Kinetics of Esterification of Isobutyl Alcohol with Palmitic Acid Using Sulfuric Acid Catalyst

Kinetics of esterification of isobutyl alcohol with palmitic acid was studied using sulfuric acid catalyst in a batch reactor. The reaction was found to be first order with respect to palmitic acid. The effects of catalyst concentration, initial reactant ratio, and temperature on the rate constant were studied. The proposed rate equation fits the experimental data within 5% error.

Isobutyl palmitate is one of the most important industrial compounds used in plastics, cosmetic, and paint industries. Loury and Mellier (1947) have studied the esterification reaction between palmitic acid and methyl and ethyl alcohols using sulfuric acid at 18–20°, but there is no published kinetic data for the esterification reaction between isobutyl alcohol and palmitic acid using sulfuric acid catalyst. It is the purpose of this investigation to study the kinetics of this reaction and to develop a rate equation useful for the design of a batch reactor for the production of isobutyl palmitate.

Experimental

Materials. Analar grade (British Drug House, India) isobutyl alcohol and CP grade palmitic acid (Calcutta Chemical Co., India) were used directly. The physical properties were compared with the literature values in Table I.

Procedure. The required amounts of the reactants were weighed into the reaction flask which was slightly warmed to make the palmitic acid completely soluble in the alcohol. The investigation was confined to reaction mixtures of C_{Bi}/C_{Ai} greater than one because palmitic acid is insoluble at $C_{Bi}/C_{Ai} \leq 1$, even after slight warming. The density of this reaction mixture was determined at 35° and is given in Table II. The reaction flask was then placed in an oil bath which was already maintained at the desired temperature and the assembly of this stirred batch reactor was completed. The temperature was maintained at ±0.01° by a temperature controller. When the temperature of the reaction mixture reached the desired value, which took about 1 hr, the required amount of sulfuric acid was added to the reaction mixture. The samples were then withdrawn at regular intervals, counting the time when the first sample was withdrawn as zero time. The samples were then chilled in ice cold water to arrest the reaction and the sample tubes were tightly stoppered.

Isobutyl alcohol and water form an azeotrope at about 89°. As the quantity of alcohol distilled over and collected was small, continuous recirculation of alcohol was not possible. In order to maintain constant composition, alcohol equivalent to the quantity distilled over, was added immediately after the sample was collected.

Analysis. The samples were titrated with a standard alkali using phenolpthalein, this titer value giving the total acidity due to palmitic acid and sulfuric acid. This titer value was corrected for the sulfuric acid from a knowledge of the weight of sulfuric acid added. The final titer value corresponds to palmitic acid alone and was used in the calculation of concentration of palmitic acid.

Results and Discussion

The order of the reaction with respect to palmitic acid was determined by taking isobutyl alcohol in large excess (run 6). Differential method used to find the order of the reaction with respect to palmitic acid gave the order to be 0.97 (Figure 1). The data of run 6 fitted the integrated rate equation (eq 1) for first order with respect to palmitic acid (Figure 2) well. The integrated rate equations used in this investigation are

$$k_{1A}'t = \ln [C_{A0}/C_A] \tag{1}$$

(first order with respect to palmitic acid)

$$k_{2A}'t = [(1/C_A) - (1/C_{A0})] \tag{2}$$

(second order with respect to palmitic acid)

The experimental data for the various runs made to study the effects of catalyst concentration, initial reactant ratio, and temperature on the rate constant k are given in Table II. In all the runs except runs 8, 9, and 10, the water of reaction was removed azeotropically making the reaction irreversible. The effect of catalyst concentration on the rate constant was

Table I. Physical Properties of Materials Used

	Exptl	Lit.
Isobutyl Alcohol		
Normal bp, °C	107.7	107.9[c]
Refractive index,[a] $n^{35}D$	1.3922	1.3923[b,c]
Density at 35°, g/ml	0.7899	0.7906[b,c]
Palmitic Acid		
Mp, °C	60.7	62.9[d]
Acid value	217.1	218.8[d]
Saponification value	216.9	

[a] Determined with Abbe refractometer. [b] Corrected for temperature. [c] Bailey, "Industrial Oil and Fat Products," Interscience, New York, N.Y., 1964. [d] Weissberger, A., Proskauer, E. S., Riddick, J. H., Toops, E. E., "Organic Solvents," 2nd ed, Interscience, New York, N.Y., 1955.

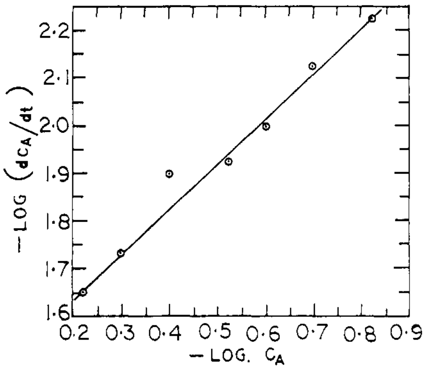

Figure 1. Determination of order of reaction with respect to palmitic acid by differential method: $C_{Bi}/C_{Ai} \approx 10$, 107°, $W = 0.1\%$, water of reaction removed

Table II. Experimental Data

Run no.	C_{Bi}/C_{Ai}	Temp, °C	Wt % of catalyst, W	Density at 35°, g/ml	C_{A0}	k_{exptl}'	$k_{calcd}'^{a}$	Deviation	% deviation^{b}
1	5	107	0.11	0.8194	0.9237	0.0426	0.0436	−0.0010	−2.35
2	5	107	0.05	0.8194	0.9196	0.0215	0.0202	+0.0013	+6.05
3	5	107	0.03	0.8194	1.2008	0.0123	0.0124	−0.0001	−0.813
4	5	107	0.00	0.8194	1.2930	0.0070	0.0007	0.0000	
5	8	107	0.11	0.8140	0.8392	0.0403	0.0392	+0.0011	+2.73
6	10	107	0.11	0.8088	0.6963	0.0374	0.0363	+0.0011	+2.94
7	12	107	0.12	0.8044	1.8657	0.0351	0.0369	−0.0013	−3.70
8^{c}	5	85	0.10	0.8194	1.1927	0.0125	0.0116	+0.0009	+7.20
9^{c}	5	95	0.10	0.8194	1.1919	0.0297	0.0198	−0.0001	−5.08
10^{c}	5	107	0.10	0.8194	0.9127	0.0388	0.0397	−0.0009	−2.32

[a] Calculated from eq 7. [b] % deviation = $(k_{exptl}' - k_{calcd}')/k_{exptl}'$. [c] Water of reaction not removed.

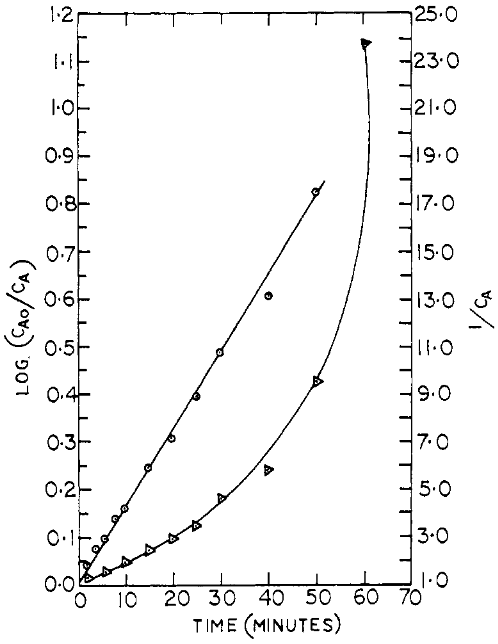

Figure 2. Determination of order of reaction with respect to palmitic acid by integral method: $C_{Bi}/C_{Ai} \approx 10$, 107°, W = 0.1%, water of reaction removed

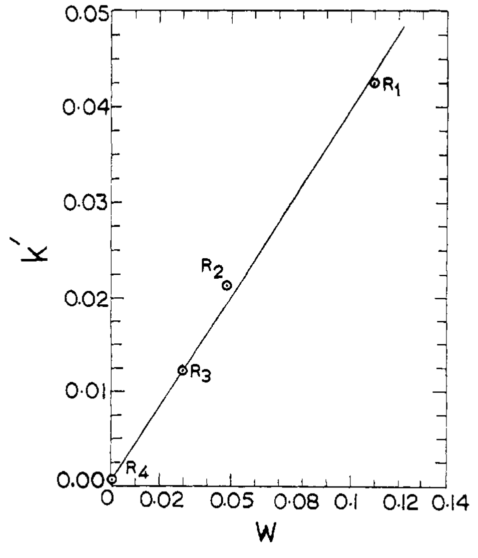

Figure 3. Effect of catalyst concentration on rate constant k': $C_{Bi}/C_{Ai} \approx 5$, 107°, water of reaction removed

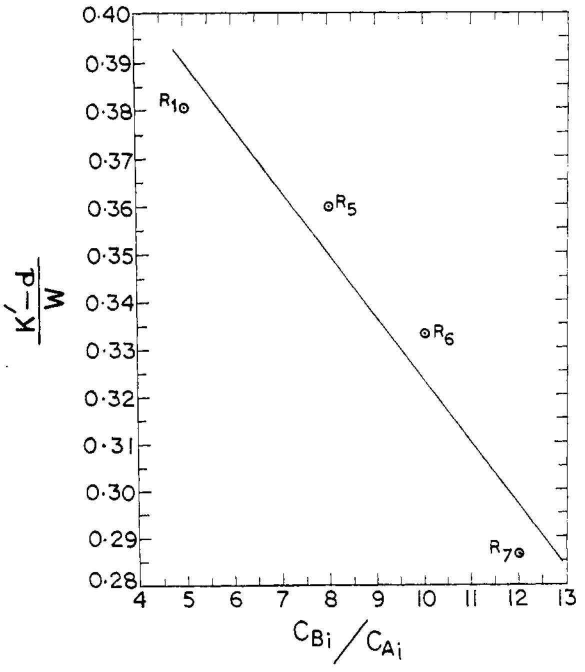

Figure 4. Effect of initial reactant ratio on rate constant k': 107°, W = 0.1%, water of reaction removed

investigated using a composition of alcohol to acid ratio of five and using catalyst concentrations of 0.00, 0.03, 0.05, and 0.11 wt % (runs 1, 2, 3, and 4). The rate constant values plotted in Figure 3, against the weight per cent of catalyst, were fitted into a best straight line by the method of least squares, resulting in

$$k' = 0.3855W + 0.0007 \qquad (3)$$

A study on the effect of initial reactant ratio on the rate constant, made by plotting $(k' - d/W)$ vs. (C_{Bi}/C_{Ai}) for runs 1, 5, 6, and 11 in Figure 4, gave eq 4 obtained by drawing the best straight line by the method of least squares

$$(k' - d)/W = 0.4558 - 0.0132(C_{Bi}/C_{Ai}) \qquad (4)$$

where d is the rate constant at 107°, using zero concentration of catalyst, and is equal to 0.0007.

The standard deviation for the rate constant was obtained as ±0.0031. Figure 5 shows Arrhenius plot for runs 8, 9, and 10. In runs 8 and 9, the water of reaction could not be removed even though the boiling point of the azeotrope is 89°. Run 10 was also conducted without water removal. The

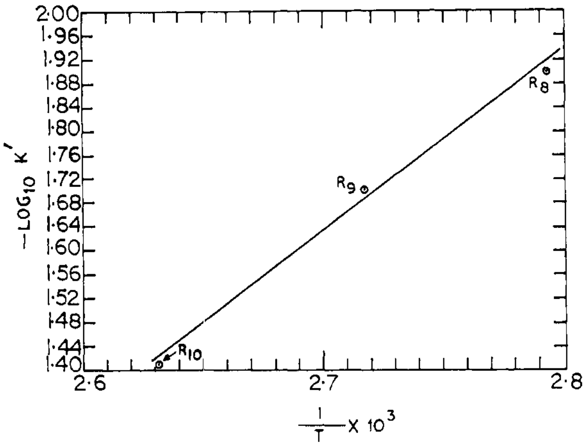

Figure 5. Effect of temperature on rate constant k': $C_{Bi}/C_{Ai} \approx 5$, $W = 0.1\%$, water of reaction not removed

rate constants k' for runs 8, 9, and 10 were obtained from the initial data upto which the linear nature of the plot of log (C_{A0}/C_A) *vs.* time exists, indicating that the amounts of products formed upto this period are negligible. The best straight line was drawn through the data points in Figure 5 by the method of least squares and eq 5 was obtained.

$$k_T' = e^{15.08} - (6992/T) \qquad (5)$$

The overall equation (eq 7) incorporating the effects of the catalyst concentration, initial reactant ratio, and temperature was obtained from eq 5 and 6.

$$k_{380°\mathrm{K}}' = (0.4558 - 0.0132C_{Bi}/C_{Ai})W + 0.0007 \qquad (6)$$

$$k_T' = [(0.4558 - 0.0132C_{Bi}/C_{Ai})W + 0.0007] \times \exp(18.32 - 6992/T) \qquad (7)$$

The standard error was calculated by using

$$\text{standard error} = [\Sigma(k_{\text{exptl}} - k_{\text{calcd}})^2/\text{no. of observations}]^{1/2} \qquad (8)$$

The standard error for the runs 1–3 and 5–8 was calculated and found to be ±0.0010 and the standard error for runs 8–10 was ±0.0009. The rate constant values calculated by eq 7 agreed with the experimental values within 5% error.

Nomenclature

C = concentration, M
d = density of the reaction mixture, g/ml
k' = pseudo-first-order rate constant, min^{-1}

SUBSCRIPTS

A = palmitic acid
B = isobutyl alcohol
0 = zero time
i = initial value

Literature Cited

Loury, M., Mellier, M. T., *Bull. Soc. Chim. Fr.*, 349 (1947).

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Transformation of Bounded Variables in Simplex Optimization Techniques

A simple and reliable technique has been found for handling bounded variables when using simplex optimization techniques. The bounded variable, X_i, is transformed into an unbounded one by the single valued expression: $Z_i = \log [(X_i - L)/(U - X_i)]$, L and U being the lower and upper bounds, respectively.

We have read with interest the description of the "Simpat" optimization technique developed by Keefer (1973) and the pattern search strategy used therein to handle bounds of constraint on the independent variables. The combination of Pattern and Simplex searching is unquestionably superior to either technique alone when the independent search variables must be bounded, though it does lead to a rather complicated optimization program.

There is, however, a very simple way of handling bounds for the Simplex method alone through the transformation of the bounded search space into an infinite one. Several years ago, we converted McCabe–Thiele vapor–liquid equilibrium plots (bounded by zero and unity) to unbounded space by applying logarithmic hyperbolic transforms to the graphical axes (1965). Identical transforms were found useful to unbound Simplex search space. These are special cases of the singly-valued Johnson (1949) S_B translation

$$Z_i = \gamma + \delta \log\left(\frac{X_i - \epsilon}{\epsilon + \lambda - X_i}\right) \qquad (1)$$

For our purposes, both scale and location parameters are arbitrary, so we set $\delta = 1$ and define γ so as to make the transform as simple as possible. If we call the upper bound U and the lower bound L, then we have for the case where both bounds are used

$$Z_i = \log\left(\frac{X_i - L}{U - X_i}\right) \qquad (2)$$