Kinetics of Esterification of Levulinic Acid with *n*-Butanol by Homogeneous Catalysis

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Kinetic data on the esterification of levulinic acid with *n*-butanol, catalyzed by sulfuric acid, have been obtained using a stirred batch reactor. Several experiments have been carried out with different initial molar ratios and different amounts of sulfuric acid at various temperatures. The conversion to *n*-butyl levulinate at 25–118 °C follows a first-order rate expression with respect to each component. The resultant kinetic equation fitted the experimental data quite well and is given by the expression $dc_{C_9H_{16}O_3}/dt = c_{H_2SO_4}[286087e^{-54275/RT}c_{C_5H_8O_3}c_{C_4H_{10}O} - 15312e^{-48431/RT}c_{C_9H_{16}O_3}c_{H_2O}]$. Experiments have shown that $\Delta H° = 7.14 \pm 0.87$ kJ mol^{-1}, $\Delta S° = 78.6 \pm 2.1$ J mol^{-1} K^{-1}, $\Delta H_1^* = 51.4 \pm 0.4$ kJ mol^{-1}, and $\Delta H_2^* = 45.4 \pm 0.7$ kJ mol^{-1}. The equilibrium constants at 25, 50, 75, 90, and 100 °C were found to be 0.33, 0.75, 1.50, 2.17, and 2.73, respectively.

Introduction

Kinetic data on homogeneous esterification of fatty acids are scarce in literature. In the early 1980s, Zhou et al. (1984) determined kinetic data of esterification of oleic acid with methanol by the semibatch method. For liquid–vapor equilibrium data, the UNIQUAC estimation method derived from UNIFAC has been used. Zaidan et al. (1986) studied the operation of an esterification process of oleic acid by different light alcohols and proposed a simulation model in order to determine the optimal operation conditions. The kinetics of esterification of oleic acid and mixtures of fatty acids with methanol using sulfuric acid and *p*-toluenesulfonic acid as catalyst were explored by Unnithan and Tiwari (1987). For fatty acid esterification with methanol *p*-toluenesulfonic acid was found to be a better catalyst than sulfuric acid. Recently studies on sulfuric acid catalyzed esterification of palmitic acid with isobutyl alcohol were presented by Goto et al. (1991).

n-Butyl levulinate is produced by Chemie Linz AG and is used as an important intermediate product of organic synthesis. It is also a basic material in order to produce plasticizing agents, solvents, and odorous substances. Levulinic acid is commonly used in textile printing. In addition the calcium salts of levulinic acid are essential parts of various calcium preparations.

The liquid-phase esterification of levulinic acid in the presence of a suitable acid catalyst, such as sulfuric acid, yields *n*-butyl levulinate as the main reaction product. The esterification of levulinic acid with *n*-butanol proceeds by the following stoichiometric equation:

$$C_5H_8O_3 + C_4H_{10}O \overset{H_2SO_4}{\rightleftharpoons} C_9H_{16}O_3 + H_2O \qquad (1)$$
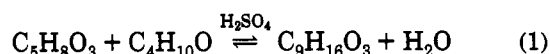
Esterification of the carboxyl group is relatively slow and needs activation either by high temperature or by a catalyst to achieve equilibrium conversion in a reasonable amount of time.

To get the appropriate kinetic parameters, the initial materials react in a discontinuous agitation vessel as described below. The aim of the investigation is to present a general kinetic equation and the result of the kinetic

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Table 1. Physical Properties of Levulinic Acid and *n*-Butyl Levulinate

constant	levulinic acid		*n*-butyl levulinate	
	lit.	detd	lit.	detd
refractive index				
n_D^{20}	1.4396[a]	1.4425	1.4290[a]	1.4285
n_D^{25}		1.4408		1.4262
density (20 °C) (g/cm^3)	1.1335,[a] 1.140[b]	1.135	0.9735[a]	0.972
bp (K)	518–519,[a] 306.5[b]		510.95[a]	
mp (K)	299–305,[c] 306–308[d]	303–306	<253[e]	
surface tension (37.5 °C) (mN/m)	not reported	40.8	not reported	27.7

[a] Handbook of Chemistry and Physics (1976). [b] Perry's Chemical Engineers' Handbook (1984). [c] Merck (1990/91). [d] Merck Index (1989). [e] Chemie Linz AG (1990).

and thermodynamic parameters of the esterification reaction conducted in a stirred batch reactor with sulfuric acid as catalyst, i.e., reaction constant, equilibrium constant, reaction order, activation energy, frequency factor, reaction enthalpy, reaction entropy, and activation enthalpy.

Experimental Procedure

Apparatus. The experimental assembly consisted of a 1-L reaction vessel fitted with a reflux condenser to prevent any loss of products, a thermometer pocket, and a dropping funnel. An anchor-type glass stirrer driven by a stirring motor was fixed to the reactor through a glass gland. The reactant temperature was maintained constant (±0.1 °C) with an electronic regulator. Samples of the reaction mixture were drawn from the reactor at definite intervals using the port, which was connected at the bottom of the vessel.

Materials. Levulinic acid, above 306 K a clear colorless to light yellow liquid, and *n*-butanol were analyzed for their purity. The former was found to be 98.5% pure, the rest being water; the latter was 99.1% pure with respect to *n*-butanol. Sulfuric acid of 96% purity (rest absorbed water) was used as a catalyst. Some physical constants of levulinic acid and *n*-butyl levulinate are shown in Table 1.

Analytics. Each sample was analyzed by an Orion 960 autochemistry system, which consists of the Orion 960

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module and an EA 940 pH/ISE meter to measure the acid number; a Mettler DL 35 Karl-Fischer titrator in order to measure the water, which was formed during the reaction; and gas chromatography using a HP 5890 Series II to determine the concentration of levulinic acid, n-butanol and n-butyl levulinate.

Procedure. n-Butanol and sulfuric acid were charged into the stirring vessel in a predetermined ratio, and levulinic acid was filled into the dropping funnel. After the desired temperature was reached, levulinic acid was drained into the stirring vessel. This moment is considered as the beginning of the experiment. Several samples of approximately 5 mL each were withdrawn during the experiment, and after analysis, the residual sample amount was taken back to the reactor to minimize the loss of the initial reaction volume. The number of samples in each experiment was approximately 20. A sample was drawn off every 5–10 min during the first hour of the reaction, during the next four hours every 20–30 min and thereafter every hour. Once the sample was taken from the vessel it was maintained at a temperature below 0 °C in order to stop continuity of the reaction.

Results and Discussion

Experiments were conducted with various molar ratios of levulinic acid and n-butanol in the range of 0.0204–1 at different temperatures (25, 50, 75, 90, 100, and 118 °C) using catalyst concentrations of 0, 0.05, 0.1, 0.25, 0.5, and 1 mol % to discern the kinetics.

The basic reaction is represented by the following stoichiometric equation:

$$LS + BuOH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} LSBE + H_2O \qquad (2)$$
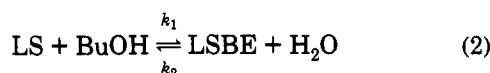
where k_1 is the forward reaction rate constant and k_2 is the reverse reaction rate constant.

The rate expression for eq 2 may be written:

$$dc_{LSBE}/dt = k_1 c_{LS}{}^a c_{BuOH}{}^b - k_2 c_{LSBE}{}^c c_{H_2O}{}^d \qquad (3)$$

To obtain a first estimation of the reaction order, the procedure Ulrich and Dietze (1964) suggested in their studies was followed. Afterward reaction time and concentration of levulinic acid were standardized, and the received plots were compared with curves of known reaction orders. The obtained overall reaction order of each experiment was related to c_∞/c_0 in another diagram and the reaction order of the forward and reverse reactions was readable.

order of the forward reaction: $a = b = 1$

order of the reverse reaction: $c = d = 1$

To estimate the rate of reaction, the following considerations were carried out:

The equilibrium state, which occurs when reaction velocity goes to zero, is described by the law of mass action

$$K = \frac{k_1}{K_2} = \frac{c_{LSBE} c_{H_2O}}{c_{LS} c_{BuOH}} \qquad (4)$$

where K is the constant that characterizes the equilibrium of the reaction, which is obtained from eqs 14 and 15 by setting $K_1 K_2 = K$.

The rate expression eq 5 proposed for the above system eq 2 as described is

$$dc_{LSBE}/dt = k_1 c_{LS} c_{BuOH} - k_2 c_{LSBE} c_{H_2O} \qquad (5)$$

where

$$c_{LS} = c_{LS}{}^\circ - c_{LSBE} \qquad (6)$$

$$c_{BuOH} = c_{BuOH}{}^\circ - c_{LSBE} \qquad (7)$$

$$c_{LSBE} = c_{H_2O} \qquad (8)$$

yields

$$dc_{LSBE}/dt = k_1(c_{LS}{}^\circ - c_{LSBE})(c_{BuOH}{}^\circ - c_{LSBE}) - k_2 c_{LSBE}{}^2 \qquad (9)$$

By integrating (dc_{LSBE}/dt) and rearranging eq 9, the ensuing analytical expression is given by

$$c_{LSBE}(t) = [(e^{t(-\Delta)^{1/2}} - 1)(k_1{}^2(c_{LS}{}^\circ - c_{BuOH}{}^\circ)^2 - \Delta)]/\{2(k_1 - k_2)[(k_1(c_{LS}{}^\circ + c_{BuOH}{}^\circ) + (-\Delta)^{1/2})e^{t(-\Delta)^{1/2}} - (k_1(c_{LS}{}^\circ + c_{BuOH}{}^\circ) - (-\Delta)^{1/2})]\} \qquad (10)$$

where

$$\Delta = 4(k_1 - k_2)k_1 c_{LS}{}^\circ c_{BuOH}{}^\circ - k_1{}^2(c_{LS}{}^\circ + c_{BuOH}{}^\circ)^2 \qquad (11)$$

Equation 10 is put into a data fitting program to get the k-values. These k-values were used as starting values in the following model.

Reaction Model. In a first reversible reaction step the carboxyl group of levulinic acid is protonated by sulfuric acid to form a reaction intermediate, which cannot be isolated.

$$LS + H_2SO_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} LSH^+ \cdot HSO_4{}^- \qquad (12)$$

In a rate-determined second one the protonated acid and n-butanol give n-butyl levulinate, water, and the regenerated catalyst.

$$LSH^+ \cdot HSO_4{}^- + BuOH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} LSBE + H_2O + H_2SO_4 \qquad (13)$$
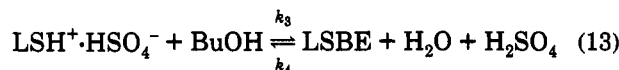
The equilibrium constants of eqs 12 and 13 result in

$$K_1 = \frac{c_{LSH^+ \cdot HSO_4{}^-}}{c_{LS} c_{H_2SO_4}} \qquad (14)$$

$$K_2 = \frac{c_{LSBE} c_{H_2O} c_{H_2SO_4}}{c_{LSH^+ \cdot HSO_4{}^-} c_{BuOH}} \qquad (15)$$

The rate expression proposed for this system from eq 13 is

$$dc_{LSBE}/dt = k_3 c_{LSH^+ \cdot HSO_4{}^-} c_{BuOH} - k_4 c_{LSBE} c_{H_2O} c_{H_2SO_4} \qquad (16)$$

Rearranging eq 14 gives

$$c_{LSH^+ \cdot HSO_4{}^-} = K_1 c_{LS} c_{H_2SO_4} \qquad (17)$$

Substituting eq 17 into eq 16 leads to

$$dc_{LSBE}/dt = k_3 K_1 c_{LS} c_{H_2SO_4} c_{BuOH} - k_4 c_{LSBE} c_{H_2O} c_{H_2SO_4} \qquad (18)$$

Setting $k_3 K_1 = k_5$ and simplifying eq 18, eq 19 is obtained

$$dc_{LSBE}/dt = c_{H_2SO_4}[k_5 c_{LS} c_{BuOH} - k_4 c_{LSBE} c_{H_2O}] \qquad (19)$$

After the mathematical models were proposed, the desired k-values were computed with aid of the integrated multifunctional simulation software package SIMUSOLV (trademark of The Dow Chemical Company). Figure 1 shows one example of data fitting for an arbitrary
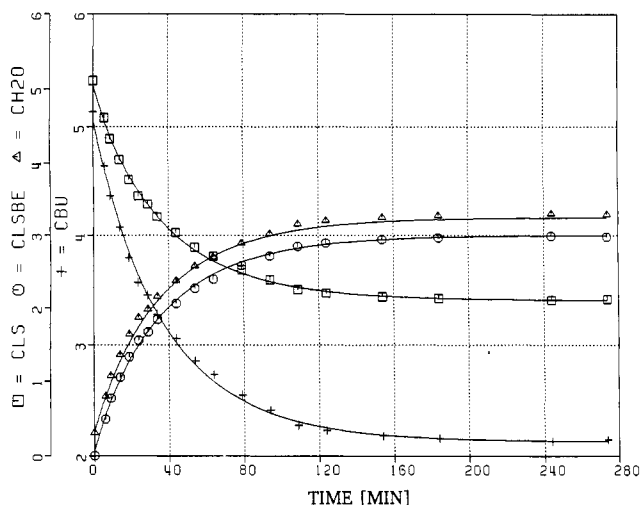
Figure 1. Graphical presentation of the data fit of experiment L5.

Table 2. Calculated Values of Equilibrium and Reaction Rate Constants

expt	T (°C)	catal concn (mol L^{-1})	k_5 (m^3)^2 kmol^{-2} s	k_4 (m^3)^2 kmol^{-2} s	K_{calc}	K_{exp}
6	25	0.010 79	1.156 × 10^{-4}			
14	25	0.010 89	1.274 × 10^{-4}			
64	25	0.051 37	8.781 × 10^{-5}		0.33	0.45
50	25	0.053 19	6.932 × 10^{-5}			
L4	50	0.005 15	3.430 × 10^{-4}	1.826 × 10^{-4}		
L6	50	0.012 87	3.855 × 10^{-4}	1.904 × 10^{-4}	0.75	0.63
L9	50	0.025 72	3.927 × 10^{-4}	1.942 × 10^{-4}		
L1	75	0.005 15	1.908 × 10^{-3}	1.001 × 10^{-3}		
54	75	0.005 33	1.887 × 10^{-3}	1.301 × 10^{-3}		
37	75	0.005 39	1.945 × 10^{-3}	1.586 × 10^{-3}		
59	75	0.010 29	1.975 × 10^{-3}			
45	75	0.010 66	1.761 × 10^{-3}	6.364 × 10^{-4}		
8	75	0.010 79	1.522 × 10^{-3}	2.382 × 10^{-3}		
15	75	0.010 89	3.034 × 10^{-3}		1.5	1.77
56	75	0.025 72	1.866 × 10^{-3}	4.548 × 10^{-4}		
42	75	0.026 63	1.816 × 10^{-3}	5.012 × 10^{-4}		
40	75	0.026 95	2.439 × 10^{-3}			
63	75	0.051 37	1.956 × 10^{-3}	5.324 × 10^{-4}		
48	75	0.053 19	2.386 × 10^{-3}	9.148 × 10^{-4}		
3	75	0.053 82	1.762 × 10^{-3}	4.815 × 10^{-4}		
L8	90	0.002 57	5.623 × 10^{-3}	2.895 × 10^{-3}		
L2	90	0.005 15	4.554 × 10^{-3}	2.517 × 10^{-3}		
L5	90	0.012 87	4.475 × 10^{-3}	2.056 × 10^{-3}	2.17	2.31
L7	90	0.025 72	4.747 × 10^{-3}	2.327 × 10^{-3}		
61	100	0.005 15	8.931 × 10^{-3}	2.195 × 10^{-3}		
53	100	0.005 33	1.009 × 10^{-2}	3.735 × 10^{-3}		
38	100	0.005 39	8.025 × 10^{-3}	3.173 × 10^{-3}		
58	100	0.010 29	8.642 × 10^{-3}	1.631 × 10^{-3}		
46	100	0.010 66	6.317 × 10^{-3}	2.380 × 10^{-3}	2.73	2.80
57	100	0.025 72	8.385 × 10^{-3}	2.312 × 10^{-3}		
43	100	0.026 63	7.383 × 10^{-3}	1.685 × 10^{-3}		
4	100	0.053 82	7.613 × 10^{-3}			
70	118	0.002 57	1.356 × 10^{-2}	4.009 × 10^{-3}		
62	118	0.005 15	1.712 × 10^{-2}	4.412 × 10^{-3}		
L3	118	0.005 15	1.581 × 10^{-2}	9.707 × 10^{-3}		
49	118	0.005 33	1.510 × 10^{-2}	6.509 × 10^{-3}		
39	118	0.005 39	1.539 × 10^{-2}	3.970 × 10^{-3}		
60	118	0.010 29	1.460 × 10^{-2}	3.991 × 10^{-3}	3.42	3.21
47	118	0.010 66	1.213 × 10^{-2}	4.966 × 10^{-3}		
7	118	0.010 79	1.446 × 10^{-2}	5.204 × 10^{-3}		
16	118	0.010 89	1.885 × 10^{-2}			
55	118	0.025 72	1.517 × 10^{-2}	3.178 × 10^{-3}		

experiment. The curves represent the calculated values of levulinic acid, n-butanol, n-butyl levulinate, and water, while the symbols represent the experimental data. In Table 2 the k-values of all experiments are collected. The heart of this program is its ability to solve sets of differential equations through numerical integration techniques. Results of the integrations can be compared with experimental data either graphically or quantitatively and used
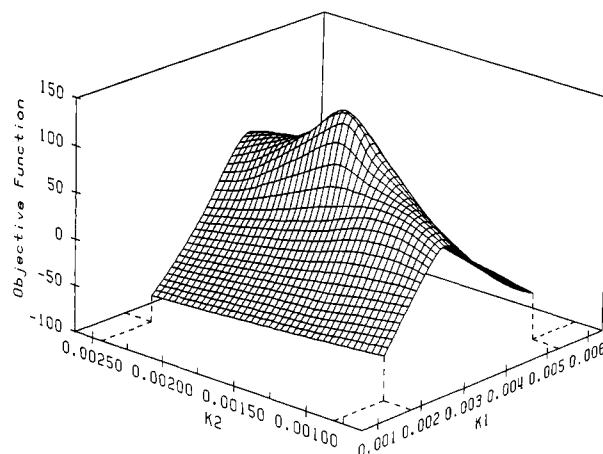

Figure 2. Surface plot of experiment L5.

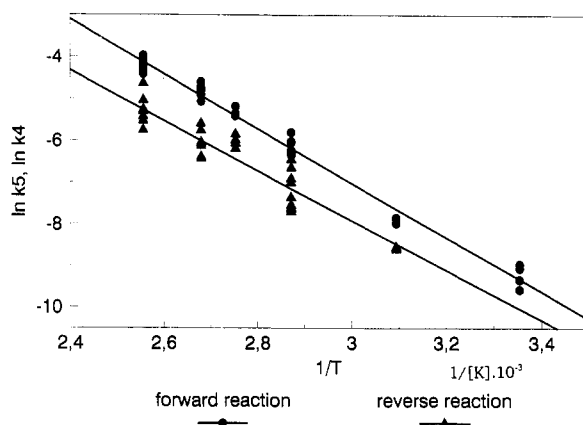forward reaction   reverse reaction

Figure 3. Relationship between forward and reverse reaction rate constants and temperature.

to estimate values for adjustable parameters which best fit the mathematical model to the data. The fitting is done through the statistically valid method of maximum log likelihood, which is a criterion for judging whether a set of parameter values or a model is the best one. The program is caused to adjust parameter values so as to maximize the value of the log likelihood function. The overall value of the maximized log likelihood function of experiment L5 is 139.9; this means that the experimental data may be predicted with an accuracy of 99.793%. Figure 2, a surface plot of the same experiment, points out the maximum where calculated and experimental data correlate best.

Activation Energy and Frequency Factor. The parameters of the Arrhenius (eqs 20 and 21), activation energy (E) and frequency factor (A), were determined for the forward and reverse reactions from reaction experiments which were carried out at different temperatures.

$$k_1 = A_1 e^{-E_1/RT} \qquad (20)$$

$$k_2 = A_2 e^{-E_2/RT} \qquad (21)$$

The data of ln k against T^{-1} [K^{-1}] were fitted by linear regression, and the result of this procedure is plotted in Figure 3. The activation energy and frequency factor of the forward reaction were estimated from this figure as 54 275 kJ kmol^{-1} and 286 087 (m^3)^2 kmol^{-2} s^{-1} using the least squares method. For the reverse reaction, a similar plot is also given in Figure 3. The activation energy was found to be 48 431 kJ kmol^{-1} and the frequency factor 15 312 (m^3)^2 kmol^{-2} s^{-1}.
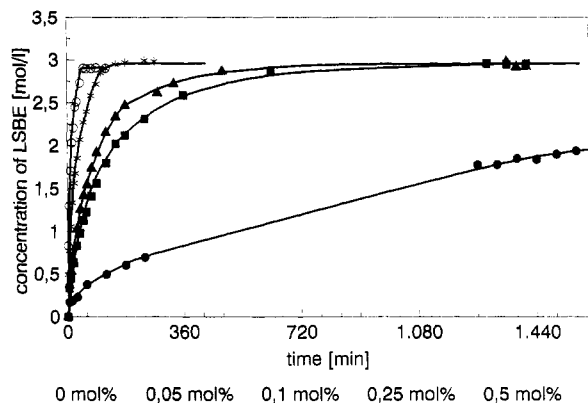
Figure 4. Effect of variation in catalyst concentration on establishment of equilibrium (molar ratio 1; temperature 90 °C).
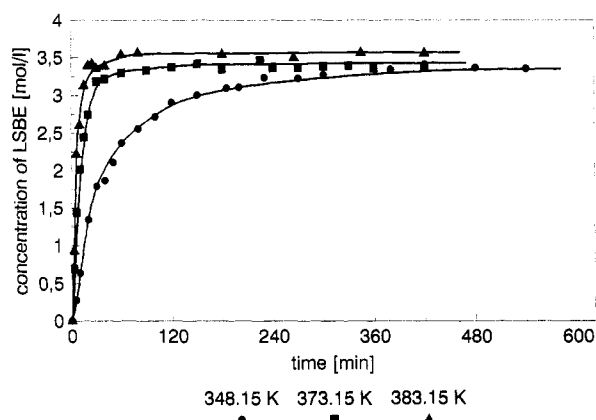

Figure 5. Effect of variation in temperature on equilibrium position (molar ratio 0.2; catalyst concentration 0.25 mol %).

Since the influence of the temperature on the forward and reverse reaction rate constants has been obtained, a generalized equation that may be applicable to all variations in catalyst concentration at 0–1 mol %, in temperature, and in reactant ratio will involve the activation energy (E) and frequency factor (A) and can be written as

$$dc_{LSBE}/dt = c_{H_2SO_4}[28607e^{-54275/RT}c_{LS}c_{BuOH} -$$
$$15312e^{-48431/RT}c_{LSBE}c_{H_2O}] \quad (22)$$

Effect of Catalyst Concentration and Temperature. Figure 4 shows the effect of amount of catalyst. Catalyst concentrations were varied at constant values of temperature. As proposed in the literature before, the establishment of equilibrium accelerates with the increase of concentration of catalyst. Even if no sulfuric acid catalyst existed, the reaction proceeded although the reaction rate was very low. In the same way the effect of temperature was investigated by varying reaction temperature at constant concentrations of catalyst. With increasing temperature the equilibrium position increased as presented in Figure 5.

Equilibrium Constant. As is well-known, the equilibrium of esterification may be affected by reaction conditions [e.g., Zey (1978)]. Goto, Tagawa, and Yussoff (1977) proposed in their studies that the composition of the reactants, the kind and amount of the catalyst, as well as the reaction temperature affected the equilibrium constant K. The experimental equilibrium constants were measured for various reaction conditions, and eq 4 was used to reckon the equilibrium constants for different temperatures. K_{calc} was obtained by division of the
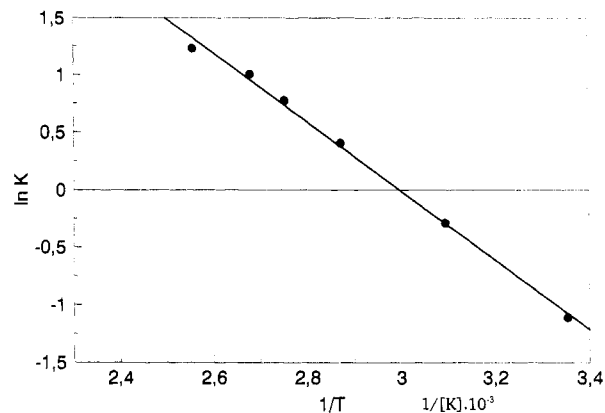

Figure 6. Relationship between equilibrium constant and temperature.

simulated forward and reverse reaction rate constants of each experiment, while K_{exp} was received by the law of mass action using the experimental determined equilibrium concentrations of each reactant. The mean values of K_{calc} and K_{exp} are listed in Table 2.

Reaction Enthalpy and Reaction Entropy. Reaction enthalpy at standard conditions indicates whether a reaction is endothermic or exothermic. It can be computed either from the formation enthalpy of each reactant and product or by setting the experimental equilibrium constants into eq 23. According to eq 23 reaction enthalpy

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (23)$$

and reaction entropy could be estimated by plotting $\ln K$ vs T^{-1} [K^{-1}] as presented in Figure 6. By use of the least squares method reaction enthalpy is evaluated from this figure as 7.14 ± 0.87 kJ mol^{-1}. The positive value of reaction enthalpy ($\Delta H°$) shows that the reaction is endothermic. Reaction entropy ($\Delta S°$) can also be obtained and was found to be 78.60 ± 2.1 J mol^{-1} K^{-1}.

Activation Enthalpy. Activation enthalpy of forward and reverse reactions in liquid or solid systems can be approximately obtained from eqs 24 and 25 or graphically

$$\Delta H_1^* = E_1 - RT \quad (24)$$

$$\Delta H_2^* = E_2 - RT \quad (25)$$

from the Eyring plot relating $\ln(k/T)$ and T^{-1} [K^{-1}] as suggested by Connors (1990). By use of the former method, activation enthalpy of the forward reaction was calculated as 51.4 ± 0.4 kJ mol^{-1} and activation enthalpy of the reverse reaction was calculated as 45.4 ± 0.7 kJ mol^{-1}.

Conclusion

The reaction of levulinic acid with n-butanol by using sulfuric acid as a catalyst was studied in detail. The kinetic parameters were quickly determined with high certainty with the help of a simulation software package. A theoretical rate equation was derived on the basis of the following reaction mechanism, which was chosen by a model discrimination process: (1) the carboxyl group of levulinic acid is protonated by sulfuric acid to give a reaction intermediate; (2) the reversible reaction of protonated acid and n-butanol gives n-butyl levulinate, water, and the regenerated catalyst. The rate equation of this mechanism obtained the best fitting to all the experimental results among the discriminated models. A final form of a generalized rate equation could be expressed

by eq 22. The kinetic information indicates that the reaction is reversible and first order with respect to each component. The values of reaction constant, equilibrium constant, reaction order, activation energy, frequency factor, reaction enthalpy, reaction entropy, and activation enthalpy can be determined with reasonable accuracy.

Acknowledgment

Nomenclature

LS = levulinic acid
LSBE = n-butyl levulinate
K = equilibrium constant
R = gas constant [J K^{-1} mol^{-1}]
T = reaction temperature [K]
$\Delta H°$ = reaction enthalpy [kJ mol^{-1}]
ΔH_1^* = activation enthalpy of forward reaction [kJ mol^{-1}]
ΔH_2^* = activation enthalpy of reverse reaction [kJ mol^{-1}]
$\Delta S°$ = reaction entropy [J mol^{-1} K^{-1}]
E_1 = activation energy of forward reaction [kJ kmol^{-1}]
E_2 = activation energy of reverse reaction [kJ kmol^{-1}]
A_1 = frequency factor of forward reaction [(m^3)^2 kmol^{-2} s^{-1}]
A_2 = frequency factor of reverse reaction [(m^3)^2 kmol^{-2} s^{-1}]
k_1 = forward reaction constant [(m^3)^2 kmol^{-2} s]
k_2 = reverse reaction constant [(m^3)^2 kmol^{-2} s]
c_{LS} = concentration of levulinic acid [kmol m^{-3}]
c_{BuOH} = concentration of n-butanol [kmol m^{-3}]
c_{LSBE} = concentration of n-butyl levulinate [kmol m^{-3}]
c_{H_2O} = concentration of water [kmol m^{-3}]
$c_{LS}°$ = initial concentration of levulinic acid [kmol m^{-3}]
$c_{BuOH}°$ = initial concentration of n-butanol [kmol m^{-3}]

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