k_4c_Dc_E \quad (2)$$

$$\frac{dc_D}{d\theta} = \frac{dc_E}{d\theta} = k_3c_C - (k_4 + k_5)c_Dc_E \quad (3)$$

$$\frac{dc_F}{d\theta} = \frac{dc_G}{d\theta} = k_5c_Dc_E \quad (4)$$

where  $c$  means the concentrations of chemical compounds or ions, and where the suffixes A, B, C, ... denote the compounds or ions shown above. The  $k$ 's indicate the reaction rate constants;  $k_1$  and  $k_2$  are the rate constants for the forward and reverse reactions of  $A + B \rightleftharpoons C$ ,  $k_3$  and  $k_4$  are the rate constants of the forward and reverse reactions of  $C \rightleftharpoons D + E$ , and  $k_5$  is that of the  $D + E \rightarrow F + G$  reaction. The reaction rates were assumed to be proportional to the concentrations of all the reacting compounds.  $\theta$  denotes the time.

The deviation from the second-order rate form which we observed seems to give the key to the analysis of the mechanism of the reaction. As the reaction proceeds, the concentration of the ester and hydroxide ions become very small; the effect of the reverse reaction rate of the addition complex on the total rate will therefore become remarkable.

Of course, there are many possible causes of the deviation of the rate from the second-order form. The  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$  equilibrium suggests the reverse reaction of the products. However, the deviation of the rate could not be due to this effect for the following reasons. According to the effect of this reverse reaction, the overall reaction rate would be retarded by the addition of the reaction product. We measured the reaction rate in the presence of

3) S. Lee and H. Kawakami, *Kogyo-Kagaku Zasshi*, **43**, 551 (1940).

4) J. Murto, *Chem. Abstr.*, **55**, 24549 d (1961).

5) E. Tommila, *ibid.*, **40**, 4591<sup>4</sup> (1946); E. Tommila and S. Hietara, *ibid.*, **48**, 11888 e (1954).

6) H. A. Smith and H. S. Levenson, *J. Am. Chem. Soc.*, **61**, 1172 (1939).

7) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

8) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951).

9) F. Swarts, *Bull. soc. chim. Belges*, **35**, 414 (1926).

sodium acetate or ethanol. The addition of the products actually retarded the overall reaction rate, but it is too small to illustrate the deviation from the second-order form. Experimentally the deviation is most remarkable when the concentrations of the ester and the base are close. We tried to estimate the rate constant of the reverse reaction by making an analysis using an analog computer, this gave a good coincidence with the experimental results, but we could not obtain the rate constant independent of the change in the ester concentration.

Moreover, the salt effect of the sodium acetate produced, the solvent effect of the ethanol produced, and other effects due to the decrease in the concentration of the reactants were discussed and checked by experiments, although we could not illustrate the deviation of the reaction rate satisfactorily.

To analyze the above reaction path, it is necessary to solve the mathematical equations, 1, 2, 3, and 4, but it would be meaningless to solve the whole system by assuming many rate constants arbitrarily. It seems to be more reasonable to assume the following approximations, which are based on the usual consideration of ionic reactions. First, the rate of the reaction IV is very slow and negligible compared to the rate of the reaction III. Second, the reaction V is regarded to be very rapid.

Therefore, the overall reaction may be expressed more simply as follows:

$$\frac{dc_A}{d\theta} = \frac{dc_B}{d\theta} = -k_1c_Ac_B + k_2c_C \quad (1)$$

$$\frac{dc_C}{d\theta} = k_1c_Ac_B - (k_2 + k_3)c_C \quad (2')$$

$$\frac{dc_F}{d\theta} = \frac{dc_G}{d\theta} = k_3c_C$$

If the stationary state approximation is applied, the overall rate may be written:

$$\frac{dc_A}{d\theta} = -k_1 \left(1 - \frac{1}{k_2 + k_3}\right) c_Ac_B$$

and expressed as a second-order rate equation such as was obtained experimentally at the initial stage of the reaction.

However, as the concentration of the reactants becomes small, the balance of the addition complex concentration is gradually broken and the process is not expressed by the approximation any more. This discussion does not necessarily depend on the assumption of the existence of a large amount of the addition complex, but it does depend on the relative scale of  $k_1c_A$ ,  $k_2$ , and  $k_3$ .

Without the stationary state approximation, Eqs. 1 and 2' are not solved analytically because of their nonlinearity.

If  $c_A \gg c_B$ , then the change of  $c_A$  on the right

hand of Eqs. 1 and 2' can be neglected and the equations can be approximated as:

$$\frac{dc_B}{d\theta} = -k_1c_{A_0}c_B + k_2c_C \quad (1')$$

$$\frac{dc_C}{d\theta} = k_1c_{A_0}c_B - (k_2 + k_3)c_C \quad (2'')$$

The initial conditions are:

$$\theta = 0 \quad c_B = c_{B_0} \quad c_C = 0 \quad (5)$$

$$\frac{dc_B}{d\theta} = -\frac{dc_C}{d\theta} = -k_1c_{A_0}c_{B_0}$$

The solutions are:

$$c_B = \frac{k_1c_{A_0}c_{B_0} - (\alpha - \beta)c_{B_0}}{2\beta} e^{-\alpha\theta} + \frac{-k_1c_{A_0}c_{B_0} + (\alpha + \beta)c_{B_0}}{2\beta} e^{-\beta\theta} \quad (6)$$

$$c_C = \frac{k_1c_{A_0}c_{B_0}}{2\beta} (e^{-\alpha\theta} - e^{-\beta\theta}) \quad (7)$$

where:

$$\alpha = (k_1c_{A_0} + k_2 + k_3)/2 \quad (8)$$

$$\beta = (\alpha^2 - k_1c_{A_0}k_3)^{1/2} \quad (9)$$

Fig. 7, where the experimental results when  $c_A - c_B$  are plotted on semi-logarithmic graph paper, shows that the whole process may be expressed by two straight lines, at the initial and final stages. These results coincide with Eqs. 7.

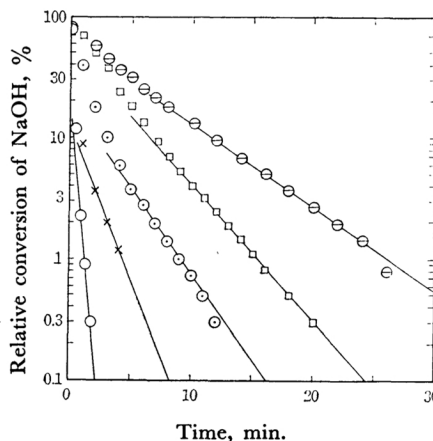


Fig. 7. Observation of  $\alpha - \beta$  using the thermal rates of the reaction (temp. 30.5~30.7°C).

Initial ester concentration

- 0.01985 mol./l.
- 0.04959 mol./l.
- ⊙ 0.09897 mol./l.
- × 0.24211 mol./l.
- 0.48422 mol./l.

Here let us survey the meaning of the time constants,  $\alpha + \beta$  and  $\alpha - \beta$ .  $\beta$  has a rather complicated form, but noting  $\alpha \gg k_1k_3c_{A_0}$  and using the Taylor expansion:



$(1-x)^{1/2} = 1 - x/2 - x^2/8 + x^3/16 - x^4/128 + \dots$   
 $\beta$  reduces to:

$$\beta \doteq \frac{k_1 c_{A_0} + k_2 + k_3}{2} - \frac{k_1 k_3 c_{A_0}}{k_1 c_{A_0} + k_2 + k_3} \quad (10)$$

Consequently:

$$\alpha + \beta \doteq k_1 c_{A_0} + k_2 + k_3 - \frac{k_1 k_3 c_{A_0}}{k_1 c_{A_0} + k_2 + k_3} \\ \doteq k_1 c_{A_0} + k_2 + k_3 \quad (11)$$

$$\alpha - \beta \doteq \frac{k_1 k_3 c_{A_0}}{k_1 c_{A_0} + k_2 + k_3} = \frac{1}{1/k_3 + \frac{1}{k_1 c_{A_0}} \left(1 + \frac{k_2}{k_3}\right)} \quad (12)$$

If  $k_3 \gg k_1 c_{A_0}$  then:

$$\alpha - \beta \doteq \frac{k_1 c_{A_0}}{1 + k_2/k_3} \quad (13)$$

This is the time constant at the final stage of the

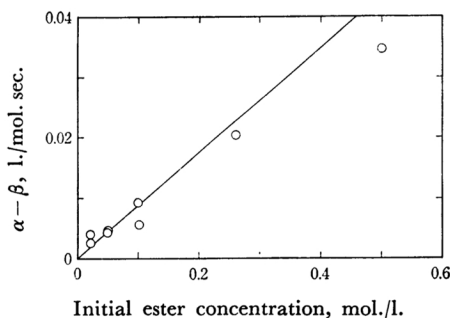


Fig. 8. The terminal reaction rate constants  $\alpha - \beta$  (30.5–30.7°C)

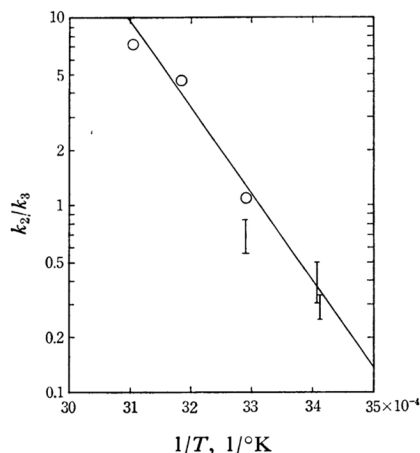


Fig. 9. The calculated values of  $k_2/k_3$ .

- Means of all experiments
- Range of the calculated values for typical experiments (Calculated with an analog computer)

The difference of the activation energy  $E_{k_2} - E_{k_3} = 20$  kcal./mol.

reaction. The experimental measurements of  $\alpha - \beta$  at 30°C are shown in Fig. 8. The  $k_2/k_3$  values are calculated from Eqs. 11 at 30, 40, and 50°C and are shown in Fig. 9. The difference in the activation energies,  $k_2$  and  $k_3$ , is obtained as 20 kcal./mol. from Fig. 9.

At lower temperatures,  $k_2/k_3$  is small and the overall reaction rate is regarded as a second-order reaction, as usual.<sup>10</sup>

**The Confirmation of the Mechanism by an Analog Computer.**—In order to confirm the above-mentioned mechanism at low concentrations of ester and base, Eqs. 1 and 2' were solved directly by an analog computer. The boundary conditions were:

$$\theta = 0 \quad c_A = c_{A_0} \quad c_B = c_{B_0} \quad c_C = 0 \quad (14)$$

The block diagram for the calculation is shown in Fig. 10. The "experimental chart reader" in Fig. 10 is used to read the results of the experiments into the computer and to compare them with the calculated results. An example of the calculation is shown in Fig. 11. In this calculation we must assume  $k_2$  and  $k_3$  respectively; the curve shown in Fig. 11 is an example. However, the main part of the curve is determined by the  $k_2/k_3$  ratio, as may be understood from Eqs. 13; the absolute values of  $k_2$  and  $k_3$  in the reacting system could not be determined independently.

The calculated curve can be matched within a 3% error with such experiments.

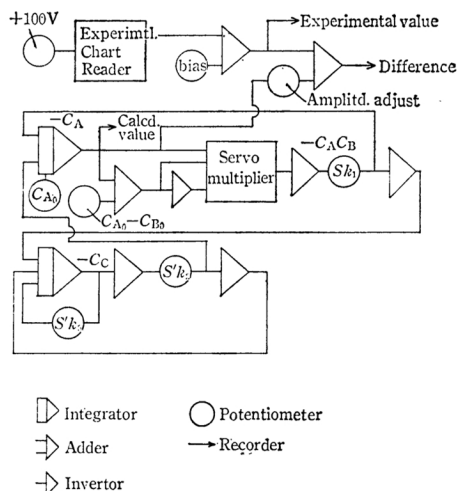


Fig. 10. The analog computer circuit for the calculation.

Calculation rate

$$c_A, c_B \quad 1 \text{ mol./l.} = 4000 \text{ V.} \\ \text{time} \quad 1 \text{ min.} = 1.078 \text{ sec.} \\ S(\text{time scale factor}) = 1.078 \\ S'(\text{time, concentration scale factor}) = 1.078/4000$$

10) J. D. Potts, Jr., and E. S. Amis, *J. Am. Chem. Soc.*, **71**, 2112 (1949).

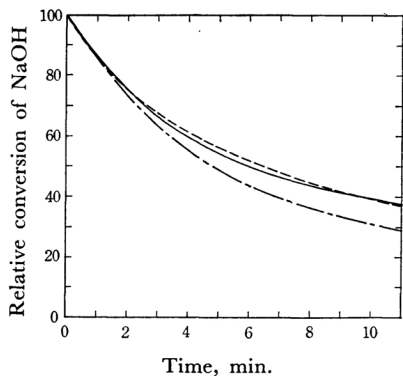


Fig. 11. Comparison of the experimental and the calculated curves of the reaction.

- Experimental
- - - Theoretical as the pure 2nd order reaction.
- . - . Calculated with an analog computer ( $k_2=2.0$ ,  $k_3=7.21$ /mol. sec.)

### Conclusion

It has been observed that the reaction rate of the basic hydrolysis of ethyl acetate is not expressed satisfactorily by a second-order rate equation, and it has been proved, from the kinetic analysis of the reaction rate, that the mechanism of the hydrolysis is the sequential reaction process through the addition complex. We have obtained  $k_1$  and  $k_2/k_3$  values for several temperatures. These results correspond well with the conclusion obtained in the general nucleophilic reaction of carboxylic acid derivatives,<sup>11)</sup> though the difference between the activation energies for  $k_2$  and  $k_3$  is too large in comparison with the results obtained by the hydrolysis of ethyl benzoate.<sup>11)</sup> This may be due to the approximation used to get  $\alpha-\beta$  from the experimental data.

11) M. L. Bender, R. D. Ginger and J. P. Unik, *J. Am. Chem. Soc.*, **80**, 1044 (1958).