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159. **Kazuya Kunugi** : Studies on the Syntheses of Sucrose Fatty Acid Esters. IV. Velocity of Alcoholysis Reaction.

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Generally, one of the most important factors in the process of chemical change is the speed with which it takes place, the velocity of the reaction. Obviously, the economic success of a chemical process must depend, in great measure, on the rate at which the product is formed. In the case of the syntheses of sucrose esters, the study of chemical kinetics, or the velocity of the reaction is also of great importance in industry. From the industrial aspect, it supplies a fundamental data for designing the apparatus, *e.g.*, the fractionating column.

Osipow, *et al.*,1) developed a method for the alcoholysis of methyl ester of fatty acid with sucrose to synthesize sucrose fatty acid esters, and the reaction was completed by elimination of methyl alcohol formed during reaction through a fractionating column.

Concerning with the reaction rate of this synthesis, almost no report is available in the literature, especially in the case of the reaction to eliminate methyl alcohol. Osipow, *et al.*,2) performed an equilibrium and a rate study about only one reaction using a ratio of three moles of sucrose to one mole of methyl stearate at 90°, without vacuum, and tried to obtain the equilibrium consant. In this study, many factors were considered separately, *e.g.*, the reaction of sucrose with methyl stearate, of monostearate with methyl stearate or of sucrose with distearate, etc. However, owing to the complication of the reactions, successful data was not obtained.[*2]

The author attempted to investigate the velocity of alcoholysis reaction at various molar ratios with respect to the standard procedure, but not to the reaction reached to equilibrium. The velocity constant was obtained by simplifying the interpretation of the reaction as described later.

In general, most bimolecular reactions are considered to be of the second order. If C_a and C_b are the initial concentrations of the reactants, and if C_x is the amount changed at any given time t, the velocity of reaction k is given by the following expression,

$$\frac{C_a-C_b}{2.303}kt=\log\frac{C_b(C_a-C_x)}{C_a(C_b-C_x)} \qquad (1)$$

If the volume of the system V(L.) is constant, the amount of the reactants a, b, and x (moles) can be used instead of C_a, C_b, and C_x, and the equation (1) is written as follows :

$$\frac{a-b}{V}\cdot\frac{k}{2.303}t=\log\frac{b(a-x)}{a(b-x)} \qquad (2)$$

In a certain bimolecular reacion, if a straight line is obtained by a graphic method in which t is plotted against $\log\frac{b(a-x)}{a(b-x)}$, it is proved to be of the second order, and k

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[*2] Various constants were obtained under various assumptions.

1) L. Osipow, *et al.* : Ind. Eng. Chem., **48**, 1459 (1956); J. Am. Oil Chem. Soc., **34**, 185 (1957).

2) *Idem* : "Progress reports, thirteenth quarters, to Suger Research Foundation on detergents from sugar." p. 14, F.D. Snell INC, New York, N.Y. (1956).

can be obtained from the slope of the line. In this case, k must be constant for any combination of a and b.

Methyl stearate were alcoholized by sucrose in dimethyl formamide at various molar ratios. When the alcoholysis reaction was analyzed from above point of view, it was regarded to be a bimolecular reaction between hydroxyl and stearoyl radicals. In fact, methyl stearate will react not only with sucrose but also with various partially-substituted stearates of sucrose produced. However, as described in the previous paper[*3] concerning with the random distribution rule, the reacted acyl radicals may migrate. Thus, the interpretation of this reaction can be simplified by the consideration that methyl stearate will react with free hydroxyl radicals instead of molecules of sucrose and its derivatives.

Table I. Amounts Neccessary for Analysis of Reaction Rate (cf. equation (2))

No.		1	2	3	4	5
Initial sucrose	[s] (mole)	0.6	0.5	0.2	0.15	0.10
Initial OH group	[a] (mole)	4.8	4.0	1.6	1.20	0.80
Initial methyl stearate	[b] (mole)	0.3	0.5	0.4	0.45	0.50
Average volume of reaction mixture	[V] (L.)	1.23	1.33	0.70	0.68	0.68

The initial amounts of sucrose and, in consequence, hydroxyl groups, the initial amounts of methyl stearate and the volumes of the systems are shown in Table I. In this table, an initial amount of hydroxyl groups were $8s$ (moles), where s (moles) was an initial amount of corresponding sucrose, assuming that sucrose had eight reactive hydroxyl radicals in a molecule.
That is :

$$a=8s \qquad (3)$$

Although the volume of the system must be constant, it decreased gradually as a result of stripping methyl alcohol with dimethylformamide. However, as the decrease of the volume was relatively small, only negligible error was regarded to be occurred and the volume was assumed to be unchanged, and so, in Table I, average volumes during reactions were given for values of V.

During the reaction the amount of methyl alcohol formed and stripped out of the system was observed once per hour. Data were shown in Table II.

Table II. Amounts (moles) of Methyl Alcohol distilled off during Reaction

Period (hr.) \ No.	1	2	3	4	5
1	0.206	0.206	0.206	0.198	0.155
2	0.274	0.371	0.314	0.309	0.270
3	0.290	0.447	0.354	0.367	0.346
4	0.300	0.476	0.370	0.395	0.389
5		0.491	0.377	0.415	0.420
6		0.499	0.380	0.426	0.440
7			0.382	0.438	0.464
8			0.385	0.444	0.497
Methyl stearate used (mole)	0.3	0.5	0.4	0.45	0.5

From a and b in Table I, and x corresponding to the amount of methyl alcohol in Table II, t was plotted against $\log\frac{b(a-x)}{a(b-x)}$ graphically according to equation (2). As shown in Fig. 1, the straight line was obtained in every case. In order to obtain the

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[*3] Part III : This Bulletin, **11**, 486 (1963).

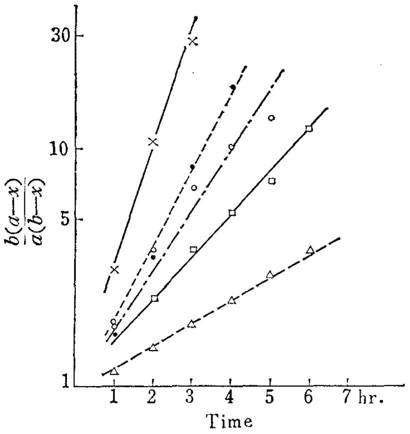

Fig. 1. $\log \frac{b(a-x)}{a(b-x)}$ versus t

No.	1	2	3	4	5
$\frac{\text{sucrose}}{\text{methyl stearate}}$ molar ratio	2	1	½	⅓	⅕

—×———×— No. 1
—•– – – –•— No. 2
—○– – – –○— No. 3
—□———□— No. 4
—△– – – –△— No. 5

slopes of these lines, the method of least squares was applied to the experimental results.

When a slope of the line was K, following relation was derived from equation (2) :

$$K=\frac{a-b}{V}\cdot\frac{k}{2.303} \qquad (4)$$

K, and k obtained from (4), are shown in Table III.[*4]

Table III. Velocity Constant (k) at a Various Molar Ratio (cf. equation (4))

No.	1	2	3	4	5
$\frac{\text{sucrose}}{\text{methyl stearate}}$ molar ratio	2	1	½	⅓	⅕
K	0.490	0.324	0.260	0.172	0.077
$\frac{a-b}{V}$	3.66	2.64	1.71	1.10	0.44
k	0.31	0.28	0.35	0.36	0.40

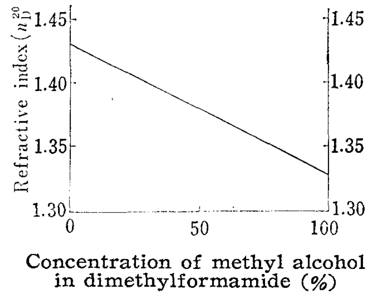

Fig. 2. Calibration Curve, Concentration of Methyl Alcohol *versus* Refractive Index

It was concluded that the alcoholysis reaction of methyl stearate by sucrose was of the second order. The velocity constant was 0.3~0.4 L. mole^{-1} hr^{-1}.

[*4] Although it was assumed in above discussion that sucrose had eight reactive hydroxyl radicals in a molecule, there remained a question in this assumption as reported in the previous paper of this series. However, the following fact can be suggested. On this assumption, the velocity constant gave a good accordance for the wide range of molar ratios as shown in Table III. On the other hand, if it was assumed that less, *e.g.*, six hydroxyl radicals in sucrose were reactive, the velocity constant calculated from the data of No. 5, in which the molar ratio of sucrose/methyl stearate was 1/5, was much larger than the velocity constant obtained from other conditions. Therefore, it was regarded that the assumption of eight reactive hydroxyl radicals had more wide validity.

Experimental

Alcoholyses Reactions——The amounts of sucrose and methyl stearate used in each reaction were shown in Table I. The initial volume of dimethylformamide in each reaction was about three times of the amounts of sucrose plus methyl stearate. Six grams of K_2CO_3 was used as catalyst in each reaction. The mixture of four components was dissolved in a flask equipped with a fractionating column, and boiled under 90 mm. ±5 of mercury pressure. MeOH formed during reaction was stripped out of the system through the fractionating column.

Measurements of the Amounts of Methyl Alcohol——The amounts of MeOH distilled off were measured once per hour during a reaction. Each distillate was a solution of MeOH in dimethylformamide. To determine the content of MeOH, the weight and the refractive index of a solution were measured. As the refractive index of the solution of MeOH in dimethylformamide has the additional nature, the concentration of MeOH in the distillate can be determined from the refractive index. The calibration curve was given in Fig. 2, and the experimental results were shown in Table II.

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Summary

Concerning with the alcoholyses reactions of methyl stearate by sucrose, rate study was carried out. Sucrose and methyl stearate were alcoholized in dimethylformamide at various molar ratios. The rates of reactions were analyzed assuming that they were of the second order, and the validity of this assumption was proved. The velocity constant at any molar ratio gave a good accordance and was determined to be 0.3~0.4 L. $mole^{-1}$ hr^{-1}.

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