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Thermokinetic investigation of the alcoholysis of acyl chlorides

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Abstract

The alcoholysis of acetyl chloride, propionyl chloride and butyryl chloride with some alcohols in acetone and toluene has been investigated by means of calorimetric measurements. Furthermore a comparison with benzoyl chloride has been made.

In the case of *i*-propanol in acetone, a smaller rate constant has been found for the alcoholysis of propionyl chloride than for butyryl chloride. In contrast to this, almost equal rate constants have been determined for the reactions of these acyl chlorides with *n*-propanol and ethanol.

In toluene, the rate constants for the reaction of acetyl chloride with all considered alcohols has the highest values under similar conditions but then decrease from acetyl chloride to butyryl chloride. The observed differences and the changes of rate constants are discussed and compared with literature data. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alcoholysis; Acyl chloride; Benzoyl chloride; Kinetics; Enthalpy; Solvent

1. Introduction

Whereas the solvolysis of benzoyl chloride and its substituted derivates has been frequently investigated in the past (e.g. [1–6]), aliphatic acyl chlorides are rarely the subject of systematic investigations [7]. The number of publications treating the comparison of the reactions of acetyl, propionyl and butyryl chloride [7–10], or even only two of them [11], is restricted to very few examples, even if partial hydrolysis [10] and naphtholysis [9] are included. An analysis of these examples is given in [12].

Surprisingly, in none of these publications, has the alcoholysis of butyryl chloride been found to have the lowest reaction rate, although this is expected from electronic and steric considerations, because the volume of the alkyl group and also the positive inductive effect should increase or at least remain constant. But instead, a higher rate constant for the reaction of butyryl chloride with the corresponding alcohol, compared to propionyl chloride, has been found [7], although frequently ignored. Except for Leimu [8], authors are inclined to ignore this observation and consider it as a measuring error [9]. But, as discussed later, this contrasts with the maximum measuring error of 10%, which is in general discussed as the maximum deviation from the true value. On the basis of this background, some reactions of the named acyl chlorides have been investigated in toluene and

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acetone, as examples for a nonpolar solvent and a polar solvent, respectively.

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/pyridine/methanol and subjecting them to HPLC-analysis. More details are given in [12,13]. The program TA-kin 3.3 [12] has been applied for the kinetic evaluation.

3. Results

Fig. 1 represents the temperature-time curves for the reactions of acetyl chloride and benzoyl chloride, respectively, with *i*-propanol in acetone.

Kinetic evaluation with TA-kin shows that the rate constants differ by some orders of magnitude. So rate constants $k_2 = 1.18 \times 10^{-3}$ 1/mol s for acetyl chloride and $k_2 = 4.9 \times 10^{-6}$ 1/mol s for benzoyl chloride have been found (factor of about 240). So the order of magnitude found by Branch (factor 172) [14], who was not able to measure this high reaction rate properly, has been confirmed.

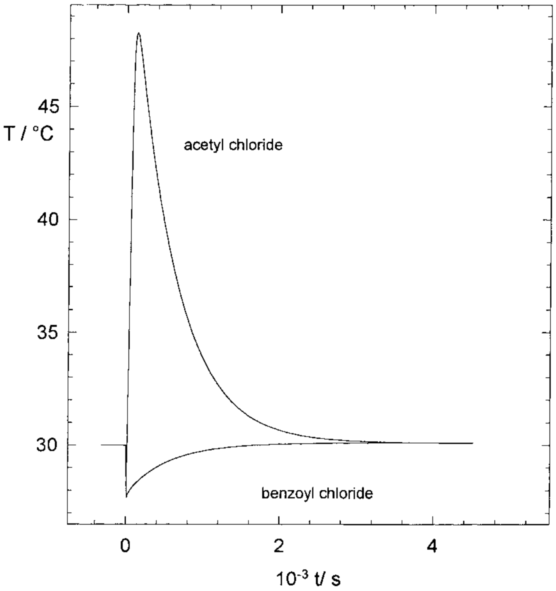

Fig. 1. Temperature-time curves for the alcoholysis of benzoyl chloride (1 mol/l) and acetyl chloride (1 mol/l) with *i*-propanol (6 mol/l) in acetone.

In Figs. 2 and 3 the measured temperature and concentration data of the *i*-propanolysis of butyryl chloride and propionyl chloride in toluene are represented, as well as the corresponding simulated data, calculated by TA-kin with the kinetic parameters determined.

Fig. 4a shows the temperature-time curves for the *i*-propanolysis of acetyl chloride, propionyl chloride and butyryl chloride in acetone.

As the calorimetric curves suggest by their increases, the overall kinetic evaluation with TA-kin delivers a higher value of the rate constant for the alcoholysis of butyryl chloride than for propionyl chloride, which was first discovered for the 2-chlorethanolysis in dioxane [7] by Leimu et al. in 1927.

Our results confirm the data of Leimu et al. Neither his nor the data of the other authors could be affected by a significant measuring error because:

1. The resulting error of generally 20% relative to the value of the alcoholysis of propionyl chloride is double the maximum error which is normally discussed for the techniques applied.
2. In the case of the data of Palomaa and Leimu [7], the rate constants (15, 25, 35°C) have correlation coefficients of 1.0.
3. As realized by Leimu [8] the phenomenon observed can be related to the pK_a values, which show the same change.

In contrast to this, in toluene (Fig. 4b) the rate constant of the *i*-propanolysis of butyryl chloride is practically the same as that for propionyl chloride. This is also indicated by the calorimetric curves.

This has to be expected because, in contrast to the alkyl chlorides [15], the *n*-propyl group and the ethyl group should not differ much in their steric or electronic influence on the acid chloride group [16].

Other measurements show that, in contrast to the reaction of acyl chlorides with *i*-propanol, primary alcohols show no such difference between the rate constants for propionyl and butyryl chloride.

The evaluation of the reactions of these acyl chlorides with ethanol in acetone (Fig. 5a) and in toluene (Fig. 5b), as well as those with *n*-propanol in these

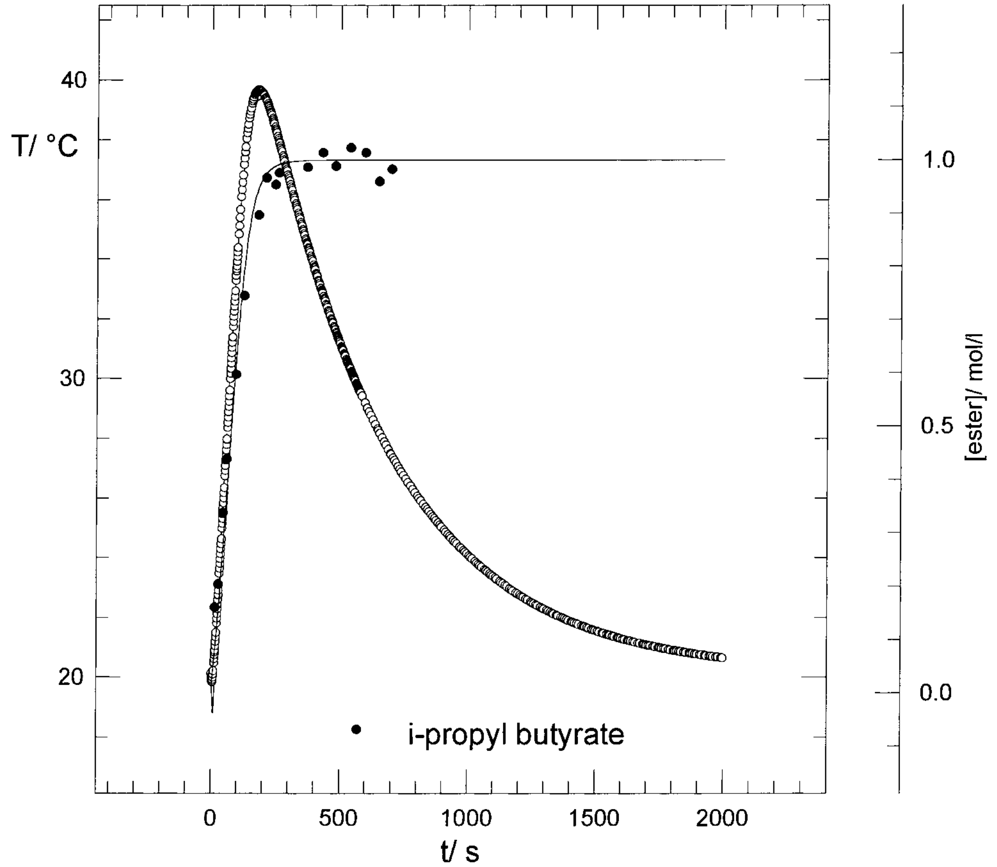

Fig. 2. Temperature-time curves and concentration data for the alcoholysis of butyryl chloride (0.5 mol/l) with *i*-propanol (6 mol/l) in toluene — experimental and simulated data.

solvents (Fig. 6a and b) gives practically the same values for the rate constants.

This can only be interpreted as a dependence of the reactivity sequence on the rate of the reaction. So, the reaction with *i*-propanol is much slower in acetone than in toluene, therefore, in this case, two different sequences are found. For the reactions with primary alcohols, the same sequence as with *i*-propanol in toluene is obtained in both solvents, because the reactions are very fast. A further indication is that Palomaa and Leimu [7] also found this phenomenon for a system with quite a slow reaction.

Tables 1–3 summarize the rate constants and kinetic parameters found by the overall kinetic evaluation of the ethanolysis, the *n*-propanolysis and the *i*-propanolysis with TA-kin. As discussed extensively in [12], there is evidence that, under the given conditions, the enolic form of the acyl chlorides is present. The change of the structure might be responsible for the observations given before. One hint on this is the fact that the homologous acyl chlorides of butyryl chloride have similar values of rate constants to butyryl chloride, which can be seen from Table 4.

Table 4 gives some of the rate constants published by Palomaa and Leimu [7], which are needed for further analysis and also the corresponding Arrhenius parameters, calculated from these data and unpublished yet. In contrast to the activation parameters (Table 4), which are difficult to analyze, an analysis of the rate constants delivers interesting facts. First of all, comparing butyryl chloride (k_1 (25°C) $= 16.2\times 10^{-5}\,\mathrm{s}^{-1}$) and 3-methylbutyryl chloride (k_1 (25°C) $= 14.8\times 10^{-5}\,\mathrm{s}^{-1}$), it is remarkable that their rate constants are larger than that of propionyl chloride

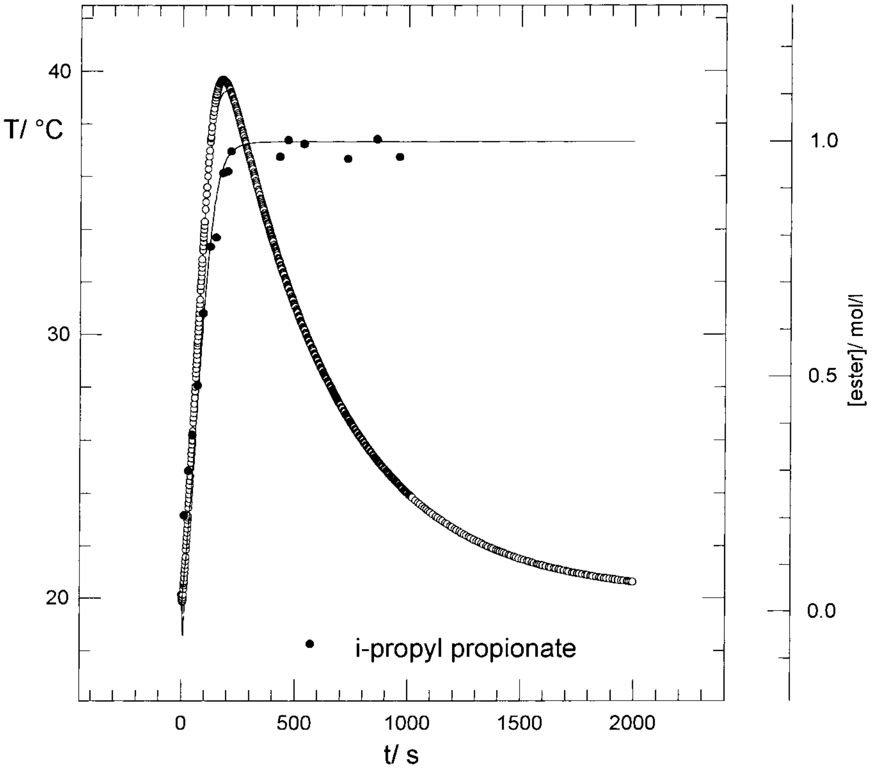

Fig. 3. Temperature-time curves and concentration data for the alcoholysis of propionyl chloride (0.5 mol/l) with *i*-propanol (6 mol/l) in toluene — experimental and simulated data.

(k_1 (25°C) = $13.2 \times 10^{-5}\,s^{-1}$). This excludes important steric influences. The methyl group in 2-methylpropionyl chloride reduces the reactivity from 5.4% (k_1 (25°C) = $12.5 \times 10^{-5}\,s^{-1}$) to 10% ($k_1$ (35°C) = $22.5 \times 10^{-5}\,s^{-1}$), depending on the temperature.

Based on theoretical considerations and on literature data, which indicate that the enol of the acyl chloride is present in the reaction mixture [12] (p. 168), relations between the rate constants of the 2-chlorethanolysis of some of the acyl chlorides investigated by Palomaa and Leimu [7] (Table 4) have been found.

Assuming only electronic influences for the reason given above, it is possible to estimate approximately the value of the 3-methyl compound on the basis of the data of butyryl chloride (Table 5). Supposing that the added methyl group (passing from propionyl chloride to butyryl chloride) is responsible for the higher reaction rate of the alcoholysis of butyryl chloride [12], the same increasing influence (difference of rate constants) might occur on passing from butyryl chloride to 3-methyl butyryl chloride, resulting in a fictitious compound (k_1 (25°C) = $19.2 \times 10^{-5}\,s^{-1}$), in which only the rate-increasing influence is present but not the inductive effect of the added methyl group. Supposing that the inductive influence is as big as that of the methyl group passing from acetyl chloride (k_1 (25°C) = $16.8 \times 10^{-5}\,s^{-1}$) to propionyl chloride (k_1 (25°C) = $13.2 \times 10^{-5}\,s^{-1}$) and subtracting the difference of the rate constant of the fictitious compound results in a value of $15.6 \times 10^{-5}\,s^{-1}$, which lies 5.4% above the experimental value of k_1(25°C) = $14.8 \times 10^{-5}\,s^{-1}$ of 3-methylbutyryl chloride. If this calculation is performed in the same way for the values obtained at 15°C, a value of k_1(15°C) = $9.7 \times 10^{-5}\,s^{-1}$ results for the fictitious compound. This leads to a value of k_1(15°C) = $7.7 \times 10^{-5}\,s^{-1}$ for 3-methylbutyryl chloride, which is 3.9% above the experimental value (Table 5). The positive differences being of the same order of magnitude, indicate that the rate-increasing influence is expectedly smaller than

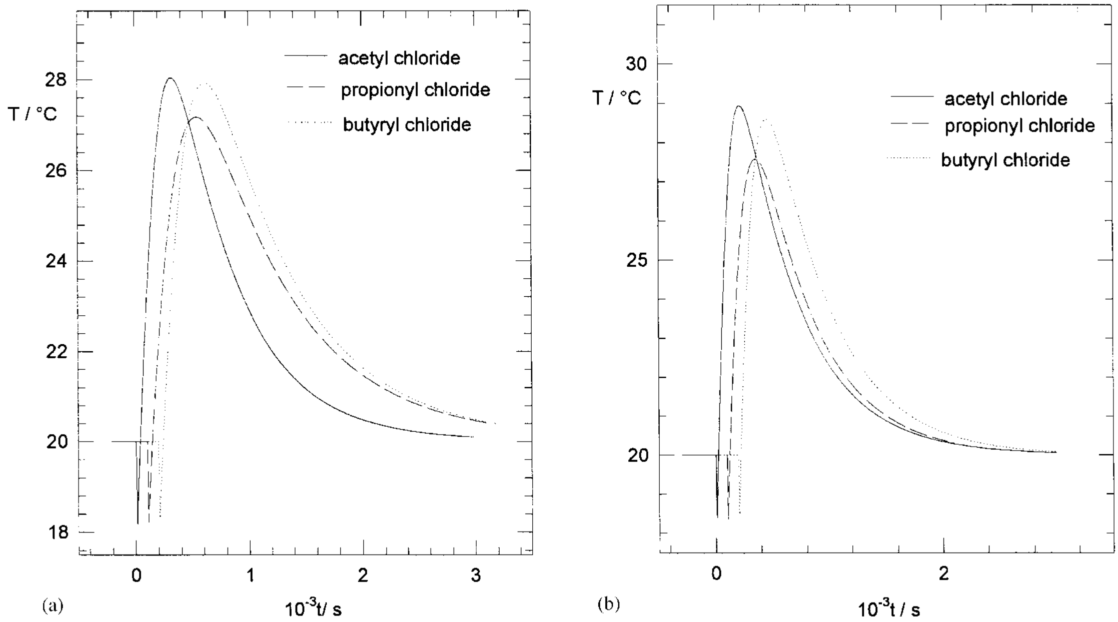

Fig. 4. (a) Temperature-time curves for the alcoholysis of acetyl chloride, propionyl chloride and butyryl chloride (0.5 mol/l) with *i*-propanol (6 mol/l) in acetone. (b) Temperature-time curves for the alcoholysis of acetyl chloride, propionyl chloride and butyryl chloride (0.5 mol/l) with *i*-propanol (6 mol/l) in toluene.

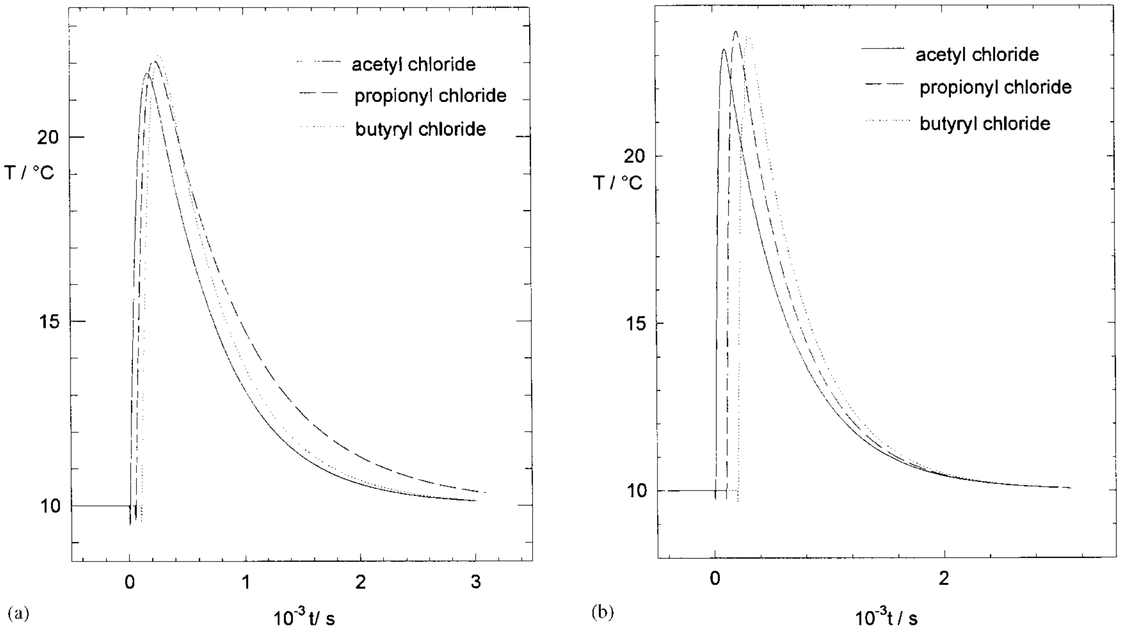

Fig. 5. (a) Temperature-time curves for the alcoholysis of acetyl chloride, propionyl chloride and butyryl chloride (0.5 mol/l) with ethanol (6 mol/l) in acetone. (b) Temperature-time curves for the alcoholysis of acetyl chloride, propionyl chloride and butyryl chloride (0.5 mol/l) with ethanol (6 mol/l) in toluene.

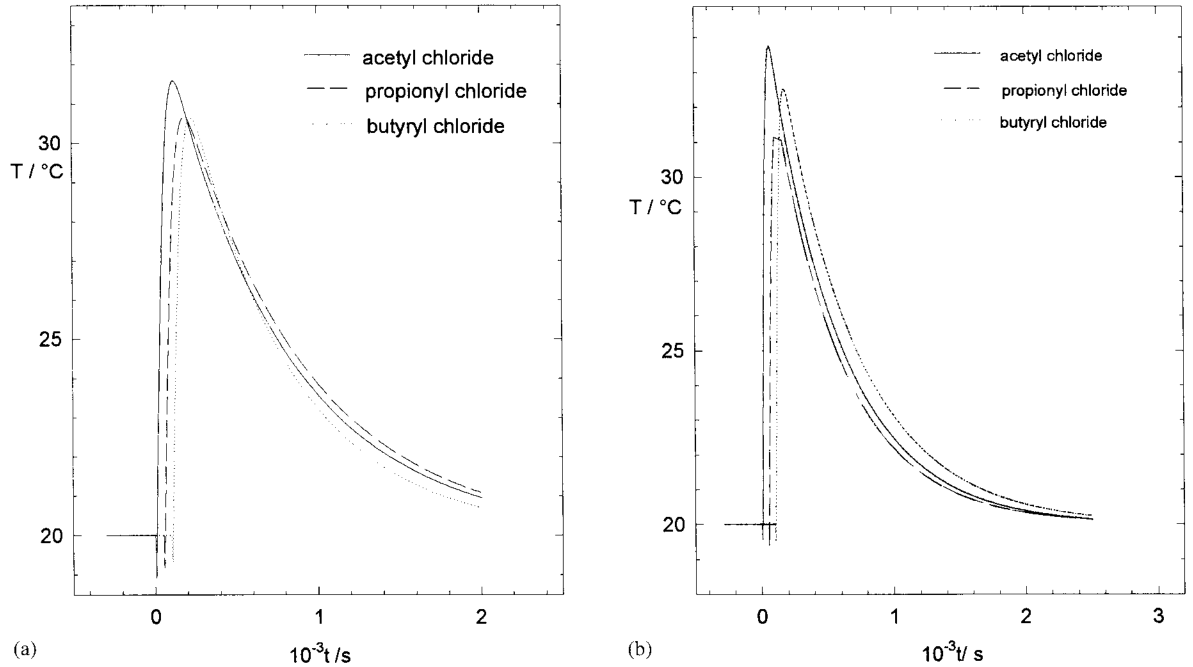

Fig. 6. (a) Temperature-time curves for the alcoholysis of acetyl chloride, propionyl chloride and butyryl chloride (0.5 mol/l) with *n*-propanol (6 mol/l) in acetone. (b) Temperature-time curves for the alcoholysis of acetyl chloride, propionyl chloride and butyryl chloride (0.5 mol/l) with *n*-propanol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

presupposed. In a similar way it is possible to calculate an approximate value for the rate constant for the reaction of 1,2-dichlorpropionyl chloride with 2-chlorethanol in dioxane as given in Table 5.

Due to electronic reasons, the rate constant [7] for the alcoholysis of 3-chlorpropionyl chloride is lower than that of propionyl chloride, so because this influence should be additive ([12], p. 168), it is possible to substract the difference of the values for these acyl chlorides from the value given for 2-chlorpropionyl chloride to obtain the value of the rate constant for the 2-chlorethanolysis of 2,3-dichlorpropionyl chloride.

On the basis of the inductive effect or field effects only, it is not possible to explain why the alcoholysis of 3-chlorpropionyl chloride is even slower than that of propionyl chloride, or why the alcoholysis of the 2-chlorderivate is faster than that of the 2,3-dichlor-compound. As explained in [12] (p. 168), formation of enols may explain not only the given reactivities and the correlation given above, but also the non-linearly changing reactivities of butyryl chloride, propionyl chloride and acetyl chloride.

So based on structural considerations, for two cases of reactions, mathematical correlations between several rate constants could be established which have not been described before. Unfortunately the procedure does not describe the data at 35°C, which may be due to a change of the influences determining the reaction kinetics.

A problem concerning the rate constants is the fact that they are determined by a rate equation of first order instead of second order. On the other hand, comparisons are in most cases not performed at the real order of the reaction, as has been shown in [17], because the order changes easily and can be determined only by an overall evaluation of several data sets, with various concentrations of the alcohol.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 given in the tables. For the reproducibility of the finding of the activation parameters from several measurements for a simple alcoholysis, the

Table 1
Activation parameters and reaction enthalpies for the ethanolysis of acyl chlorides[a]

ACl	[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)
AcCl	0.25	13.24	46.3	−90.1	4.35E−3	5.23/1172	14.14	46.7	−117.2	9.03E−3	29.4/1116
	0.50	14.26	48.6	−82.3	4.79E−3	57.40/1134	16.70	53.0	−108.1	9.20E−3	50.24/1140
	1.00	15.11	50.6	−74.0	5.00E−3	196.75/1202	16.78	52.8	−99.4	1.11E−2	146.6/1140
PrCl	0.25	11.71	42.6	−90.7	4.28E−3	6.12/817[b]	16.88	53.5	−110.6	9.12E−3	8.03/1092
	0.50	12.50	44.3	−87.0	4.61E−3	62.34/1209	14.19	47.0	−92.7	8.38E−3	49.82/1058
	1.00	14.50	49.1	−74.2	4.98E−3	186.3/1254	–	–	–	–	–
BuCl	0.25	10.78	40.5	–88.3	3.86E−3	4.27/834[b]	17.34	54.9	−102.4	8.31E−3	12.85/1083
	0.50	15.00	50.5	−88.3	4.61E−3	21.44/ 758[b]	15.42	50.1	−90.2	8.19E−3	29.85/911[c]
	1.00	12.08	43.2	−79.5	4.84E−3	27.36/700[b]	–	–	–	–	–

[a] Results of the overall evaluation at different starting temperatures T_0 with TA-kin [EtOH]: 6 mol/l; ESS: result of the minimization of the error square sum (nonlinear regression); m: number of error equations (uncertainties: $\ln k_0 < \pm 0.1$; E_A: $< \pm 0.2$ kJ/mol; $\Delta_R H < \pm 1.0$ kJ/mol).

[b] Evaluation of two measurements (10 and 20°C).

[c] Measurements at 10 and 30°C.

Table 2
Activation parameters and reaction enthalpies for the *n*-propanolysis of acyl chlorides[a]

ACl	[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)
AcCl	0.25	15.29	51.3	−89.1	4.29E−3	8.3/973	10.70	38.8	−102.6	7.07E−3	11.75/587
	0.50	13.58	47.1	−82.8	4.45E−3	24.7/994	15.65	50.7	−89.3	8.28E−3	20.73/1087
	1.00	14.95	50.2	−78.6	4.92E−3	90.8/1049	14.83	48.5	−79.2	8.85E−3	121.25/1039
PrCl	0.25	13.61	47.8	−76.1	3.49E−3	16.21/1018	16.51	53.1	−81.3	7.25E−3	11.32/1088
	0.50	13.28	46.7	−76.1	3.89E−3	19.24/887	16.19	52.5	−78.4	6.88E−3	63.35/956
	1.00	13.03	46.2	−70.9	4.38E−3	44.06/1003	14.77	49.0	−72.4	6.83E−3	160.8/1041
BuCl	0.25	13.61	47.8	−73.6	3.45E−3	2.43/438[b]	15.51	50.7	−84.5	7.22E−3	9.63/825[b]
	0.50	13.28	46.6	−82.7	3.96E−3	2.66/436[b]	16.47	53.2	−85.3	6.83E−3	98.86/1128
	1.00	13.03	45.8	−74.7	4.39E−3	9.09/392[b]	17.03	54.5	−77.4	7.00E−3	178/991

[a] Results of the overall evaluation at different starting temperatures T_0 with TA-kin [*n*-prOH]: 6 mol/l; ESS: result of the minimization of the error square sum (nonlinear regression); *m*: number of error equations (uncertainties: $\ln k_0 < \pm 0.1$; E_A: $< \pm 0.2\,\mathrm{kJ/mol}$; $\Delta_R H < \pm 1.0\,\mathrm{kJ/mol}$).

[b] Evaluation of two measurements (10 and 20°C).

Table 3
Activation parameters and reaction enthalpies for the *i*-propanolysis of acyl chlorides[a]

ACl	[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)
AcCl	0.25	14.68	53.4	−71.6	1.07E−3	34.4/1224	19.32	63.6	−90.0	1.81E−3	10.1/1129
	0.50	15.03	54.1	−69.1	1.13E−3	66.3/929	17.56	59.1	−84.4	1.91E−3	52.7/1114
	1.00	16.29	57.1	−66.1	1.18E−3	160.51/1173	16.59	56.4	−79.9	2.11E−3	146.8/1208
PrCl	0.25	12.64	49.2	−70.9	7.50E−4	24.3/930	14.64	52.6	−81.9	1.37E−3	23.71/1058
	0.50	16.56	58.6	−71.1	8.40E−4	13.3/847[b]	15.53	54.8	−71.3	1.42E−3	38.34/976
	1.00	14.59	53.5	−67.9	9.12E−4	175/1111	14.57	52.0	−73.3	1.64E−3	121/1039
BuCl	0.25	11.91	47.1	−74.1	8.23E−4	13.67/1176	14.43	52.0	−80.8	1.46E−3	9.74/1002
	0.50	15.78	56.6	−74.1	8.76E−4	34.05/1297	14.56	52.3	−74.4	1.45E−3	33.6/1360
	1.00	16.65	58.4	−74.8	9.85E−4	108.6/1102	17.53	59.4	−69.8	1.64E−3	78.27/864

[a] Results of the overall evaluation at different starting temperatures T_0 with TA-kin [*i*-prOH]: 6 mol/l; ESS: result of the minimization of the error square sum (nonlinear regression); *m*: number of error equations (uncertainties: $\ln k_0 < \pm 0.1$; E_A: $< \pm 0.2\,\mathrm{kJ/mol}$; $\Delta_R H < \pm 1.0\,\mathrm{kJ/mol}$).

[b] Evaluation of measurements at 20 and 30°C.

Table 4
Rate constants for the alcoholysis of acyl chlorides with 2 mol/l 2-chlorethanol in dioxane (activation parameters calculated from the rate constants of Leimu in s^{-1})

R (RCOCl)	ln k_0	E_A (kJ/mol)	k_1 (15°C) × 10^{-6} (s^{-1})	k_1 (25°C) × 10^{-6} (s^{-1})	k_1 (35°C) × 10^{-6} (s^{-1})
CH_3	11.32	49.76	85	168	323
CH_3CH_2	11.08	49.80	65	132	250
$CH_3CH_2CH_2$	10.22	47.18	81	162	290
$CH_3(CH_2)_3$	11.69	50.53	77	160	305
$CH_3(CH_2)_4$	12.08	51.76	79	160	318
$(CH_3)_2CH$	10.35	48.17	61	125	225
$CH_3(C_2H_5)CH$	11.83	52.65	42	88	173
$(CH_3)_2CHCH_2$	12.14	52.06	74	148	300
$CH_3)_3C$	10.22	52.42	9	18	37

Table 5
Derivation of the rate constants k_{cal} for 2,3-dichlorpropionyl chloride and methylbutyryl chloride at 15 and 25°C on the basis of structural similar compounds[a]

Values	k_1 (15°C) × 10^{-5} (s^{-1})	k_1 (25°C) × 10^{-5} (s^{-1})
Derivation of the rate constant of methylbutyryl chloride		
k_1(BuCl) from Leimu	8.1	16.2
$\Delta k_1 = k_1(\mathrm{BuCl}) - k_1(\mathrm{PrCl})$	1.6	3.0
$k_1(\mathrm{BuCl}) + \Delta k_1 = k_1(\mathrm{MeBuCl})$ fictitous	9.7	19.2
$\Delta k_2 = k_1(\mathrm{AcCl}) - k_1(\mathrm{PrCl})$	2.0	3.6
$k_1(\mathrm{MeBuCl})$ calculated $= k_1(\mathrm{MeBuCl})$ fictitious $- \Delta k_2$	7.7	15.6
k_{exp} (MeBuCl) from Leimu	7.4	14.8
Deviation ($k_{cal} - k_{exp}$)	3.9%	5.4%
Derivation of the rate constant of 2,3-dichlorpropionyl chloride		
k_1(2-ClPrCl) from Leimu	20.6	35.2
$\Delta k = k_1(\mathrm{PrCl}) - k_1(\text{3-ClPrCl})$ exp k_1 values from Leimu	4.2	8.3
$k_1(\text{2-ClPrCl}) - \Delta k = k_1(\text{DiCl-PrCl})$ calculated	16.4	26.9
k_{exp} (DiCl-PrCl) from Leimu	15.8	27.3
Deviation ($k_{cal} - k_{exp}$)	3.8%	1.5%

[a] Butyryl chloride: BuCl; *x*-chlorpropionyl chloride: *x*-ClPrCl ($x = 2$ or 3); propionyl chloride: PrCl; 2,3-dichlorpropionyl chloride: DiCl-PrCl; methylbutyryl chloride: MeBuCl.

following values have been obtained (standard deviation σ)

$$\sigma(E_A) = \pm 0.06\,\mathrm{kJ/mol}, \quad \sigma(\Delta_R H) = \pm 1.80\,\mathrm{kJ/mol} \quad (\text{fixed } \ln k_0 = 20)$$

For more details, see [12,17].

4. Conclusions

The reactions of acetyl chloride and benzoyl chloride have been compared. A factor of about 240 times is found for the reaction rate constant of the alcoholysis of acetyl chloride, relative to benzoyl chloride, which is expectedly higher than that estimated in literature from experimental data.

Unfortunately the reactions of acetyl chloride, propionyl chloride and butyryl chloride with alcohols are quite rarely investigated kinetically yet. Furthermore, kinetic evaluation results in apparently strange parameter changes.

In the case of slow alcoholysis reactions (e.g. with secondary alcohols in polar sovents) there is evidence that the frequently observed order:

$$\text{acetyl chloride} \geqslant \text{propionyl chloride} < \text{butyryl chloride}$$

is due to the formation of the enolic form of the acyl chlorides. On the basis of this theory [12], an increment system has been found to be applicable to the rate constants for some acyl chlorides determined by Palomaa and Leimu [7].

In this work, the sequence of the values of rate constants for pure alcoholysis[1] of acyl chlorides:

$$\begin{aligned}\text{acetyl chloride} &\gg \text{propionyl chloride}\\ &> \text{butyryl chloride}\end{aligned}$$

as required by theory due to the inductive effect, has been observed for the first time. For *i*-propanol as a secondary alcohol this result is only found in the case of nonpolar conditions, but for reactive primary alcohols like ethanol and *n*-propanol, this is the normal sequence in acetone and toluene.

Results show that modern calorimetric methods are powerful tools, useful for investigating systems which have not been accessible before.

Precision calorimetry has proved to be a good tool for differentiating the reactivities of acyl chlorides in the reactions with several alcohols.

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[1] Ref. [10] reports the investigation of the alcoholysis of the given acyl chlorides, but only relative constants referring to the hydrolysis are determined [12].