Kinetics of Esterification of Succinic Anhydride with Methanol by Homogeneous Catalysis

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Abstract

Kinetic data on the esterification of succinic anhydride with methanol catalyzed by sulfuric acid have been obtained using a stirred batch reactor. In addition to get a precise ascertainment of the parameters the esterification of monomethyl succinate with methanol has been studied separately. Several experiments have been carried out with different initial molar ratios and different amounts of sulfuric acid at various temperatures. The conversion to dimethyl succinate at 30–65°C follows a first-order rate expression with respect to each component. A theoretical rate equation is derived by the following reaction mechanism: (1) succinic anhydride is protonated by sulfuric acid to form a reaction intermediate, (2) irreversible esterification to monomethyl succinate, (3) protonation of the monoester, and (4) the esterification to dimethyl succinate proceeds reversibly. The resultant kinetic equation fitted the experimental data quite well and is given by the expression:

$$\frac{dc_{CH_3OH}}{dt} = c_{H_2SO_4}\left[-4.344 * 10^8 e^{-65239/RT} c_{C_4H_4O_3} c_{CH_3OH} - 2.457 * 10^6 e^{-57732/RT} c_{C_5H_8O_4} c_{CH_3OH} \right.$$
$$\left. + 229 e^{-34361/RT} c_{C_6H_{10}O_4} c_{H_2O} \right]$$

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Introduction

Kinetic data on homogeneous esterification of anhydrides of dicarboxylic acids are scarce and contradictory in literature. Dharwadkar and Hussain [1] determined kinetic data of maleic anhydride with butanol, catalyzed by *p*-toluenesulphonic acid, by using a batch reactor. It was found that the conversion of mono to dibutyl maleate in excess butanol follows a second-order rate expression with respect to the monoester concentration. In the early 1980s Chawla and Hussain [2] presented their studies on sulfuric acid catalyzed esterification of maleic anhydride with ethanol. The kinetic information obtained indicated that the reaction is reversible and first-order with respect to each reactant. Bhutada and Pangarkar [3] studied the kinetics of esterification of phthalic anhydride with 2-ethylhexanol using various catalysts; terabutyl titanate, tetrabutyl zirconate, and paratoluene sulphonic acid. The reaction is in general first-order in monoester and alcohol. The titanates and zirconates were found to be better then conventionally used acidic catalysts in order to produce di-2-ethylhexyl phthalate. The influence of sulfuric acid as a catalyst on the preparation of diethyl maleate from maleic anhydride and ethanol was explored by Alvarez and Alvarez Jr. [4].

Dimethyl succinate is produced by Chemie Linz AG and is used as an important intermediate product of organic synthesis. It is also used as additive in synthetic

lubricants and gasoline, miticide, crystal habit modifier for gypsum, and in absorption refrigeration.

The liquid phase esterification of succinic anhydride in the presence of a suitable acid catalyst, such as sulfuric acid, yields dimethyl succinate as the main reaction product. The esterification of succinic anhydride with methanol proceeds in two steps represented by the following stoichiometric equations:
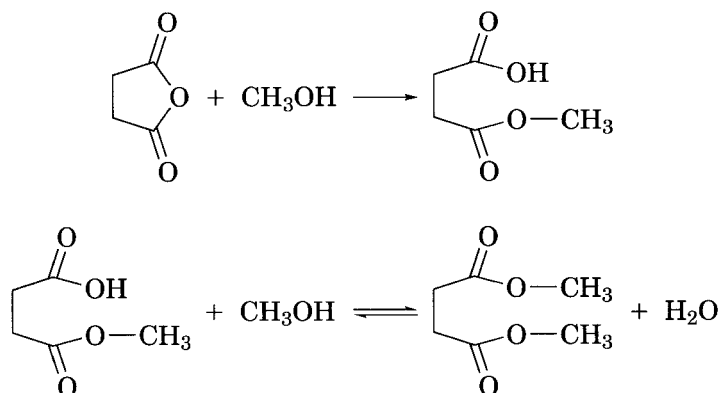
The first step which is exothermic, proceeds to complete conversion almost immediately and never went beyond about 15 to 20 min after catalyst addition. Esterification of the second carboxyl group is relatively slow and needs activation either by high temperature or by a catalyst to achieve equilibrium conversion in reasonable 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 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

Apparatus

The experimental assembly consisted of a 1 liter 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 ($\pm 0.1°C$) 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

Succinic anhydride forms rhombic pyramidal or bipyramidal crystals and is relatively insoluble in water and ether, but soluble in boiling chloroform, ethyl acetate, and alcohol. The anhydride and methanol were analyzed for their purity. The former was found to be 99.6% pure, the rest being water, the latter 99.8% pure with respect to methanol. Sulfuric acid of 96% purity (rest absorbed water) was used as a catalyst.

Analytics

Each sample was analyzed by an ORION 960 autochemistry system, which consists of the ORION 960 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 SERIE II to determine the concentration of succinic anhydride, methanol, monomethyl succinate, and dimethyl succinate.

Procedure

Succinic anhydride and methanol were charged into the stirring vessel in a predetermined ratio and a mixture of sulfuric acid and methanol was filled into the dropping funnel. After reaching the desired temperature the catalyst 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 analyzing, 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.

Preparation of dimethyl succinate by using monomethyl succinate and methanol as reactants happened in the analogous way.

Results and Discussion

Experiments were conducted with various molar ratios of succinic anhydride and methanol in the range of 0.02 to 0.5 at different temperatures (30, 50, and 65°C) using catalyst concentrations of 0.5, 0.2, 0.5, and 1 mol% to discern the kinetics.

The reaction order was obtained by following a procedure as previously proposed in details [10]. It was found that the reaction is first-order with respect to each component.

For a first estimation of the values of the reaction rate constants the esterification of monomethyl succinate and methanol catalyzed by sulfuric acid was investigated as described in [10], because it can be treated like a monobasic esterification reaction. The determined k-values were used as starting values in the following model.

Reaction Model

In a first reversible reaction step succinic anhydride is protonated by sulfuric acid to form an uninsulatable reaction intermediate.
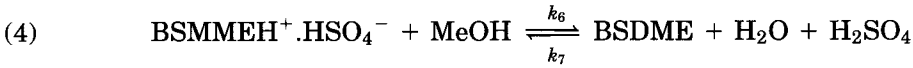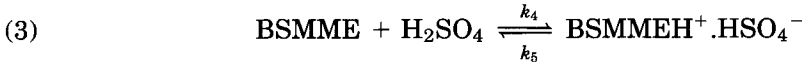
(1) $$\text{BSA} + \text{H}_2\text{SO}_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{BSAH}^+.\text{HSO}_4{}^-$$
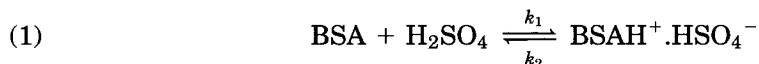
The irreversible second step leads to monomethyl succinate and regenerated catalyst.

(2) $$\text{BSAH}^+.\text{HSO}_4{}^- + \text{MeOH} \xrightarrow{k_3} \text{BSMME} + \text{H}_2\text{SO}_4$$
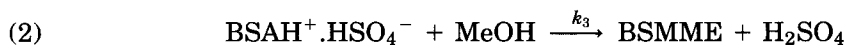
In an additional reversible reaction step the carboxyl group monomethyl succinate is protonated by the catalyst to form a reaction intermediate, which also cannot be

isolated, followed by a rate determined one, where the protonated monoester and methanol gives dimethyl succinate, water and the regenerated catalyst.

$$(3) \qquad\qquad \text{BSMME} + \text{H}_2\text{SO}_4 \underset{k_5}{\overset{k_4}{\rightleftharpoons}} \text{BSMMEH}^+.\text{HSO}_4^-$$

$$(4) \qquad \text{BSMMEH}^+.\text{HSO}_4^- + \text{MeOH} \underset{k_7}{\overset{k_6}{\rightleftharpoons}} \text{BSDME} + \text{H}_2\text{O} + \text{H}_2\text{SO}_4$$

The equilibrium constants of eqs. (1), (3), and (4) result in

$$(5) \qquad\qquad\qquad K_1 = \frac{c_{\text{BSAH}^+.\text{HSO}_4^-}}{c_{\text{BSA}}c_{\text{H}_2\text{SO}_4}}$$

$$(6) \qquad\qquad\qquad K_2 = \frac{c_{\text{BSMMEH}^+.\text{HSO}_4^-}}{c_{\text{BSMME}}c_{\text{H}_2\text{SO}_4}}$$

$$(7) \qquad\qquad\qquad K_3 = \frac{c_{\text{BSDME}}c_{\text{H}_2\text{O}}c_{\text{H}_2\text{SO}_4}}{c_{\text{BSMMEH}^+.\text{HSO}_4^-}c_{\text{MeOH}}}$$

The rate expression proposed for this system from eqs. (2) and (4) is:

$$\frac{dc_{\text{MeOH}}}{dt} = -k_3 c_{\text{BSAH}^+.\text{HSO}_4^-}c_{\text{MeOH}} - k_6 c_{\text{BSMMEH}^+.\text{HSO}_4^-}c_{\text{MeOH}}$$

$$(8) \qquad\qquad\qquad + k_7 c_{\text{BSDME}}c_{\text{H}_2\text{O}}c_{\text{H}_2\text{SO}_4}$$

Rearranging eqs. (5) and (6) gives:

$$(9) \qquad\qquad c_{\text{BSAH}^+.\text{HSO}_4^-} = K_1 c_{\text{BSA}}c_{\text{H}_2\text{SO}_4}$$

$$(10) \qquad\qquad c_{\text{BSMMEH}^+.\text{HSO}_4^-} = K_2 c_{\text{BSMME}}c_{\text{H}_2\text{SO}_4}$$

Substituting eqs. (9) and (10) into eq. (8) leads to:

$$\frac{dc_{\text{MeOH}}}{dt} = -k_3 K_1 c_{\text{BSA}}c_{\text{H}_2\text{SO}_4}c_{\text{MeOH}} - k_6 K_2 c_{\text{BSMME}}c_{\text{H}_2\text{SO}_4}c_{\text{MeOH}}$$

$$(11) \qquad\qquad\qquad + k_7 c_{\text{BSDME}}c_{\text{H}_2\text{O}}c_{\text{H}_2\text{SO}_4}$$

Setting $k_3^* K_1 = k_8$ and $k_6^* K_2 = k_9$, the simplified eq. (12) is obtained:

$$(12) \qquad \frac{dc_{\text{MeOH}}}{dt} = c_{\text{H}_2\text{SO}_4}[-k_8 c_{\text{BSA}}c_{\text{MeOH}} - k_9 c_{\text{BSMME}}c_{\text{MeOH}} + k_7 c_{\text{BSDME}}c_{\text{H}_2\text{O}}]$$

After proposing the mathematical models 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 experiment. The curves represent the calculated values of succinic anhydride, methanol, monomethyl succinate, dimethyl succinate, and water, while the symbols represent the experimental data. In Table I 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.

Dharwadkar and Hussain [1] suggested a mechanism for a similar esterification of dibasic acids, where the conversion to dibutylmaleate follows a second-order rate expression with respect to the monoester concentration. This proposal, which takes the second order expression of the monoester into account, was tested, but the data could not be fitted efficiently.
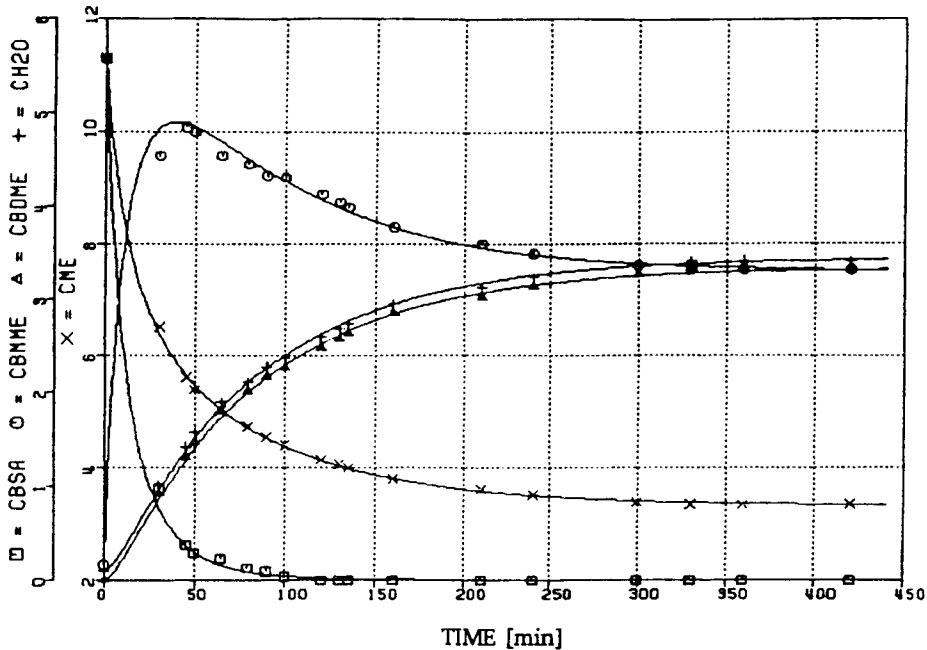
Figure 1. Graphical presentation of the data fit of Experiment 1 (molar ratio 0.5, catalyst concentration 0.5 mol%, reaction temperature 30°C).

Activation Energy and Frequency Factor

The parameters of the Arrhenius eqs. (13), (14), and (15), activation energy (E), and frequency factor (A), were determined for the irreversible, forward, and reverse reaction from reaction experiments which were carried out at different temperatures.

$$(13) \qquad\qquad k_1 = A_1 e^{-E_1/RT}$$

$$(14) \qquad\qquad k_2 = A_2 e^{-E_2/RT}$$

$$(15) \qquad\qquad k_3 = A_3 e^{-E_3/RT}$$

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 2. Activation energy and frequency factor of the first reaction step were estimated from this figure as 65239 kJ kmol^{-1} and 4.344*10^8 (m^3)^{2}kmol^{-2}s^{-1} and of the forward reaction of the second one as 57732 kJ mol^{-1} and 2.4569*10^6 (m^3)^{2}kmol^{-2}s^{-1} using the least-squares method. For the reverse reaction, a similar plot is also given in Figure 2. The activation energy was found to be 34361 kJ kmol^{-1} and the frequency factor 229 (m^3)^{2}kmol^{-2}s^{-1}.

Since the influence of the temperature on the reaction rate constants has been obtained, a generalized equation that may be applicable to all variations in catalyst concentration in the range of 0.05 to 1 mol%, temperature and reactant ratio will involve activation energy (E) and frequency factor (A) and can be written as:

$$\frac{dc_{\mathrm{MeOH}}}{dt} = c_{\mathrm{H_2SO_4}}[- 4.34 * 10^8 e^{-65239/RT} c_{\mathrm{BSA}} c_{\mathrm{MeOH}}$$

$$(16) \qquad\qquad - 2.457 * 10^6 e^{-57732/RT} c_{\mathrm{BSMME}} c_{\mathrm{MeOH}} + 229 e^{-34461/RT} c_{\mathrm{BSDME}} c_{\mathrm{H_2O}}]$$

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TABLE I. Calculated values of equilibrium and reaction rate constants.

Experiment	T [°C]	Kat.conc. [mol%]	$k8$ $(m^3)^2kmol^{-2}s$	$k9$ $(m^3)^2kmol^{-2}s$	$k7$ $(m^3)^2kmol^{-2}s$	K calc	K exp
13	30	0.05	$2.381 \ 10^{-3}$	$4.89 \ 10^{-4}$	$4.96 \ 10^{-4}$	1.00	0.99
77	30	0.2	$2.271 \ 10^{-3}$	$3.65 \ 10^{-4}$	$3.74 \ 10^{-4}$		
01	30	0.5	$2.441 \ 10^{-3}$	$2.86 \ 10^{-4}$	$2.72 \ 10^{-4}$		
12	30	1	$1.986 \ 10^{-3}$	$6.13 \ 10^{-4}$	$5.85 \ 10^{-4}$		
05	30	0.05	$1.999 \ 10^{-3}$	$2.51 \ 10^{-4}$	$2.46 \ 10^{-4}$		
32	30	0.2	$2.498 \ 10^{-3}$	$2.48 \ 10^{-4}$	$2.65 \ 10^{-4}$		
07	30	0.5	$2.646 \ 10^{-3}$	$2.41 \ 10^{-4}$	$2.45 \ 10^{-4}$		
10	30	1	$2.041 \ 10^{-3}$	$2.41 \ 10^{-4}$	$2.38 \ 10^{-4}$		
48	30	0.05	$2.495 \ 10^{-3}$	$2.55 \ 10^{-4}$	$2.40 \ 10^{-4}$		
45	30	0.2	$1.623 \ 10^{-3}$	$2.78 \ 10^{-4}$	$3.73 \ 10^{-4}$		
41	30	0.5	$2.369 \ 10^{-3}$	$2.74 \ 10^{-4}$	$2.78 \ 10^{-4}$		
43	30	1	$1.522 \ 10^{-3}$	$2.69 \ 10^{-4}$	$2.74 \ 10^{-4}$		
02	50	0.05	$4.464 \ 10^{-3}$	$1.771 \ 10^{-3}$	$8.26 \ 10^{-4}$	1.96	2.05
72	50	0.2	$2.127 \ 10^{-2}$	$1.502 \ 10^{-3}$	$7.00 \ 10^{-4}$		
15	50	0.5	$1.5611 \ 10^{-2}$	$1.360 \ 10^{-3}$	$6.14 \ 10^{-4}$		
17	50	1	$1.3643 \ 10^{-2}$	$1.429 \ 10^{-3}$	$4.97 \ 10^{-4}$		
03	50	0.05	$1.4873 \ 10^{-2}$	$1.138 \ 10^{-3}$	$5.16 \ 10^{-4}$		
31	50	0.2	$1.4130 \ 10^{-2}$	$9.930 \ 10^{-4}$	$5.19 \ 10^{-4}$		
06	50	0.5	$1.4186 \ 10^{-2}$	$9.710 \ 10^{-4}$	$4.83 \ 10^{-4}$		
11	50	1	$1.4706 \ 10^{-2}$	$9.380 \ 10^{-4}$	$4.98 \ 10^{-4}$		
37	50	0.05	$9.9760 \ 10^{-3}$	$1.199 \ 10^{-3}$	$7.22 \ 10^{-4}$		
38	50	0.2	$1.3748 \ 10^{-2}$	$1.174 \ 10^{-3}$	$1.447 \ 10^{-3}$		
42	50	0.5	$1.2969 \ 10^{-2}$	$1.586 \ 10^{-3}$	$5.33 \ 10^{-4}$		
44	50	1	$1.5510 \ 10^{-2}$	$1.070 \ 10^{-3}$	$7.51 \ 10^{-4}$		
14	65	0.05	$3.7432 \ 10^{-2}$	$3.273 \ 10^{-3}$	$1.078 \ 10^{-3}$	2.65	2.82
71	65	0.2	$3.9449 \ 10^{-2}$	$3.227 \ 10^{-3}$	$1.266 \ 10^{-3}$		
16	65	0.5	$3.6623 \ 10^{-2}$	$3.991 \ 10^{-3}$	$1.465 \ 10^{-3}$		
18	65	1	$3.4097 \ 10^{-2}$	$3.119 \ 10^{-3}$	$9.97 \ 10^{-4}$		
04	65	0.05	$3.0746 \ 10^{-2}$	$2.292 \ 10^{-3}$	$8.87 \ 10^{-4}$		
33	65	0.2	$2.8152 \ 10^{-2}$	$2.402 \ 10^{-3}$	$9.61 \ 10^{-4}$		
08	65	0.5	$2.8987 \ 10^{-2}$	$2.036 \ 10^{-3}$	$7.29 \ 10^{-4}$		
09	65	1	$3.0648 \ 10^{-2}$	$2.379 \ 10^{-3}$	$1.004 \ 10^{-3}$		
39	65	0.05	$1.7444 \ 10^{-2}$	$3.224 \ 10^{-3}$	$4.481 \ 10^{-3}$		
40	65	0.2	$1.5323 \ 10^{-2}$	$2.540 \ 10^{-3}$	$1.626 \ 10^{-3}$		
46	65	0.5	$2.7058 \ 10^{-2}$	$3.156 \ 10^{-3}$	$1.530 \ 10^{-3}$		
47	65	1	$3.1560 \ 10^{-2}$	$2.747 \ 10^{-3}$	$1.240 \ 10^{-3}$		

Effect of Catalyst Concentration and Temperature

Figure 3 shows the effect of amount of catalyst. Catalyst concentration was varied at constant values of temperature. As proposed in literature before, the establishment of equilibrium accelerate with the increase of concentration of catalyst. 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 4.

Equilibrium Constant

As is well known, the equilibrium of esterification may be affected by reaction conditions [11]. Goto, Tagawa, and Yusoff [12] proposed in their studies that the
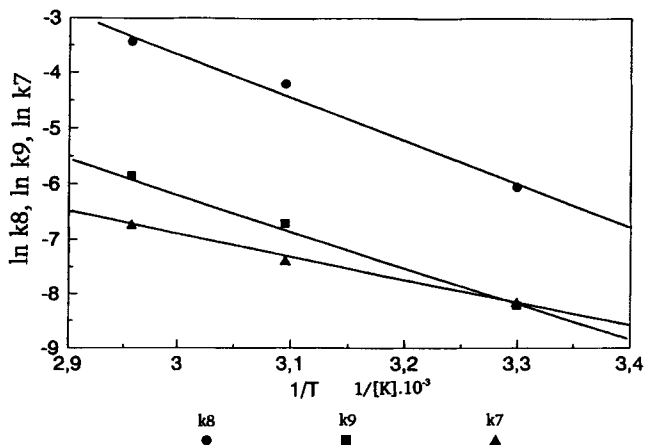
Figure 2. Relationship between the reaction rate constants and temperature.

composition of the reactants, the kind and amount of the catalyst as well as reaction temperature affected the equilibrium constant K. The equilibrium constants were measured for various reaction conditions and different temperatures. K_{calc} was obtained by division of the 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 I. The discrepancy between the two methods in determining K_{calc} and K_{exp} is a result of the well known experimental difficulties by using a batch reactor.

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
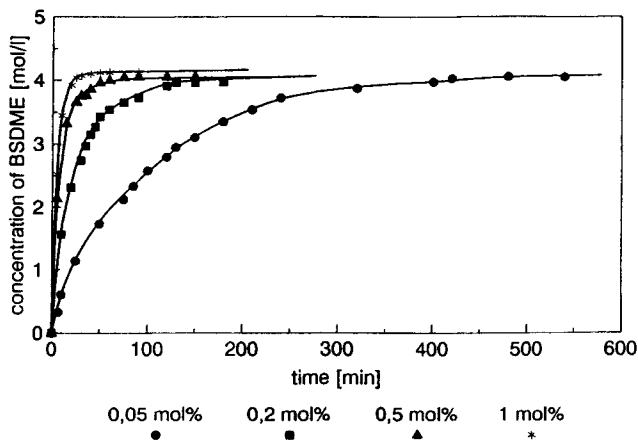

Figure 3. Effect of variation in catalyst concentration on establishment of equilibrium (molar ratio 0.5, temperature 65°C).
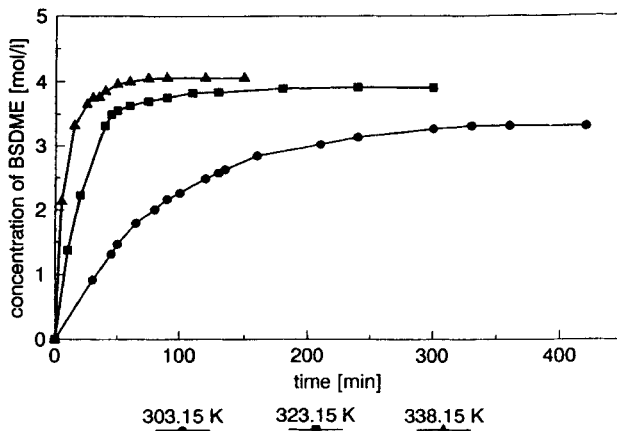
Figure 4.   Effect of variation in temperature on equilibrium position (molar ratio 0.5, catalyst concentration 0.5 mol%).

reactant and product or by setting the experimental equilibrium constants into eq. (17).

$$(17) \qquad\qquad \ln K = -\frac{\Delta H_R^0}{RT} + \frac{\Delta S^0}{R}$$

According to eq. (17) reaction enthalpy and reaction entropy could be estimated by plotting $\ln K$ vs. $T^{-1}[K^{-1}]$ as presented in Figure 5. By using the least-squares method reaction enthalpy is evaluated from this figure as 23.96 kJ mol^{-1} $\pm$ 1.91. The positive value of reaction enthalpy (ΔH_R^0) shows that the reaction is endothermic. Reaction entropy (ΔS^0) can also be obtained and was found to be 79.27 J mol^{-1} K^{-1} $\pm$ 2.21.

Activation Enthalpy

Activation enthalpy of the various reactions in liquid or solid systems can be approximately obtained from eqs. (18), (19), and (20)
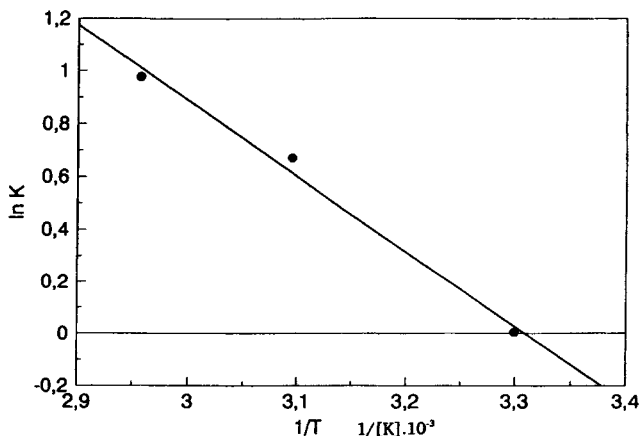
$$(18) \qquad\qquad \Delta H_1^* = E_1 - RT$$

Figure 5.   Relationship between equilibrium constant and temperature.

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

(20) $$\Delta H_3^* = E_3 - RT$$

or graphically from the Eyring plot relating $\ln(k/T)$ and $T^{-1}[K^{-1}]$ as suggested by K. A. Connors [13]. By using the former method activation enthalpy of the irreversible reaction was calculated as 62.55 kJ mol^{-1} ± 1.84, of the forward reaction as 55.05 kJ mol^{-1} ± 1.12 and as 31.67 kJ mol^{-1} ± 0.76 with respect to the reverse reaction.

Conclusion

The reaction of succinic anhydride with methanol by using sulfuric acid as a catalyst was studied in detail. The kinetic parameters were quickly determined with help of a simulation software package with high certainty. A theoretical rate equation was derived based on the following reaction mechanism, which was chosen by a model discrimination process: (1) the carboxyl group of succinic anhydride is protonated by sulfuric acid to give a reaction intermediate, (2) exothermic formation of monomethyl succinate, (3) protonation of the carboxyl group of the monomethyl succinate and (4) the reversible reaction of protonated monoester and methanol gives dimethyl succinate, 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. (16). The kinetic information indicated that the reaction is 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

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