

Calorimetric investigation of complex reaction courses in organic chemistry¹

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Abstract

Acetylation of different hexanediols as a complex reaction has been investigated by calorimetry. The calorimetric curves demonstrate that the reaction rate depends on the molecular structure. In case of 1,6- and 2,5-hexanediols, the activation parameters have been obtained by nonlinear evaluation procedures with the program TA-kin v3.3. The kinetic results show, that the formation of the diester is characterized by higher activation energies than that of the monoester. © 1998 Elsevier Science B.V.

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1. Introduction

In the past, the alcoholysis of acyl chlorides has been the subject of many kinetic investigations [1–3]. Especially for the alcoholysis of benzoyl chloride, some of its derivatives [4,5] and some aliphatic acyl chlorides [6,7], the influence of the kind of alcohols has been studied. Furthermore, a review is presented by Norris and Cortese [8]. Accordingly, the decrease in the rate of alcoholysis due to a methyl group becomes smaller with increasing distance to the C(1)-atom in the alcohol. Results are limited to alcohols with several hydroxyl groups.

Chemical or physical processes are generally accompanied with changes in temperature. Therefore, calorimetric methods are suitable for their investigation. An advantage is the possibility of determining the

kinetic parameters and the reaction enthalpy by the temperature data set of one experiment.

An isoperibolic glass calorimeter was used [9]. The reaction calorimeter containing the reactor is connected with a burette to add the second component. The calorimeter and the burette are integrated in a thermostated circuit. The effective volume of the reactor is ca. 40 ml; it contains a Pt-sensor, a calibration heater and a stirrer. After the thermostating, the second component will be added in batch mode. The temperature of the reactor is measured and stored by the hard- and software of the ACTRON calorimeter [10]. The registered temperature data sets can be evaluated kinetically by the software package TA-kin [11]. The program allows the definition of any simple or complex reaction model. Using this nonlinear evaluation procedure, the simultaneous kinetic evaluation of reactions, up to four steps, is possible. Concentration values can be included in the evaluation procedure beside the temperature data. This is recommended in the case of complex reactions because

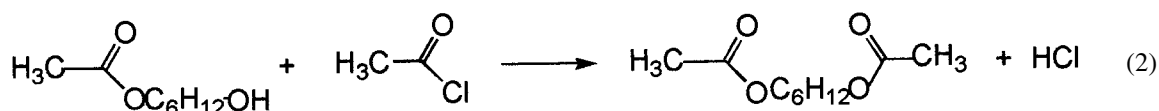
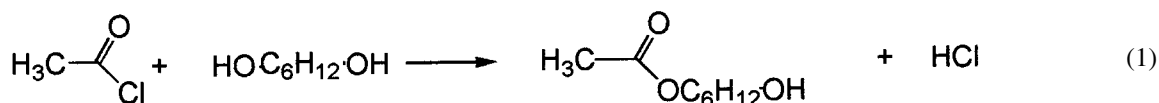
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the temperature is the sum of all processes in the system.

2. Experimental and results

For the kinetic investigation of the alcoholysis with an alcohol containing two hydroxyl groups, the turnover of hexanediol with acetyl chloride was selected. In this way, two steps of reaction occur. First, the monoester is formed, reacting in a second step to form the diester. This is given by the reaction Eqs. (1) and (2).



The kinetics of the reaction depends on the structure of the molecule, e.g. on the distance between the hydroxyl groups. In the case of the 1,6-hexanediol, both steps should occur nearly independently.

The kinetics of 1,6-, 2,5- and 1,5-hexanediols has been investigated by calorimetry, using acetonitrile (HPLC-grade) as solvent. The starting temperature, as well as the concentration of hexanediol and of acetyl chloride have been varied.

As the acetylation of hexanediol is a complex reaction, the concentration course of the esters had to be determined by HPLC to assist the significance of kinetic evaluation. GC/MS was used to analyze the final composition of the reaction mixture. In the case of 1,5-hexanediol it could be observed that, beside the diester, at least two monoesters will be formed because of its asymmetrical molecular structure. Hence, acetylation with of 1,5-hexanediol has to be described by a minimum of three kinetic equations. The concentration data are needed especially for this alcohol. But, up to now, it was not possible to synthesize each of the monoesters sufficiently pure. On the other hand, the HPLC peaks of the diester and the two monoesters are not yet separable.

Fig. 1 shows the calorimetric curves of the reaction of acetyl chloride with several hexanediols at a starting temperature of 30°C. Therefore, a solution of the hexanediol in acetonitrile was introduced in the reactor. To start the reaction, the acetyl chloride solution was added as the second component in batch mode. A calibration was carried out to determine the apparatus constants at the end of the reaction. During the conversion, ca. 20 samples, each of 100 µl, were taken and quenched immediately with 250 µl of a solution of ammonia in water (30% acetonitrile). Concentrations of esters have been obtained by HPLC, using a reverse phase C18-column and a mixture of aceto-

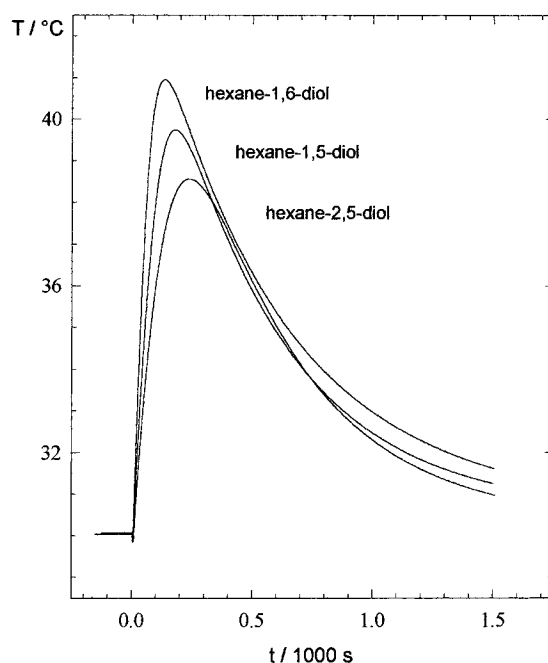


Fig. 1. Calorimetric curves of the reaction of 0.5 M acetyl chloride and 1 M hexanediols at 30°C in acetonitrile as a function of the structure of the diol.

nitrile (67%) and water as eluent. To evaluate the concentrations of the reaction products from the chromatogram, the diesters and the monoesters of the 1,6- and 2,5-hexanediols have been synthesized as reference materials and verified by GC/MS.

The calorimetric curves show the influence of the number of primary hydroxyl groups on the reaction rate. As an alcohol with two primary hydroxyl groups, 1,6-hexanediol is characterized by a higher reaction rate than 1,5-hexanediol. The temperature maximum of the alcoholysis with the 1,6-hexanediol is higher and shifted to shorter reaction times. Because 2,5-hexanediol contains two secondary hydroxyl groups, 1,5-hexanediol shows a higher reaction rate than 2,5-hexanediol.

The influence of the temperature on the acetylation of 2,5-hexanediol in acetonitrile is represented in Fig. 2. The maximum difference of temperature increases with the starting temperature. Whereas the maximum difference of temperature of only 9 K is reached at 10°C after 400 s, only 90 s are needed for a difference of 19 K in the case of a starting temperature

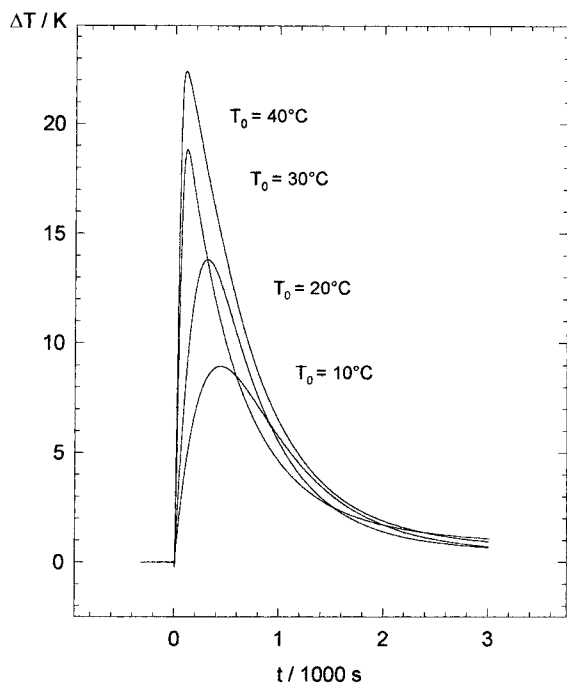


Fig. 2. Calorimetric curves of the reaction of 1 m 2,5-hexanediol and 1 m acetyl chloride in acetonitrile as a function of the starting temperature.

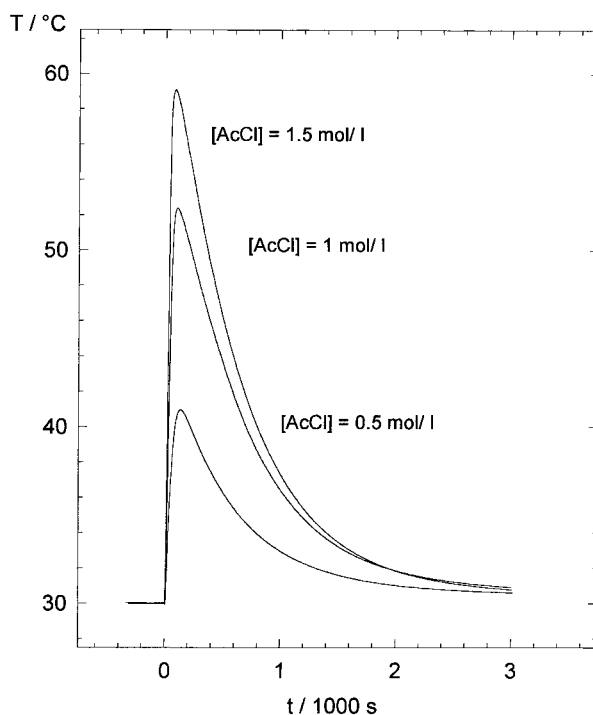


Fig. 3. Calorimetric curves of the acetylation of 1 m 1,6-hexanediol in acetonitrile as a function of the concentration of acetyl chloride.

of 30°C. Comparing the starting temperatures of 30° and 40°C, no further shift in time for the maximum temperature could be found, but the temperature jump amounted to ca. 22.5 K.

Fig. 3 shows the temperature vs. time curves of the reaction of 1,6-hexanediol (1 mol/l) on varying the concentration of acetyl chloride at a starting temperature of 30°C. The maximum difference and the rate of the temperature change grow with the concentration of acetyl chloride. The reaction at an initial concentration of 1.5 mol/l reaches the temperature maximum after 80 s, whereas 120 s are necessary in case of 0.5 mol/l.

3. Conclusions

The calorimetric curves demonstrate that the reaction rates depend on the isomeric structure of the hexanediol, the starting temperature and the molar ratio between hexanediol and acetyl chloride.

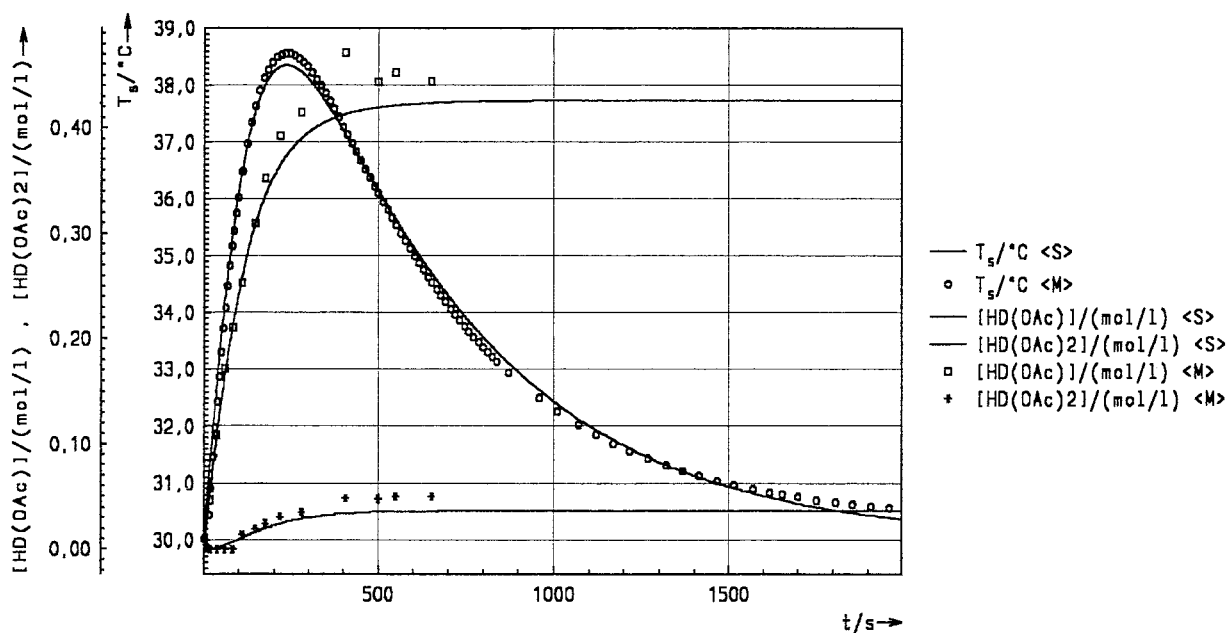


Fig. 4. Kinetic evaluation of temperature–time and concentration–time courses of the reaction of 0.5 mol/l acetyl chloride and 1 mol/l 2,5-hexanediol in acetonitrile obtained by TA-kin v3.3

Table 1

Results of the kinetic evaluation obtained by TA-kin v3.3 $\ln k_0 = 20$ (fixed), R1 = formation of monoester, R2 = formation of diester

Hexandiol	T_0 °C	[Hexandiol]/ mol l ⁻¹	[Acetylchloride]/ mol l ⁻¹	E_A (R1) kJ mol ⁻¹	E_A (R2)	ΔH (R1)	ΔH (R2)
	20	0.25	0.13	63.7	—	-73.0	—
			0.25	63.5	66.5	-65.8	-62.0
			0.50	63.7	65.7	-65.0	-61.7
2,5-diol	1.00	1.00	0.25	63.2	67.6	-74.0	-72.0
			0.50	62.7	67.0	-69.8	-72.7
			1.00	62.8	65.3	-60.4	-60.0
	30	1.00	0.25	63.7	64.5	-71.4	-67.8
			0.50	63.2	66.8	-69.6	-67.8
			1.00	63.0	65.3	-66.0	-67.8
1,6-diol	20	0.25	0.13	62.6	65.6	-64.8	-60.0
			0.25	61.5	65.5	-68.6	-75.5
			0.50	62.2	64.3	-60.3	-60.5
	30	1.00	0.25	61.4	69.2	-77.4	-77.5
			0.50	60.9	65.0	-78.9	-77.8
			1.00	60.0	69.9	-82.9	-83.9

Measurements show that the starting temperature has a stronger effect on the reaction rate than the molar ratio between the reaction components. The influence of these conditions on the reaction can be described by the kinetic activation parameters. The kinetic evaluation was carried out by the nonlinear program TA-kin.

As already mentioned, the acetylation of hexanediols is a complex reaction. Therefore, only 1,6- and 2,5-hexanediols have been evaluated, because the temperature–time-data and the concentration–time data could be obtained completely only for these. Fig. 4 shows a typical example for the kinetic evaluation of the acetylation of 2,5-hexanediol (1 mol/l) with acetyl chloride (0.5 mol/l) obtained by TA-kin v3.3. Table 1 summarizes the results of the kinetic evaluation. To compare the parameters, the value of $\ln k_0$ was fixed at 20. At low concentrations, namely 0.25 mol/l of 2,5-hexanediol and 0.125 mol/l of acetyl chloride, the second step of reaction could be neglected in the kinetic evaluation procedure, because the diester was not detectable by HPLC. Contrary to this, in the case of 1,6-hexanediol, up to 7% diester was formed. This fact demonstrates the higher reactivity of 1,6-hexanediol as shown in Fig. 1.

Under similar conditions, activation energy of the first step of the acetylation of the 2,5-hexanediol is

higher than that of the 1,6-hexanediol. The primary alcohols are characterized by a lower activation energy as compared to the secondary ones. It has been found, by the evaluation procedure, that the activation energy of the first reaction step is lower than that of the second. Between the two steps, a difference in the activation energy of ≈ 3 kJ/mol was obtained.

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