

Cases of pronounced extended π ,n-participation in solvolysis of *tert*-butyl and benzyl chloride derivatives

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Received 02 May 2004; revised 07 July 2004; accepted 13 July 2004

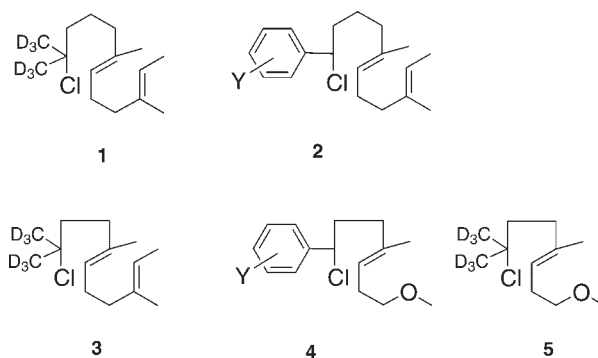
ABSTRACT: Solvolysis rates of chlorides that share the same side-chain comprising two neighboring groups [tertiary chloride **10**, 2-chloro-2,6-dimethyl-9-methoxy-(6*E*)-nonene, and benzyl chlorides **11**, 1-chloro-1-aryl-5-methyl-8-methoxy-(5*E*)-octene, with various phenyl substituents ($Y = p\text{-OCH}_3$, $p\text{-CH}_3$, H, $p\text{-Br}$ and $m\text{-Br}$)], were measured in 80% (v/v) aqueous ethanol. Both the tertiary substrate **10** and the benzyl substrates **11** solvolyze with smaller entropy and enthalpy of activation than the corresponding reference analogs with one neighboring group, **6** and **8**, respectively ($\Delta\Delta H^\ddagger = -34 \pm 6 \text{ kJ mol}^{-1}$, $\Delta\Delta S^\ddagger = -122 \pm 19 \text{ J K}^{-1} \text{ mol}^{-1}$ with **10**; $\Delta\Delta H^\ddagger = -33 \pm 6 \text{ kJ mol}^{-1}$, $\Delta\Delta S^\ddagger = -95 \pm 17 \text{ J K}^{-1} \text{ mol}^{-1}$ with **11**), indicating that in addition to the double bond, the methoxy group also participates in the rate-determining step. Chloride **10** has a significantly reduced secondary β -deuterium kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.07 \pm 0.01$ in 80E; $k_{\text{H}}/k_{\text{D}} = 1.05 \pm 0.1$ in 97T) in comparison with the typical value for the tertiary chlorides ($k_{\text{H}}/k_{\text{D}} = 1.80$), as a consequence of the less positive charge on the reaction center in the transition state. The slope of the Hammett plot ρ^+ value obtained with the series of **11** is considerably smaller than that obtained with the reference chlorides **8**-Y ($\rho^+ = -1.29 \pm 0.11$ vs -3.93 ± 0.10), confirming that benzyl substrates also solvolyze with extended π ,n-participation. On both types of substrates, **10** and **11**, the kinetic parameters indicate that very pronounced assistance of both neighboring groups occurs in the rate-determining step. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: secondary β -deuterium isotope effects; tertiary chlorides; benzyl chlorides; extended π ,n-participation; Hammett correlation; solvolysis

INTRODUCTION

The outstanding problem with the biomimetic cyclization mechanism is whether cyclization occurs in a stepwise or concerted manner upon the formation of the carbocation intermediate. We have reported on numerous squalene derivatives¹ and model compounds² that solvolyze by way of the k_{A} process in which two neighboring groups take part in the rate-determining step, i.e. extended participation occurs. For example, in solvolysis of chlorides **1**,³ **2**,^{4,5} and **3**,⁶ both double bonds participate their electrons in the rate-determining displacement of chloride ion. We have also demonstrated that in chlorides **4**⁷ and **5**,⁸ which have a methoxy group as second neighboring group, the double bond and the n-

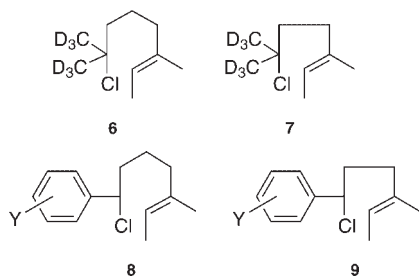
electrons of the methoxy group take part in the reaction, hence the reaction proceeds by way of extended π ,n-participation.



Kinetic data are considered to provide an indication of the extended participation mechanism if they show specific variations from those obtained with the corresponding model compound lacking the second neighboring group (e.g. chlorides **6**–**9**). Typically, the most pertinent variations are as follows: (a) decrease of $\Delta H^\ddagger$ and $\Delta S^\ddagger$; (b) depression of the secondary β -deuterium kinetic isotope effect (KIE) (two deuteromethyl groups, as

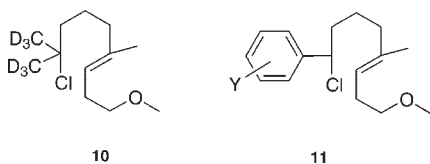
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Contract/grant sponsor: Ministry of Science and Technology of the Republic of Croatia; Contract/grant number: 0006451.

shown in, e.g. structures **1**, **3** and **5**); and (c) lowering the slope of Hammett ρ^+ plot for benzyl derivatives (substrates **2** and **4**).



Even though the participation of the second neighboring group in **1–5** has been proved without ambiguity, its assistance is not the same in magnitude in all substrates. It generally appears that the delocalization of the second neighboring group is more efficient in substrates which have the first participating group (double bond) located at C-5 from the reaction center (as in **1** and **2**) than in the substrates which have the double bond located at C-4 (as in **3–5**). For example, the depression of the β -deuterium KIE in the solvolysis of **1** is much more pronounced [$k_H/k_D = 1.01 \pm 0.02$ vs 1.37 ± 0.03 for the reference compound **6** in 80% (v/v) ethanol at 50°C]^{3,9} than that of **3** and **5**, respectively [$k_H/k_D = 1.14 \pm 0.01$ and 1.16 ± 0.03 , respectively, vs $k_H/k_D = 1.30 \pm 0.03$ for the reference compound **7** in 80% (v/v) ethanol at 50°C]^{6,8} indicating less positive charge on the reaction center in the transition structure of **1** than that of **3** and **5**, i.e. more extensive charge delocalization in **1**. Similarly, the slope of Hammett plot is 2.3 units less for **2** than for the reference chloride **8**,¹⁰ whereas it is only 1.1 units less for **4** than for reference compound **9**.

Since, to the best of our knowledge, substrates **4** and **5** are the only cases reported in which the methoxy group as a second neighboring group acts with the double bond in a concerted manner, in a logical extension of our work we set out to design substrates in which we predict very distinct extended charge delocalization of π - and n-electrons in the transition state. According to the above considerations, a suitable candidate for a structure is one in which the double bond is located on C-5 from the reaction center, which leads to the formation of a cyclohexyl-like transition structure. It is known that methoxy group participation is very efficient if the transition state is a tetrahyrofuran-like structure.¹¹ Therefore, we assumed that the tertiary chloride **10** and the benzyl chlorides **11** should unambiguously give kinetic evidence of a very pronounced extended π ,n-participation mechanism.



RESULTS AND DISCUSSION

The protio and hexadeuterated isotopomers of chloride **10** and benzyl chlorides **11** ($Y = p\text{-OCH}_3, p\text{-CH}_3, \text{H}, p\text{-Br}$ and $m\text{-Br}$) were prepared according to procedures presented in detail in the Experimental section.

Chlorides **10**, **10-d₆** and the series of **11** were subjected to solvolysis in 97% (w/w) aqueous 2,2,2-trifluoroethanol (97T) and/or 80% (v/v) aqueous ethanol (80E). Solvolysis rates were followed by means of a pH-stat. The extrapolated or measured rate constants and the activation parameters are presented in Table 1. The activation parameters were calculated from the rate constants determined at different temperatures. The rates for the corresponding unsaturated compound were calculated according to the empirical equation presented earlier that takes into account the length of the side-chain of tertiary and benzyl chlorides.¹² The Hammett ρ^+ values for the chlorides **11** were calculated using simple regression analysis. Rate effects (k_U/k_S , where k_U is the rate for the unsaturated compound and k_S is the rate for the saturated reference compound), secondary β -deuterium KIEs (k_H/k_D) or reaction constants (ρ^+) of **10** and **11**, along with the same data for some relevant reference compounds are given in Table 2.

Both substrates **10** and **11** show a moderate rate enhancement relative to saturated analogs (Table 2). However, the simple participation cannot be distinguished from the extended participation mechanism, so these results are not conclusive.

A concerted bicyclization mechanism for **10** and all derivatives of **11** can be deduced with great certainty on the basis of the activation parameters. It is well known that neighboring group participation lowers $\Delta H^\ddagger$. Also, the k_A process involves bridging and loss of some degrees of rotational freedom of the alkenyl chain in the transition state, which results in a more negative $\Delta S^\ddagger$.¹³ Therefore, we compared the activation parameters of tertiary chloride **6**⁹ with those of tertiary chloride **10** and of benzyl chloride **8**¹⁰ with benzyl chloride **11**, respectively. The methoxy group in both types of substrate has a substantial influence on activation parameters. Thus, the enthalpy and the entropy of activation are considerably lower for both the tertiary substrate **10** ($\Delta\Delta H^\ddagger = \Delta H^\ddagger_{10} - \Delta H^\ddagger_6 = -34 \pm 6 \text{ kJ mol}^{-1}$, $\Delta\Delta S^\ddagger = \Delta S^\ddagger_{10} - \Delta S^\ddagger_6 = -122 \pm 19 \text{ J K}^{-1} \text{ mol}^{-1}$ in 80EtOH) and the benzyl substrate **11** ($\Delta\Delta H^\ddagger = \Delta H^\ddagger_{11} - \Delta H^\ddagger_8 = -33 \pm 6 \text{ kJ mol}^{-1}$; $\Delta\Delta S^\ddagger = \Delta S^\ddagger_{11} - \Delta S^\ddagger_8 = -95 \pm 17 \text{ J K}^{-1} \text{ mol}^{-1}$ in 80EtOH). These values are consistent with the rate-determining extended participation mechanism, in which the high degree of order required in the transition state (large negative $\Delta S^\ddagger$) is overcompensated by a rather small $\Delta H^\ddagger$.

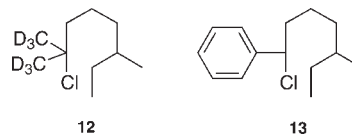


Table 1. Solvolysis rate constants and activation parameters for chlorides **10** and **11**

Compound	Solvent ^a	<i>t</i> /(°C)	<i>k</i> (10 ^{−4} s ^{−1}) ^b	Δ <i>H</i> [‡] (kJ mol ^{−1}) ^c	Δ <i>S</i> [‡] (J K ^{−1} mol ^{−1}) ^c
10	80E	50	4.26 (2)	39 ± 4	−190 ± 13
		40	2.37 (5)		
		30	1.53 (3)		
		25	1.127		
	97T	55	65.5 (6)	50 ± 3	−135 ± 10
		45	33.2 (2)		
		35	18.6 (1)		
10-d₆	80E	50	1.43 (2)	54 ± 2	−122 ± 6
	97T	35	1.78 (1)		
	80E	50	48.1 (2)		
11-<i>p</i>-OCH₃	80E	40	23.5 (1)	36 ± 0.1	−189 ± 0.2
		30	11.9 (2)		
		25	8.05		
		60	16.6 (3)		
11-<i>p</i>-CH₃	80E	50	10.7 (1)	43 ± 5	−179 ± 14
		40	6.69 (9)		
		25	3.13		
		70	8.72 (5)		
11	80E	60	5.89 (3)	46 ± 1	−171 ± 2
		50	3.24 (7)		
		25	0.805		
		70	6.44 (3)		
11-<i>p</i>-Br	80E	60	3.88 (9)	52 ± 2	−155 ± 7
		50	2.21 (1)		
		25	0.479		
		70	5.58 (2)		
11-<i>m</i>-Br	80E	60	2.98 (2)		
		50	1.68 (2)		
		25	0.297		
		70			

^a 80E is 80% (v/v) aqueous ethanol; 97T is 97% (w/w) aqueous 2,2,2-trifluoroethanol.^b The uncertainties of the last reported figure (standard deviation of the mean) are given in parentheses. The rate constants lacking standard errors are extrapolated.^c Uncertainties are standard deviations.**Table 2.** Relative solvolysis rates, β-deuterium secondary kinetic isotope effects and Hammett ρ⁺ values of some tertiary and benzyl chlorides

Compound	Solvent ^a	<i>k_U</i> / <i>k_S</i> ^b	<i>k_H</i> / <i>k_D</i> ^c	−ρ ⁺ ^d
12	80E		1.80 ± 0.03 ^e	6.28 ± 0.25 ^f
13	97T			
6	80E	32.7	1.37 ± 0.03 ^e	
8	97T	16.1		3.93 ± 0.10 ^f
5	80E	3.7	1.16 ± 0.1	
	97T		1.12 ± 0.1	1.45 ± 0.03
4	80E	11.9		
10	80E	10.4	1.07 ± 0.01	1.29 ± 0.11
	97T		1.05 ± 0.01	
11	80E	55.9		

^a 80E is 80% (v/v) aqueous ethanol; 97T is 97% (w/w) aqueous 2,2,2-trifluoroethanol.^b Rate constant of unsaturated vs the rate constant of the corresponding saturated chloride at 25 °C; rate constants of saturated chlorides having the same size of the side-chain were either measured or calculated according to the equation given in Ref. 12.^c In 80E determined at 50 °C, in 97T determined at 30 °C; uncertainties are standard errors of the estimate.^d Determined from the rate constants extrapolated to 25 °C; uncertainties are standard errors of the estimate.^e Ref. 9.^f Ref. 10.

Charge delocalization from the reaction center in benzyl systems can be proved with the Hammett ρ⁺ parameter, which is a measure of the charge ‘seen’ by the aromatic ring at the reaction center, i.e. a measure of charge delocalization.¹⁴ The assistance of one double bond in **6** lowers the ρ⁺ value by ~2 units in comparison with the saturated analog **13** (−3.93 vs −6.28, Table 2), while the methoxy group in **11** has a further dramatic influence, so the ρ⁺ value decreases by another 2.5 units. It is worth noting that the Hammett parameter obtained is similar to that with substrate **2**, which ρ⁺ was proposed as a reference value for the extended participation mechanism.⁵ The different solvolysis mechanisms of **8** and **11** are supported by the fact that with **8** breakdown of the Hammett plot occurs, whereas with **11** all data correlate well with the σ⁺ values. In the case of **8**, the double bond assistance is very attenuated by the strongly electron-donating *p*-methoxy substituent, whereas with derivatives of structure **11** the ‘stronger’ neighboring group participation is not overcome even by the *p*-methoxy group.

In conclusion, kinetic parameters obtained with **10** and **11** are fundamentally the same as those obtained earlier with chlorides **1** and **2**, indicating that the side-chain

takes part in a similar manner regardless of whether the second neighboring group is a double bond or a methoxy group, i.e. under given conditions the methoxy group and the double bond have comparable electron-donating abilities. The results presented for **10** and **11** further support the observation that in the transition state the charge is more efficiently delocalized from the reaction center if the double bond is located at C-5 than at C-4. Hence the more reduced KIE with **10** than **5** and the more reduced slope of the Hammett plot with **11** than **5** (Table 2) could be attributed to less charge on the reaction center. Efficient charge delocalization could occur from the optimal preorganized structure, which probably cannot be achieved with **5** and **4** because of the angle strain. Therefore, in the solvolysis of **10** and **11**, the participation of the second double bond is more important. The results obtained could also be interpreted in terms of 'early' and 'late' transition states. The 'earlier' transition state exists in the case of **4** and **5** and the 'later' state in the case of **10** and **11**.

EXPERIMENTAL

Substrate preparation

1-Bromo-4-methyl-7-methoxy-4-heptene. To a stirred solution of primary alcohol (4-methyl-7-methoxy-4-heptanol, 5 g, 0.032 mol) and carbon tetrabromide (13.6 g, 0.041 mol) in 50 ml of dry methylene chloride, a solution of triphenylphosphine (9.95 g, 0.038 mol) in 50 ml of the same solvent was added dropwise at room temperature. After the addition was completed, the reaction mixture was refluxed and stirred for 2–3 h. After completion of the reaction (checked with TLC), light petroleum was added and the volatiles were evaporated. The crude product was purified by column chromatography on silica gel by eluting the product with light petroleum. The yield of pure bromide was 5.39 g (76.5%). ^1H NMR (CDCl_3), δ (ppm) 1.53 (s, 3H), 1.83–2.08 (m, 6H), 3.28 (s, 3H), 3.59–3.65 (m, 4H), 5.12–5.15 (t, 1H); ^{13}C NMR (CDCl_3), δ (ppm) 12.90, 30.44, 32.74, 34.37, 37.39, 51.16, 67.51, 125.39, 134.94.

2,6-Dimethyl-9-methoxy-6-nonen-2-ol. Grignard reagent, prepared from Mg (1.35 g, 54.00 mmol) and 1-bromo-4-methyl-7-methoxy-4-heptene (3 g, 14.00 mmol) in THF (10 ml), was cooled to 0 °C and a solution of acetone (0.80 g, 14.00 mmol) in 10 ml of THF was added dropwise. Stirring was continued at room temperature for 1 h. The Grignard complex was hydrolyzed with saturated aqueous NH_4Cl . The water layer was washed with diethyl ether three times and the combined ether layers were washed with brine and dried over Na_2SO_4 . The crude product was purified by column chromatography on silica gel. The pure alcohol obtained (1.15 g, 41.1%) was in the form of a viscous oil. ^1H NMR (CDCl_3), δ (ppm) 1.33–

1.37 (m, 2H), 1.43–1.65 (m, 11H), 1.93–2.08 (m, 4H), 3.54–3.65 (m, 5H), 5.12–5.15 (t, 1H); ^{13}C NMR (CDCl_3), δ (ppm) 14.90, 16.20, 25.97, 34.12, 39.05, 41.15, 53.28, 68.50, 71.55, 122.44, 136.91.

1-Phenyl-8-methoxy-5-methyl-5-octenol. A suspension of lithium powder (332 mg, 0.048 mol), granulated Li (332 mg, 0.048 mol), dry THF (5 ml) and very little (10 μL) CH_3I was refluxed under a slow stream of argon for 10–15 min in an ultrasonic bath, then a solution of 1.1 g (0.005 mol) of 1-bromo-4-methyl-7-methoxy-4-heptene and benzaldehyde (0.575 g, 0.005 mol) in 20 ml of dry THF was added dropwise to the stirred mixture at 0 °C. After all the solution had been added, the reaction mixture was by turns stirred with the magnetic stirrer and the ultrasonic bath for 3 h. The progress of the reaction was checked by TLC. The excess of Li was filtered off and the filtrate was treated with a saturated aqueous solution of NH_4Cl . The alcohol was extracted with diethyl ether and dried over anhydrous Na_2SO_4 . The diethyl ether was evaporated and the product was purified on a silica gel column. Unreacted bromide was removed with light petroleum and the pure alcohol was eluted with dichloromethane. The yield of pure alcohol was 0.25 g (20.2%). ^1H NMR (CDCl_3), δ (ppm) 1.38–1.52 (m, 5H), 1.89–1.99 (m, 4H), 2.46–2.50 (q, 2H), 3.26 (s, 3H), 3.54–3.57 (t, 2H), 4.53–4.57 (t, 1H), 5.10–5.13 (t, 1H), 7.17–7.26 (m, 5H); ^{13}C NMR (CDCl_3), δ (ppm) 17.08, 20.57, 26.16, 39.02, 39.29, 51.22, 67.49, 73.88, 123.99, 125.51, 127.84, 134.43, 135.17.

1-(4-Methoxyphenyl)-8-methoxy-5-methyl-5-octenol. The procedure is the same as described above. From 221 mg, (32.00 mmol) of Li powder, 221 mg (32.00 mmol) of granulated Li, 1.10 g (5.00 mmol) of 1-bromo-7-methoxy-4-methyl-4-heptene and 0.74 g (5.00 mmol) of anisaldehyde was obtained 0.27 g (19.4%) of pure alcohol. ^1H NMR (CDCl_3), δ (ppm) 1.55–1.58 (m, 2H), 1.66–1.96 (m, 7H), 2.41–2.23 (q, 2H), 3.73–3.97 (m, 8H), 4.60–4.63 (t, 1H), 5.19–5.21 (t, 1H), 7.12–7.14 (d, 2H), 7.21–7.23 (d, 2H); ^{13}C NMR (CDCl_3), δ (ppm) 16.00, 23.81, 26.33, 39.46, 39.72, 55.00, 59.00, 67.66, 76.47, 118.80, 123.49, 129.75, 143.38, 158.81.

1-(4-Methylphenyl)-8-methoxy-5-methyl-5-octenol. The procedure is the same as described above. From 221 mg (32.00 mmol) of Li powder, 221 mg (32.00 mmol) of granulated Li, 1.10 g (5.00 mmol) of 1-bromo-7-methoxy-4-methyl-4-heptene and 0.65 g (5.00 mmol) of *p*-toluylaldehyde was obtained 0.18 g (13.7%) of pure alcohol. ^1H NMR (CDCl_3), δ (ppm) 1.35–1.79 (m, 5H), 1.84–2.07 (m, 7H), 3.69–3.978 (m, 5H); ^{13}C NMR (CDCl_3), δ (ppm) 15.50, 20.73, 20.84, 25.36, 39.46, 53.33, 67.72, 74.00, 118.00, 124.00, 124.26, 134.46, 136.63, 141.91.

1-(4-Bromophenyl)-8-methoxy-5-methyl-5-octenol. The procedure is the same as described above. From 221 mg (32.00 mmol) of Li powder, 221 mg (32.00 mol) of granulated Li, 1.10 g (5.00 mmol) of 1-bromo-7-methoxy-4-methyl-4-heptene and 0.92 g (5.00 mmol) of 4-bromobenzaldehyde was obtained 0.29 g (17.8%) of pure alcohol. ^1H NMR (CDCl_3), δ (ppm) 1.18–1.25 (m, 7H), 1.42–1.45 (t, 2H), 1.63–1.69 (q, 2H), 3.42–3.50 (m, 5H), 7.18–7.20 (d, 2H), 7.42–7.44 (d, 2H); ^{13}C NMR (CDCl_3), δ (ppm) 15.07, 25.10, 29.26, 30.15, 37.05, 58.57, 64.10, 65.68, 121.07, 125.33, 131.33, 131.77, 131.91.

1-(3-Bromophenyl)-8-methoxy-5-methyl-5-octenol. The procedure is the same as described above. From 62.5 mg (9.00 mmol) of Li powder, 62.5 mg (9.00 mol) of granulated Li, 0.44 g (2.00 mmol) of 1-bromo-7-methoxy-4-methyl-4-heptene and 0.35 g (52 mmol) of 3-bromobenzaldehyde was obtained 0.18 g (27.5%) of pure alcohol. ^1H NMR (CDCl_3) δ (ppm) 1.29–1.35 (m, 2H), 1.52–1.60 (m, 5H), 1.95–2.06 (m, 4H), 3.27 (s, 3H), 3.51–3.54 (t, 2H), 5.05–5.09 (t, 1H), 7.20–7.42 (m, 4H); ^{13}C NMR (CDCl_3), δ (ppm) 13.02, 24.93, 26.83, 39.50, 55.21, 64.00, 66.02, 121.20, 122.55, 124.50, 126.33, 129.45, 130.95, 139.52, 141.20.

Chlorides 10, 10-d₆ and 11. The parent alcohol was dissolved in 10–15 ml of light petroleum, the solution was cooled to -15°C and SOCl_2 was added dropwise. The reaction mixture was stirred for 2 h under reduced pressure (about 520–560 mmHg) to remove the liberated HCl and SO_2 continuously. The light petroleum was then evaporated and the crude chloride was used for kinetic measurements. Further purification proved to be unnecessary because the solvolysis rates were found to be independent on contamination.

Kinetic measurements

Solvolysis rates were followed in 80% (v/v) aqueous ethanol (80E) and 97% (w/w) aqueous 2,2,2-trifluoroethanol (97T) titrimetrically by means of a pH-stat (end-point titration, $\text{pH} = 6.85$). Typically, 0.02 mmol of

the chloride **1** was dissolved in 20 ml of the solvent at the required temperature thermostated to $\pm 0.05^\circ\text{C}$, and the liberated HCl was continuously titrated by using a 0.008 M solution of NaOH in the same solvent mixture. Individual measurements could be described by the first-order law from 15% up to at least 80% completion. First-order rate constants were calculated from about 100 determinations by using a non-linear least-squares program. Measurements were usually repeated 3–7 times. Activation parameters were calculated from rate constants at three different temperatures.

Acknowledgement

We gratefully acknowledge the financial support of this research by the Ministry of Science and Technology of the Republic of Croatia (Grant No. 0006451).

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