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Kinetic and thermodynamic study of 2-bromo-2-methylbutane, 2-chloro-2-methylbutane and 3-chloro-3-methylpentane in diols

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ABSTRACT: Rate constants, *k*, were determined for the solvolytic reactions of 2-bromo-2-methylbutane, 2-chloro-2-methylbutane and 3-chloro-3-methylpentane in 10 pure diols at 298.15 K. The Gibbs energies of activation were calculated in order to study the influence of the solvent and to provide mechanistic information about the activation process. By combining these values with a set of infinite dilution activity coefficients, γ^{∞}, the transfer Gibbs energies of the reactants (initial state) and of the activated complex (transition state) were obtained, which allowed the solvent effects on both states to be quantitatively analysed. The γ^{∞} values were calculated using the UNIFAC group contribution method. The modified Flory–Huggins equation was used in the combinatorial term. The interaction parameters were taken from the specific UNIFAC γ^{∞} interaction parameter table, except for the γ^{∞} values of 2-chloro-2-methylbutane and 3-chloro-3-methylpentane in diethylene glycol and triethylene glycol, which were obtained using the γ^{∞} UNIFAC–VLE interaction parameter tables. For comparative purposes all the other infinite dilution activity coefficients of the three solutes in the diols were also calculated using the UNIFAC–VLE parameter tables. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: haloalkanes; diols; kinetics; thermodynamics

INTRODUCTION

In previous papers[1–4] concerning the solvolysis of *tert*-butyl halides in pure and binary mixtures of alcohols and the Menschutkin reaction of triethylamine with ethyl iodide, we provided a useful quantitative procedure for examining solvent effects on the rate constants, *k*, through the calculation of the transfer Gibbs energies of activation, $\delta\Delta^{\neq}G$, of the transfer Gibbs energies of the reactants, δG_i, and of the transfer Gibbs energies of the activated complex, δG_t.[5]

In order to gain a more thorough understanding of the thermodynamic Gibbs energy of transfer values, we have undertaken a kinetic investigation at 298.15 K using 2-bromo-2-methylbutane (2-Br-2-MeBu), 2-chloro-2-methylbutane (2-Cl-2-MeBu) and 3-chloro-3-methylpentane (3-Cl-3-MePe) as substrates and 10 pure diols as solvents.

The reactions follow first-order kinetics, which were monitored by measuring the conductance, *G*, at regular intervals of time. The data were analysed according to the Kezdy–Swinbourne method:[6]

$$G_t = G_{t\infty}\ (1 - e^{k\Delta t}) + e^{k\Delta t}\ G_{t+\Delta t} \qquad (1)$$

where G_t, $G_{t\infty}$ and $G_{t+\Delta t}$ denote the conductance of the solution at time *t*, infinite time and $t+\Delta t$ (Δt is a constant period of time), respectively. A computer program gives the value of *k* from the straight line with a correlation coefficient *r* always better than 0.9990 for a number of pairs of points (G_t, $G_{t+\Delta t}$) between 50 and 600, and a value of Δt from 8 to 10300 min, depending on the system under study and, consequently, on the rate of the reaction.

The Gibbs energies of activation for solvolysis of the three substrates in the diols were obtained from the following transition state theory relationship:

$$\Delta^{\neq} G = - R\ T\ \text{In}\ (h\ k / k_B\ T)_{\text{p}} \qquad (2)$$

where *R*, *h* and k_B are the universal gas, Planck and Boltzmann constants, respectively, and *T* is the absolute temperature.

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Table 1. Dielectric constants, rate constants and Gibbs energies of activation for the solvolysis of alkyl halides in diols at 298.15 K

		2-Br-2-MeBu		2-Cl-2-MeBu		3-Cl-3-MePe	
Solvent	ε	10^6k (s^{-1})	$\Delta^{\neq}G$ (kJ mol^{-1})	10^6k (s^{-1})	$\Delta^{\neq}G$ (kJ mol^{-1})	10^6k (s^{-1})	$\Delta^{\neq}G$ (kJ mol^{-1})
1,2-Et$(OH)_2$	37.7	142×10	89.3	49.7	97.6	71.8	96.7
1,2-Pr$(OH)_2$	28.59	155	94.8	3.75	104.0	4.88	103.3
1,3-Pr$(OH)_2$	34.98	384	92.5	7.71	102.2	14.9	100.6
1,2-Bu$(OH)_2$	22.35	43.6	97.9	1.31	106.6	2.02	105.5
1,3-Bu$(OH)_2$	28.57	64.9	96.9	2.08	105.5	2.52	105.0
1,4-Bu$(OH)_2$	30.86	96.7	95.9	2.68	104.8	3.79	104.0
2,3-Bu$(OH)_2$	21.65	20.7	99.8	1.07	107.1	1.35	106.5
1,5-Pe$(OH)_2$	27.17	37.7	98.3	1.12	107.0	1.72	105.9
Diethylene glycol	31.69	178	94.4	3.21	104.4	3.66	104.1
Triethylene glycol	23.69	103	95.8	1.32	106.6	3.04	104.5

Since the transfer Gibbs energy of the reactants is given by:

$$\delta G_i = R\ T\ \mathrm{In}\ (\gamma^{\infty}{}_j/\gamma^{\infty}{}_r) \qquad (3)$$

where the subscript *j* refers to a chosen solvent and *r* to a reference solvent, we first need to obtain the infinite dilution activity coefficients, γ^{∞}.

In this work, the γ^{∞} values of the solutes in the pure diols at 298.15 K were calculated using the UNIFAC group contribution method,[7,8] due to the non-availability of experimental data. For the combinatorial term, as suggested by Kikic *et al.*,[9] the modified Flory–Huggins equation in the Staverman–Guggenheim expression was used. For the residual term, group interaction parameters from the UNIFAC γ^{∞} specific table[10] were used, except for the solutes 2-Cl-2-MeBu and 3-Cl-3-MePe in diethylene and triethylene glycol because the specific γ^{∞} UNIFAC parameters for the relevant groups are not available.[10] Therefore, the γ^{∞} values of 2-Cl-2-MeBu and 3-Cl-3-MePe in diethylene and triethylene glycol were calculated using the UNIFAC interaction parameters from the VLE tables.[8,11–15] For comparison, all the other infinite dilution activity coefficients were also predicted on the basis of UNIFAC–VLE parameter tables.

Finally, through the relationship that correlates the respective transfer Gibbs energies:

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

it was possible to calculate the Gibbs energies of transfer for the activated complex.

In the following sections the new experimental *k* values are presented, γ^{∞} calculations are detailed, then the calculation of transfer Gibbs energies is described and finally solvent effects on the initial state and the transition state are discussed.

EXPERIMENTAL

The diols used were ethane-, propane- and butane-1,2-diol [1,2-Et$(OH)_2$, 1,2-Pr$(OH)_2$ and 1,2-Bu$(OH)_2$, respectively], propane- and butane-1,3-diol [1,3-Pr$(OH)_2$ and 1,3-Bu$(OH)_2$, respectively], butane-1,4-diol [1,4-Bu$(OH)_2$], butane-2,3-diol [2,3-Bu$(OH)_2$], butane-1,5-diol [1,5-Bu$(OH)_2$], diethylene glycol [$CH_2OCH_2(CH_2OH)_2$] and triethylene glycol [$(CH_2OCH_2)_2(CH_2OH)_2$]. They were obtained from BDH and Merck and they were carefully dried over appropriate molecular sieves to keep the content of water less than 0.02%.[16]

The substrates, 2-bromo-2-methylbutane (2-Br-2-MeBu), 2-chloro-2-methylbutane (2-Cl-2-MeBu) and 3-chloro-3-methylpentane (3-Cl-3-MePe), of the highest purity commercially available (>99%), all from BDH, were used without further purification.

Conductance measurements were carried out with a Wayne-Kerr B905 bridge regulated and controlled by a computer. The measurements were performed at least in triplicate. The temperature in the reaction cells was maintained constant at 25.00 ± 0.01 °C.

RESULTS AND DISCUSSION

The rate constants for the three substrates in the diols, given in Table 1, are the means of the separate kinetic runs; the accuracy is better than 2%. Equation (2) was used to calculate the Gibbs energies of activation, which are also given in Table 1.

The rate data in Table 1 can be analysed through two different approaches: substrate and solvent effects.

Substrate effects

From the point of view of substrate effects, it is worth pointing out that, first, *k* values always increase from 2-Cl-2-MeBu to 2-Br-2-MeBu. The order of the rate ratio has a mean value of 40 when 2,3-Bu$(OH)_2$, diethylene and triethylene glycol are excluded. In a previous study we compared the rate constants of *tert*-butyl chloride (*t*-BuCl) and *tert*-butyl bromide (*t*-BuBr) in mono- and dialcohols.[17] The rate ratio obtained for the same set of diols is similar: 37. The three mentioned solvents exhibit

Table 2. Infinite dilution activity coefficients γ^{∞} for the alkyl halides in diols at 298.15 K

	2-Br-2-MeBu		2-Cl-2-MeBu		3-Cl-3-MePe	
Solvent	UNIFAC	UNIFAC–VLE	UNIFAC	UNIFAC–VLE	UNIFAC	UNIFAC–VLE
1,2-Et(OH)$_2$	53.5	26.6	18.2	26.5	31.2	44.9
1,2-Pr(OH)$_2$	24.4	14.3	9.8	13.9	15.3	21.4
1,3-Pr(OH)$_2$	24.3	14.3	9.8	13.9	15.3	21.4
1,2-Bu(OH)$_2$	14.2	9.3	6.5	8.9	9.4	12.8
1,3-Bu(OH)$_2$	14.2	9.3	6.5	8.9	9.4	12.8
1,4-Bu(OH)$_2$	14.2	9.3	6.5	8.9	9.4	12.8
2,3-Bu(OH)$_2$	14.2	9.3	6.5	8.9	9.4	12.8
1,5-Pe(OH)$_2$	9.5	6.8	4.8	6.4	6.6	8.8
Diethylene glycol	4.4	9.3	—	13.6	—	20.9
Triethylene glycol	2.0	5.6	—	9.6	—	14.0

different values from the mean: the smallest value for 2,3-Bu(OH)$_2$ (*ca* 20) and the highest values for diethylene glycol and triethylene glycol (*ca* 80). The agreement between these variations and those presented before[17] is satisfactory, showing a consistent behaviour of the different substrates. Second, when comparing the experimental rate constants for 2-Cl-2-MeBu and 3-Cl-3-MePe, the situation is similar, although the rate ratios are substantially smaller. Again, an exceptionally high value is obtained for triethylene glycol. It should be noted that these considerations also apply to *t*-BuCl and *t*-BuBr. Third, is found that the influence of the substituents (Cl → Br) is more important than the replacement of a methyl group by an ethyl group in the substrate molecule.

The results can be summarized as $k_{2\text{-}Cl} << k_{2\text{-Br}}$ and $k_{2\text{-Cl}} < k_{3\text{-Cl}}$ for the solvolytic reactions of *tert*-alkyl halides in diols. The molar volumes for the three solutes are 123 cm^3 mol^{-1} for 2-Cl-2-MeBu, 128 cm^3 mol^{-1} for 2-Br-2-MeBu and 136 cm^3 mol^{-1} for 3-Cl-3-MePe. It is interesting that the change of the halide ion is more important than the change of the molar volume.

Solvent effects

A different approach to the problem is the analysis of solvent effects. Among the various solvent effects that influence the rate constants, we note the following. (i) When the solvolysis is performed in alcohols with neighbouring OH groups (1,2- and 1,3-), an acceleration in reaction rates with a decrease in the length of the carbon chain is observed for all substrates. This is a consequence of steric hindrance, which is more important when the increase of the carbon chain takes place in the two terminal carbons. Analysis of the results in Table 1 in Ref. 17, concerning the solvolysis of *t*-BuCl and *t*-BuBr in the same diols, leads to similar conclusions. (ii) When each member of the alcoholic series differs from the next lower one by the addition of a methylene group, the increase in the number of these groups leads to a large steric inhibition of solvation, which causes a decrease in *k* values. This is also true on going from diethylene to triethylene glycol. (iii) An interesting conclusion that can be drawn from the rate constants for the reaction in butanediols is that the reaction in 2,3-Bu(OH)$_2$ proceeds differently. In other words, the position of the functional groups is the most sterically hindered, which is in some way responsible for the lowest *k* value. The same can be observed for propanediols on going from 1,3- to 1,2-Pr(OH)$_2$. Diols are associated through inter- and intramolecular hydrogen bonds. When the two hydroxyl groups are situated in adjacent positions, a strong intramolecular interaction exists, weakening the intermolecular cohesion.

UNIFAC γ^{∞} values

In Table 2 are summarized the infinite dilution activity coefficients for the three alkyl halides in the 10 pure diols at 298.15 K. This table contains the γ^{∞} values obtained from the UNIFAC group contribution method,[7,8] as mentioned before. The model has already been used previously,[1–4] and a brief description and presentation of the relevant equations were given in Gonçalves *et al.*[1]

For the combinatorial term, the modified Flory–Huggins equation was used in the Staverman–Guggenheim expression.[9] For the residual term, group interaction parameters from the UNIFAC γ^{∞} parameter table[10] were used, except for 2-Cl-2-MeBu and 3-Cl-3-MePe in diethylene and triethylene glycol, owing to the non-availability of parameters for the relevant groups. For these two γ^{∞} values UNIFAC–VLE parameters were used.[8,11–15] For comparison, all the other infinite dilution activity coefficients were also calculated using the UNIFAC–VLE parameter tables (Table 2).

It should be noticed that for the solvent 1,2-ethanediol, interaction parameters for the hydroxy group (‘OH’) were used, instead of the diol group (‘DOH’), because relevant parameters are not available. The solvents

Table 3. Gibbs energies of transfer for the solvolysis of alkyl halides in diols at 298.15 K (kJ mol^{-1})

	2-Br-2-MeBu			2-Cl-2-MeBu			3-Cl-3-MePe		
Solvent	$\delta\Delta^{\neq}G$	$-\delta G_i^a$	δG_t^a	$\delta\Delta^{\neq}G$	$-\delta G_i^a$	δG_t^a	$\delta\Delta^{\neq}G$	$-\delta G_i^a$	δG_t^a
1,2-Et(OH)$_2$	0	0	0	0	0	0	0	0	0
1,2-Pr(OH)$_2$	5.5	2.0	3.5	6.4	1.5	4.9	6.7	1.8	4.9
		1.5	4.0		1.6	4.8		1.8	4.9
1,3-Pr(OH)$_2$	3.2	2.0	1.2	4.6	1.5	3.1	3.9	1.8	2.1
		1.5	1.7		1.6	3.0		1.8	2.1
1,2-Bu(OH)$_2$	8.6	3.3	5.3	9.0	2.6	6.4	8.8	3.0	5.8
		2.6	6.0		2.7	6.3		3.1	5.7
1,3-Bu(OH)$_2$	7.6	3.3	4.3	7.9	2.6	5.3	8.3	3.0	5.3
		2.6	5.0		2.7	5.2		3.1	5.2
1,4-Bu(OH)$_2$	6.7	3.3	3.4	7.2	2.6	4.6	7.3	3.0	4.3
		2.6	4.1		2.7	4.5		3.1	4.2
2,3-Bu(OH)$_2$	10.5	3.3	7.2	9.5	2.6	6.9	9.8	3.0	6.8
		2.6	7.9		2.7	6.8		3.1	6.7
1,5-Pe(OH)$_2$	9.0	4.3	4.7	9.4	3.3	6.1	9.2	3.9	5.3
		3.4	5.6		3.5	5.9		4.0	5.2
Diethylene glycol	5.2	6.2	−1.0	6.8	—	—	7.4	—	—
		2.6	2.6		1.6	5.2		1.9	5.5
Triethylene glycol	6.5	8.2	−1.7	9.0	—	—	7.8	—	—
		3.9	2.6		2.5	6.5		2.9	4.9

a Values in the first row from γ^{∞} (UNIFAC) and in the second row from γ^{∞} (UNIFAC–VLE) in Table 2.

diethylene and triethylene glycol were considered to be built from the structural groups ‘CH$_2$,’ ‘OH’ and the ether group ‘CH$_2$O.’ Although in the UNIFAC γ^{∞} specific parameter table[10] both solvents are recommended to be considered as only one group each (group ‘DEG’ and group ‘TEG,’ respectively), no parameters for the relevant interactions are available. In the UNIFAC–VLE parameter tables these two groups, ‘DEG’ and ‘TEG,’ are not defined.

As can be seen from Table 2, for some infinite dilution activity coefficients different results are obtained when using the two UNIFAC interaction parameters tables, γ^{∞} and VLE. This has already been pointed out by Bastos *et al.*[10] for high values of γ^{∞}. This is probably a good indication that the γ^{∞} values calculated using the UNIFAC γ^{∞} specific parameter table are more reliable than those calculated from the UNIFAC–VLE parameter tables.

It is interesting that, except for the outstanding case of diethylene and triethylene glycol on passing from 2-Cl-2-MeBu to 2-Br-2-MeBu, the γ^{∞} values behave similarly to k values: $\gamma^{\infty}{}_{\text{2-Cl}} < \gamma^{\infty}{}_{\text{2-Br}}$ and $\gamma^{\infty}{}_{\text{2-Cl}} < \gamma^{\infty}{}_{\text{3-Cl}}$. On the other hand, we may observe that, as expected the γ^{∞} values always decrease with an increase in the carbon chain length.

Gibbs energies of transfer

The solvolytic reactions were also analysed by the method of initial state and transition state contributions, equations (3) and (4). Values for the various hydroxylic solvents are presented in Table 3, with 1,2-Et(OH)$_2$ as the reference solvent.

The transfer Gibbs energies of activation, $\delta\Delta^{\neq}G$, measure the difference between the Gibbs energy of the reaction in a chosen solvent and that in the reference solvent. Therefore, for the structural reasons presented above, 2,3-Bu(OH)$_2$ shows the highest values.

Table 3 shows that δG_i are always negative and δG_t are, in general, positive. The effects on the Gibbs energies of activation are, in most cases, mainly due to transition state effects, although the solvent effects on the reactants are not negligible. It is important to mention that, although γ^{∞} values from both sources may differ considerably, the transfer Gibbs energies for the initial state and for the transition state follow the same pattern and lead to a common interpretation. It would be interesting to treat transfer values for diethylene and triethylene glycol, but we contend that this is not yet possible. The inclusion of these values, however, can be interesting for testing different models, particularly if experimental γ^{∞} values could be obtained.

A number of other conclusions can be drawn from the thermodynamic results. (i) From the δG_i and δG_t contributions, it can be deduced that the initial state is more stabilized in 1,2-Et(OH)$_2$ than in the other diols and, conversely, the transition state is more stabilized in all the other alcohols than in 1,2-Et(OH)$_2$. The Gibbs energies of stabilization for the transition state are explained by the expenditure of less energy in solvents of lower dielectric constant. Some correlation exists, in fact, between δG_t and ε values,[17] as can be seen from the data in Tables 1 and 3. (ii) At the molecular level, the results can be discussed in terms of dipolarity and also in terms of hydrogen-bond properties of the solvents. Two effects appear to be important: the interactions between solvent molecules and the interactions between solvent and substrate–activated complex molecules. It seems that, in the initial state, the clevage of hydrogen bonds and cavity formation are more relevant than dipole–dipole interactions between the substrate and solvent molecules (alkyl halides have small dipole moments). A comparison of solvent effects on the activated complex with solvent effects on substrates shows an opposite situation. Since the activated complex is close to an ion pair, the free molecules of the most polar alcohols interact strongly with the activated complex and can even increase solvent–solvent interactions inside the cybotatic region. (iii) The Gibbs energy of transfer, for each solvent, is almost insensitive to the nature of the alkyl halide.

CONCLUSION

The preceding discussion shows the possibility of distinguishing solvent effects on the initial state and activated complex. Although a critical point involves the large differences provided by the two computations used to obtain the activity coefficients, the sequence of the transfer Gibbs energies for the initial state and for the transition state follow the same pattern and lead to a common interpretation.

Mechanistic differences are probably the basis of the observed data. This is why we chose a ‘wellknown’ reaction to perform the first studies. In future work, however, we hope to analyse in more detail possible differences in the reaction pathways of the substrates and their significance.

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