



INFLUENCE OF SOLVENT AND TEMPERATURE ON THE GROUND STATE AND ON THE TRANSITION STATE OF *tert*-BUTYL CHLORIDE ALCOHOLYSIS

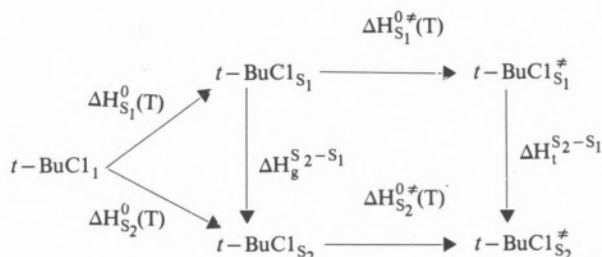
Thermodynamic enthalpies of activation, as well as standard solutions enthalpies, calculated from experimental values for the solvolysis of tert-butyl chloride in methanol, ethanol, iso-propanol and tert-butanol were used together to study the influence of the solvent and of the temperature on the ground and transition states of the reaction.

Some mechanistic conclusions are drawn.

1 — INTRODUCTION

Appropriate thermodynamic cycles to discriminate solvent involvement in the ground and in the transition states of chemical reactions were developed by different authors [1-8].

At constant temperature, several solvolysis of *tert*-butyl chloride have been studied from the following scheme [1, 2, 8]:

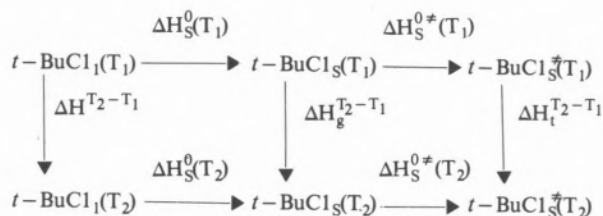


and equations (1) and (2) are derived:

$$\Delta H_g^{S_2-S_1} = \Delta H_{S_2}^0(T) - \Delta H_{S_1}^0(T) \quad (1)$$

$$\Delta H_t^{S_2-S_1} = \Delta H_{S_2}^{0*}(T) - \Delta H_{S_1}^{0*}(T) + \Delta H_g^{S_2-S_1} \quad (2)$$

A similar cycle, considering the same solvent at two different temperatures, may be constructed [9]:



from which, the following temperature coefficients can be derived:

$$\Delta H_g^{T_2-T_1} = \Delta H_{S_1}^0(T_2) - \Delta H_{S_1}^0(T_1) + \Delta H^{T_2-T_1} \quad (3)$$

$$\Delta H_t^{T_2-T_1} = \Delta H_{S_1}^{0*}(T_2) - \Delta H_{S_1}^{0*}(T_1) + \Delta H_g^{T_2-T_1} \quad (4)$$

The two sets of equations permit to study solvent and temperature influence on both ground and transition states of *tert*-butyl chloride solvolysis.

For this purpose, enthalpies of activation and standard enthalpies of solution of *t*-BuCl in several alcohols were determined and interpreted.

2 — EXPERIMENTAL

A conductimetric technique, previously described [10], was used to evaluate the rate constants of the system *t*-BuCl — *i*-PrOH, between 25 and 60 °C.

A method, based on equation $\ln k = \frac{A}{T} + B \ln T + C$, described elsewhere [11, 12], was used to calculate the enthalpies of activation as well as their standard deviations.

Standard solution enthalpies, at two different temperatures, were obtained by a calorimetric technique using a calorimeter LKB 8700. *Tert*-butyl chloride concentration range, 0.02 M — 0.04 M, was low enough to permit to consider the total heat of solution identical to the solute partial molar enthalpy, at infinite dilution. Two series, each one of four independent determinations, were performed for each system solute-solvent and a maximum deviation of 40 J mol⁻¹ from the mean value was observed. Calorimeter accuracy was tested using the values of solution heats of Tris in HCl 0.01 M. The results were in accordance with those of WADSÖ and col. [13]. Cylindrical ampoules, flame closed as described by SUNNER and WADSÖ [14], were used.

All reagents were BDH products of high purity grade. The solvents were distilled and dried over molecular sieve. IR spectroscopy and gas chromatography were used to test the purification degree.

3 — RESULTS AND DISCUSSION

Rate constants and the best equation fitting ($\ln k$, T) variation for the system *t*-BuCl — *i*-PrOH are presented in Table 1.

Enthalpies of activation and solution enthalpies values are shown in Table 2. Those solutions enthalpies already published by ABRAHAM [15] are in accordance with our correspondent values.

From equations (1) to (4), using MeOH as reference solvent and accepting $\Delta H^{T_2-T_1}$ equal to zero for comparative purposes, different ΔH_g and ΔH_i values were calculated (Tables 3 and 4).

Standard solution enthalpies are essentially function of two contributions: one, endothermic in character, due to the rupture of some hydrogen bonding when the solute is added; another, an exothermic component, resulting from solvent reorganization on account of solute-solvent and solvent-solvent interactions.

According to the values shown in Table 2, the first contribution to ΔH_g^0 is always the most important. Several reasons can account for it.

A great number of hydrogen bonding is expected to be broken in methanol and ethanol when the substratum is added; however, *iso*-propanol and specially *tert*-butanol, are much less associated by

Table 1
Solvolysis of *t*-BuCl in *i*-PrOH

t(°C)	25.00	30.00	35.00	40.00	45.00	50.00	55.00	60.00
— $\ln k^*$	14.41	13.60	12.68	12.15	11.31	10.72	10.21	9.69
$\Delta \ln k^{**}$	0.07	0.10	0.17	0.02	0.01	0.05	0.04	0.02

* mean value from four to eight experiments

** maximum deviation from the mean value

$$\ln k = \frac{A}{T} + B \ln T + C$$

A = -61691.3	$\sigma(A) = 13916.3$	cov(A,B) = 1.13201×10^6
B = -153.167	$\sigma(B) = 44.1732$	cov(B,C) = -2.42689×10^4
C = 1065.17	$\sigma(C) = 154.600$	cov(A,C) = -7.64501×10^6

Correlation coefficient = 0.999.

Table 2
 $\Delta H^{0\ddagger}$ and ΔH_S^0 (kJ mol^{-1}) of *t*-BuCl in alcohols

	t(°C)	MeOH	EtOH	<i>i</i> -PrOH	<i>t</i> -BuOH	<i>n</i> -BuOH
$\Delta H^{0\ddagger}$	25.0	93.7 _(a)	109 _(b)	130	116* _(c)	—
	40.0	104 _(a)	—	111	75 _(c)	—
ΔH_S^0	25.0	1.51 1.506 _(d)	1.418 _(d)	3.43 3.498 _(d)	6.28**	2.218 _(d)
	40.0	1.97	—	4.10	6.11	—

(a) Ref. [12, 16]; (b) Ref. [17]; (c) Ref. [10]; (d) Ref. [15].

* Extrapolated value from Ref. [10].

** Value obtained at 30.0 °C.

Table 3
 Values of $\Delta H^{S_2-S_1}$ (kJ mol^{-1})

t(°C)	$\Delta H^{S_2-S_1}$	MeOH ^(a)	EtOH	<i>i</i> -PrOH	<i>t</i> -BuOH
25	$\Delta H_g^{S_2-S_1}$	0	− 0.08	+ 1.92	+ 4.85 ^(b)
	$\Delta H_t^{S_2-S_1}$	0	+ 15	+ 39	+ 28
40	$\Delta H_g^{S_2-S_1}$	0	—	+ 2.13	+ 4.14
	$\Delta H_t^{S_2-S_1}$	0	—	+ 9.6	− 25

(a) Reference solvent.

(b) Extrapolated value.

TABLE 4
 Values of ΔH^{40-25} (kJ mol^{-1})

ΔH^{40-25}	MeOH	<i>i</i> -PrOH	<i>t</i> -BuOH
ΔH_g^{40-25}	+ 0.46	+ 0.69	− 0.25*
ΔH_t^{40-25}	+ 10	− 18	− 41.8

* Extrapolated value

hydrogen bonding than other alcohols [18, 19]. In fact, ΔH_S^0 large values for these solvents are mainly a consequence of a small interaction between solvent and solute molecules, probably due to steric hindrance. The small ΔH_S^0 value for *n*-BuOH (2218 J mol^{−1}) seems to confirm such point of view. Transfer enthalpies in Table 3 show that the solvent influence on the transition state structure is larger than on the ground state at both temperatures. $\Delta H_g^{S_2-S_1}$ increases along the serie,

$$\text{MeOH} \approx \text{EtOH} < i\text{-PrOH} < t\text{-BuOH}$$

probably due to the decreasing solute-solvent interaction. However, this is only true for the ground state; actually, $\Delta H_t^{S_2-S_1}$ is smaller than expected for the solvolysis in *tert*-butanol, specially at the highest temperature.

Having in account ΔH^{40-25} values presented in Table 4, a higher temperature effect on the transition state than on the initial state is observed. A maximum influence of such effect is observed with *tert*-butanol.

An exceptionally high negative value of $\Delta C_p^{0\ddagger}$ (− 2743 J mol^{−1}K^{−1}) and a very small negative volume of activation (− 5 cm³mol^{−1} at 313 and 323 K) for this system was already reported by us [10, 11]. The same type of argument used above leads to the explanation that these values are probably related to the small hydrogen bonding of *t*-BuOH [18, 19] and, consequently, to an easy solvation of the

substract molecules specially in the transition state, as well as to the small free volume associated to the solvent molecules which approximately have a globular shape and a close packing structure [20, 21].

Received 14. November. 1980

ACKNOWLEDGMENTS

The authors thank Prof. J. Moura Ramos for the determination of standard enthalpies of solution.

GLOSSARY

$\Delta H_{S_x}^0(T)$ — Standard solution enthalpy of *t*-BuCl in the solvent S_x , at temperature T .

$\Delta H_{S_x}^{0*}(T)$ — Standard enthalpy of activation of *t*-BuCl solvolysis in solvent S_x , at temperature T .

$\Delta H_g^{S_2-S_1}$; $\Delta H_t^{S_2-S_1}$ — Enthalpy variation of *t*-BuCl from solvent S_1 to solvent S_2 , in the ground and in the transition state, respectively, at temperature T .

$\Delta H_S^0(T_X)$ — Standard solution enthalpy of *t*-BuCl in the solvent S , at temperature T_X .

$\Delta H_S^{0*}(T_X)$ — Standard enthalpy of activation of *t*-BuCl solvolysis in solvent S , at temperature T_X .

$\Delta H^{T_2-T_1}$; $\Delta H_g^{T_2-T_1}$; $\Delta H_t^{T_2-T_1}$ — Enthalpy variation of *t*-BuCl from temperature T_1 to temperature T_2 in the pure liquid, in the ground state and in the transition state, respectively, in the solvent S .

MeOH — Methanol.

EtOH — Ethanol.

i-PrOH — Propanol.

t-BuOH — *tert*-Butanol.

t-BuCl — *tert*-butyl chloride.

REFERENCES

- [1] E. M. ARNETT, P. McC. DUGGLEBY, J. J. BURKE, *J. Amer. Chem. Soc.*, **85**, 1350 (1963).
- [2] E. M. ARNETT, W. G. BENTRUDE, J. J. BURKE, P. McC. DUGGLEBY, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).
- [3] E. S. RUDAKOV, V. P. TRETYAKOV, *Org. React.*, **2**, 174 (1965).
- [4] J. G. MARTIN, R. E. ROBERTSON, *J. Amer. Chem. Soc.*, **88**, 5353 (1966).
- [5] H. S. GOLINKIN, I. LEE, J. B. HYNE, *J. Amer. Chem. Soc.*, **89**, 1307 (1967).
- [6] P. HABERFIELD, *J. Amer. Chem. Soc.*, 2091 (1971).
- [7] W. DRENTH, M. COCIVERA, *Can. J. Chem.*, **54**, 3944 (1976).
- [8] M. H. ABRAHAM, *J. Chem. Soc. Perkin II*, 1028 (1977).
- [9] R. M. C. GONÇALVES, Ph. D. Thesis, University of Lisbon (1978).
- [10] C. A. N. VIANA, R. M. C. GONÇALVES, *J. C. S. Faraday Trans. I.*, **72**, 1541 (1976).
- [11] C. A. N. VIANA, R. M. C. GONÇALVES, *J. C. S. Faraday Trans. I.*, **76**, 753 (1980).
- [12] C. A. N. VIANA, R. M. C. GONÇALVES, L. M. P. C. ALBUQUERQUE, *Rev. Port. Quím.*, **22**, 117 (1980).
- [13] J. O. HILL, G. ÖJELUND, I. WADSÖ, *J. Chem. Thermodynamics*, **1**, 111 (1969).
- [14] S. SUNNER, I. WADSÖ, *Acta Chem. Scand.*, **13**, 97 (1959).
- [15] M. H. ABRAHAM, *J. Chem. Soc. Perkin II*, 1028 (1977).
- [16] C. A. N. VIANA, M. I. L. T. CALADO, *Rev. Port. Quím.*, **16**, 198 (1974).
- [17] S. WINSTEIN, A. H. FAIBERG, *J. Amer. Chem. Soc.*, **79**, 5937 (1957).
- [18] W. DANNHAUSER, L. W. BAHE, *J. Chem. Phys.*, **40**, 3058 (1964).
- [19] W. STOREK, H. KRIEGSMANN, *Ber. Bunseng. Phys. Chem.*, **72**, 706 (1968).
- [20] J. TIMMERMANS, *J. Phys. Chem. Solids*, **18**, 1 (1961).
- [21] F. L. OETTING, *J. Phys. Chem.*, **67**, 2757 (1963).

RESUMO

Influência do solvente e da temperatura sobre os estados inicial e de transição de alcoólises do cloreto de butilo terciário.

Determinam-se valores de entalpias de activação e de entalpias padrão de solução para a solvólise do cloreto de butilo terciário em metanol, etanol, iso-propanol e butanol terciário, com o fim de estudar a influência do solvente e da temperatura nos estados inicial e de transição da reacção.

Deduzem-se algumas conclusões sobre o mecanismo reaccional.