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Thermokinetic investigation of the reaction of acetyl chloride with different alcohol types — Part II

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Abstract

The ethanolysis of acetyl chloride has been compared to the methanolysis and the hydrolysis, as well as to the reaction with *n*-propanol, *n*-butanol and *n*-pentanol in acetone and in toluene, to reveal chain-length effects. Pentanol, heptanol and nonanol have been included as well in the investigation, but at lower concentrations.

Structural influences on the alcoholysis of acetyl chloride have been studied with the isomeric C_3 and C_4-alcohols in acetone and in toluene. Furthermore, alcoholysis of acetyl chloride with some C_7-alcohols and the reaction of benzoyl chloride with different types of alcohols have been investigated. © 2000 Published by Elsevier Science B.V.

Keywords: Acetyl chloride; Alcoholysis; Kinetics; Reaction enthalpies; Butanol; Propanol; Benzyl alcohol; Cyclohexyl methanol; *n*-Heptanol

1. Introduction

Esters are applied in many fields of modern industry. This is not only valid for esters with short *n*-alkyl chains like ethyl acetate and methyl acetate which are used as solvents, but also for the esters of pentanol, heptanol or other long-chain *n*-alcohols. Some octyl esters serve as plastics softeners and pentyl acetate is used for the extraction of penicillin in the biotechnological production procedure [1]. Although there are some publications about the alcoholysis of aromatic acyl chlorides, the reaction of aliphatic acyl chlorides with different alcohols has hardly been investigated yet, which could be due to the fact that reaction rates are relatively high and the reactions are quite exothermic.

2. Experimental

The reaction has been performed in an isoperibolic glass calorimeter with a magnetic stirrer. Concentration data were obtained by taking samples, quenching them with a mixture of acetonitrile/ammonia and subjecting them to HPLC-analysis. Whereas for all lower alcohols a concentration of 6 mol/l could be applied, this was not possible for *n*-heptanol and *n*-nonanol, because the volume required would have been to much to obtain comparable conditions. So these experiments have been performed at 4 mol/l and, additionally, some with *n*-pentanol under the same conditions. Measurements were evaluated kinetically by the program TA-kin 3.3 [1]. Details are given in [1–3].

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3. Results

In general, kinetic parameters showed the same tendencies as the appearance of the temperature curves suggests. Fig. 1 represents the temperature–time curves of the hydrolysis, the methanolysis and the ethanolysis of acetyl chloride in acetone.

The temperature maximum is shifted to longer reaction times with increasing chain length. Furthermore, the slopes of the calorimetric curves are decreasing.

Using the value $\ln k_0 = 16$, given by other authors for the hydrolysis of acetyl chloride [4], the activation energy ($E_a = 50.3\,\mathrm{kJ/mol}$) determined is comparable to that ($E_a = 51.0$) found by this author. The experimental reaction enthalpy of 120 kJ/mol, which results from the kinetic evaluation, has been calculated from the enthalpies of formation, taking into account the presence of water and the corresponding solvation enthalpies of HCl and acetic acid. For further discussion see [1].

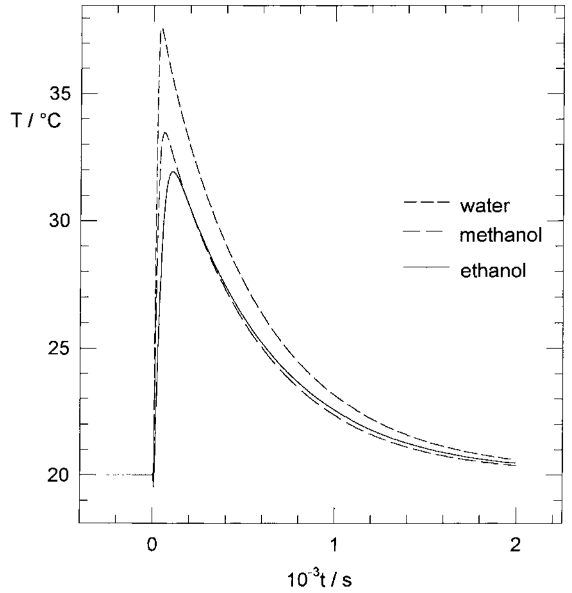

Fig. 1. Temperature–time curves for the alcoholysis of acetyl chloride (0.5 mol/l) with water, methanol and ethanol (6 mol/l) in acetone.

The decrease of the reaction rate is related to the length of the molecule in the case of water, methanol, and ethanol, so a statistical effect has to be included, which is given by the probability of collision of the active center of an acetyl chloride molecule with an alcohol molecule. This decreases with the chain length [5]. Fig. 2a represents the temperature–time curves of

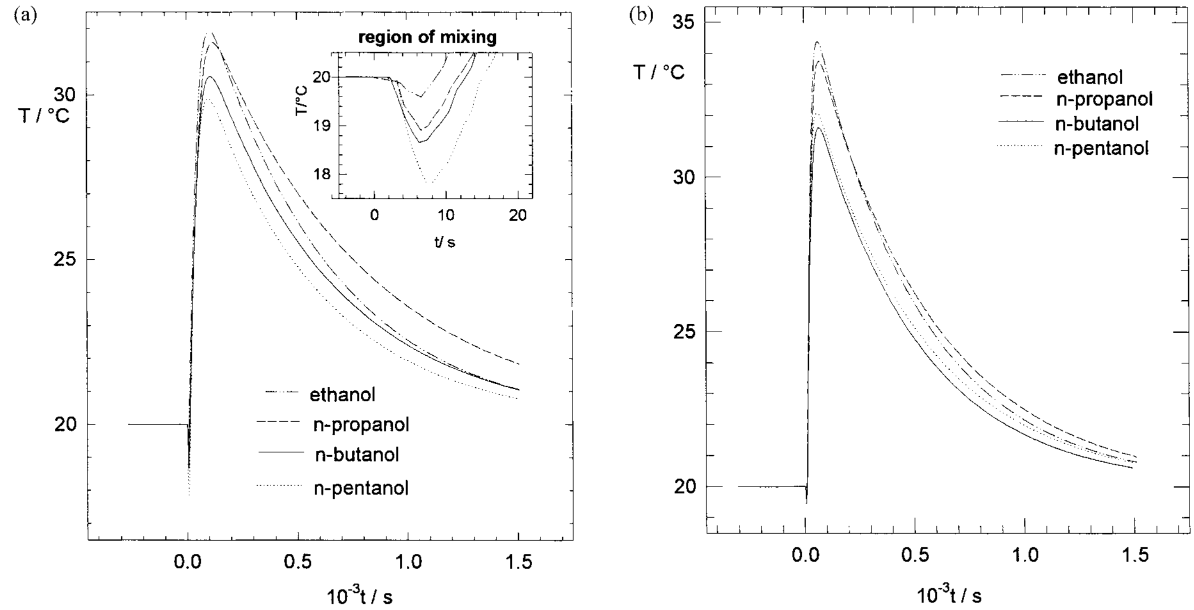

Fig. 2. Temperature–time curves for the reaction of acetyl chloride (0.5 mol/l) with primary alcohols (6 mol/l) in (a) acetone, and (b) toluene.

Table 1
Activation energies and reaction enthalpies for the alcoholysis of acetyl chloride with primary alcohols at 20°C with $\ln k_0 = 20$ (constant) (uncertainties: $E_a < \pm 0.1$ kJ/mol, $\Delta_R H < \pm 2.8$ kJ/mol)

ROH	[AcCl] (mol/l)	Acetone		Toluene	
		E_a (kJ/mol)	$\Delta_R H$ (kJ/mol)	E_a (kJ/mol)	$\Delta_R H$ (kJ/mol)
Water	0.5	61.2	−108.0	–	
Methanol	0.5	61.6	−78.8	–	
Ethanol	0.25	63.1	−88.8	61.6	−120.0
	0.50	63.2	−79.7	62.1	−97.4
	1.00	63.1	−73.2	61.9	−91.6
n-Propanol	0.25	63.4	−82.7	62.1	−89.0
	0.50	63.4	−76.9	61.8	−65.0
	1.00	63.4	−74.0	62.0	−70.0
n-Butanol	0.25	63.1	−82.0	62.0	−82.0
	0.50	63.2	−76.0	62.0	−77.7
	1.00	63.1	−75.0	62.5	−70.8
n-Pentanol	0.25	63.0	−78.5	61.8	−81.7
	0.50	63.0	−72.8	61.4	−97.0
	1.00	62.5	−75.8	61.1	−99.6

the ethanolysis, the *n*-propanolysis, the *n*-butanolysis and the *n*-pentanolysis of acetyl chloride in acetone, Fig. 2b shows the corresponding curves for the reaction in toluene. Some kinetic parameters for the evaluation with constant $\ln k_0$-value are given in Table 1. It is clear (Tables 1 and 2) that the rate constants can be split into two groups:

1. hydrolysis, methanolysis, ethanolysis, *n*-propanolysis: rate constants decrease for the reasons given above (in Table 1 the hydrolysis has the smallest activation energy),
2. *n*-propanolysis, butanolysis, pentanolysis: rate constants increase with the length of the alkyl group.

Increasing rate constants have been found by Norris and Cortese [6] for the alcoholysis of *p*-nitrobenzoyl chloride with higher alcohols too.

Songshou et al. [7] discovered a similar effect for the alcoholysis of acyl anhydrides [3]. They considered the reactivity as a result of two effects, namely the higher reaction enthalpy, which facilitates the reaction of lower alcohols having a higher acidity like methanol, and the auto-association of methanol, which diminishes the reaction rate. In the case of *n*-butanol this is reversed because the big alkyl chains prevent auto-association but the acidity is smaller, as is the reaction enthalpy.

The greater importance of an intermolecular complex for the alcoholysis of acyl anhydrides is due to the reaction mechanism which presupposes formation of OH-bridges and a cyclic transition-state as has been described by Hugo and Pham [8]. Thus our results represent a further hint that a cyclic complex of the alcohol and the acyl chloride could be involved in the alcoholysis of acetyl chloride, as has been deduced already in [2]. In the case of toluene as solvent, the same phenomenon can be observed. Reaction enthalpies and activation parameters for these experiments at a concentration of 6 mol/l, obtained by an overall evaluation with data sets at 10, 20 and 30°C, are given in Table 2. Fig. 3 shows the pentanolysis of acetyl chloride in toluene and in acetone.

The curve in acetone shows a lower temperature maximum as well as a smaller slope of the temperature–time curve. Apart from this, the integration of the curve results in a smaller value for the area.

Fig. 4 gives an example of the temperature–time curve and the measured concentration data for the *n*-butanolysis of acetyl chloride. Additionally, the corresponding simulated data, calculated by TA-kin with the derived parameters, are given.

Fig. 5a represents the temperature–time curves for the pentanolysis, the heptanolysis and the nonanolysis of acetyl chloride in acetone. Whereas the curves for the pentanolysis, the heptanolysis and the *n*-nonano-

Table 2
Activation parameters and reaction enthalpies of the alcoholysis of acetyl chloride with primary alcohols[a]

	[ACl] (mol/l)	In acetone					In toluene				
		ln k_0	E_a (kJ/mol)	ΔH_R (kJ/mol)	k_2 (25°C) (l/mol s)	ESS/m	ln k_0	E_a (kJ/mol)	ΔH_R (kJ/mol)	k_2 (25°C) (l/mol s)	ESS/m
EtOH	0.25	13.24	46.3	−90.1	4.35E−03	5.23/1172	14.14	46.7	−117.2	9.03E−03	29.4/1116
	0.50	14.26	48.6	−82.3	4.79E−03	57.40/1134	16.70	53.0	−108.1	9.20E−03	50.2/1140
	1.00	15.11	50.6	−74.0	5.00E−03	196.75/1202	16.78	52.8	−99.4	1.11E−02	146.6/1140
n-PrOH	0.25	15.29	51.3	−89.1	4.29E−03	8.3/973	10.70	38.8	−102.6	7.09E−03	11.8/587
	0.50	13.58	47.1	−82.8	4.45E−03	24.7/994	15.65	50.7	−89.3	8.26E−03	20.7/1087
	1.00	14.95	50.2	−78.6	4.92E−03	90.8/1049	14.83	48.5	−79.2	8.85E−03	121.3/1039
n-BuOH	0.25	14.92	49.9	−89.6	5.39E−03	25.9/996	–	–	–	–	–
	0.50	17.63	56.7	−81.7	5.37E−03	29.0/1082	15.94	51.2	−83.6	9.04E−03	29.9/1154
	1.00	20.69	64.3	−77.5	5.28E−03	26.3/762	15.57	50.4	−81.3	8.69E−03	38.6/712
n-PeOH	0.25	14.96	49.9	−91.0	5.73E−03	30.8/1001	18.43	57.4	−83.9	8.72E−03	18.7/993
	0.50	16.42	53.3	−92.7	6.26E−03	37.1/1094	15.00	48.6	−94.3	1.02E−02	48.9
	1.00	17.83	56.6	−84.6	6.75E−03	67.0/1074	16.78	52.7	−88.1	1.15E−02	142.5/1044

[a] Results of the overall evaluation over starting temperatures T_0 at different concentrations of acyl chloride with TA-kin [ROH]: 6 mol/l (ESS: result of minimization of Error square sum, m: number of error equations) (uncertainties: $\ln k_0 \leqslant \pm 0.1$, $E_a < \pm 0.2\,\mathrm{kJ/mol}$, $\Delta_R H < \pm 1.0\,\mathrm{kJ/mol}$).

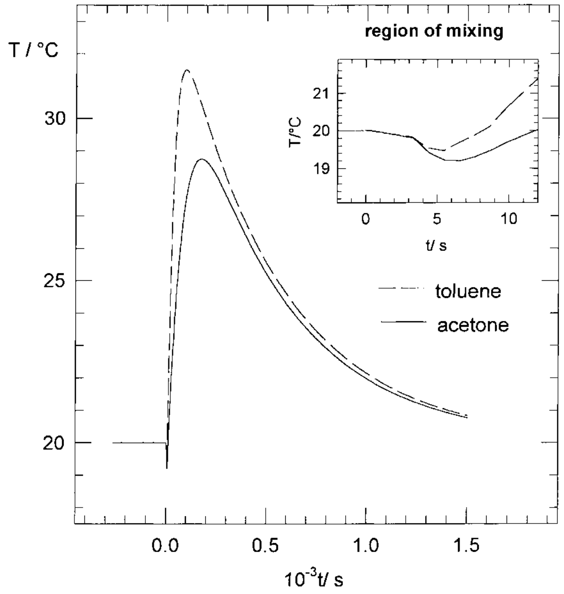

Fig. 3. Temperature–time curves for the alcoholysis of acetyl chloride (0.5 mol/l) with *n*-pentanol (4 mol/l) in acetone and toluene.

lysis of acetyl chloride in toluene are very similar (Fig. 5b), they differ considerably in acetone. The fact that, before adding the solution of acetyl chloride in acetone, only some milliliters of acetone are present in the nonanol solution, could cause the larger mixing peak. The lower polarity in the reaction mixture might explain the unusually high reaction rates, which are similar to those with lower alcohols in toluene. The parameters obtained are summarized in Table 3.

In Fig. 6 the temperature and concentration data for the 2-butanolysis of acetyl chloride are shown, as well as the corresponding simulated data. Fig. 7a shows the temperature–time curves for the *n*-butanolysis, the *i*-butanolysis and the 2-butanolysis of acetyl chloride in acetone.

In the case of primary alcohols, the temperature maximum is shifted to shorter reaction times, so the starting slope of the calorimetric curve of the 2-butanolysis in acetone, as in toluene (Fig. 7b), is lower than for *n*-butanol and *i*-butanol.

The different reactivities may be explained qualitatively by steric hindrances, but it has been shown [1]

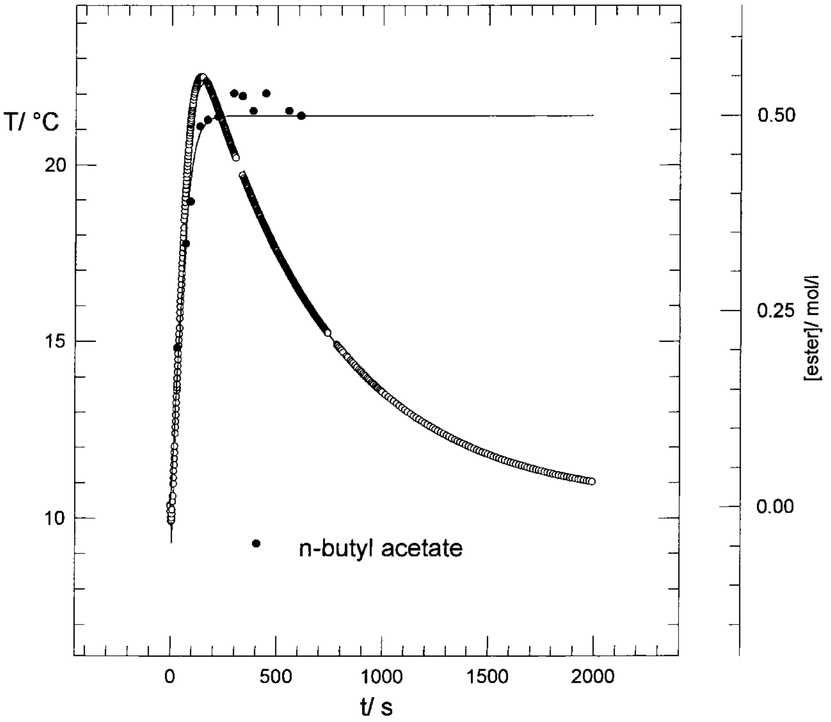

Fig. 4. Temperature–time curves and concentration data for the alcoholysis of acetyl chloride (0.5 mol/l) with *n*-butanol (6 mol/l) in acetone — experimental and simulated data.

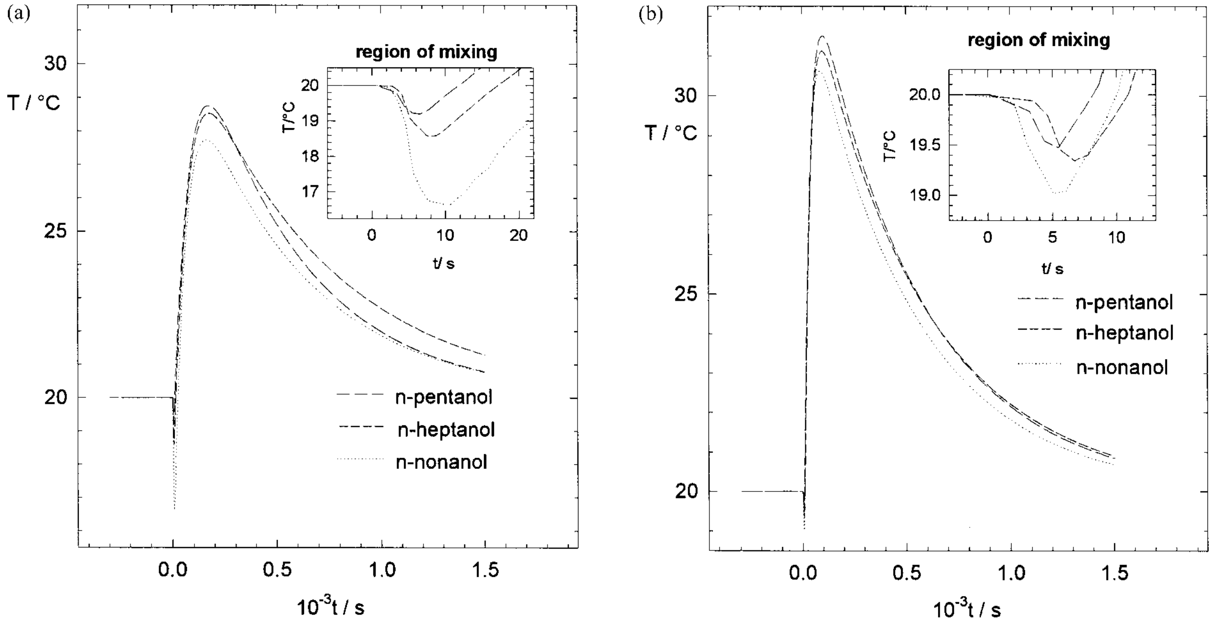

Fig. 5. Temperature–time curves for the alcoholysis of acetyl chloride (0.5 mol/l) with *n*-pentanol, *n*-heptanol and *n*-nonanol (4 mol/l) in (a) acetone, and (b) toluene.

that there is a direct relation to the basicity of the alcohol. So, whereas the pK_a-value of the primary alcohol is about 16.0, that of the secondary alcohol is about 16.5. The values of tertiary alcohols are in the range of 17–18 showing that the smaller reactivity of these compounds coincides with a larger pK_a. An analysis of the percentage rate change with the pK_a-value is given in [1].

This difference could be the reason for the fact that a relationship for the activation energies E_a of the alcoholysis of different concentrations of acetyl chloride with propanol isomers at 10 and 20°C of the following kind has been found ($\ln k_0$ = fixed to 20):

$$E_a(\text{sec. alcohol}) = E_a(\text{prim. alcohol}) + 3.3 \pm 0.1\,\text{kJ/mol}$$

Such an equation is valid too for the *i*-propanolysis in toluene at 20°C (with $3.25 \pm 0.25\,\text{kJ/mol}$). For the butanol isomers in acetone, a small amount has to be added on the right ($3.6 \pm 0.2\,\text{kJ/mol}$ for 20 and 30°C).

Table 3
Activation energies and reaction enthalpies for the alcoholysis of acetyl chloride with 4 mol/l alcohol (*n*-C_5 to *n*-C_9) at 20°C with $\ln k_0 = 20$ (constant) (uncertainties: $E_a < \pm 0.1\,\text{kJ/mol}$, $\Delta_R H < \pm 2.8\,\text{kJ/mol}$)

ROH	[AcCl] (mol/l)	Acetone		Toluene	
		E_a (kJ/mol)	$\Delta_R H$ (kJ/mol)	E_a (kJ/mol)	$\Delta_R H$ (kJ/mol)
n-Pentanol	0.25	63.5	−79.7	61.7	−86.4
	0.50	63.3	−70.1	61.7	−78.9
	1.00	63.5	−68.3	62.0	−78.3
n-Heptanol	0.50	63.3	−68.4	61.8	−75.4
n-Nonanol	0.25	62.8	−81.1	61.0	−93.3
	0.50	62.6	−78.4	61.4	−77.8
	1.00	62.5	−73.2	61.5	−87.0

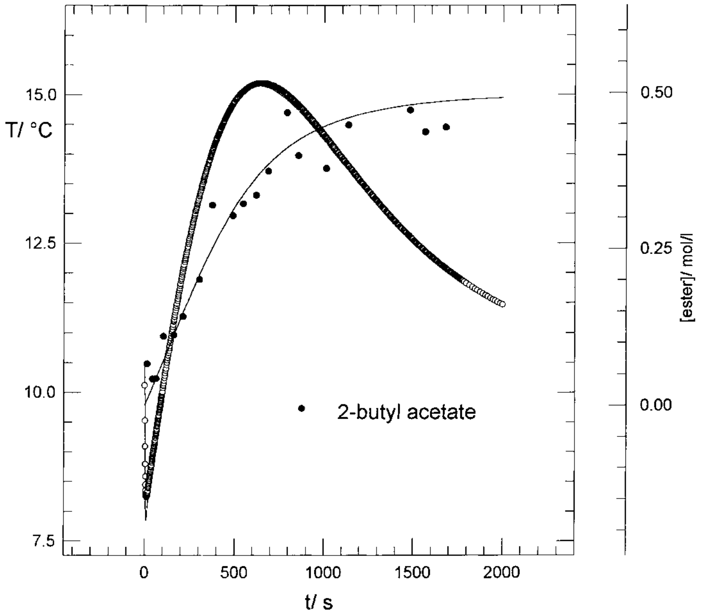

Fig. 6. Temperature–time curves and concentration data for the alcoholysis of acetyl chloride (0.5 mol/l) with 2-butanol (6 mol/l) in acetone — experimental and simulated data.

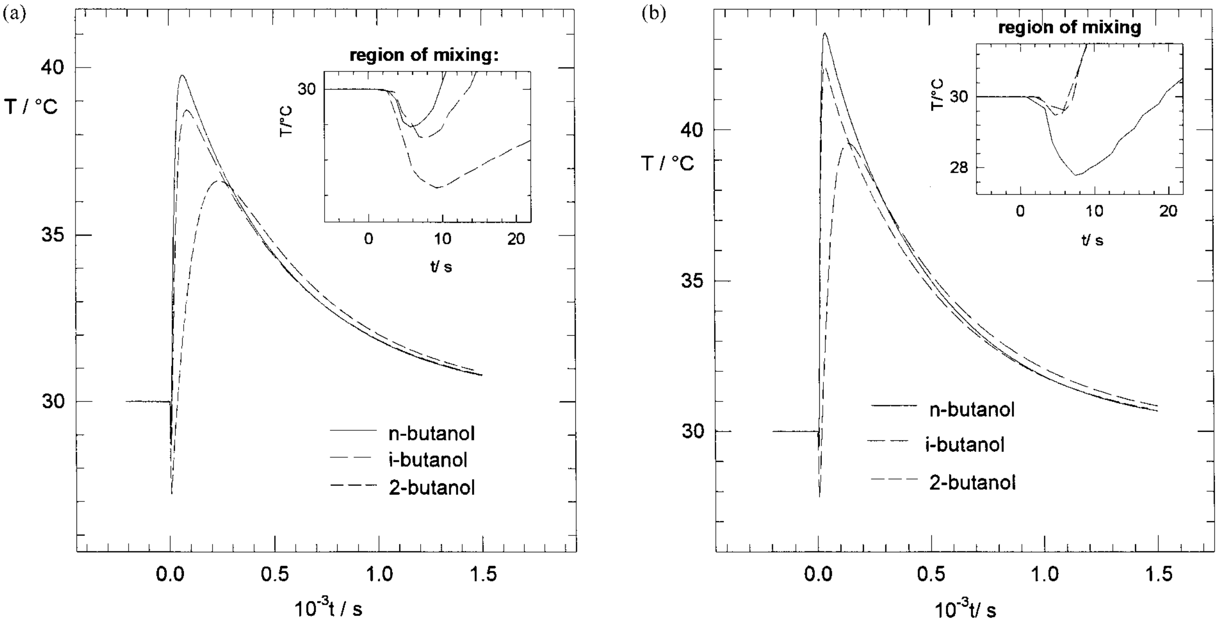

Fig. 7. Temperature–time curves for the alcoholysis of acetyl chloride (0.5 mol/l) with butanol isomers (6 mol/l) in (a) acetone, and (b) toluene.

Table 4

Activation parameters and reaction enthalpies of the alcoholysis of acetyl chloride with butanol isomers and *i*-propanol[a]

	[ACl] (mol/l)	In acetone					In toluene				
		ln k_0	E_a (kJ/mol)	ΔH_R (kJ/mol)	k_2 (25°C) (l/mol s)	ESS/*m*	ln k_0	E_a (kJ/mol)	ΔH_R (kJ/mol)	k_2 (25°C) (l/mol s)	ESS/*m*
n-BuOH	0.25	14.92	49.9	−89.6	5.39E−03	25.9/996	–	–	–	–	–
	0.50	17.63	56.7	−81.7	5.37E−03	29.0/1082	15.94	51.2	−83.6	9.04E−03	29.9/1154
	1.00	20.69	64.3	−77.5	5.28E−03	26.3/762	15.57	50.4	−81.3	8.69E−03	38.6/712
i-BuOH	0.25	9.23	36.7	−93.2	3.76E−03	47.08/1132	15.12	49.5	−102.3	7.84E−03	32.8/1015
	0.50	12.82	45.3	−81.9	4.35E−03	22.26/729	14.75	48.3	−92.5	8.65E−03	40.03/1189
	1.00	15.05	51.0	−81.2	3.99E−03	43.9/953	15.85	51.1	−87.7	8.53E−03	180.32/796
2-BuOH	0.25	15.24	55.1	−70.2	9.20E−04	23.7/1169	14.14	50.9	−81.0	1.69E−03	23.8/879
	0.50	14.78	53.9	−70.9	9.65E−04	46.4/1141	17.12	58.2	−79.5	1.71E−03	47.9/943
	1.00	15.59	55.4	−69.0	1.17E−03	85.9/1023	16.39	56.2	−76.9	1.90E−03	130.1/1168
i-PrOH	0.25	14.68	53.4	−71.6	1.07E−03	34.4/1224	19.32	63.6	−90.0	1.81E−03	10.1/1129
	0.50	15.03	54.1	−69.1	1.13E−03	66.3/929	17.56	59.1	−84.4	1.91E−03	52.7/1114
	1.00	16.29	57.1	−66.1	1.18E−03	160.51/1173	16.59	56.4	−79.9	2.11E−03	146.8/1208

[a] Results of the over-all-evaluation over starting temperatures T_0 at different concentrations of acyl chloride with TA-kin [ROH]: 6 mol/l (ESS: result of minimization of Error square sum, *m*: number of error equations) (uncertainties: $\ln k_0 < \pm 0.1$, $E_a < \pm 0.2\,\mathrm{kJ/mol}$, $\Delta_R H < \pm 1.0\,\mathrm{kJ/mol}$).

Table 5
Activation energies and reaction enthalpies of the alcoholysis of acetyl chloride with C_7-alcohols in acetone at 20°C with $\ln k_0 = 20$ (constant) (uncertainties: $E_a < \pm 0.1$ kJ/mol, $\Delta_R H < \pm 2.8$ kJ/mol)

ROH	[AcCl] (mol/l)	E_a (kJ/mol)	$\Delta_R H$ (kJ/mol)
n-Heptanol	0.50	63.4	−76.9
Cyclohexyl methanol	0.25	62.7	−85.2
	0.50	63.0	−74.7
	1.00	63.0	−69.9
Phenyl methanol	0.25	64.9	−71.5
	0.50	64.7	−62.7
	1.00	64.5	−59.2

Under different conditions the deviations are higher, so that in toluene (10°C) for the acetylation of *n*-butanol and 2-butanol such an equation can only be established if a larger error is accepted ($\approx 3.5 \pm 0.5$ kJ/mol).

As the following shows, the effective basicity is decreased less in toluene, which may be the reason that reaction rates from chemically similar alcohols generally seem to be more similar in nonpolar than in polar solvents.

Fig. 7b also shows that, in contrast to the reaction in acetone, the temperature curves of the primary butanols differ less in toluene, which is confirmed by the kinetic parameters obtained by TA-kin (Tables 4 and 5). This suggests that the lower reaction rate in acetone is probably only partly caused by steric hindrance from the methyl group, but to a greater part by a solvent effect. This conclusion is substantiated by the fact that both phenomena are observed independently for similar reactions by other authors [6,9]. Percentage values of rate changes are given in [1].

Alternatively, there is evidence that the basicity of alcohols measured in solution is influenced by sterical phenomena anyway, because in the vaporized state, *t*-butanol is a much stronger acid than *n*-butanol [10]. So steric hindrance, which is difficult to measure, should be indirectly included in our considerations.

Fig. 8a demonstrates the temperature–time curves for the *n*-propanolysis, the *i*-propanolysis and the 2-butanolysis of acetyl chloride in acetone. In Fig. 8b, the curves for the reaction with the same alcohols in toluene are given.

These figures show that the temperature–time curves of the propanols differ in the same way as those of the corresponding butanols. Furthermore, a comparison of the calorimetric curves of 2-butanol and *i*-propanol is possible. Again, the curve widths in toluene are narrower than in acetone, which provides further evidence for the foregoing generalization. In contrast to the examples given before, the difference of the rate constants reveals, in the case of the secondary alcohols, only partly the difference which is suggested by the calorimetric curves. Reaction enthalpies and activation parameters for these experiments at a concentration of 6 mol/l are arranged in Table 4.

Fig. 9 shows the temperature–time curves of the reaction of acetyl chloride with *n*-heptanol, cyclohexyl methanol and benzyl alcohol in acetone. It is remarkable that the calorimetric curve of the reaction with cyclohexyl methanol shows the steepest slope, whereas the *n*-heptanolysis appears to be much slower. This may be explained by the compact structure of the molecule of cyclohexyl methanol, compared to *n*-heptanol, which increases the probability of collisions with the acetyl chloride molecule. The reactivity of benzyl alcohol appears, according to the calorimetric curves, considerably lower than that of cyclohexyl methanol, which should be caused by the electronic structure of the phenyl group because the cyclohexyl group has a bigger volume than the flat phenyl ring, but nevertheless causes a higher reaction rate. Thus steric hindrance cannot be decisive and the electron-withdrawing effect of the phenyl group could be responsible. Parameters are given in Table 5. Fig. 10 shows the alcoholysis of benzoyl chloride with *i*-propanol, *n*-propanol and ethanol. Again there is a big difference in reactivity between the *i*-propanolysis and the *n*-propanolysis (Table 6).

The uncertainties of the parameters of the measurements are varying depending on the number of free parameters and on the kind of the parameter, the order of magnitude of the errors of the measurements is

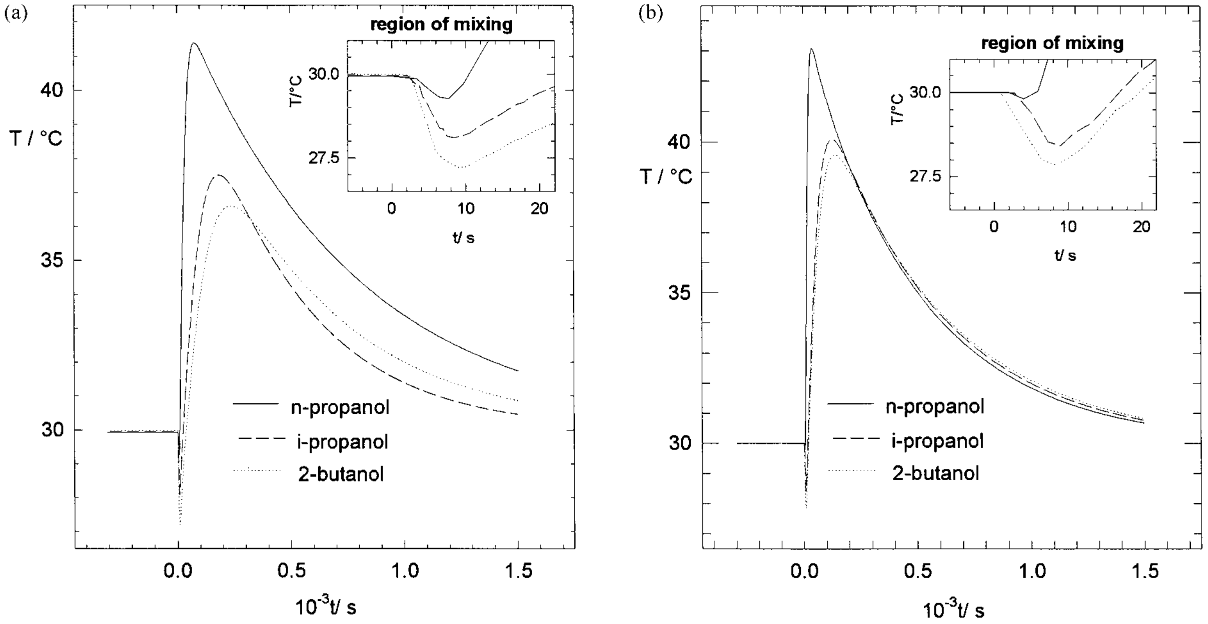

Fig. 8. Temperature–time curves for the alcoholysis of acetyl chloride (0.5 mol/l) with 2-butanol, *n*-propanol and *i*-propanol (6 mol/l) in (a) acetone, and (b) toluene.

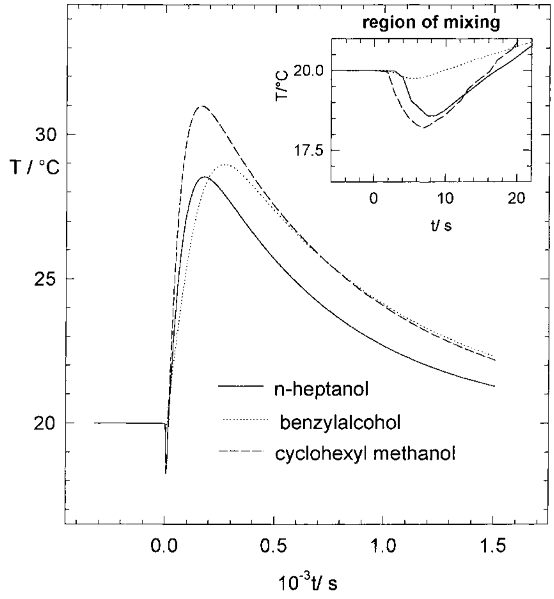

Fig. 9. Temperature–time curves for the alcoholysis of acetyl chloride (0.5 mol/l) with heptanol, benzylalcohol and cyclohexyl methanol (4 mol/l) in acetone.

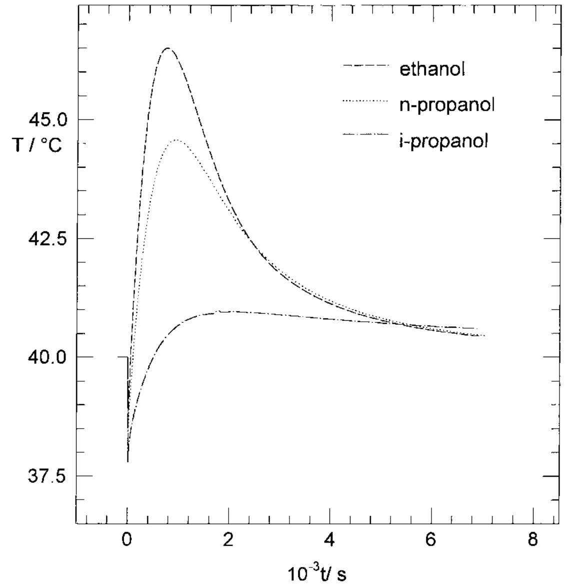

Fig. 10. Temperature–time curves for the alcoholysis of benzoyl chloride (1 mol/l) with ethanol, *n*-propanol and *i*-propanol (6 mol/l) in acetone.

Table 6
Results of the evaluation of the alcoholysis of benzoyl chloride and acetyl chloride in acetone (uncertainties: $E_a < \pm 0.1\,\mathrm{kJ/mol}$, $\Delta_R H < \pm 2.8\,\mathrm{kJ/mol}$)

ROH in acetone	[ACl] (mol/l)	Acetyl chloride at 30°C				Benzoyl chloride at 40°C			
		$\ln k_0$	E_a (kJ/mol)	$\Delta_R H$ (kJ/mol)	k_2 (30°C) (l/mol s)	$\ln k_0$	E_a (kJ/mol)	$\Delta_R H$ (kJ/mol)	k_2 (30°C) (l/mol s)
Ethanol	1.00	20.0	63.8	−73.2	4.93E−03	11.60	53.0	−75.1	5.95E−05
n-Propanol	1.00	20.0	64.1	−72.2	4.38E−03	11.60	55.0	−82.5	3.64E−05
i-Propanol	1.00	20.0	66.8	−63.8	1.50E−03	11.60	59.0	−73.0	7.45E−06

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 deviation σ)

$$\sigma(E_a) = \pm 0.06\,\mathrm{kJ/mol},$$

$$\sigma(\Delta_R H) = \pm 1.80\,\mathrm{kJ/mol} \quad (\text{fixed} \ln k_0 = 20)$$

For more details, see [1,2].

4. Conclusions

It has been shown that even small differences in activation parameters are detectable by modern calorimetric methods and kinetic evaluation software, complex processes taking place during the reaction of the alcohols with acetyl chloride have been found by the effects of varying the chain length of the alcohol.

The unusual change in the activation parameters going from the *n*-propanolysis to the *n*-butanolysis was explained by decreasing auto-association, which facilitates the formation of the intermolecular complex. This interpretation was transferred from an investigation of the alcoholysis of acyl anhydrides [7].

Expectedly, the difference between the curves of the pentanolysis, heptanolysis and the nonanolysis is small, especially in toluene the curves are nearly identical. The lower reactivity of secondary alcohols compared to primary ones was confirmed by modern calorimetric methods. It has been shown that reactivity depends on the basicity of the alcoholic hydroxyl group.

In nonpolar solvents, the rate constant seems to be determined exclusively by the basicity of the alcohol if reaction conditions are similar, whereas in polar solvents the activation energy is influenced by the OH-bridge to the solvent [2]. But as indicated in [2], a change of the rate law due to an additional process is probably more important. It has been shown by the calorimetric curves, and by the kinetic parameters, determined by means of TA-kin, that the difference in reactivity between *n*-butanol and *i*-butanol is larger in acetone than in toluene [1]. So the lower reaction rate could not be due only to a steric hindrance as has been accepted but, to a greater extent, also to a solvent effect. For the rate constants of the 2-butanolysis and *i*-propanolysis of acetyl chloride only a small difference has been found in both solvents.

Compared to benzyl alcohol, cyclohexyl methanol gives a much higher reaction rate with acetyl chloride under similar conditions. This supports the interpretation that the lower reactivity is due to the electron-withdrawing effect of the phenyl group and shows the smaller steric influence of the ring. On the other hand, cyclohexyl methanol also gives a larger rate constant than heptanol which may be caused by its greater compactness which facilitates the reaction compared to the long-chained heptanol.

As described for acetyl chloride, decreasing reaction rate constants for the reactions of benzoyl chloride with ethanol, propanol and *i*-propanol have been found. Precision calorimetry has proved to be a good tool to differentiate the reactivities of alcohols against acetyl chloride.

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