Solvent and Temperature Effects on the Rate Constants of Solvolysis of *tert*-Butyl Bromide in Mono- and Di-alcohols

Raquel M. C. Gonçalves,[a] **Ama M. N. Simões,**[a] **Lídia M. P. C. Albuquerque**[a] **and Sebastião J. Formosinho**[b]
[a] *Departamento de Química, Faculdade de Ciências de Lisboa – CECUL, Cd. Bento da Rocha Cabral, 14, 1200 Lisboa, Portugal*
[b] *Departamento de Química, Universidade de Coimbra, 3049 Coimbra Codex, Portugal*

Rate constants, *k*, for the solvolytic reactions of 2-bromo-2-methylpropane (Bu^{t}Br) in the monoalcohols propan-1-ol and butan-1-ol and in the dialcohols ethane-1,2-diol, propane-1,3-diol and butane-1,4-diol are reported, at different temperatures. These values, the Arrhenius activation energies, E_a, and the thermodynamic functions of activation, Gibbs energy ($\Delta^{\ddagger}G^{\circ}$), enthalpy ($\Delta^{\ddagger}H^{\circ}$) and entropy ($\Delta^{\ddagger}S^{\circ}$) are interpreted and compared with previous results in methanol and ethanol. According to the Intersecting-state model, the reaction-energy profile is shaped and the solvent effect on the Gibbs energy of activation, $\Delta^{\ddagger}G^{\circ}$, is analysed.

At the molecular level, the dominant solvent–solute interactions are examined. The results show that changes in E_a (or $\Delta^{\ddagger}H^{\circ}$) most affect the changes in the *k* values when dialcohols are used in place of monoalcohols; $\Delta^{\ddagger}S^{\circ}$ seems to control the differences in the *k* values within the set of monoalcohols.

In spite of the valuable contribution made by non-kinetic studies, there is no doubt that temperature and solvent studies are essential in providing evidence concerning the mechanisms of reactions; mechanistic proposals can only be made after careful kinetic investigation.

Although some controversy still remains about the best method of dealing with the problem of temperature dependence of the rate constants, the influence of temperature is usually interpreted in terms of the Arrhenius equation.[1,2] On the other hand, solvent effects on rate constants are many and varied. Nucleophilic substitutions, for instance, are very sensitive to changes in solvent polarity.

The kinetics of the solvolytic reactions of 2-chloro-2-methylpropane in pure alcohols have been extensively studied.[3,4] However, for 2-bromo-2-methylpropane (*tert*-butyl bromide, Bu^{t}Br) data for alcohol solutions, at temperatures other than 25 °C, are only available from the studies of Fainberg and Winstein[5] and Virtanen,[6] (methanol and ethanol), Biordi and Moelwyn-Hughes,[7] (methanol) and Viana and Gonçalves[8] (*tert*-butyl alcohol).

In this paper we report new kinetic data for Bu^{t}Br in the monoalcohols propan-1-ol (PrOH) and butan-1-ol (BuOH) and in the dialcohols ethane-1,2-diol (1,2-ED), propane-1,3-diol (1,3-PD) and butane-1,4-diol (1,4-BD), at different temperatures. Comparisons of data for mono- and di-alcohols with the same number of carbon atoms are made, as well as with previous results for the reactions of the same substrate in other solvents, in an attempt to gain more insight into the mechanism of these reactions.

The Arrhenius energy of activation, E_a, was calculated and is interpreted in terms of the predominant solvent–solute interactions; the transition-state approach also gives results which provides useful information.

The Intersecting-state model (ISM), developed by Formosinho and Varandas,[9,10] was used to determine the reaction-energy profile and, according to this model, the solvent effect on the Gibbs energy of activation, $\Delta^{\ddagger}G^{\circ}$, is discussed.

Experimental

The kinetic runs were carried out by means of the conductimetric technique already described.[11] In fact, the chemical change in our reactions is associated with changes in the electrical conductance of the solution (due to the production of the ions H^+ and Br^-) which permits the use of this technique; moreover, conductimetry has an advantage over otherwise suitable techniques in that the reacting system can be examined continuously. The conductivity bridge was a Wayne Kerr B905 (accuracy: 0.05%). The kinetic experiments were performed at Bu^{t}Br concentrations of 10^{-2} mol dm^{-3}, in the temperature range 25–60 °C, except for 1,2-ED, for which the temperature interval was 5–50 °C. This is because, at higher temperatures, Bu^{t}Br reacts too rapidly to allow precise velocity measurements to be made by the conductimetric technique. The vapour space above the reacting solution within the conductivity cells was minimized in order to avoid kinetic complexities[2] and the temperature control of the thermostatic vessel was better than 0.01 °C.

At least five kinetic runs were carried out at each temperature. The reagents were from BDH (min. 99.5%), Merck (min. 99.5%) and Fluka (min. 99%).

Results and Discussion

The Kezdy–Swinbourne method[12] was applied to the conductance values of the reaction solution in order to obtain the rate constants of the solvolysis of Bu^{t}Br, since the rate of production of H^+ and X^- ions was found to be approximately first order at all temperatures. However, to avoid possible kinetic complexities, rate constants were obtained under conditions where conductance values approaching equilibrium were not included in the calculations.[13]

The precision of each kinetic experiment was high, ± 0.2%. The mean rate constant values, *k*, for the solvolytic reactions are summarized in Table 1, together with some previously reported experimental data for these kinds of reaction. Fig. 1 shows the influence of temperature on the rate constants of the various reaction systems.

The Arrhenius Activation Energy.—Within the precision of the calculated kinetic data, all of the systems investigated obey the Arrhenius type eqn. (1) where a_0 is the logarithm of the

$$\ln k = a_0 + a_1 T^{-1} \qquad (1)$$

Table 1 Rate constants for the solvolytic reactions of Bu^{t}Br in several alcohols at different temperatures

	$k/10^{-6}$ s^{-1}						
T/°C	MeOH	EtOH	1,2-ED	PrOH	1,3-PD	BuOH	1,4-BD
0.0	0.845^a	0.089^a	—	—	—	—	—
5.0	—	—	67.24	—	—	—	—
10.0	4.59^b	—	142.6	—	—	—	—
14.9	7.93^c	—	—	—	—	—	—
15.0	—	—	280.1	—	—	—	—
20.0	17.3^b	—	540.7	—	—	—	—
25.0	34.4^a	4.40^a	954.0^d	3.638^d	202.8^d	2.481^d	53.73^d
25.1	36.04^c	—	—	—	—	—	—
30.0	70.0^b	9.70^b	1 972	8.364	380.4	4.413	108.5
35.0	—	—	3 464	17.00	681.4	7.238	224.2
39.9	246.0^c	—	—	—	—	—	—
40.0	252^b	37.2^b	6 726	31.06	1 269	16.62	426.6
45.0	—	—	9 964	59.02	2 136	31.74	764.0
45.2	464.0^c	—	—	—	—	—	—
50.0	790^a	128^b 118.5^c	13 838	102.8	3 348	54.16	1 285
55.0	—	—	—	179.2	5 185	92.20	2 304
60.0	—	407^b	—	319.1	10 399	185.5	3 667

^{a} Ref. 5. ^{b} Ref. 6. ^{c} Ref. 7. ^{d} Ref. 14.

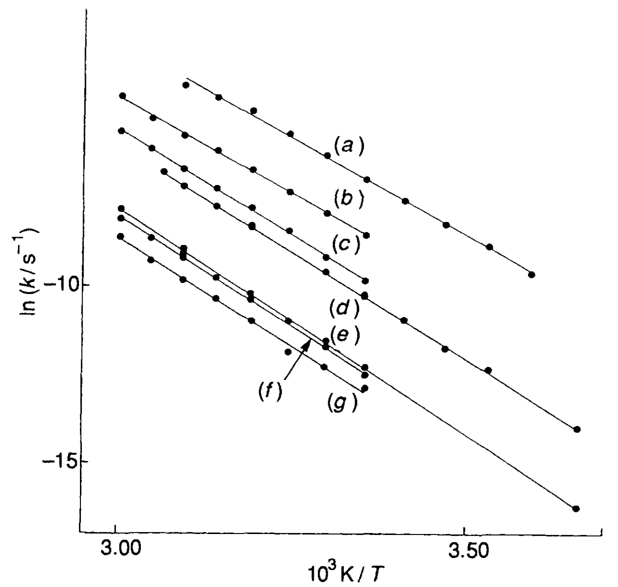

Fig. 1 Influence of temperature on the rate constants of Bu^{t}Br solvolysis in (*a*) ethane-1,2-diol; (*b*) propane-1,3-diol; (*c*) butane-1,4-diol; (*d*) methanol; (*e*) ethanol; (*f*) propan-1-ol; (*g*) butan-1-ol

pre-exponential factor and a_1 is related to the Arrhenius activation energy, E_a, through the expression $a_1 = -E_a/R$ (R = gas constant).

In Table 2 are recorded the sets of a_0 and a_1 parameters for the systems studied, obtained by applying a linear regression analysis and the least-squares method to the pairs of points (ln k, T^{-1}). The temperature interval and the number of pairs of points, N, used in the regression, the standard deviation of the parameters, $\sigma(a_0)$ and $\sigma(a_1)$, the covariance between a_0 and a_1, $\sigma^2(a_0,a_1)$, and the correlation coefficient, r, and the standard deviation, σ, of the fit are also shown in Table 2.

The Arrhenius activation energy, E_a, and its standard deviation, $\sigma(E_a)$, for all of the solvolytic reactions are listed in Table 3. This table shows how E_a changes with the solvent and the temperature interval.

When comparing different samples of data by means of statistical methods, the significance increases if the number of pairs of points, their regularity and temperature interval are similar. This is why we present two different sets of estimated parameters (Table 2) and E_a values (Table 3) for the solvents methanol, ethanol and ethane-1,2-diol. However, as regards to the values shown in both tables, we conclude that this is irrelevant for our particular reacting systems.

The first fact to note is that, with Bu^{t}Br, a change in the composition of the solvent from a particular monoalcohol to the corresponding dialcohol causes the first-order rate constants to increase dramatically: from a factor of 20 for butanols to a factor of 200 for ethanols. In contrast, only a small decrease is observed in the Arrhenius energy of activation: the mean E_a value for monoalcohols is 103.1 ± 1.8 while for dialcohols it is 93.9 ± 3.8 kJ mol^{-1}, the mean deviations being of the same order of magnitude of $\sigma(E_a)$.

If one assumes that the rate-determining path of the solvolytic reaction is as shown in eqn. (2) and in accordance with

$$\mathrm{Bu^tBr} \longrightarrow \mathrm{Bu^{t+}Br^-} \qquad (2)$$

Abraham[15,16] who reported, on the apportionment of Gibbs energy of activation of the solvolysis of *tert*-butyl chloride into initial and transition-state contributions, which suggest that in alcohols solvent effects predominate in the transition state, we may conclude that the activated complex is much more strongly stabilized by the dialcohols than by monoalcohols. With regard to the solvents properties, this preferential stabilization can be accounted for by two main reasons: (*i*) non-specific, long-range intermolecular forces, solvent-activated complex interactions, mainly dipolar in nature and (*ii*) specific, short-range intermolecular forces, also solvent-activated complex interactions, arising from the presence of the two OH groups which are able to participate in hydrogen bonds. Furthermore, the charge separation of the substrate is only small (μ = 2.21 D*), the activated complex is ion-pair like in nature, as will be discussed later. The increase in charge separation during the activation process depends on the solvent, as has been shown before for Bu^{t}Cl and Bu^{t}Br solvolysis in several polar and non-polar solvents.[15,16] Thus, the dipole moment of the Bu^{t}Br transition state in dialcohols should be higher than that of the transition state in monoalcohols, which is consistent with the solvent–solute interactions described before.

---

* 1 D = *ca.* 3.335 × 10^{-3} C m.

Table 2 Parameters of the Arrhenius plot for the solvolysis of Bu^{t}Br ($\ln k = a_0 + a_1 T^{-1}$)

Solvent	T/°C	N	a_0	$\sigma(a_0)$	a_1	$\sigma(a_1)$	$\sigma^2(a_0,a_1)$	r	σ
MeOH	0–55	12	30.23	0.24	−12 071	72	−17.0	0.999	0.050
	25–55	8	30.26	0.48	−12 080	142	−68.4	1.000	0.024
EtOH	0–60	7	30.52	0.26	−12 768	79	−20.5	1.000	0.051
	25–60	6	30.57	0.33	−12 781	100	−32.9	0.999	0.055
1,2-ED	5–50	10	29.68	0.66	−10 911	198	−131	0.997	0.100
	25–50	6	30.66	0.54	−11 198	157	−84.6	0.988	0.128
PrOH	25–60	8	29.39	0.61	−12 465	193	−118	0.999	0.064
1,3-PD	25–60	8	27.93	0.44	−10 855	208	−137	0.998	0.068
BuOH	25–60	8	28.25	0.81	−12 301	284	−256	0.997	0.092
1,4-BD	25–60	8	30.45	0.37	−11 990	192	−117	0.999	0.062

Table 3 Arrhenius activation energy for the solvolysis of Bu^{t}Br

Solvent	T/°C	E_a /kJ mol^{-1}	$\sigma(E_a)$ /kJ mol^{-1}
MeOH	0–55	100.4	0.6
	25–55	100.4	1.2
EtOH	0–60	106.1	0.7
	25–60	106.3	0.8
1,2-ED	5–50	90.7	1.6
	25–55	93.1	1.3
PrOH	25–60	103.6	1.6
1,3-PD	25–60	90.2	1.7
BuOH	25–60	102.2	2.4
1,4-BD	25–60	99.7	1.6

The Transition-state Approach.—If we assume that the Transition-state theory can be applied to our systems we may then calculate the enthalpies and the entropies of activation.

As expected, the enthalpy of activation values, $\Delta^{\ddagger}H^{\ominus}$, are almost constant within the set of monoalcohols ($\Delta^{\ddagger}H^{\ominus}_{298.15}$ = 101 ± 2 kJ mol^{-1}) and dialcohols ($\Delta^{\ddagger}H^{\ominus}_{298.15}$ = 91 ± 4 kJ mol^{-1}), and similar to the E_a values. Moreover, they do not change significantly with changes in temperature; changes of less than 1 kJ mol^{-1} for the temperature intervals studied were observed. The difference between both sets of solvents exceeds the standard deviations of the mean, which is of statistical and physico-chemical significance. Thus, we may say that, owing to the solvent–solute interactions particularly in the transition state, the breakage of the C–Br substrate bond seems to be facilitated when dialcohols are used as solvents. Conversely, the enthalpy of activation does not seem to play an important role in the observed differences in k (or $\Delta^{\ddagger}G^{\ominus}$) within each set of solvents.

Values for the entropy of activation, $\Delta^{\ddagger}S^{\ominus}$, for all of the alcohols are generally small and negative (from 0 to −20 J K^{-1} mol^{-1}) and show little temperature dependence. At 298.15 K, the mean $\Delta^{\ddagger}S^{\ominus}$ values for mono- and di-alcohols are of the same order of magnitude: −7 ± 6 J K^{-1} mol^{-1} for monoalcohols and −9 ± 6 J K^{-1} mol^{-1} for dialcohols. Although there is a discernible tendency for $\Delta^{\ddagger}S^{\ominus}$ to decrease when the length of the carbon chain of the alcohols (especially for monoalcohols) is increased, we feel that further conclusions based on these values would be unreliable on account of their standard deviations (from 4 to 7 J K^{-1} mol^{-1}).

The Reaction-energy Profile.—We now discuss the relative constancy of the activation energy for *tert*-butyl bromide solvolysis in mono- and di-alcohols. To address this problem it is important to determine the position of the transition state along the reaction co-ordinate as a function of the solvent and to assess the contribution of the Gibbs reaction energy, $\Delta_rG^{\ominus}$, as a driving force for the reaction.

A convenient model to determine the reaction-energy profile for the rate-determining step in terms of the sum of the bond extensions (d) of the initial and product states at the transition state, is the Intersecting-state model (ISM) developed by Formosinho and Varandas.[9,10] Considering the ionization in eqn. (2), and according to ISM, the intersecting potential-energy curves for our solvolytic reactions can be represented as shown in Fig. 2. The potential-energy curve for the reagent may be taken as that of the harmonic oscillator for the reactive bond C–Br. If we now assume $x = r^{\ddagger} - l_{\text{C-Br}}$ and $y = r' - r^{\ddagger}$, the bond distensions of the reagent and of the product (the ion pair C^+Br^-), respectively, where $l_{\text{C-Br}}$ is the bond length of C-Br and r' is the sum of the ionic radius of the carbon and of the halogen atom,* the ISM will give the reduced bond extension $\eta = d/(l_{\text{C-Br}} + r')$. The sum of the bond distensions from reagent and product to the transition state, $d = x + y$, is also the separation of the minima of the potential-energy curves as stated before.

For dissociative processes, such as those described in this paper, we may consider $\lambda \gg |\Delta_rG^{\ominus}|$ (λ is the 'entropy of mixing' or 'configuration entropy', defined by Agmon and Levine,[19] which has energy dimensions) and, thus, $\eta = 0.108/n^{\ddagger}$, where $n^{\ddagger}$ is the bond order of the transition state.

At the crossing point of the potential-energy curves there is a resonance effect (2ε) which splits the curves and decreases the reaction energy barrier. As Evans and Warhurst[20,21] have shown such an effect can be very significant when there are 'mobile electrons'. Within the ISM formalism, the transition state can be characterized by a chemical bond order $n^{\ddagger}$. When the resonance effect is negligible, $n^{\ddagger}$ is identical with the order of the bond about to be broken, *i.e.*, $n^{\ddagger} = 1$; however, $n^{\ddagger}$ increases with increased resonance energy.

Although there is insufficient realistic data to construct the repulsion curve for C^+Br^-, we may use the C–Br curve as a reasonable approximation. If so eqn. (3) is valid where the

---

* r_{C^+} = 0.29 Å[17] and r_{Br^-} = 1.96 Å.[18]

Table 4 Parameters for the reaction $Bu^tBr \longrightarrow Bu^{t+}Br^-$, at 25 °C

			eqn. (3)		eqn. (5)	
Solvent	$\Delta^‡G$/kJ mol^{-1} [a]	$\Delta_rG°$/kJ mol^{-1} [a]	η	ε/kJ mol^{-1}	η	ε/kJ mol^{-1}
Water	73.6	47.7	0.1064	1.3	0.0874	14.5
Methanol	98.2	84.4	0.1061	1.4	0.0875	16.7
Ethanol	103.2	96.1	0.0999	4.9	0.0842	19.7
Acetonitrile	106.2	97.4	0.1033	2.9	0.0867	17.8
Dimethylformamide	104.9	94.9	0.1044	2.3	0.0871	17.4

[a] Ref. 22.

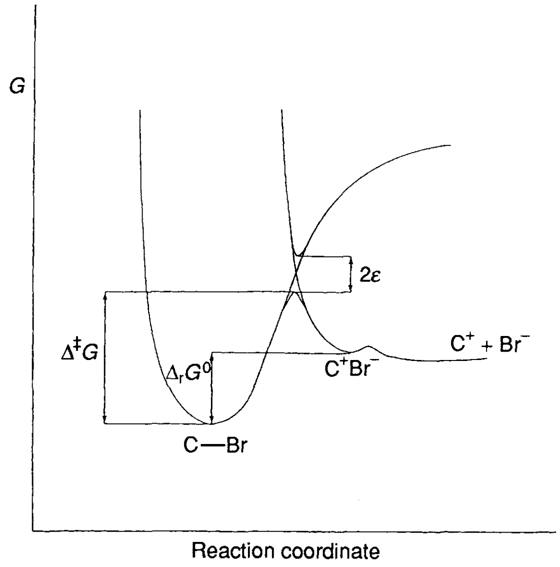

Fig. 2 Intersecting potential energy curve diagram for the reaction $Bu^tBr \longrightarrow Bu^{t+}\,Br^-$

$$\tfrac{1}{2}f_{C\text{–}Br}\,x^2 = \tfrac{1}{2}f_{C\text{–}Br}\,(d-x)^2 + \Delta_rG° \qquad (3)$$

harmonic force constants of the reagent and of the product are both represented by $f_{C\text{–}Br}$.

Table 4 shows the Gibbs energy of reaction and of activation for the solvolysis of *tert*-butyl bromide in several polar solvents at 25 °C, as well as the resonance splitting ε (see Fig. 2), which was estimated by comparison of the energy for $n^‡ = 1$ and the experimental $\Delta^‡G°$ value. The η values were calculated from eqn. (3).

From these results we may conclude that the reaction is essentially adiabatic in nature with resonance factors $\leqslant 5$ kJ mol^{-1} which is much less than $\Delta^‡G°$. Thus, the solvent effect arises mainly from the change in $\Delta_rG°$ and from the corresponding change in $\Delta^‡G°$. For the solvents reported in Table 4, the change in $\Delta_rG°$ can account for variations in k of about eight orders of magnitude where the variation which can be attributed to the resonance effect at the transition state (ε) accounts at most for variations in the rate constants by a factor of five. Similar conclusions can be drawn if one employs an exponential repulsion curve. In this case, the intersection of the potential-energy curves leads to eqns. (4) and (5) where b and

$$\Delta^‡G° = b\exp(-r'/p) - \exp(-r/p) + \Delta_rG° \qquad (4)$$

$$\Delta^‡G° = \tfrac{1}{2}f_{C\text{–}Br}\,x^2 \qquad (5)$$

p are constants. For the reactions under study, Ogg and Polanyi[17] used the following values: $b = 7.96 \times 10^4$ kJ mol^{-1} and $p = 0.345$ Å. The values of η and ε, estimated by means of eqn. (4), are also presented in Table 4. Although the calculated energy of resonance is considerably higher than that for the harmonic curve of the products, the solvent effects on $\Delta^‡G°$ are essentially a consequence of the changes in $\Delta_rG°$, as previously found.

Within the ISM formalism we have shown that the Hammond postulate and the Brønsted relation are valid under such conditions.[23] In consequence, because one is dealing with endothermic processes, the closer charge separation of the transition state is to the one of the products, the higher is $\Delta_rG°$; furthermore, $\Delta^‡G° = \alpha\,\Delta_rG°$ where α is the Brønsted coefficient.

The comparison between the solvolytic behaviour in mono- and di-alcohols on these grounds, cannot be performed because $\Delta_rG°$ is not available for polyalcohols, but one would expect that it controls the variations in the rate constants.

We are now able to interpret the constancy of E_a in different solvent media. By expressing the Gibbs energy of activation in terms of entropy and enthalpy of activation, eqn. (6), and

$$\Delta^‡G° = \Delta^‡H° - T\Delta^‡S° \qquad (6)$$

recognizing that the relation of Brønsted is valid for reaction (2), eqn. (7), and that $E_a \simeq \Delta^‡H°$, we obtain eqn. (8).

$$\alpha\,\Delta_rG° = \Delta^‡H° - T\Delta^‡S° \qquad (7)$$

$$\alpha\,\Delta_rG° = E_a - T\Delta^‡S° \qquad (8)$$

If one considers the variation of the thermodynamic function when there is a change in solvent medium, at constant temperature eqn. (9) holds. This expression can be rewritten as eqn. (10).

$$\alpha\,\delta\Delta_rG° = \delta E_a - T\delta\Delta^‡S° \qquad (9)$$

$$\delta E_a = \alpha\,\delta\Delta_rH° - \alpha\,T\delta\Delta_rS° + T\delta\Delta^‡S° \qquad (10)$$

Since $\delta E_a \simeq 0$ and appears to be independent of the temperature within the temperature range studied, eqn. (10) is valid for our reactions with $\delta\Delta_rH° = 0$. Eqn. (11) thus

$$\delta\Delta^‡S° = \alpha\,\delta\Delta_rS° \qquad (11)$$

represents a linear entropy relationship.

It must be pointed out that Abraham[22] has reported a small change (2.5%) in $\Delta_rH°$ for the dissociation of Bu^tBr from methanol to ethanol ($\delta\Delta_rH° = -0.5$ kcal mol^{-1}). For Bu^tCl the change is even smaller (1.9%; $\delta\Delta_rH° = -0.3$ kcal mol^{-1}), but it is more significant (14%) for water, $\delta\Delta_rH°$ (methanol/water) $= -3$ kcal mol^{-1}.

In conclusion, the constancy of E_a for the solvolysis of Bu^tBr in monoalcohols appears to imply that the changes in the Gibbs reaction energy as a function of the solvent are virtually all accounted for by the changes in entropy. Furthermore, a linear entropy relationship, eqn. (11), is verified for the activation entropy.

Conclusions

In order to gain a better understanding of the solvolytic reactions of *tert*-butyl bromide, we investigated the rate constants as a function of the temperature and the solvent.

From the analysis of the data in terms of the Arrhenius behaviour and using the transition-state theory, we conclude that the activated complex is more stabilized in dialcohols than in monoalcohols, and that this can be attributed mainly to enthalpic factors. This is probably due to dipolar, intermolecular solvent–substrate interactions *e.g.* hydrogen bonds occurring predominantly in the transition state. Conversely, changes in the solvation of the activated complex in entropic terms, seems to dominate the activation process when the number of carbon atoms of the solvent molecule is changed.

Within a set of monoalcohols, the analysis of solvent effects according to the ISM formulation reveals that $\Delta^{\ddagger}G^{\ominus}$ changes are essentially a consequence of the changes in $\Delta_r G^{\ominus}$, which are virtually all accounted for by changes in entropy.

Acknowledgements

We are grateful to the *Instituto Nacional de Investigação Científica* for financial support.

References

1 M. J. Blandamer, J. Burgess and J. B. F. N. Engberts, *Chem. Soc. Rev.*, 1985, **14**, 237.
2 W. Bentley and G. E. Carter, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 1633.
3 R. M. C. Gonçalves, A. M. N. Simões and C. A. N. Viana, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1923.
4 M. J. Blandamer, J. M. W. Scott and R. E. Robertson, *Prog. Phys. Org. Chem.*, 1985, **15**, 149.
5 A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 1957, **79**, 1602.
6 O. I. Virtanen, *Suom. Kemistil. B*, 1967, **40**, 178.
7 J. Biordi and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1962, 4291.
8 R. M. C. Gonçalves and C. A. N. Viana, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 753.
9 A. J. C. Varandas and S. J. Formosinho, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 953.
10 S. J. Formosinho and A. J. C. Varandas, *Educ. Chem.*, 1989, **26**, 118.
11 C. A. N. Viana, L. M. P. C. Albuquerque and M. I. M. A. Montenegro, *Rev. Port. Quím.*, 1971, **76**, 753.
12 E. S. Swinbourne, *Analysis of Kinetic Data*, Thomas Nelson, Melbourne, 1971, p. 81.
13 R. M. C. Gonçalves, F. E. L. Martins and A. M. N. Simões, *Rev. Port. Quím.*, in press.
14 R. M. C. Gonçalves, A. M. N. Simões and L. M. P. C. Albuquerque, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1379.
15 M. H. Abraham, *Prog. Phys. Org. Chem.*, 1974, **11**, 1.
16 M. H. Abraham, *Pure Appl. Chem.*, 1985, **57**, 1055.
17 R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.
18 *Handbook of Chemistry and Physics*, ed. R. C. Weast, 59th edn., CRC, Boca Raton, 1978/79.
19 N. Agmon and R. D. Levine, *Chem. Phys. Lett.*, 1977, **52**, 197.
20 M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, 1938, **34**, 614.
21 M. G. Evans, *Trans. Faraday Soc.*, 1939, **35**, 824.
22 M. H. Abraham, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1893.
23 S. J. Formosinho, *J. Chem. Soc., Perkin Trans. 2*, 1988, 839.

Paper 0/02241A
Received 21*st May* 1990
Accepted 29*th January* 1991