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Thermochimica Acta 447 (2006) 57–63

thermochimica acta

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Autocatalytic behaviour in esterification between anhydrides and alcohols

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Received 2 December 2005; received in revised form 20 March 2006; accepted 2 May 2006
Available online 11 May 2006

Abstract

In this work the Arrhenius parameters and heat of reaction for the esterification of acetic anhydride by methanol and the esterification of propionic anhydride by 2-butanol were determined using a CPA 202 reaction calorimeter (ChemiSens). Three reaction rate models were tested for each of the esterification reactions, two of which assumed autocatalytic behaviour. The autocatalytic models were based on a carboxylic acid dependency; acetic acid and propionic acid being side products in the reactions studied. The two catalytic models gave excellent fits to the experimental results thus indicating autocatalytic behaviour.

Keywords: Esterification; Autocatalysis; Calorimetry; Kinetics

1. Introduction

In this paper investigations of the esterification of acetic anhydride by methanol and propionic anhydride by 2-butanol are described, concerning the reaction mechanism and certain reaction parameters. Many previous investigators have proposed a reaction rate expression based on the reactant concentrations. In this study two kinds of autocatalytic reaction mechanisms are proposed, in which the carboxylic acid formed catalyses the esterification. Strong mineral acids, such as sulphuric acid, have been used as catalysts for a long time in this kind of esterification. It is generally accepted that these strong acids protonate and activate the anhydride in the esterification between anhydrides and alcohols. However, a significant catalytic effect of the carboxylic acid formed is not often reported.

The reaction for the esterification of acetic anhydride by methanol is often written:

$$A + B \rightarrow C + D \tag{a}$$

where A is methanol, B acetic anhydride, C acetic acid and D is methyl acetate. But in reality the reaction mechanism is more complex, and several reactions may be involved. Balland et al. [1] proposed the following reaction path:

$$A + B \rightarrow C + D \tag{b}$$

$$A + C \rightarrow H_2O + D \tag{c}$$

$$B + H_2O \rightarrow 2C \tag{d}$$

The reaction between propionic anhydride and 2-butanol is a common one in safety studies. The main product is sec-butyl propionate but propionic acid is also formed. The reaction can be written:

$$A + B \rightarrow C + D \tag{e}$$

where A is 2-butanol, B propionic anhydride, C propionic acid and D is sec-butyl propionate. Also in this esterification process the reaction scheme is in reality more complex, and involves a reaction between the side product propionic acid and 2-butanol to form the same ester and water. The water can then hydrolyse some of the propionic anhydride. However, the reaction rate between propionic acid and 2-butanol is negligible when propionic anhydride is present [2].

2. Method

Since almost all chemical and physical processes are associated with the absorption or release of heat, reaction calorimetry

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doi:10.1016/j.tca.2006.05.003

Nomenclature

A	heat transfer area (m^2)
c	concentration (M)
d	distance between measurement points (m)
E_a	activation energy (J/mole)
h_r	heat transfer coefficient on the reactor side ($W/(m^2\,K)$)
k	reaction rate constant (s^{-1}, $l\,mole^{-1}\,s^{-1}$, $l^2\,mole^{-2}\,s^{-1}$)
k_0	frequency factor (s^{-1}, $l\,mole^{-1}\,s^{-1}$, $l^2\,mole^{-2}\,s^{-1}$)
K_a	acid constant (dissociation constant) (M)
$n_{i,0}$	initial amount of component i (mole)
P	heat flow (W)
Q_{mix}	energy absorbed/generated due to mixing (J)
r	reaction rate of chemical reaction (mole/(l s))
R	gas constant (J/(mole K))
T	temperature (K or °C)

Greek letter

λ	specific heat conductivity (W/(m K))
ΔH_r	heat of reaction (kJ/mole)

is a suitable tool to investigate such processes. The reactions were studied in a CPA 202 reaction calorimeter (ChemiSens) which is based on a heat flow principle. This reactor is a small-scale reactor with a working volume of 40–180 ml. The main output signal from the calorimeter is the heat flow associated with chemical and physical processes. One significant difference between the CPA 202 and ordinary heat flow calorimeters is the method of temperature measurement on which the heat flow rate is based. The heat flow signal is based on temperature measurements at certain strategic locations. In ordinary heat flow reaction calorimeters the reaction temperature, T_r, and the jacket temperature, T_j, are measured. In the CPA 202 calorimeter the temperature is measured at two points in the reactor base, T_1 and T_2. Thus, changes in the heat transfer coefficient, h_r, and the heat transfer area A (constant in CPA 202) do not affect the heat flow measurements and the baseline is therefore known throughout the whole experiment. The CPA 202 calorimeter is pre-calibrated, which means that the instrument presents the heat evolution rate directly on-line, and takes the variation in heat conductivity as a function of temperature into account.

A Peltier element is inserted underneath the reactor. This is not involved in the temperature measurement, but controls the temperature in the reactor by heating or cooling. The main heat flow sensor measures the temperatures T_1 and T_2 and is located between the reactor bottom and the Peltier element (see Fig. 1).

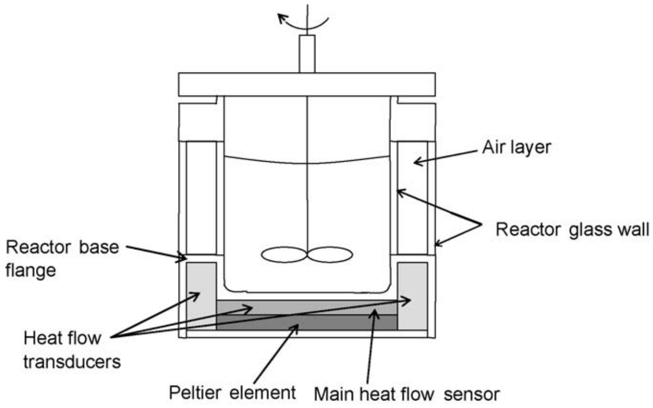

Fig. 1. Schematic of the CPA 202 reaction calorimeter.

All the heat flow out of the reactor is through the reactor bottom since the rest of the reactor is insulated. The reactor is submerged in a thermostat-controlled bath at a temperature 0.2 °C higher than the reactor temperature in order to provide active insulation. Because of this temperature difference between the reactor and its surroundings, a small amount of heat flows into the reactor through the reactor base flanges. Sensors in the flanges measure this heat flow and compensate for it. The reactor wall consists of a double glass wall and is therefore also passively insulated [3].

The experiments with acetic anhydride and methanol were performed in the isothermal mode at three temperatures (55, 60 and 65 °C). The reactor was initially loaded with about 50 g acetic anhydride (≥98.5%, Sigma–Aldrich) and heated to the reaction temperature. About 3.2 g methanol (>99%, Sigma–Aldrich) was pre-heated to the reaction temperature in the thermostat-controlled unit and injected into the reactor using a syringe. The initial molar ratio was 5:1, with acetic anhydride in excess. Water was used as thermostat liquid. To ensure a homogeneous liquid phase, the stirrer was set to 500 rpm.

Additional tests with different initial concentrations of acetic acid were performed in order to study the impact of acid in the acetic anhydride–methanol system. Two tests were performed at 60 °C, with the same initial concentration of methanol (2.0 M) as the previous tests but at initial acetic acid concentrations of 0.58 and 1.95 M, respectively. In the first of these experiments the reactor was loaded with 6.4 g of methanol (>99.8%, Merck), 98.4 g of acetic anhydride (>99%, Riedel-de Haën) and 3.6 g of acetic acid (>99.8%, Riedel-de Haën). In the second test the reactor was loaded with 6.4 g of methanol, 89.7 g of acetic anhydride and 12.0 g of acetic acid.

The esterification of propionic anhydride by 2-butanol was also performed in the isothermal mode, at 90, 100 and 105 °C. The reactor was initially loaded with 65 g propionic anhydride (97%, Sigma–Aldrich). Then 37 g 2-butanol (>99.5%, Sigma–Aldrich) was pre-heated and slowly injected into the reactor during a period of 45 min (90 min in one case) with a pump. The total molar ratio was 1:1. Since 2-butanol at atmospheric pressure has a boiling point of 99.5 °C, the reactor pressure had to be increased before 2-butanol was added at 100 and 105 °C. The reactor pressure was increased to 2 bar by the addition of nitrogen. At these relatively high temperatures a kind of oil with a boiling point of approximately 180 °C was chosen as the thermostat liquid. As in the acetic anhydride–methanol system, the stirrer speed was set to 500 rpm.

3. Theory

The measured heat flow in this study is denoted P_{flow} (W), and can be expressed:

$$P_{\mathrm{flow}} = \frac{\lambda}{d} A (T_2 - T_1) \tag{1}$$

where λ ($\mathrm{W\,m^{-1}\,K^{-1}}$) is the specific heat conductivity of the construction material through which the heat flows on its way from the reactor through the Peltier element to the thermostat-controlled bath. A (m^2) is the heat transfer area and d (m) is the distance between the points at which the temperatures (T_1 and T_2) are measured. The total energy balance can be written:

$$P_{\mathrm{flow}} + P_{\mathrm{lid}} = P_{\mathrm{react}} + P_{\mathrm{mix}} + P_{\mathrm{phase}} + P_{\mathrm{dos}} + P_{\mathrm{stirr}} \tag{2}$$

where P_{react} (W) is the reaction heat flow, P_{mix} (W) is the heat flow rate due to mixing enthalpies when different fluids are mixed, and P_{phase} (W) is the heat flow rate due to phase changes. The parameters P_{dos} (W) and P_{stirr} (W) are the heat flows corresponding to dosing and stirring, respectively, and P_{lid} (W) describes the heat flow rate through the reactor lid. In this study, the heat flow is equal to the reaction heat flow since all other sources of heat are small and can be neglected. The heat of reaction for isothermal batch experiments is therefore calculated using the following expression:

$$\Delta H_{\mathrm{r}} = \frac{\int_0^\infty P_{\mathrm{flow}}\,\mathrm{d}t}{n_{i,0}} \tag{3}$$

where $n_{i,0}$ (mole) is the initial amount of the reactant not in excess. The heat of reaction for isothermal semi-batch experiments is calculated with the following expression:

$$\Delta H_{\mathrm{r}} = \frac{\int_0^\infty P_{\mathrm{flow}}\,\mathrm{d}t - Q_{\mathrm{mix}}}{n_{i,0}} \tag{4}$$

where Q_{mix} (J) is the energy absorbed/generated from mixing. The term Q_{mix} is not present in the batch experiment calculations because the mixing enthalpy has been eliminated in the evaluation of the curves. The mixing enthalpy only affects the output data immediately after injection into the calorimeter, and this affected interval (0–120 s) has been extrapolated in the evaluation.

Activation energies and frequency factors are calculated with Arrhenius plots and the Arrhenius equation:

$$k = k_0 \mathrm{e}^{-E_{\mathrm{a}}/(RT)} \tag{5}$$

where k is the rate constant, k_0 the frequency factor and E_{a} is the activation energy.

4. Results and discussion

4.1. Acetic anhydride–methanol system

The side reaction between the acid formed and methanol should be very limited, and by ensuring a large excess of the anhydride in the reaction mixture this side reaction and following reactions will be even more suppressed. In one experiment, acetic acid was added to a large amount of methanol at 60 °C and atmospheric pressure. Under these conditions no detectable reaction occurred. The conclusion was that the acetic acid–methanol reaction is very slow compared with the acetic anhydride–methanol reaction.

Since the acetic anhydride was in “sufficient” excess the reaction was assumed to be of pseudo-first-order with respect to methanol. The percentage change in concentration of acetic anhydride as a function of the reaction time was relatively small compared with the corresponding change for methanol, and methanol was thus rate determining. The reaction rate for the pseudo-first-order reaction is expressed:

$$r = k c_{\mathrm{A}} \tag{6}$$

where the index A denotes methanol. The rate constant, k, for each temperature was determined by fitting the theoretical model to the experimental results. Curve fitting was simulated by a program in Matlab® toolbox called “NLINFIT”. This program fits data and estimates the coefficients of a non-linear function using a least-squares (Gauss–Newton method). The output from this program consists of the fitted coefficients, the residuals and the Jacobian. The estimated coefficients, which in this case were the rate constants, were then used in Excel® to plot graph.

The activation energy was calculated and found to be 68.1 kJ/mole, and the frequency factor was found to be $3.07 \times 10^7\ \mathrm{s}^{-1}$ for the isothermal experiments. The simulated curves agreed fairly well with the experimental curves (see Figs. 2–4). The heat of reaction of esterification was found to be -67.1 ± 2.0 kJ/mole, which agrees well with values found in the literature. A comparison was made between different experiments and the results are summarised in Table 1.

A sigmoid profile of the heat flow curve indicated that something else was affecting the reaction rate. The reaction rate expression gave a much better fit to the experimental curves when the reaction order was in the range 0.70–0.75, which also indicated that something else was affecting the reaction rate. This profile was more obvious in the experiments performed at the lower temperatures, where the reaction rate is relatively low,

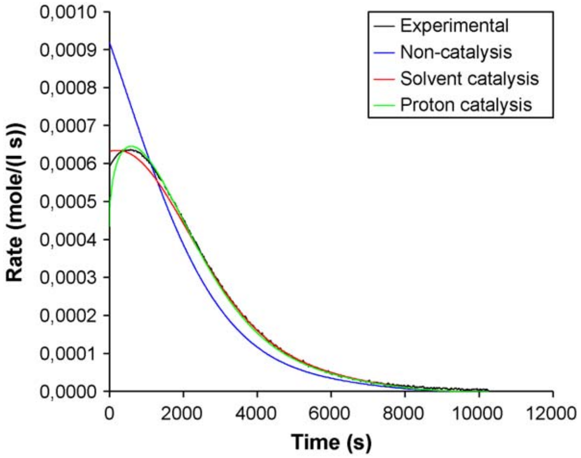

Fig. 2. The graph shows the fits for a non-catalytic reaction, a solvent-catalytic reaction and a proton-catalytic reaction, respectively, at 55 °C.

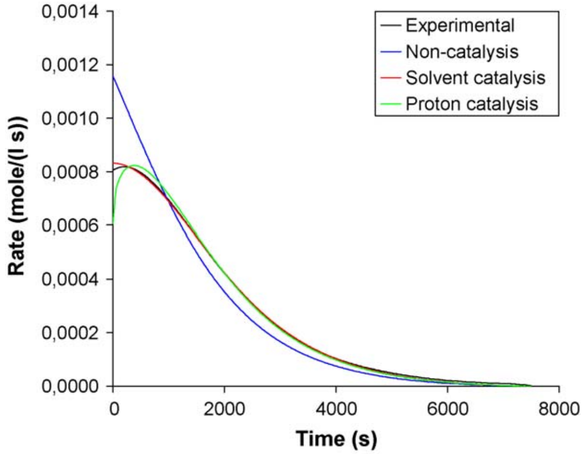

Fig. 3. The graph shows the fits for a non-catalytic reaction, a solvent-catalytic reaction and a proton-catalytic reaction, respectively, at 60 °C.

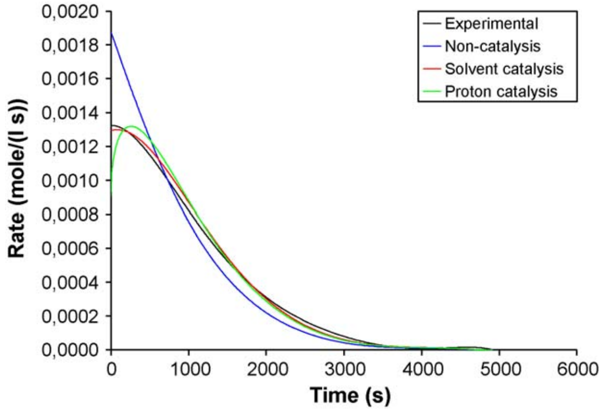

Fig. 4. The graph shows the fits for a non-catalytic reaction, a solvent-catalytic reaction and a proton-catalytic reaction, respectively, at 65 °C.

but the tendency was clear even at higher temperatures. Three things that could affect the profile of the curve are mass transport resistance, chemical equilibrium and catalytic effects. The first is not likely since the agitation was good, and the second is not likely since the reaction is not known to be an equilibrium reaction. The third one is interesting as an acid is formed as a side product. If sulphuric acid had been added as a catalyst, the catalytic effect of the strong inorganic acid would have been protonation of the anhydride. The consequence of this would have been weakened chemical bonding and therefore also a decrease in activation energy. Two theories were investigated concerning the catalytic mechanism in which acetic acid serves as a catalyst. The first was protonation of the anhydride with protons from dissociated acetic acid with the following proposed reaction rate model:

$$r = k_1 c_\mathrm{A} + k_2 c_\mathrm{A} c_{\mathrm{H}^+} \tag{7}$$

where the concentration of protons was assumed to follow an equilibrium:

$$K_\mathrm{a} = \frac{[\mathrm{H}^+][\mathrm{CH_3COO}^-]}{[\mathrm{CH_3COOH}]} \tag{8}$$

As can be seen, the model above describes two parallel reactions, one catalytic and one non-catalytic. The simulated curves were in excellent agreement with the experimental curves (see Figs. 2–4). The activation energies for the two reactions were found to be 70.3 and 66.4 kJ/mole, respectively. The activation energy for the catalytic reaction was lower than the activation energy for the non-catalytic reaction, which agrees with the theory of catalysis. The frequency factor was determined to be $3.43 \times 10^7\ \mathrm{s}^{-1}$ for the non-catalytic reaction and $2.50 \times 10^9\ \mathrm{l\,mole}^{-1}\ \mathrm{s}^{-1}$ for the catalytic reaction. To calculate the concentration of H^+ the dissociation constant for acetic acid at 25 °C was used. An error can be expected as the constant may vary with temperature and the solvent used. It is also assumed that all the free protons protonate the anhydride, which could give rise to an error.

Table 1
Comparison of frequency factor, activation energy and heat of reaction between different experiments

Experiment	k_0 (s^{-1})	E_a (kJ/mole)	ΔH_r (kJ/mole)
CPA 202 test[a]	3.07×10^7	68.1	−67.1
CPA 202 test[b]	9.75×10^6		
[4][c]	3.6×10^7	72.6	−67.3
[4,5]	1.8×10^7	68.2	−61.9
[4,5]	3.94×10^7	71.6	−63.2
[4,5]	5.48×10^7	71.6	−62.8
[4,6]	4.67×10^7	71.6	−66.3
[4,7][c]	8.97×10^6	73.8	−64.9
[4,8][c]	1.05×10^7	73.2	−64.4
[4,5]	2.47×10^7	69.5	−64.9
[9]	–	–	−67.7

[a] Pseudo-first-order reaction.

[b] Second-order reaction calculated from pseudo-first-order reaction with a median value of the almost constant anhydride concentration.

[c] Second-order reaction with rate constant in units $\mathrm{l\,mole}^{-1}\ \mathrm{s}^{-1}$.

In many reactions the choice of solvent affects the reaction rate. The second theory was based on the assumption that the acetic acid formed acts like a solvent and increases the contact between the reactants. The proposed reaction rate expression for this theory is:

$$r = k_1 c_\mathrm{A} + k_2 c_\mathrm{A} c_\mathrm{C} \tag{9}$$

This model also gave excellent agreement between simulated and experimental curves (see Figs. 2–4). The activation energy was determined to be 68.3 kJ/mole for the non-catalytic reaction and 68.6 kJ/mole for the reaction where acetic acid acted as solvent. The frequency factors were found to be $2.36 \times 10^7\ \mathrm{s}^{-1}$ and $1.44 \times 10^7\ \mathrm{l\,mole}^{-1}\ \mathrm{s}^{-1}$ for the non-catalytic and the catalytic reactions, respectively.

To investigate if there is a connection between the by-product (acetic acid) and reaction rate, the esterification reaction was performed with different initial concentrations of acetic acid. The result is shown in Fig. 5.

The experiment showed that there is a connection between the rate and the acetic acid concentration. The reaction rate increases with higher acetic acid concentration. The calculated Arrhenius parameters above were used for evaluation of the two catalytic models proposed, and the results are shown in Figs. 6 and 7.

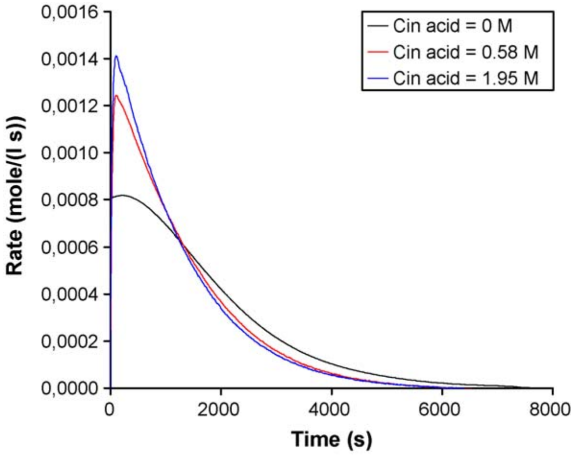

Fig. 5. The graph shows the reaction rates for different initial concentrations of acetic acid.

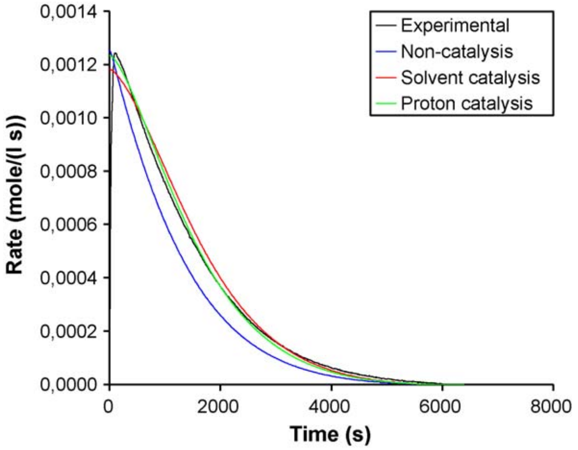

Fig. 6. The fits for a non-catalytic reaction, a solvent-catalytic reaction and a proton-catalytic reaction, respectively, at 60 °C and an initial acetic acid concentration of 0.58 M.

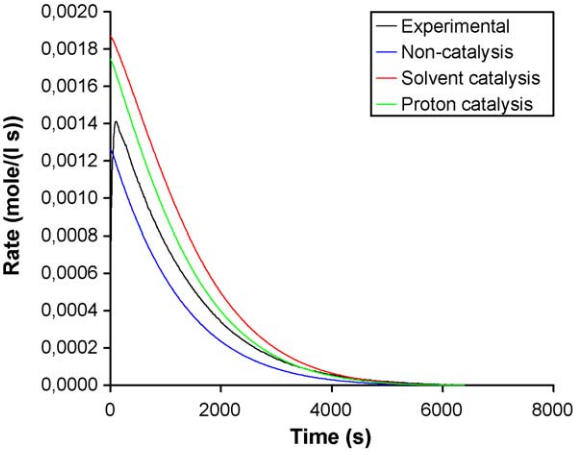

Fig. 7. The fits for a non-catalytic reaction, a solvent-catalytic reaction and a proton-catalytic reaction, respectively, at 60 °C and an initial acetic acid concentration of 1.95 M.

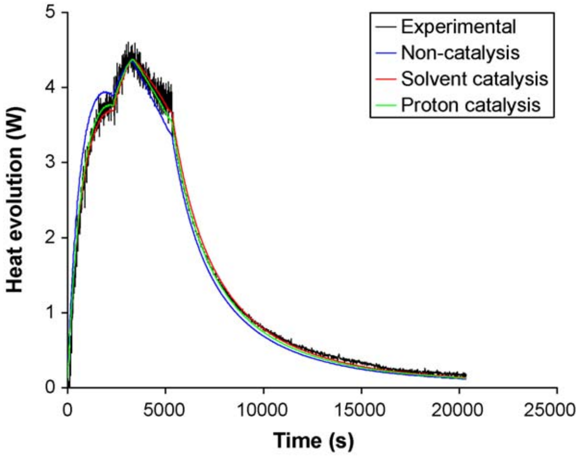

Fig. 8. The fits for a non-catalytic reaction, a solvent-catalytic reaction and a proton-catalytic reaction, respectively, at 90 °C.

The catalytic models gave good agreement between simulated and experimental curves for the initial acetic acid concentration of 0.58 M. For the higher initial concentration, the agreement was quite poor between the models and the experimental data. Perhaps a maximum catalytic effect was reached in this case. The heat of reaction was found to be −67.0 kJ/mole for both of the acetic acid response tests.

4.2. Propionic anhydride–butanol system

Since there seemed to be a relation between the reaction rate and the acid formed in the esterification between acetic anhydride and methanol, three similar rate models were proposed for the reaction between propionic anhydride and 2-butanol. The first does not take any catalytic behaviour into account, and only the concentrations of the reactants determine the reaction rate:

$$r = kc_\mathrm{A}c_\mathrm{B} \qquad (10)$$

where the index A denotes 2-butanol and index B propionic anhydride. The activation energy was found to be 80.8 kJ/mole and the frequency factor $5.17 \times 10^7\,\mathrm{l\,mole^{-1}\,s^{-1}}$ when the results from the experiment at 105 °C were excluded. These values agree well with values found in the literature. The results at 105 °C were excluded from the first calculation due to the relatively poor fit of the simulated curve to the experimental curve (see Fig. 10), which affected the estimated rate constant significantly. When the experiment at 105 °C was included, the activation energy and the frequency factor were 78.8 kJ/mole and $2.67 \times 10^7\,\mathrm{l\,mole^{-1}\,s^{-1}}$, respectively. The fits of the curves at 90 and 100 °C were very good, but not as good as when the catalytic models were used (see Figs. 8–10). The heat of reaction was found to be -65.7 ± 0.3 kJ/mole. This value agrees very well with values found in the literature. As the heat of mixing +4.2 kJ/mole was used, taken from Ubrich et al. [10]. A comparison was made between different experiments and the results are summarised in Table 2.

The other two models are based on different kinds of catalytic behaviour, as in the case of acetic anhydride–methanol esterification; two parallel reactions, one of which is non-catalytic and

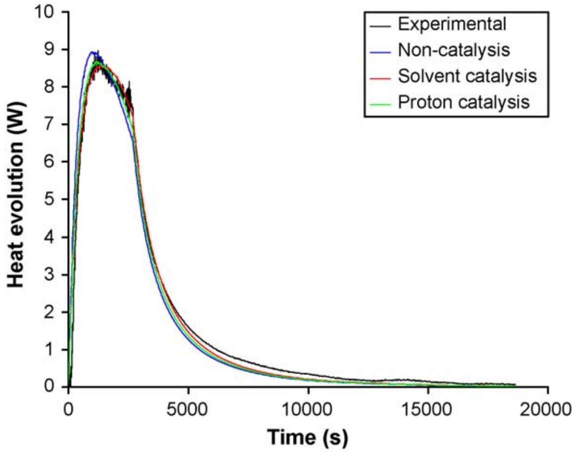

Fig. 9. The fits for a non-catalytic reaction, a solvent-catalytic reaction and a proton-catalytic reaction, respectively, at 100 °C.

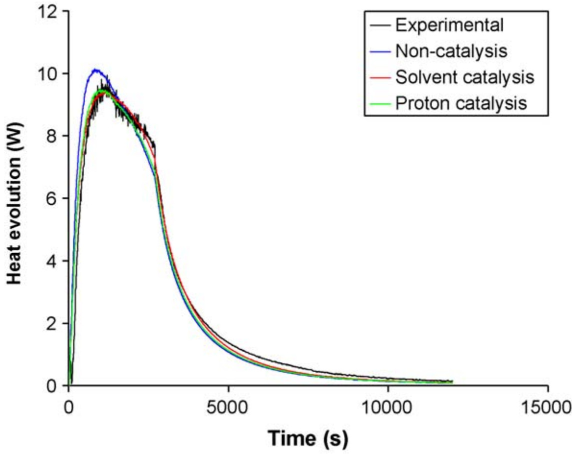

Fig. 10. The fits for a non-catalytic reaction, a solvent-catalytic reaction and a proton-catalytic reaction, respectively, at 105 °C.

the other catalytic. The two models are the following:

$$r = k_1 c_A c_B + k_2 c_A c_B c_{H^+} \tag{11}$$

$$r = k_1 c_A c_B + k_2 c_A c_B c_C \tag{12}$$

The first of these models, which assumes a proton-catalysed effect, gave activation energies of 79.0 and 69.9 kJ/mole for the non-catalytic and catalytic reactions, respectively. The activation energy for the catalytic reaction is lower than that of the non-catalytic reaction, as predicted by the theory of catalysis. The frequency factors were determined to be 2.20×10^7 l mole^{-1} s^{-1} and 4.56×10^7 l^2 mole^{-2} s^{-1} for the non-catalytic and catalytic reactions, respectively, and the fits were excellent when this model was used (see Figs. 8–10). The second of the catalysis models, which assumed that the propionic acid formed acts as a solvent, gave an activation energy of 77.4 kJ/mole and a frequency factor of 1.36×10^7 l mole^{-1} s^{-1} for the non-catalytic reaction. For the catalytic reaction these values were 82.5 kJ/mole and 4.30×10^6 l^2 mole^{-2} s^{-1}. The curve fits were also excellent when this model was used (see Figs. 8–10).

Table 2
Comparison of frequency factor, activation energy and heat of reaction between different experiments

Experiment	k_0 (l mole^{-1} s^{-1})	E_a (kJ/mole)	ΔH_r (kJ/mole)
CPA 202 test[a]	5.17×10^7	80.8	−65.7
[2]	5.36×10^7	80.5	–
[11]	–	84.4	−61.6
[11]			−60
[11]			−64
[11]			−63.7 to −69.5
[10]	9.55×10^7	82.5	−62.5
[10]			−63.0

[a] Second-order reaction without catalytic effect and experiment at 105 °C excluded.

5. Conclusions

The results of the experiments indicate that thermal processes other than the main reaction between alcohol and anhydride are taking place. Several factors, such as chemical equilibrium, mass transport resistance, side reactions and catalytic effects, can influence the rate profile. In this study chemical equilibrium is not a relevant factor since the esterification reactions are not known to be equilibrium reactions. Significant mass transport resistance in the liquid–liquid system under good agitation is not likely either. Side reactions cannot be excluded since contamination with, for example, water would give rise to hydrolysis reactions. Moreover, in the propionic anhydride–butanol system, propionic acid is in high excess at the end of the reaction, compared with propionic anhydride, so despite the fact that the anhydride is more reactive with butanol, the reaction between propionic acid and butanol cannot be excluded. However, the anhydride-alcohol reactions are believed to proceed much faster than the acid–alcohol reactions.

In this study a sigmoid profile was obtained, leading to the theory of autocatalysis in the reaction system investigated. It is obvious that the two catalytic models give a better fit to the experimental results than the non-catalytic model. The reaction rate in the acetic anhydride–methanol system showed a dependency of the acetic acid concentration. The rate increased when the initial acetic acid concentration was raised, strongly indicating autocatalysis. It is difficult to determine which of the catalysis models gives the best fit to the experimental data; both of them agree very well with the experimental results. A combination of the two theories may well be closer to the truth. However, proton catalysis is a known phenomenon in esterification reactions, especially when strong mineral acids are used as catalysts. Moreover, two things speak against the solvent catalysis theory; the relatively small amount of acetic acid in comparison with anhydride in the acetic anhydride–methanol system and the difference in polarity between acid, alcohol and anhydride in both of the studied reaction systems. Both acetic acid and propionic acid have lower dielectric constants than the anhydrides and alcohols involved in the studied reactions, and should therefore not act as solvent.

We consider the explanation involving autocatalytic behaviour to be most interesting. It is well known that this kind of esterification proceeds faster in acidic environments. As the reaction proceeds and the pH falls, autocatalysis may thus be taking place.

Acknowledgement

The authors would like to thank ChemiSens (www.chemisens.se) for providing the reaction calorimeter and associated equipment.

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