

# Thermokinetic investigation of the alcoholysis of acetyl chloride — Part I

T. Willms<sup>1</sup>, H.L. Anderson<sup>\*</sup>, K. Heldt, B. Hinz

*Institute of Physical Chemistry, University of Greifswald, Soldtmannstr. 23, D-17489 Greifswald, Germany*

Received 16 June 2000; received in revised form 16 June 2000; accepted 1 September 2000

## Abstract

The alcoholysis of acetyl chloride under various reaction conditions has been investigated by isoperibolic calorimetry and HPLC-analysis. Non-linear kinetic evaluation has been realized by the program TA-kin 3.3 on the basis of temperature and concentration data. Depending on the excess of alcohol, different partial reaction orders are found. The reaction rate also depends on the basicity of the solvent. This could be caused by H-bonding with the alcohol increasing the activation energy.

It was possible to distinguish between the kinetic parameters of the ethanolysis and the *i*-propanolysis of acetyl chloride in the evaluation of the alcoholysis of acetyl chloride by alcoholic mixtures at stoichiometric concentrations of the reagents. A partial order of  $n = 0.5$  for the alcohol, as determined in the evaluation of the single alcoholysis under these conditions, has been confirmed. The results show that heat accumulations are an important feature for the kinetic evaluation of reactions under the concentration conditions described. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Acetyl chloride; Alcohol mixtures; Calorimetry; Kinetics; Solvent

## 1. Introduction

In the past, the alcoholysis of acyl chlorides has been frequently a subject of publications [1–5], but due to the exothermic character of the reaction, investigations have generally been restricted to conditions which slow down the rate of reaction to permit the reaction course to be followed with the methods available at that time. Nowadays, alcoholysis of acyl chlorides is still of interest because the reaction is useful to convert alcohols into their esters which are frequently used as solvents, fragrances and additives to drugs and perfumes, as well on an industrial scale. But for an economic realization of this reaction,

high concentrations of the starting products are desired so that parameters in the literature are not necessarily appropriate. Therefore the alcoholysis of acyl chlorides had been investigated by means of modern calorimetric methods, that are not affected by the disadvantages of the former methods and are also favoured by the developments in measuring techniques and computer technology.

## 2. Experimental

A glass reactor with the alcoholic mixture (30 ml) is placed in a water cooled, double walled vessel which, after closing, is connected to a burette with the acyl chloride solution. The vessel and the burette of this isoperibolic reaction calorimeter [6] are integrated in a thermostated circuit. The effective volume of the reactor is 40 ml and it contains a Pt-sensor, a calibration

<sup>\*</sup> Corresponding author. Present address: Rembrandtstr. 9, 18057 Rostock, Germany. Tel./fax: +49-381-2089988.

E-mail address: t.willms@fz.rossendorf.de (T. Willms).

<sup>1</sup> Tel.: +49-351-2600; fax: +49-351-2603651.

heater and a stirrer. After thermal equilibration has been reached, the acyl chloride is added using the batch mode. The temperature of the reaction medium is measured and stored by the software of the ACTRON calorimeter [7].

The investigation of the reaction of acetyl chloride (1 mol/l) with mixtures of *i*-propanol and ethanol has been performed, varying the alcohol concentrations as follows:

1.  $[\text{etOH}] + [i\text{-prOH}] = 1 \text{ mol/l}$ ,  $[\text{etOH}] = 0.2, \dots, 0.8 \text{ mol/l}$ , step 0.2;
2.  $[i\text{-prOH}] = 0.8 \text{ mol/l}$ ,  $[\text{etOH}] = 0.4, 0.6 \text{ and } 0.8 \text{ mol/l}$ .

To investigate the complex reactions, as well as to verify the simulated conversion data from simple reactions, it is necessary to measure concentration data because the temperature change is due to the sum of all heat releasing processes in the system.

To support the evaluation of temperature data, samples have been taken, quenched and subjected to HPLC-analysis to get concentration data for *i*-propyl acetate and ethyl acetate, respectively. Quenching was realized by an aqueous ammonia solution.

The recorded temperature data and concentration data sets can be evaluated kinetically by the software package TA-kin [6,8]. This program allows definition of most reaction models. Using this non-linear evaluation procedure, the simultaneous kinetic evaluation of reactions with up to four steps is possible.

Traces of condensation products in the solvent acetone could disturb the evaluation of the chromatogram, because the peaks of these lie near that of *i*-propyl acetate in the HPLC-chromatogram. So the acetone was checked before use and it was found that samples should not be taken after a period of more than 1 h. Furthermore, for this reason, drying is restricted to a short period of time and is only possible with non-reacting reagents such as molecular sieves. Details are described in [6], pp. 30, 59.

### 3. Results

#### 3.1. Alcoholysis with one alcohol

Figs. 1 and 2 show the temperature–time curves of the ethanolysis of acetyl chloride in acetone and

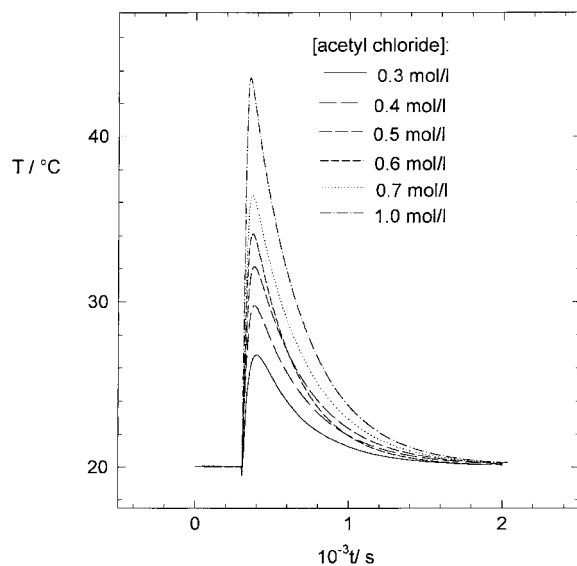


Fig. 1. Temperature–time curves of the alcoholysis of acetyl chloride with ethanol (6 mol/l) in acetone.

toluene, respectively, with varying concentrations of acetyl chloride.

Primary alcohols produce a temperature jump proportional to the concentration of acetyl chloride because the release of heat is high enough to create

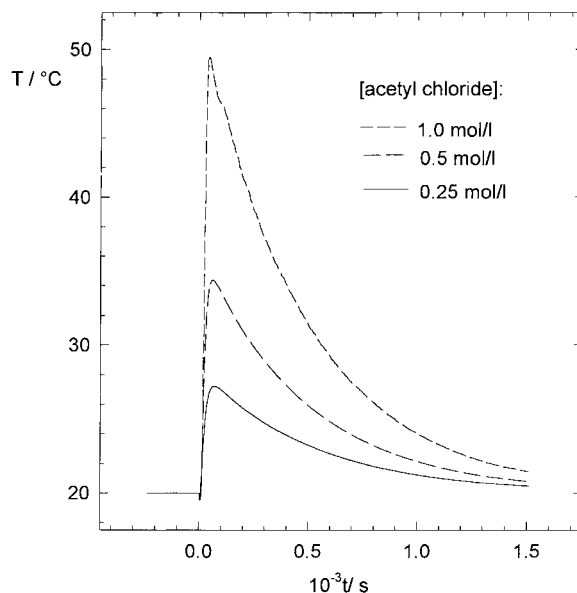


Fig. 2. Temperature–time curves of the alcoholysis of acetyl chloride with ethanol (6 mol/l) in toluene.

practically an adiabatic state. This corresponds to the observed chemical conversion curves which reaches 100% just after the maximum of the temperature curve ([6], p. 97). The temperature curve of the ethanolysis of 1 mol/l acetyl chloride in toluene (Fig. 2) shows, in contrast to all other experiments, a phenomenon at the maximum of the temperature signal which may be called “needle effect”. Later a normal cooling curve could be observed. This occurred only in one case of extremely high heat production (high concentration of acyl chloride and ethanol, toluene) and a low cooling constant, respectively, which indicates local overheating as an explanation. From Fig. 2 it can be seen, as well, that the increase and the maximum are generally much higher in toluene than in acetone under comparable conditions. In contrast to this, none of the temperature–time curves of the reaction with secondary alcohols (Fig. 3) shows this proportionality, which is due to the lower reaction rate and heat production. Besides this, Fig. 3 shows the decreasing endothermic starting signal which is characteristic for all measurements, only varying in magnitude depending on the alcohol, its concentration and the acetyl chloride concentration. Secondary alcohols produce a stronger endothermic signal than primary alcohols.

The kinetic evaluation of temperature–time curves with varying acyl chloride concentrations leads to different reaction enthalpies, which may be the consequence of a solvation effect of the acyl chloride and its reaction products with the alcohol. But because there is also the endothermic effect of dilution of alcohol by the acetone of the acyl chloride solution (Fig. 3), it is difficult to determine which solvation effect is responsible for these differences. It can be shown that the amount of the endothermic signal is approximately proportional to the acetone content in the acetyl chloride solution ([6], p. 43).

Overall evaluations of a group of curves (e.g. Fig. 1) do not give satisfactory results, because the varying

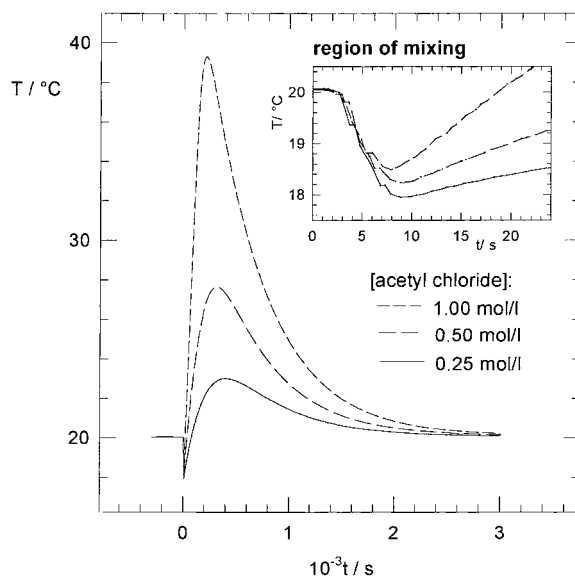


Fig. 3. Temperature–time curves of the alcoholysis of acetyl chloride with *i*-propanol (6 mol/l) in acetone.

reaction enthalpy leads to relatively large differences between the simulated and experimental temperature curves if a constant enthalpy is presupposed. In Table 1 the result of overall evaluations (varying the temperature) at constant acyl chloride concentrations are given for the ethanolysis (6 mol/l) of acetyl chloride in acetone. Table 2 shows the result of the overall evaluations varying the acyl chloride concentration and the temperature simultaneously. If the concentration of alcohol at a constant acyl chloride concentration is increased, the maximum of the temperature curve is shifted to earlier reaction times and the increase grows. This can be seen in Fig. 4 which represents the temperature–time curves for the alcoholysis of 0.5 mol/l acetyl chloride with various ethanol concentrations. Due to the change of the kinetic rate laws of the alcoholysis, the reactions with

Table 1

Parameters of the overall evaluation of the *i*-propanolysis of acetyl chloride in acetone varying the starting temperature (10, 20, 30°C) (*m*: number of equations of equations) ESS: result of the non-linear regression (minimization of error square sum)

[AcCl]	$\ln k_0$	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)	ESS/ <i>m</i>
0.25	$8.95 \pm 0.022$	$40.54 \pm 0.064$	$-78.50 \pm 0.33$	13.92/1010
0.50	$10.96 \pm 0.032$	$45.41 \pm 0.088$	$-76.99 \pm 0.31$	17.13/1010
1.00	$15.56 \pm 0.058$	$56.99 \pm 0.150$	$-74.13 \pm 0.30$	177.48/872

Table 2

Parameters of the overall evaluation of the *i*-propanolysis of acetyl chloride in acetone varying the concentration of acetyl chloride and the temperature

$\ln k_0$	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)	$n_1$ (AcCl)	$n_2$ ( <i>i</i> -PrOH)	ESS/ <i>m</i>
$15.44 \pm 0.017$	$55.72 \pm 0.043$	$-74.26 \pm 0.33$	$1.0327 \pm 0.0017$	$0.986 \pm 0.013$	200.998/1135

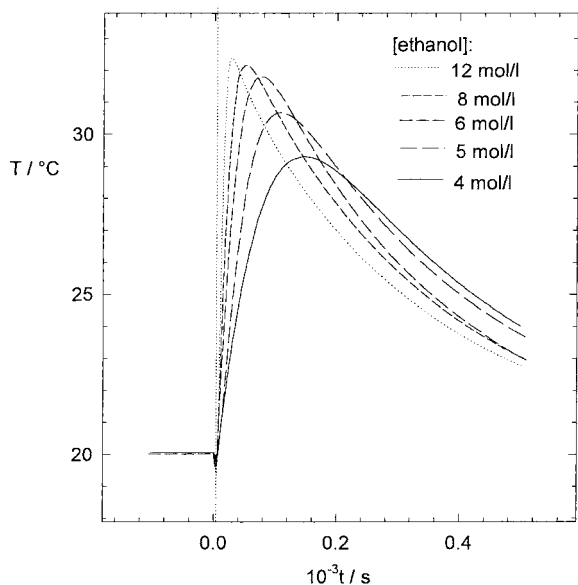


Fig. 4. Temperature–time curves of the alcoholysis of acetyl chloride (0.5 mol/l) with ethanol in acetone.

stoichiometric, or nearly stoichiometric, alcohol concentrations and those with higher alcohol concentrations (Table 3) are treated separately.

If no activation parameter or reaction order is kept constant in the user-defined reaction model of TA-kin 3.3, the kinetic evaluation results in a kinetic law (1) with a partial order of 1.5–1.9 depending on the alcohol, e.g. for ethanol (Table 3):

$$r = k_5 [\text{AcCl}] [\text{ROH}]^{1.6} \quad (1)$$

It has been shown for the first time that the fractional order with respect to alcohol in this rate law is a consequence of a mixed kinetic law (2) consisting of two terms with the partial orders 1 and 2 for the alcohol, respectively (Tables 4 and 5):

$$r = k_2 [\text{AcCl}] [\text{ROH}]^2 + k_1 [\text{AcCl}] [\text{ROH}] \quad (2)$$

This law has been found by several authors [1,6,9,10]. It has been interpreted as the involvement of two mechanisms. The first mechanism includes the

Table 3

Parameters of the overall evaluation of the ethanolysis of acetyl chloride in acetone varying the concentration of ethanol (2, 4, 6 mol/l) with free and fixed order of reaction

$\ln k_0$	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)	$n_1$	$n_2$	ESS/ <i>m</i>
$12.83 \pm 0.18$	$47.78 \pm 0.22$	$-79.10 \pm 0.20$	1.00 (fixed)	$1.624 \pm 0.016$	35.8/779
$11.93 \pm 0.16$	$45.61 \pm 0.40$	$-79.02 \pm 0.22$	$0.979 \pm 0.014$	$1.625 \pm 0.015$	36.1/779

Table 4

Parameters of different evaluations of the ethanolysis of 0.5 mol/l acetyl chloride at 20°C varying the concentration of ethanol (2, 4, 6 mol/l),  $r_{\text{total}}$ : definition of the rate law

Evaluation with $r_{\text{total}}$	Rate law	$\ln k_0$	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)	$n_2$
$r_{\text{total}} = r$	$r = k [\text{A}] [\text{B}]_2^n$	11.9	45.6	-79.0	1.6
$r_{\text{total}} = r_1 + r_2$	$r_1 = k_1 [\text{A}] [\text{B}]$	$9.96 \pm 0.28$	$53.3 \pm 1.7$	$-72.8 \pm 2.2$	–
	$r_2 = k_2 [\text{A}] [\text{B}]^2$	$9.95 \pm 0.23$	$51.4 \pm 0.84$	$-76.9 \pm 1.8$	–

Table 5

Parameters of the evaluation of the *i*-propanolysis of 0.5 mol/l acetyl chloride at 20°C in acetone varying the concentration of *i*-propanol (2, 4, 6 mol/l),  $r_{\text{total}}$ : definition of rate law

Evaluation with $r_{\text{total}}$	Rate law	$\ln k_0$	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)	$n_2$
$r_{\text{ges}} = r$	$r = k[A][B]^n$	18.55	66.73	-72.7	1.9
$r_{\text{ges}} = r_1$ and $r_2$	$r_1 = k_1[A][B]$	$13.9 \pm 0.1$	$66.33 \pm 0.58$	$-67.24 \pm 0.47$	-
	$r_2 = k_2[A][B]^2$	$15.3 \pm 0.1$	$76.40 \pm 0.40$	$-51.27 \pm 0.40$	-

reaction of an acyl chloride molecule with two alcohol molecules (second-order law), the second molecule serving as the acceptor for the proton released in the reaction. In the second mechanism the proton is accepted by a solvent molecule (first-order law). This explains, to some extent, a dependence of the mechanism on the alcohol concentration, because, whether the first or the second mechanism dominates, depends on the concentration of alcohol and the solvent. So, the result of Gilkerson [11], who found a partial order of 2 for the alcohol can be explained by the small  $pK_a$ -value of the solvent acetonitrile ( $pK_a(\text{CH}_3\text{CNH}^+) = -10.1$ ) which prevents the solvent molecules from acting as efficient proton acceptors, therefore mainly the mechanism with two molecules of alcohol occurs.

Fig. 5 shows the concentration- and the temperature-time curves of the ethanolysis of acetyl chloride with a stoichiometric concentration of alcohol which gave the kinetic parameters and reaction enthalpies summarized in Table 6. In this case a different rate law (3) with a partial order of  $n(\text{ROH}) = 0.5$  has been found:

$$r = k_5[\text{AcCl}][\text{ROH}]^{0.5} \quad (3)$$

Angelidou and Hugo [12] also found that simple reaction laws are not capable of describing the temperature curves, especially if the alcohol concentration is less than twice that of the acyl chloride. As shown in [12], these curves can be better evaluated on the basis of complex formulas consisting of a fractional kinetic

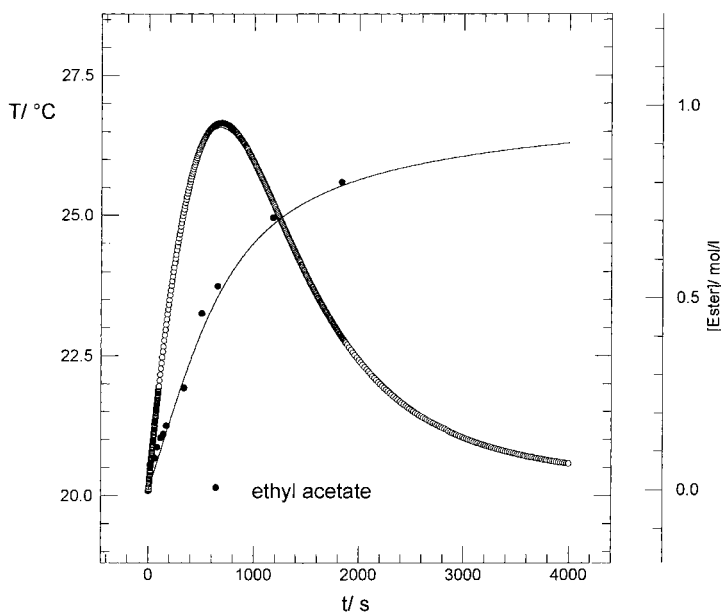


Fig. 5. Temperature–time curves and concentration courses of the alcoholysis of acetyl chloride (1 mol/l) with ethanol (1 mol/l) in acetone — experimental and simulated data.

Table 6

Parameters of the overall evaluation (temperature and acetate concentration curve) of the ethanolysis of acetyl chloride in acetone (1 and 0.2 mol/l)

[AcCl] = 1 mol/l [ROH]	$\ln k_0$	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)	$n_1$ (fixed)	$n_2$
1 mol/l	$20.52 \pm 0.30$	$67.2 \pm 0.8$	$-61.0 \pm 0.26$	1.00	$0.485 \pm 1.6 \times 10^{-2}$
0.2 mol/l	$19.50 \pm 0.03$	$68.4 \pm 0.07$	$-72.8 \pm 0.12$	1.00	$0.612 \pm 2.7 \times 10^{-2}$

law, but an explanation for the partial orders in this law could not be given.

Supposing a steady state in each step, as has been done by Turkewitch and Makitra [13], and taking into account the mechanism described above, which includes the reaction with one molecule and two molecules of alcohol, respectively, it is possible to derive Eq. (4) which gives on simplification (omitting  $k_3$  and representing the counter by one term)

$$r = \frac{k_1[\text{AcCl}][\text{ROH}]^1 + k_2[\text{AcCl}][\text{ROH}]^2}{k_3 + k_4[\text{ROH}]} \quad (4)$$

Eq. (3). Because of the resemblance with the equation resulting on simplification of the rate law given in [10], Eq. (4) might well describe the data given by Angelidou and Hugo [12], who found several equations to be appropriate to describe his measurements.

Eq. (4) should be able to describe the rate law of any alcoholysis of acyl chlorides. For higher concentrations the counter terms dominate ( $k_3$  can be neglected), that is why the evaluation of measurements with a simple second-order law is also successful.

For stoichiometric starting product concentrations, any other simple rate law with an order  $n \neq 0.5$  (Eq. (3)) does not fit simultaneously the temperature changes and the course of the acetate concentration. Different ways of evaluation, as was also found for the corresponding *i*-propanolysis experiment, gave similar results. Unfortunately, the fractional law (4) could not be tested in the kinetic evaluation, because only reaction laws with products of concentrations can be used in the definition of the reaction model in TA-kin 3.3. Furthermore, it does not make sense to evaluate the experiments on the basis of the underlying six partial reactions (implying two back-reactions) as reaction model, because there are not enough data available (e.g. concentrations of the transition states) to support the resulting kinetic parameters (17 free variables).

As demonstrated in Fig. 6, the solvent has a distinct influence which follows as well from the considerations above. In toluene, higher reaction enthalpies and reaction rates than in acetone have been found. In general, non-polar solvents increase the reaction rates, whereas in polar solvents lower reaction rates are found (Table 7). The reaction rate in non-polar solvents is correlated to the dielectric constant. In polar solvents the rate depends on the basicity of the solvent in such a way that the rate is increased by weak bases (CH<sub>3</sub>CN) and decreased by stronger basic solvents like ether (not by amines which attack the acyl chloride). In [13] this decrease is explained by H-bonding between the transition state and the solvent, which decreases with the  $pK_a$ -value. Although this might be

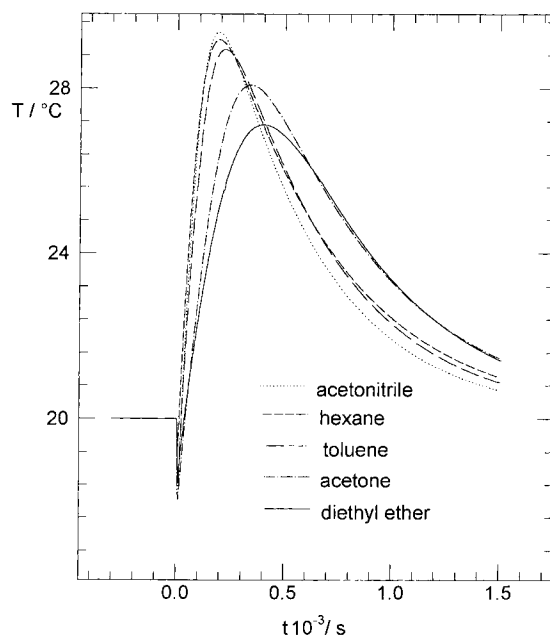


Fig. 6. Temperature–time curves of the alcoholysis of acetyl chloride (0.5 mol/l) with *i*-propanol (6 mol/l) in different solvents.

Table 7

Parameters of the *i*-propanolysis (6 mol/l) of 0.5 mol/l acetyl chloride at 20°C in different solvents with  $\ln k_0 = 20$  (constant) (uncertainties:  $E_a < \pm 0.1$  kJ/mol,  $\Delta_R H < \pm 1.8$  kJ/mol)

Solvent	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)
Hexane	65.0	-71.0
Toluene	65.3	-82.9
Acetonitrile	64.8	-84.6
Acetone	66.7	-76.2
Diethyl ether	67.2	-68.8

an explanation, this could not be confirmed because of the following facts (Table 7):

- At high excess of alcohol, the probability of collision of the molecules of the intermediate with those of the alcohol is much higher than with solvent molecules.
- The alcohol is more polar than the solvent so an interaction between the alcohol and the intermediate should be more stable because it is strongly polar.
- If the reaction takes place in toluene there is no important interaction of the intermediate or the alcohol with the solvent. But because alcohols are more basic (e.g. protonated form:  $pK_a(i\text{-PrOH}_2^+) = -3.2$ ,  $pK_a(\text{EtOH}_2^+) = -2.4$ ,  $pK_a(\text{MeOH}_2^+) = -2.2$  [14]) than most non-protic solvents, there is a certain contradiction because solvents with higher basicities (ether:  $pK_a(\text{Et}_2\text{OH}_2^+) = -3.6$ ) cause lower reaction rates. In contrast to this, the solution in toluene gives higher reaction rates.

Apparently, solvation with other alcohol molecules neither stabilizes the intermediate complex nor increases the activation energy as the interactions with other solvents do. But, supposing that the properties of protonation of aprotic solvents ( $\text{Et}_2\text{OH}_2^+$ ) and alcohols with comparable  $pK_a$ -values are similar ( $i\text{-PrOH}_2^+$ ), they should have the same effect on the reaction intermediate. Such a stabilization is obviously not important, which might be due to special properties of the alcoholic group (e.g. autoprotolysis of the alcohol, a transport mechanism for the proton, etc.). Instead, a second alcohol molecule obviously serves as an acceptor for the proton. As indicated by the

second-order law in Eq. (2), it should play an important role in the mechanism.

These facts make a mechanism probable which includes a cyclic transition state formed by two alcohol molecules and an acetyl chloride molecule. Cyclic transition states frequently play an important role in organic reactions because of the lower activation energy of such an arrangement, but normally this does not consist of three partners.

On the other hand, the lower activation energy of the term  $r_2$  in Eq. (2) with  $n_2 = 2$  in the case of the ethanolysis in Table 5 is a further hint on the proposed mechanism. Thus the lower total reaction rate in polar solvents should be due to a disturbing influence on this cyclic transition state. From the foregoing, it follows that H-bonding between the alcohol and the solvent should be more important for the reaction rate than H-bonding between the solvent and the intermediate [13]. Thus the activation energy is increased by the amount necessary for the desolvation of the alcohol molecule.

Fig. 7 shows the influence of the addition of pyridine and triethylamine, respectively, compared to the

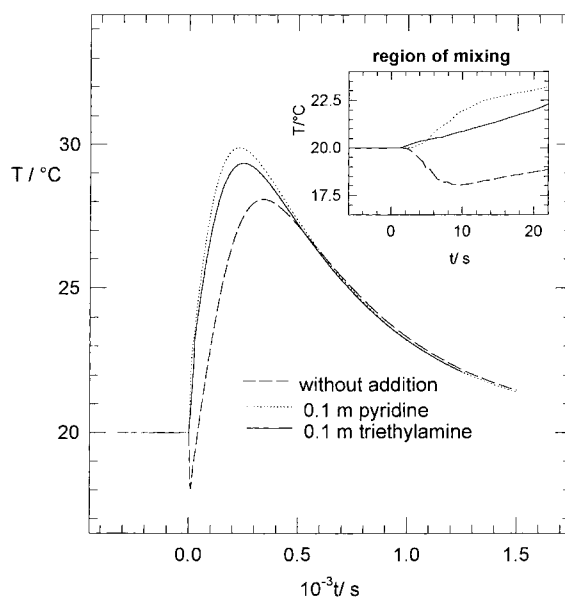


Fig. 7. Effect of pyridine and triethylamine on the temperature–time curves of the alcoholysis of acetyl chloride (0.5 mol/l) with *i*-propanol (6 mol/l) in acetone.

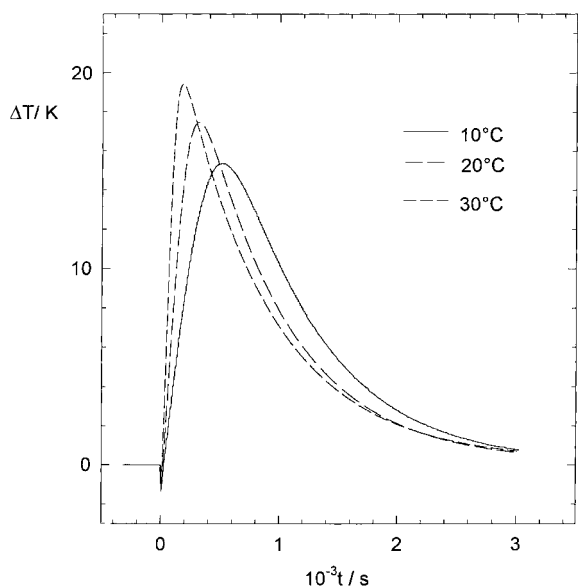


Fig. 8. Temperature–time curves of the alcoholysis of propionyl chloride (1 mol/l) with *i*-propanol (6 mol/l) in acetone at different starting temperatures.

reaction without any amine. The higher reaction rate in the presence of pyridine should be due to a different reaction mechanisms. Whereas triethylamine eliminates one H-atom of acetyl chloride to give the ketene,

which is a relatively slow process, pyridine attacks the keto-bond giving the acylammonium chloride which, reacting with the alcohol, easily eliminates pyridinium chloride. Fig. 8 shows the temperature–time curves at different starting temperatures. The slope increases about 2–3 times by varying the starting temperature by an amount of 10 K as normally expected.

### 3.2. Alcoholysis with binary alcohol mixtures

As has been shown before, the calorimetric curves of ethanol are characterized by a steeper temperature increase than that of *i*-propanol under comparable conditions, due to a higher reaction rate. This has been found too in the case of alcoholic mixtures.

For stoichiometric alcohol mixtures (Fig. 9a) as for the reaction with a small excess of ethanol (Fig. 9b), the temperature–time curves show a steeper temperature jump with increasing ethanol concentration. As it has been found for the simple alcoholysis, the maximum of the temperature–time curves increases with the starting temperature and is shifted to shorter reaction times in the case of higher concentrations of ethanol.

Fig. 10a and b shows examples of the results of the simultaneous kinetic evaluation of temperature–time and concentration–time curves for the

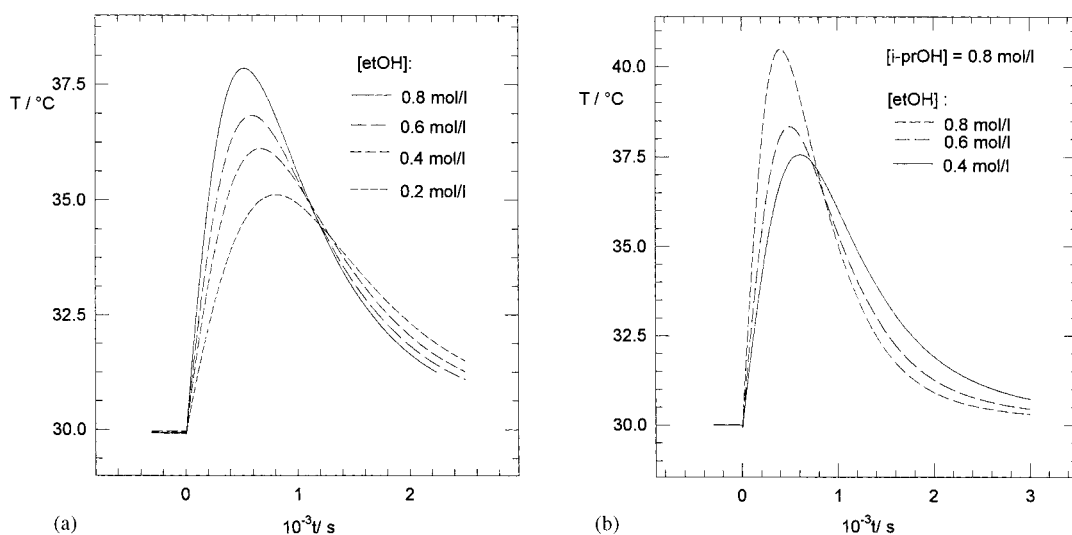


Fig. 9. Temperature–time curves of the alcoholysis of acetyl chloride (1 mol/l) with a mixture of: (a) *i*-propanol and ethanol at a total concentration of 1 mol/l in acetone varying the ethanol concentration; (b) *i*-propanol (0.8 mol/l) and ethanol in acetone varying the ethanol concentration.



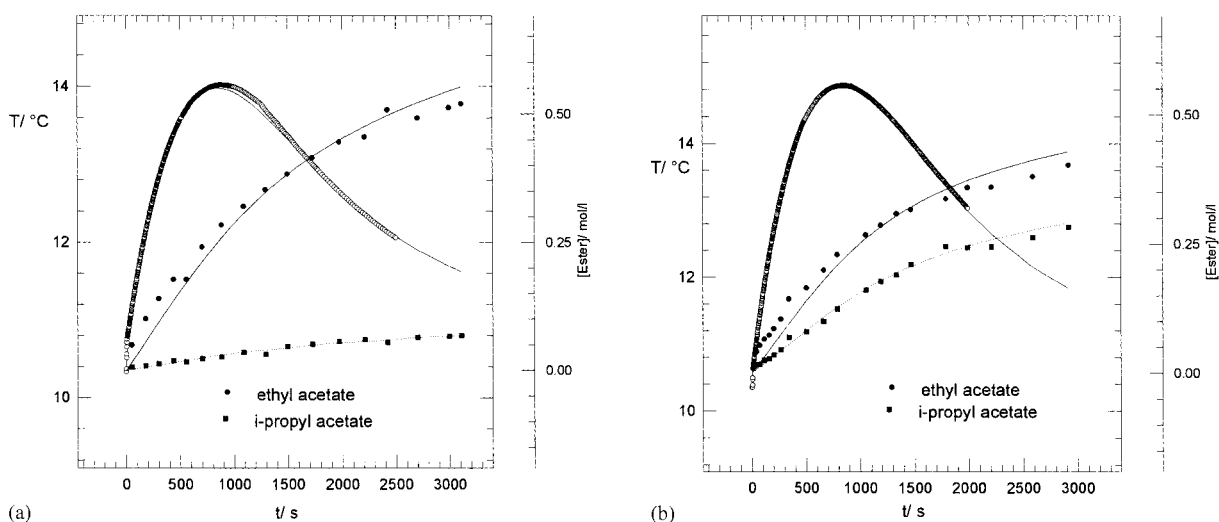


Fig. 10. Temperature–time curves and concentration courses of the alcoholysis of acetyl chloride (1 mol/l) with a mixture of: (a) *i*-propanol (0.2 mol/l) and ethanol (0.8 mol/l); (b) *i*-propanol (0.8 mol/l) and ethanol (0.6 mol/l) in acetone — experimental and simulated data.

stoichiometric and the over stoichiometric cases of alcohol, respectively.

The kinetic analysis of temperature data and concentration data led in nearly all cases of alcohol mixtures to the conclusion that the reaction order is  $n_2 = 0.5$ . As described before, this has been found for the conversions with stoichiometric concentrations of ethanol and of *i*-propanol, as well. Another important observation is the temperature jump which frequently occurs during the time of mixing of the reagent solutions.

In contrast to the dilution of higher concentrations of alcohol which produce greater endothermic signals, experiments with stoichiometric (or nearly stoichiometric) alcohol concentrations result frequently in exothermic temperature courses during the time of mixing. This is especially observed at 10°C. A look at the experimental curves shows that only at a temperature of 30°C does the starting signal become weakly endothermic. The exothermic temperature signal can be attributed to a heat accumulation which is a consequence of the small endothermic heat of the mixing process at low alcohol concentrations and the relatively high reaction enthalpy and rate. Because endothermic excess heats frequently increase with temperature [15], the mixing signal becomes endothermic for the experiments with a starting temperature of 30°C.

The accumulation of the reaction heat during the addition of the acyl chloride solution leads to an exothermic temperature jump in the case of stoichiometric concentrations of the adducts because of the nearly adiabatic conditions and is due to the higher acyl chloride concentration. The spontaneous heat production should be mainly due to the reaction with the more reactive ethanol, because the measured concentrations of ethyl acetate are much higher than those calculated, whereas the measured and the simulated concentration data of the ester of the less reactive *i*-propanol nearly do not deviate.

Whereas additional heat processes and the resulting temperature signals can be described by introducing appropriated amounts of heat into the model of reaction in TA-kin, as shown in [6], the preceding observations might be simulated by a change of the constant of heat exchange, because this would result in a higher temperature and thus in a concentration increase in the beginning as it has been frequently found.

Table 8 summarizes the kinetic parameters and reaction orders found. The uncertainties of the parameters of the measurements are varying depending on the number of free parameters and on the kind of the parameter, they are given in the tables. For the reproducibility of the finding of the activation parameters from several measurements for a simple alcoholysis, the following values have been obtained (standard

Table 8

Overall evaluations (including temperature courses and acetate concentrations) of the mixed ethanolysis and *i*-propanolysis of acetyl chloride (1 mol/l) in acetone with  $\ln k_0 = 20$  (uncertainties:  $E_a < \pm 0.1$  kJ/mol,  $\Delta_R H < \pm 2.8$  kJ/mol)

$T_0$ (°C)	ROH		Ethanol			<i>i</i> -Propanol				
	[etOH] (mol/l)	[ <i>i</i> -prOH] (mol/l)	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)	$n_2$	$E_a$ (kJ/mol)	$\Delta_R H$ (kJ/mol)	$n_2$		
10	0.8	0.2	67.4	−60.9	0.5	67.5	−53.1	0.5		
	0.6	0.4	67.2	−96.8		68.8	−71.1			
	0.4	0.6	67.2	−72.8		68.4	−63.1			
	0.2	0.8	66.0	−76.1		69.8	−67.6			
	0.4	0.8	66.9	−73.3		68.0	−61.6			
	0.6	0.8	66.0	−75.0		67.6	−71.7			
	0.8	0.8	65.7	−85.0		67.7	−64.9			
20	0.8	0.2	67.9	−92.7	0.5	70.9	−72.2	0.5		
	0.6	0.4	68.1	−82.7		70.3	−65.2			
	0.4	0.6	68.2	−70.8		68.9	−62.2			
	0.2	0.8	69.2	−77.8		69.8	−63.7			
	0.4	0.8	66.8	−70.1		70.8	−69.8			
	0.6	0.8	66.3	−70.7		68.3	−53.3			
	0.8	0.8	67.1 <sup>a</sup>	−60.7		1.0	66.1 <sup>a</sup>		−63.8	
30	0.8	0.2	67.3	−58.1	0.5	69.1	−61.2	0.5		
	0.6	0.4	67.7	−64.6		71.2	−63.2			
	0.4	0.6	68.9	−62.0		70.0	−62.7			
	0.2	0.8	70.4	−31.5		69.8	−63.2			
	0.4	0.8	67.2	−76.0		1.02	70.0		−71.8	0.449
	0.6	0.8	66.8	−70.0		1.22	69.3		−74.3	0.985
	0.8	0.8	66.3	−75.4		1.53	68.8		−71.8	1.488

<sup>a</sup>  $\Delta E_a = \pm 0.3$ .

deviation  $\sigma$ ) [6]:  $\sigma(E_a) = \pm 0.06$  kJ/mol,  $\sigma(\Delta_R H) = \pm 1.80$  kJ/mol ( $\ln k_0 = 20$ ).

#### 4. Conclusions

The varying reaction enthalpies, depending on the acyl chloride concentration, make the overall evaluation of groups of data sets with various acyl chloride concentrations difficult. Except for the evaluation of single data sets, a kinetic law of first- or second-order is not appropriate to be applied to kinetic evaluations of experiments of the alcoholysis of acyl chlorides with various concentrations of the alcohol. Partial reaction orders of the alcohol between one and two, in the case of a large excess of alcohol, have been explained, as well as the partial orders of  $n_2 = 0.5$  found for the stoichiometric case. The solvent determines the position of the maximum and the shape of the temperature curve to a big extent, as well. In the

case of toluene, higher reaction enthalpies have been found. For the dependence of the reaction rate on the basicity of the solvent, alternative explanations compared to the literature are given. The efficiency of amine catalysts does not depend in a simple way on the basicity of the amine but also on the reaction mechanism, which may slow down the rate compared to a weaker base.

In the present work, first hints of the formation of a cyclic transition state have been established. Furthermore, it might be possible to estimate activation energies by taking into account the strength of the present H-bonding, if the desolvation energy alone is responsible for the increase of the activation energy.

The results of the evaluation of the alcoholysis of acetyl chloride with mixtures of ethanol and *i*-propanol suggest that modern calorimetric methods permit the distinguishing between parallel reactions if the reactivity difference is big enough.

Results confirm that, for stoichiometric concentrations of alcohol and acyl chloride, a simple kinetic law cannot be presupposed as is generally done in the literature. So a partial order of  $n(\text{ROH}) = 0.5$  for the alcohol has been found, which is not the only hint on more complicated rate laws [12]. Furthermore, investigations underline the necessity of taking into account and simulating heat accumulations when modelling strong exothermic reactions.

Precision calorimetry has proved to be a good tool to differentiate the reactivities of alcohols with acetyl chloride.

## References

- [1] R.F. Hudson, B. Saville, J. Chem. Soc. 4121 (1955) 4130.
- [2] A. Kivinen, Ann. Acad. Sci. Fennicae. A 108 (1960) 77.
- [3] M.H. Palomaa, R.S. Leimu, Ber. 66 (1933) 813.
- [4] J.F. Norris, A.A. Ashdown, J. Am. Chem. Soc. 47 (1925) 837.
- [5] J.F. Norris, Blake, J. Am. Chem. Soc. 50 (1928) 1808.
- [6] T. Willms, Dissertation, EMA-Universität Greifswald, 1999.
- [7] H.L. Anderson, E. Hartmann, Thermochim. Acta 229 (1993) 229–233.
- [8] A. Kemmler, Diplomarbeit, EMA-Universität Greifswald, 1998.
- [9] S.D. Ross, J. Am. Chem. Soc. 7 (1970) 5998.
- [10] A.A. Ashdown, J. Am. Chem. Soc. 52 (1930) 268–279.
- [11] R. Gilkerson, J. Phys. Chem. 60 (1956) 1143.
- [12] M.A. Angelidou, P. Hugo, Chem. Ing. Technol. 62 (9) (1990) 741–744.
- [13] O.E. Turkewitch, P.G. Makitra, React. Sposobnost. Org. Soedin. 10 (3) (1973) 737–747 (in Russian).
- [14] A. Streitwieser, C.H. Heathcock, Organische Chemie, VCH, Weinheim, p. 541.
- [15] A. Lietzmann, B. Löwen, S. Schulz, J. Chem. Eng. Data 39 (1994) 785–788.