Alcoholysis of t-Butyl Chloride in Branched and Straight-chain Alcohols: a Kinetic and Calorimetric Study

Raquel M. C. Gonçalves, Ana M. N. Simões, and César A. N. Viana *
Centro de Electroquímica e Cinética da Universidade de Lisboa, Instituto Bento da Rocha Cabral 14, 1200 Lisboa, Portugal

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Kinetic and related calorimetric data are reported for the alcoholysis of t-butyl chloride. Heat capacities of solution and activation are used to probe the role of solvent in the activation process. Partial molar heat capacities of activation, ground, and transition states differ for reaction in normal and branched alcohols. Structural and mechanistic distinctions between the two classes of solvolytic reaction are established.

Solvolytic reactions of alkyl halides and similar compounds in different solvents, especially in water, have been frequently studied.[1,2] However, few of these reactions have been analysed using both thermodynamic and kinetic data. We have reported the kinetics of solvolysis for 2-chloro-2-methylpropane (Bu^{t}Cl) and 3-chloro-3-ethylpentane in methanol,[3,4] propan-2-ol,[5] 2-methylpropan-2-ol,[6,7] ethane-1,2-diol,[8,9] and propane-1,2,3-triol.[9]

As mentioned by Hullet,[10] the definition of reaction mechanism requires an understanding of the involvement of solvent in both ground and transition states. The main problem lies in obtaining thermodynamic functions for both states. Considerable attention has been given to enthalpies and Gibbs functions,[11–14] with rather less concern for entropies and volumes of activation.[15,16] However, as far as we are aware, no comparable study has been undertaken of heat capacities of activation despite their importance.[17] Two reasons account for this omission: (a) heat capacities of activation are difficult to obtain because they are a function of the second temperature derivative of the specific rates; (b) the required heat capacities of solution are scarce.

In this paper we report kinetic data for solvolysis of Bu^{t}Cl in normal alcohols (MeOH, EtOH, Pr^{n}OH, Bu^{n}OH, and n-C_5H_{11}OH) together with calorimetric data for this substrate in these normal alcohols and in Pr^{i}OH and Bu^{t}OH.

Calculated and previously reported heat capacities of activation[5,6] and of solution are used to obtain standard partial molar heat capacities of ground and transition states. The results are used to comment on the role of solvent in these reactions.

Experimental

A conductimetric technique[6] and the Kezdy–Swinbourne method[18,19] [equation (1) where G denotes the global

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

conductance of the system] were used to determine the specific rates for reactions in solutions containing 0.01M-Bu^{t}Cl. Solution enthalpies were obtained using a quasi-adiabatic solution calorimeter fitted with a platinum sensor (Tinsley 5187 SA), a resistance bridge (Tinsley 5840), a constantan calibration heater, a glass stirrer, and a support containing the sealed ampoule. The power supply of the calibration heater was a Philips PE 1537 apparatus and a Philips PM 2522 ammeter, was used. Calorimetric experiments were made using Bu^{t}Cl concentrations which were low enough (0.01—0.03M) to obtain directly standard partial molar heats of solution: calculated enthalpies of solution were essentially constant upon breaking six solute ampoules in the same solvent. Corrections resulting from ampoule breaking and solute vaporization were negligibly small. At least five kinetic and calorimetric experiments were performed at each temperature. Simple and multiple regressions were used to calculate heat capacities of activation and their standard deviations. All reagents were purified as described.[6]

Results and Discussion

The specific rates for solvolysis of Bu^{t}Cl at temperatures ranging from 25 to 55 °C are shown in Table 1. The conductimetric technique assumes that the conductance (G) of the system is a linear function of the hydrochloric acid concentration, the accuracy of the method depending on the HCl concentration, the viscosity, and dielectric constant. Therefore, the accuracy is very dependent on solvent and temperature. The specific rates for reaction in normal alcohols have a smaller error than those in branched alcohols; the error increases with length of carbon chain. The application of linear regression according to the Kezdy–Swinbourne method leads to the standard deviation on k [equation (2) where N represents

Table 1. $-\ln (k/s^{-1})$* of Bu^{t}Cl solvolysis

Solvent T/°C	MeOH	EtOH	Pr^{n}OH	Bu^{n}OH	n-C_5H_{11}OH	Pr^{i}OH[a]	Bu^{t}OH[b]
25.00	13.74[c]	14.49	15.24	14.80	14.86	14.41	12.40[d]
30.00	13.17[c]	14.08	14.84	14.43	14.47	13.60	11.90
35.00	12.48[c]	13.52	14.21	13.92	14.09	12.68	11.45
40.00	11.83[c]	12.94	13.56	13.38	13.58	12.15	10.84
45.00	11.15	12.43	13.01	12.90	13.04	11.31	10.37
50.00	10.56	11.86	12.48	12.39	12.55	10.72	10.06
55.00	9.89	11.28	11.88	11.89	12.16	10.21	9.75

[a] Ref. 5. [b] Ref. 6. [c] Ref. 4. [d] T 27.00 °C.

* $\delta(\ln k) \leqslant 0.5\%$.

Table 2. Application of Valentiner's equation to Bu^{t}Cl solvolysis

Solvent	MeOH	EtOH	Pr^{n}OH	Bu^{n}OH	n-C_5H_{11}OH	Pr^{i}OH	Bu^{t}OH
10^{-4} A	1.4737	3.3116	2.0679	2.5669	2.7844	−5.9746	−8.7037
10^{-1} B	8.7579	13.997	10.188	11.298	11.806	−14.691	−24.795
10^{-2} C	−5.6218	−9.2192	−6.6513	−7.4468	−7.8094	10.230	16.920
10^{-7} $\sigma_A^{\,2}$	8.0108	9.5680	31.292	10.598	25.461	47.004	34.311
10^{-2} $\sigma_B^{\,2}$	8.1933	9.7858	32.004	10.839	26.041	48.074	34.905
10^{-4} $\sigma_C^{\,2}$	2.9216	3.3922	11.412	3.8651	9.2858	16.662	12.452
10^{-5} $\sigma_{AB}^{\,2}$	2.5617	3.0596	10.006	3.3890	8.1420	15.031	10.943
10^{-6} $\sigma_{AC}^{\,2}$	−1.7281	−2.0640	−6.7501	−2.2862	−12.818	−10.140	−7.3846
$10^{-3}\sigma_{BC}^{\,2}$	−5.5269	−6.6012	−21.589	−7.3118	−17.566	−32.429	−23.555
r	1.000	0.999	0.998	0.999	0.998	0.998	0.998
$10^{-2}(\Delta C_p^{\circ\neq} \pm \sigma\Delta C_p^{\circ\neq})$/ J K^{-1} mol^{-1}	(7 ± 2)	(11 ± 3)	(8 ± 5)	(9 ± 3)	(10 ± 4)	(−12 ± 6)	(−20 ± 5)

Table 3. ΔH_s°*/J mol^{-1} values of Bu^{t}Cl solutions

T/°C \ Solvent	MeOH	EtOH	Pr^{n}OH	Bu^{n}OH	n-C_5H_{11}OH	Pr^{i}OH	Bu^{t}OH
25.00	1 565	1 494	1 619	2 104	2 561	3 565	6 326^a
30.00	2 351	1 971	2 494	2 686	2 812	4 330	6 573
35.00	2 653	2 431	2 862	3 012	3 155	5 121	7 159
40.00	3 054	2 711	3 259	3 381	3 531	5 364	7 276

^{a} T 27.00 °C.

* $\delta(\Delta H_s^{\circ}) \leqslant 2\%$.

$$\sigma_k = \frac{\left[N\sigma^2\left|N\sum_{i=1}^{N} G_{t_i+\Delta t} - \left(\sum_{i=1}^{N} G_{t_i+\Delta t}\right)^2\right|\right]^{1/2}}{\Delta t\left(N\sum_{i=1}^{N} G_{t_i}G_{t_i+\Delta t} - \sum_{i=1}^{N} G_{t_i}\sum_{i=1}^{N} G_{t_i+\Delta t}\right)} \qquad (2)$$

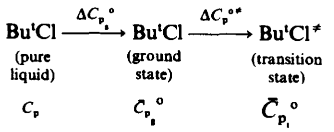
the number of pairs of points (G_{t_i}, $G_{t_i+\Delta t}$) and σ the standard deviation of each point]. The accuracy of each kinetic experiment is high, 80% of the specific rates having σ_k smaller than 0.5%.

ln k values given in Table 1 are the mean values from a set of experimental results (n) obtained at the same temperature. δ(ln k) are mean deviations from those values [equations (3) and (4)]. Corresponding rate constants reported by Swain,[20] Winstein,[21] Moelwyn-Hughes,[22] and Koppel[23] for the methanolysis and ethanolysis of Bu^{t}Cl, differ slightly from the values reported here.* For branched alcohols, however, the values reported by Rudakov[24] differ significantly.* A titration technique was used in this case[25] which is, in our opinion, much less precise that the conductimetric technique. When NaOH is added to the reaction system, competitive reactions occur. We suggest that specific rates obtained in this way are unreliable. Specific rates were measured for reactions in the alcohols at identical temperatures.[26] The data were satisfactorily fitted to Valentiner's equation, ln $k = A/T + B$ ln $T + C$. Correlation factors (r), A, B, and C parameters and their variances and covariances (σ^2) are reported in Table 2.

$$\ln k = \sum_{i=1}^{n} \ln k_i/n \qquad (3)$$

$$\delta(\ln k) = \sum_{i=1}^{n} |\ln k_i - \ln k|/n \qquad (4)$$

Heat capacities of activation for reaction in branched alcohols are negative but in all other systems these functions are positive, the mean value being (9 ± 3) × 10^2 J mol^{-1} K^{-1}. Positive values reflect an increasing energy of activation with rise in temperature. Two factors account for this behaviour: (i) decrease in the partial molar enthalpy of the activated complex, and/or (ii) increase on the partial molar enthalpy of the substrate with increasing temperature. Calorimetric data can be used to identify which explanation is correct. Consider the following Scheme where C_p is the molar heat capacity of the liquid solute and $\Delta C_{p_s}^{\circ}$ is the standard heat capacity of solution. The standard partial molar heat capacities of the ground and transition states, $\bar{C}_{p_s}^{\circ}$ and $\bar{C}_{p_t}^{\circ}$, respectively, are given by equations (5) and (6).



Scheme.

$$\bar{C}_{p_s}^{\circ} = C_p + \Delta C_{p_s}^{\circ} \qquad (5)$$

$$\bar{C}_{p_t}^{\circ} = \bar{C}_{p_s}^{\circ} + \Delta C_p^{\circ\neq} \qquad (6)$$

Standard partial molar enthalpies of solution, at different temperatures, are presented in Table 3. They are the mean values from a set of ΔH_s° values obtained at same temperatures and $\delta(\Delta H_s^{\circ})$ are the mean deviations from the media. Abraham's results are, generally, in agreement at 25 °C.[27] ΔH_s° are positive which means that endothermic solvent–solvent interactions together with a cavity creation term outweigh exothermic specific solute–solvent interactions.[28]

The high values for solution in branched alcohols are a consequence of weak solute–solvent interaction, mainly due to steric effects in the alcohols.[6] The sequence of ΔH_s° values for

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* −ln k (T 25 °C): 14.10,[21] 13.95,[22] 14.32[23] in MeOH; 16.15,[20] 16.27,[21] 16.53[23] in EtOH; 18.0[24] in Pr^{i}OH; 19.1[24] in Bu^{t}OH.[24]

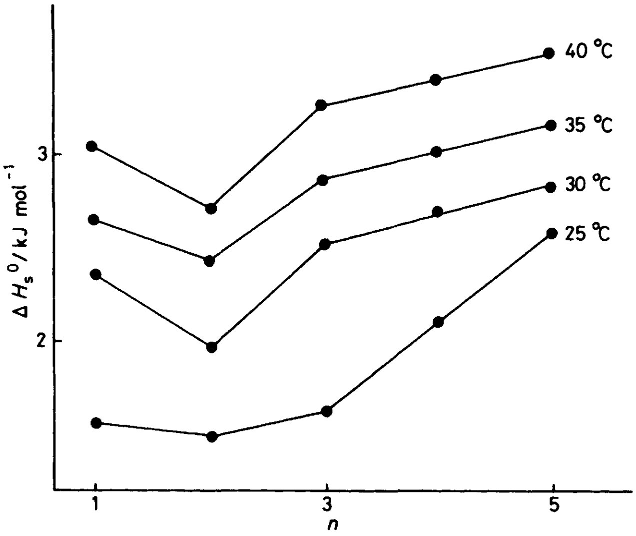

Figure 1. ΔH_s° *versus* *n* (number of carbon atoms of normal alcohols)

Table 4. $10\Delta C_{p_s}^{\circ}$/J K^{-1} mol^{-1} values

Bu^{t}Cl in normal alcohols

T/°C \ Solvent	MeOH	EtOH	Pr^{n}OH	Bu^{n}OH	n-$C_5H_{11}OH$
25—30	15	10	17	12	7
30—40	7	7	8	7	7

Bu^{t}Cl in branched alcohols

T/°C \ Solvent	Pr^{i}OH	Bu^{t}OH
25—35	15	10
35—40	5	3

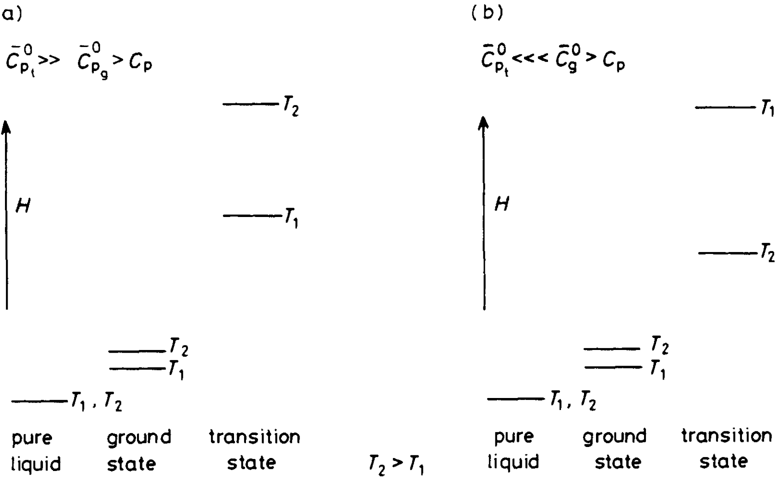

Figure 2. Solution and activation enthalpy diagrams for the system Bu^{t}Cl–alcohol: a, normal alcohols; b, branched alcohols.

normal alcohols, at each temperature (Figure 1), is explained in terms of a competition between inductive and steric factors, the latter predominating for alcohols with a carbon chain longer than EtOH. The $\Delta H_s^{\circ} - T$ dependence could not be described by a quadratic equation. A linear dependence of ΔH_s° on T in the case of normal alcohols (70 J K^{-1} mol^{-1}) is observed between 30 and 40 °C. However, the corresponding slope depends on solvent below 30 °C (Table 4). $\Delta C_{p_s}^{\circ}$ is always higher above 30 °C, except for n-$C_5H_{11}OH$. The extent of hydrogen bonding in alcohols seems to be particularly sensitive at the lower temperatures. A decrease in extent of molecular association from MeOH to n-$C_5H_{11}OH$ can account for this. The smaller $\Delta C_{p_s}^{\circ}$ value for solutions in EtOH is consistent with the assumption that inductive effects of methyl groups in this alcohol produces a stronger solute–solvent interaction. For branched alcohols, $\Delta C_{p_s}^{\circ}$ (Table 4) rapidly decreases with temperature indicating that the extent of hydrogen-bond breaking has reached a maximum; a similar trend is expected for normal alcohols but at higher temperatures.

Using equations (5) and (6) we estimate the partial molar heat capacities of ground and transition states; the heat capacity of Bu^{t}Cl (pure liquid) is *ca.* 60 J K^{-1} mol^{-1} between 25 and 40 °C.[29,30] The effect of solvent and temperature on $\Delta C_{p_s}^{\circ}$ is small for all alcohols compared with $\Delta C_p^{\circ\neq}$. A mean $\bar{C}_{p_s}^{\circ}$ for all systems of (15 ± 3) × 10 J K^{-1} mol^{-1} yielded values for $\bar{C}_{p_t}^{\circ}$ of 10 × 10^2, −10 × 10^2, and −18 × 10^2 J K^{-1} mol^{-1} for reactions in normal alcohols, Pr^{i}OH, and Bu^{t}OH, respectively.

In Figure 2 we compare, in diagrammatic form, trends in enthalpies. For Bu^{t}Cl in normal alcohols, breaking of hydrogen bonding in the solvent during the activation process is more important than for the solution process. Hence, effects of solute–solvent interactions in the activation process are marked. However, activation volumes for the Bu^{t}Cl–MeOH system are strongly negative,[3] indicating a clear difference between ground and transition states. The situation is different for the solvolysis of Bu^{t}Cl in branched alcohols. There is less association by hydrogen bonding in branched alcohols than in normal alcohols due to steric effects. This is specially so for Bu^{t}OH. Therefore, breaking of hydrogen bonds dominates the solution process relative to activation. During the activation process, the main energetic changes stem from solute–solvent interactions. Although the volume of activation for Bu^{t}Cl in Bu^{t}OH,[5] at 1 atm, is *ca.* −5 cm^3 mol^{-1} in the studied temperature range, it is considerably higher than the activation volume for solutions in MeOH,[3] pointing to a small solvation increase during the activation process.

Abraham *et al.*[31] concluded that the transition state is the same in all alcohols. This conclusion is at variance with the conclusion reached here. Abraham examined ΔG values. Gibbs energies, however, resulting from compensation between enthalpy and entropy terms, are not sensitive to mechanistic details. Besides, Abraham used the $\Delta G^{\circ\neq}$ values for solvolytic reactions in branched alcohols reported by Rudakov, which are open to the criticism mentioned above.

Finally, some conclusions can be drawn about the solution and activation processes in the limits of strongly associated and the weakly associated alcohols. The key factor in the ground state is the extent of hydrogen bonding between solvent molecules in the solvation shell. For the activated state, the key factor is the number of solvent molecules surrounding the tertiary-alkyl halide. This number increases with increase in polarity of alcohols. The solvation shell for strongly associated alcohols is built at the expenses of breaking hydrogen bonds of the solvent. For less associated alcohols the solvation shell is formed from non-hydrogen-bonded molecules.

Certain aspects of the way in which the kinetic data have been analysed may need to be reconsidered.[32–34] One question concerns the Valentiner equation because it is unsuitable for the detection of a dependence of $\Delta C_p^{\circ\neq}$ on temperature. Further, the A, B, and C parameters are linearly dependent on temperature. Nevertheless the aim of this paper is to analyse data obtained under the same experimental conditions, to use the same analytical treatment, and hence to examine mechanistic details.

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