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Kinetics and activation thermodynamics of the solvolysis of *tert*-pentyl and *tert*-hexyl halides in alcohols

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The influences of solvent and substrate were interpreted through the values of rate constants and infinite dilution activity coefficients obtained for the solutes 2-chloro- and 2-bromo-2-methylbutane and 3-chloro-3-methylpentane in several monohydric alcohols at 298.15 K.

Keywords: solvolysis of *tert*-pentyl and *tert*-hexyl halides

Investigations of the kinetic behaviour of different solvolysis of *tert*-butyl halides in pure and binary mixtures of alcohols are of great interest because these reactions serve as reaction models to improve our knowledge about solute–solvent and solvent-solvent mechanisms of interaction at the molecular level.[1–3]

Previously, a useful quantitative procedure has been reported for examining solvent effects on the rate constants, k, by means of the calculation of the transfer Gibbs energies of activation, $\delta\Delta^{\neq}G$, the transfer Gibbs energies of the reactants, δG_i, and the transfer Gibbs energies of the activated complex, δG_t.[4–6]

In this paper we present experimental results for the rate constants and Gibbs energies of activation (Table 1), as well as calculated values for the infinite dilution activity coefficients, γ^{∞}, of each solute in the various solvents (Table 2). The rate constants were obtained using a conductimetric technique[16] and the γ^{∞} values were calculated by taking advantage of a completely predictive model, the UNIFAC group-contribution method.[7,13–15] Subsequently, the transfer Gibbs energies for the reactants and activated complex were calculated according to the equations:

$$\delta G_i = RT \ln (\gamma^{\infty}_j / \gamma^{\infty}_r) \qquad (3)$$

$$\delta G_t = \delta G_i + \Delta^{\neq}G_j - \Delta^{\neq}G_r \qquad (4)$$

These values are reported (Table 3) and analysed. Ethanol was used as the reference solvent. Several trends can be deduced from the analysis of the results presented in Table 1: (i) the rate constants are extremely solvent dependent, varying by several orders of magnitude; (ii) the rate constants of solvolysis are, in general, higher for diols than for monohydric alcohols except methanol; (iii) the increase in length of the main carbon chain of the substrate (2–Cl–2–MeBu → 3–Cl–3–MePe) is accompanied by an increase in reactivity (exception for 2–Me–1–BuOH); (iv) in general, a shift towards higher rate constants was also observed on going from 3–Cl–3–MePe to 3–Cl–3–EtPe, which corresponds to an increase in the branched aliphatic chain; (v) a pronounced increase in k is always observed when Br replaces Cl in the substrate molecule. From the results presented in Table 3 we may observe that the transfer Gibbs energies of activation, $\delta\Delta^{\neq}G$, are always negative for diols. In monohydric alcohols the three chloride compounds have in general negative values of $\delta\Delta^{\neq}G$, this behaviour being opposite to the bromide compound and to the *tert*-butyl halides.[5] The highest stabilisation values of the initial state are obtained for methanol and 1,2-ethanediol. The observed data are a consequence of molecular structure, hydrogen bond association and the dipolarity properties of alcohols.[5,20] The small dipole moments of the substrates do not allow strong dipole–dipole interactions, but, since the activated complex is most probably similar to an ion pair, the interaction is strongly increased in the transition state. However, there are several exceptions to this general behaviour. In the case of the solvolysis of 2–Br–2–MeBu in monohydric alcohols the dominant interactions always occur in the initial state. This behaviour reinforces previous results concerning the *tert*-butyl bromide.[5]

For the most crowded substrate, 3–Cl–3–EtPe, the contributions of the initial state and the transition state to the energies of activation are similar. For this compound such behaviour may be due to an earlier stabilisation of the carbenium ion, the structure of the activated complex being more similar to that of the initial state than in the case of the other chlorides.

Technique used: Conductimetry

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Table 1 Rate constants and Gibbs energies of activation for the solvolysis of alkyl halides in alcohols at 298.15 K

		2–Br–2–MeBu		2–Cl–2–MeBu		3–Cl–3–MePe		3–Cl–3–EtPe	
No.	Solvent	$10^6 k$ /s	$\Delta^{\neq}G$ kJ/mol	$10^6 k$ /s	$\Delta^{\neq}G$ kJ/mol	$10^6 k$ /s	$\Delta^{\neq}G$ kJ/mol	$10^6 k$ /s	$\Delta^{\neq}G$ kJ/mol
1	MeOH	88.4	96.2	2.24	105.3	4.55	103.5	7.77^{b}	102.2^{b}
2	EtOH	13.6	100.8	0.387	109.6	0.921	107.5	1.49^{b}	106.3^{b}
3	1-PrOH	8.17	102.1	0.199	111.3	0.406	109.5	1.91^{b}	105.7^{b}
4	2-PrOH	5.63	103.0	0.688	108.2	0.784	107.9	2.05^{b}	105.5^{b}
5	1-BuOH	5.02	103.3	0.725	108.1	1.66	106.0	1.80^{b}	105.8^{b}
6	2-BuOH	2.64	104.9	2.04	105.5	3.01	104.5	2.14^{b}	105.4^{b}
7	2-Me-1-PrOH	4.18	103.7	0.804	107.8	1.01	107.2	1.42^{b}	106.4^{b}
8	2-Me-1-BuOH	3.45	104.2	0.745	108.0	0.660	108.3	1.13^{b}	107.0^{b}
9	1,2-Et(OH)$_2$	1420^{a}	89.3^{a}	49.7^{a}	97.6^{a}	71.8^{a}	96.7^{a}	63.7^{b}	97.0^{b}
10	1,2-Pr(OH)$_2$	155^{a}	94.8^{a}	3.75^{a}	104.0^{a}	4.88^{a}	103.3^{a}	5.25^{b}	103.2^{b}
11	1,3-Pr(OH)$_2$	384^{a}	92.5^{a}	7.71^{a}	102.2^{a}	14.9^{a}	100.6^{a}	16.4^{b}	100.8^{b}
12	1,2-Bu(OH)$_2$	436^{a}	97.9^{a}	1.31^{a}	106.6^{a}	2.02^{a}	105.5^{a}	1.91^{b}	105.7^{b}
13	1,3-Bu(OH)$_2$	64.9^{a}	96.9^{a}	2.08^{a}	105.5^{a}	2.52^{a}	105.0^{a}	2.94^{b}	104.6^{b}
14	1,4-Bu(OH)$_2$	96.7^{a}	95.9^{a}	2.68^{a}	104.8^{a}	3.79^{a}	104.0^{a}	4.57^{b}	103.5^{b}
15	2,3-Bu(OH)$_2$	20.7^{a}	99.8^{a}	1.07^{a}	107.1^{a}	1.35^{a}	106.5^{a}	1.48^{b}	106.3^{b}
16	1,5-Pe(OH)$_2$	37.7^{a}	98.3^{a}	1.12^{a}	107.0^{a}	1.72^{a}	105.9^{a}	2.26^{b}	105.2^{b}
17	Diethylene glycol	178^{a}	94.4^{a}	3.21^{a}	104.4^{a}	3.66^{a}	104.1^{a}	5.62^{b}	103.0^{b}
18	Triethylene glycol	103^{a}	95.8^{a}	1.32^{a}	106.6^{a}	3.04^{a}	104.5^{a}	2.51^{b}	105.0^{b}

^{a}Values from ref.1; ^{b}Values from ref.18.

Table 2 Infinite dilution activity coefficients γ^{∞} for the alkyl halides at 298.15 K (interpolated values in parentheses)

	2–Br–2–MeBu		2–Cl–2–MeBu		3–Cl–3–MePe		3–Cl–3–EtPe	
Solvent	UNIFAC	UNIFAC-VLE	UNIFAC	UNIFAC-VLE	UNIFAC	UNIFAC-VLE	UNIFAC	UNIFAC-VLE
MeOH	–	20.4	29.6	21.6	44.0	34.2	65.3	54.3
EtOH	9.8	7.1	5.0	6.6	6.7	8.9	9.0	11.8
1-PrOH	5.8	4.8	3.3	4.3	4.2	5.4	5.3	6.7
2-PrOH	5.8	4.8	3.3	4.3	4.2	5.4	5.3	6.7
1-BuOH	4.2	3.7	2.6	3.2	3.1	3.9	3.8	4.7
2-BuOH	4.2	3.7	2.6	3.2	3.1	3.9	3.8	4.7
2-Me-1-PrOH	4.2	3.7	2.6	3.2	3.1	3.9	3.8	4.7
2-Me-1-BuOH	3.3	3.1	2.2	2.6	2.6	3.1	3.0	3.6
1,2-Et(OH)$_2$	53.5	26.6	18.2	26.5	31.2	44.9	53.4	75.9
1,2-Pr(OH)$_2$	24.4	14.3	9.8	13.9	15.3	21.4	23.6	32.8
1,3-Pr(OH)$_2$	24.4	14.3	9.8	13.9	15.3	21.4	23.6	32.8
1,2-Bu(OH)$_2$	14.2	9.3	6.5	8.9	9.4	12.8	13.6	18.4
1,3-Bu(OH)$_2$	14.2	9.3	6.5	8.9	9.4	12.8	13.6	18.4
1,4-Bu(OH)$_2$	14.2	9.3	6.5	8.9	9.4	12.8	13.6	18.4
2,3-Bu(OH)$_2$	14.2	9.3	6.5	8.9	9.4	12.8	13.6	18.4
1,5-Pe(OH)$_2$	9.5	6.8	4.8	6.4	6.6	8.8	9.0	12.0
Diethylene glycol	4.4	9.3	(9.6)	13.6	(14.9)	20.9	(22.9)	31.9
Triethylene glycol	2.0	5.6	(6.9)	9.6	(10.1)	14.0	(14.8)	20.3

Table 3 Gibbs energies of transfer for the solvolysis of alkyl halides in alcohols at 298.15 K (kJ/mol)

	2–Br–2–MeBu			2–Cl–2–MeBu			3–Cl–3–MePe			3–Cl–3–EtPe		
Solvent no.	$\delta\Delta^{\neq}G$	δG_i	δG_t	$\delta\Delta^{\neq}G$	δG_i	δG_t	$\delta\Delta^{\neq}G$	δG_i	δG_t	$\delta\Delta^{\neq}G$	δG_i	δG_t
1	–4.6	–	–	–4.3	4.4	0.1	–4.0	4.8	0.8	–4.1	4.9	0.8
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	1.3	–1.3	0.0	1.7	–1.0	0.7	2.0	–1.2	0.8	–0.6	–1.3	–1.9
4	2.2	–1.3	0.9	–1.4	–1.0	–2.4	0.4	–1.2	–0.8	–0.8	–1.3	–2.1
5	2.5	–2.1	0.4	–1.5	–1.6	–3.1	–1.5	–1.9	–3.4	–0.5	–2.1	–2.6
6	4.1	–2.1	2.0	–4.1	–1.6	–5.7	–3.0	–1.9	–4.9	–0.9	–2.1	–3.0
7	2.9	–2.1	0.8	–1.8	–1.6	–3.4	–0.3	–1.9	–2.2	0.1	–2.1	–2.0
8	3.4	–2.7	0.7	–1.6	–2.0	–3.6	0.8	–2.4	–3.1	0.7	–2.7	–2.0
9	–11.5	4.2	–7.3	–12	3.2	–8.8	–10.8	3.8	–7.0	–9.3	4.4	–4.9
10	–6.0	2.3	–3.7	–5.6	1.7	–3.9	–4.2	2.0	–2.2	–3.1	2.4	–0.7
11	–8.3	2.3	–6.0	–7.4	1.7	–5.7	–6.9	2.0	–4.9	–5.5	2.4	–3.1
12	–2.9	0.9	–2.0	–3.0	0.7	–2.3	–2.0	0.8	–1.2	–0.6	1.0	–0.4
13	–3.9	0.9	–3.0	–4.1	0.7	–3.4	–2.5	0.8	–1.7	–1.7	1.0	–0.7
14	–4.9	0.9	–4.0	–4.8	0.7	–4.1	–3.5	0.8	–2.7	–2.8	1.0	–1.8
15	–1.0	0.9	–0.1	–2.5	0.7	–1.8	–1.0	0.8	–0.2	0.0	1.0	1.0
16	–2.5	–0.1	–2.6	–2.6	–0.1	–2.7	–1.6	0.0	–1.6	–1.1	0.0	–1.1
17	–6.4	–2.0	–8.4	–5.2	(1.6)	(–3.6)	–3.4	(2.0)	(–1.4)	–3.3	(2.3)	(–1.0)
18	–5	–3.9	–8.9	–3.0	(0.8)	(–2.2)	–3.0	(1.0)	(–2.0)	–1.3	(1.2)	(–0.1)