Linear Solvation-energy Relationships: Solvolytic Reactions of t-Butyl Bromide and t-Butyl Iodide in Hydroxylic Solvents

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Solvent effects on the solvolytic reactions of Bu^tBr and Bu^tI in water, and 12 monoalcohols and 10 dialcohols, from 1 to 5 carbon atoms, have been analysed in terms of linear solvation energy relationships. The experimentally determined rate constants, at 25 °C, are well correlated through equations of the form

$$\log k = a_0 + a_1 g(\eta) + a_2 E_T^N + a_3 C$$

where $g(\eta)$ is a function of the refractive index, E_T^N is the normalized Dimroth and Reichardt parameter and C is the solvent cohesive pressure. The correlation analysis revealed significant information on the solvent–solvent–solute interactions. It is also shown that results are in good agreement with previous analysis using different approaches and other sets of solvents.

Although kinetic and mechanistic aspects of the solvolytic reactions of 2-halogeno-2-methylpropane (t-butyl halides) were among the first to be studied[1,2] and form one of the cornerstones of physical organic chemistry, there is a continuing search for new data and better models[3–7] since these reactions are frequently used as testing grounds for new interpretations and new mechanistic criteria.

As a basic principle, solvent effects on chemical reactivity are similar in nature, there being only a few mechanisms of interaction between solvent and solute. Thus, we may appeal to a general way of treating the kinetic data of a given reaction in order to express the solvent–solvent–solute interactions quantitatively. A general and consistent treatment of solvent effects is given by the linear solvation-energy relationships, provided some classical considerations are taken into account.[8–10]

In spite of the observation that single empirical parameters can be used as good approximations of solvent polarity, multiple solvent effects on kinetic processes are only revealed by using linear combinations of solvent parameters, chosen according to a physico-chemical model of a particular process. Although the separation of solvent polarity into various solvent–solvent–solute interaction mechanisms is purely formal and taken for granted, the multiparameter approach to solvent effects has been shown to work quite well.

In essence, there are three types of interactions: (*i*) non-specific, long-range intermolecular forces, solvent–solute interactions, (*ii*) specific, short-range intermolecular forces, solvent–solute interactions and (*iii*) solvent–solvent interactions from the cavity effect. The most important non-specific interactions are considered to be determined by macroscopic physical parameters of the solvent, *i.e.* the relative permittivity, and the refractive index, which are connected with the molecular structure of the solute. The specific solvation is mainly determined by the acidity and basicity of the solvent, in terms of the Lewis concept, which are measures of the solvent hydrogen-bond ability to donate (HBD) and to accept (HBA) a proton, respectively. Disruption and reorganization of solvent–solvent interactions are measured by the work necessary to separate solvent molecules to create a suitable cavity, large enough to accommodate the solute.

Starting with the Grunwald and Winstein relationship,[11] several attempts have been made to correlate rate constants (or Gibbs energies of activation) for the heterolytic decomposition of 2-chloro- and 2-bromo-2-methylpropane with various solvent property scales.[11–14] Although for a restricted range of solvents, there is often a reasonable linear correlation between rate constants k and a single solvent parameter, it is now clear that k values for a wide range of different media would only be satisfactorily correlated if multiple linear correlation analysis is used. In this field, two main approaches should be mentioned: (*i*) the approach suggested by Koppel and Palm[15] [equation (1)], which relates the variation of $\log k$ to non-specific (Y-solvent polarization and P-solvent polarizability) and specific (E-electrophilic and B-nucleophilic solvating power) properties of the solvent, and (*ii*) the treatment proposed by Kamlet *et al.*[16,17] [equation (2)], where π^* is a dipolarity–polarizability parameter, δ is a discontinuous polarizability correction term and α and β are, respectively, measures of hydrogen-bond donor acidity and basicity. Later on this equation was extended by the introduction of a further parameter[18] [equation (3)]. The parameter C, equal to the square of the Hildebrand solubility parameter, δ_H, is the cohesive pressure defined by[19] equation (4). Δ_vU and Δ_vH are, respectively, the energy and the enthalpy of vaporization of the solvent to a gas of zero pressure and V is the molar volume of the solvent.

$$\log k = \log k_0 + yY + pP + eE + bB \quad (1)$$

$$\log k = \log k_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (2)$$

$$\log k = \log k_0 + s(\pi^* + d\delta) + a\alpha + b\beta + cC \quad (3)$$

$$C = \delta_H^2 = \Delta_vU/V = (\Delta_vH - RT)/V \quad (4)$$

Abraham *et al.*[18] applied equation (3) to correlate the rate constants for the solvolytic reactions of three t-butyl halides in 21 solvents (11 hydrogen-bond donor solvents—water, 8 monoalcohols, 1 dialcohol, and formamide—and 10 non-hydrogen-bond solvents). However, most of the data for Bu^tBr and Bu^tI used in that analysis was not of experimental origin. In the present paper, we extend the linear solvation-energy relation-

Table 1. Solvolysis rate constants of Bu^{t}Br and Bu^{t}I, at 25 °C.

		$-\log(k/\text{s}^{-1})$			
n	Solvent	Bu^{t}Br	Ref.	Bu^{t}I	Ref.
1	Water	0.12	23	0.19	23
2	Methanol	4.46	24	3.91[a]	
3	Ethanol	5.36	12	4.65	
4	Propan-1-ol	5.44		4.86	
5	Propan-2-ol	5.67		5.05	
6	Butan-1-ol	5.61		4.95	
7	Butan-2-ol	5.78		5.40	
8	2-Methylpropan-1-ol	5.68		5.19	
9	Pentan-1-ol	5.64		5.29	
10	Pentan-2-ol	5.98		5.57	
11	2-Methylbutan-1-ol	5.74		5.29	
12	3-Methylbutan-1-ol	5.65		5.37	
13	Pentan-3-ol	5.99		5.72	
14	Ethane-1,2-diol	3.03		2.55	
15	Propane-1,2-diol	4.03		3.56	
16	Propane-1,3-diol	3.71		2.95	
17	Butane-1,2-diol	4.57		4.16	
18	Butane-1,3-diol	4.50		4.05	
19	Butane-1,4-diol	4.27		3.81	
20	Butane-2,3-diol	4.88		4.48	
21	Pentane-1,5-diol	4.68		4.19	
22	Diethylene glycol	3.84		3.16	
23	Triethylene glycol	4.14		3.30	

[a] In order to test our experimental method, the reaction of Bu^{t}I in methanol was studied. Our rate constant agrees very well with the published value, $\log k = -3.90$.[24]

ship analysis of the heterolysis of Bu^{t}Br and Bu^{t}I in hydroxylic media, by using 12 straight- and branched-chain monoalcohols and 10 dialcohols, from 1 to 5 carbon atoms, as solvents. To perform this study a great number of rate constants were experimentally determined, at 25 °C. The results are interpreted according to the fundamental solvent–solvent–solute interactions and compared with those from previous analysis concerning this kind of reaction.

Experimental

Conductimetry was applied to obtain the solvolytic rate constants of t-butyl bromide and iodide in the various alcohols. Conductance measurements were recorded in a Wayne–Kerr B905 conductimetric bridge and used a modified version of Shedlovsky cells.[20] Since the partitioning of Bu^{t}X between liquid and vapour phases can lead to kinetic complexities,[21] the cell space above the solutions was kept as small as possible. In order to avoid photochemical decomposition of alkyl halides, which is particularly relevant for Bu^{t}I, t-butyl halides were kept in dark flasks at temperatures below 5 °C; conductivity cells were covered with aluminium foil during the kinetic runs. At least five experiments were performed for each system. The temperature control of the thermostatic bath was ∓0.01 K. The Kezdy–Swinbourne method[22] was applied to obtain the rate constants of the solvolytic reactions of Bu^{t}Br and Bu^{t}I, at 25 °C [equation (5)]. The conductance of the reacting solution

$$G_t = G_\infty(1 - e^{k\Delta t}) + G_{t+\Delta t}e^{k\Delta t} \qquad (5)$$

at time t, $t + \Delta t$ and infinity were represented by G_t, $G_{t+\Delta t}$, and G_∞, respectively, and Δt is a constant period of time.

All the observed kinetics were first-order within the experimental error of 2% in k, and used no more than 80% of the increasing values of conductance.

Results and Discussion

The mean rate constant values for the solvolytic reactions of Bu^{t}Br and Bu^{t}I are summarized in Table 1, together with some previously reported experimental data for water, methanol, and ethanol.

In order to take into consideration the different solvent–solvent–solute interaction mechanisms and attending to the available values for, in principle, independent but complementary empirical parameters of solvent polarity, we decided to test the application of equation (6) to correlate the rate

$$\log k = a_0 + a_1 f(\varepsilon) + a_2 g(\eta) + a_3 E_T^N + a_4 C \qquad (6)$$

constants shown in Table 1. $f(\varepsilon)$ is a relative permittivity function taken as $(\varepsilon - 1)/(2\varepsilon + 1)$, the so-called Kirkwood function, and $g(\eta)$ is the refractive index function $(\eta^2 - 1)/(\eta^2 + 2)$. E_T^N is the normalized Dimroth and Reichardt parameter (1 for water; 0 for tetramethylsilane),[25,26] and C is the cohesive pressure, as stated before.

The E_T^N values are dimensionless and E_T^N was, therefore, used instead of $E_T(30)$, which by definition has the dimensions of kcal mol^{-1}. The $E_T(30)$ scale, and consequently the E_T^N scale, is one of the most sensitive characterizations of the polarity of the solvents because of the exceptionally large displacement of the solvatochromic absorption band of the pyridinium *N*-phenoxide betaine dye (44). The use of E_T^N in equation (6) is in agreement with the assumption that this parameter provides a measure of the solvent HBD acidity of protic solvents;[27] furthermore, the multiparameter treatment which combines $E_T(30)$ with functions of the relative permittivity* and the index of refraction was tested by Katritzky *et al.*[28] with excellent results. On the other hand, the use of the cohesive pressure seems to be quite relevant in our case, since this parameter exhibits large values for highly structured solvents such as water, methanol, and the lower carbon-chain dialcohols.

The physico-chemical model envisaged here to connect the macroscopic solvent parameters and the microscopic details of the reaction process is very similar to that proposed by Abraham *et al.*,[10] based on the cavity theories of solution: not only the fundamental solvent–solute interaction mechanisms, which are related to the creation of a cavity of suitable size, but also the forces holding the solvent molecules are represented in the chosen multiparametric equation. The solvent hydrogen-bond acceptor basicity was not considered in equation (6) since previous studies on the solvolytic reactions of t-butyl halides have shown the irrelevance of this term.[17,18,29] A compilation of the values of the empirical solvent parameters $f(\varepsilon)$, $g(\eta)$, E_T^N, and C for the set of studied solvents are shown in Table 2.

Interrelation of Solvent Parameters.—In order to test the non-collinearity assumption for the chosen parameters, a critical comparison between any two parameters was performed. From the results shown in Table 3, we conclude that highly significant linear correlations are not observed; however, concerning the plot $f(\varepsilon)$ *vs.* E_T^N (Figure), some influence of solvent dipolarity in E_T^N values should not be excluded, as stated by several authors for other sets of solvents.[16,27,39] The results of the correlation analysis for the two t-butyl halides, through the complete and truncated versions of equation (6), are given in Table 4.

The observation of this systematic linear-regression analysis leads us to the following preliminary conclusions.

(*i*) According to the equations A to D for both substrates, uniparametric relationships have no relevant statistical meaning, except where the use of the E_T^N variable is concerned (equation C). We may then assume that the intermolecular

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* Relative permittivity was previously referred to as dielectric constant.

Table 2. Solvent parameters used in this work.[a]

n	Solvent	$f(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon + 1}^{b}$	$g(\eta) = \frac{\eta^2 - 1}{\eta^2 + 2}^{c}$	E_T^N	$C/10^3$ MPa
1	Water	0.490 48	0.205 69	1.000	2.307
2	Methanol	0.477 38	0.203 11	0.762	0.887
3	Ethanol	0.470 06	0.221 47	0.654	0.703
4	Propan-1-ol	0.464 20	0.234 67	0.617	0.590^{h}
5	Propan-2-ol	0.463 27	0.230 11	0.546	0.552^{h}
6	Butan-1-ol	0.458 36	0.242 10	0.602	0.485
7	Butan-2-ol	0.456 04	0.240 87	0.506	0.488^{h}
8	2-Methylpropan-1-ol	0.459 31	0.240 23	0.552	0.516^{i}
9	Pentan-1-ol	0.447 92	0.247 76	0.568	0.497^{h}
10	Pentan-2-ol	0.447 22	0.245 84	0.488	0.465^{j}
11	2-Methylbutan-1-ol	$0.453\,50^{d}$	$0.247\,12^{d}$	0.534^{g}	0.482^{j}
12	3-Methylbutan-1-ol	0.452 20	0.246 27	0.565	0.497^{j}
13	Pentan-3-ol	0.445 85	0.247 98	0.463	0.472^{j}
14	Ethane-1,2-diol	0.480 37	0.259 27	0.790	0.887
15	Propane-1,2-diol	$0.474\,22^{e}$	$0.259\,58^{f}$	0.722	0.881^{j}
16	Propane-1,3-diol	$0.478\,86^{e}$	$0.263\,45^{f}$	0.747	0.847^{k}
17	Butane-1,2-diol	$0.467\,18^{e}$	$0.262\,40^{f}$	0.676	$(0.60)^{l}$
18	Butane-1,3-diol	$0.474\,20^{e}$	$0.264\,07^{f}$	0.682	0.562^{h}
19	Butane-1,4-diol	$0.476\,08^{e}$	$0.266\,67^{f}$	0.704	0.738^{k}
20	Butane-2,3-diol	$0.466\,14^{e}$	$0.258\,85^{f}$	0.651	0.602^{k}
21	Pentane-1,5-diol	$0.472\,89^{e}$	$0.268\,43^{f}$	0.654^{g}	0.603^{k}
22	Diethylene glycol	0.476 70	0.267 45	0.713	0.615^{h}
23	Triethylene glycol	0.469 00	0.271 73	0.704	0.480^{h}

[a] Values are from ref. (9), except when indicated. [b] Values at 25 °C, except for diethylene and triethylene glycol which are at 20 °C. [c] Values at 20 °C, except for butane-2,3-diol which is at 25 °C. [d] Value from ref. (30). [e] Value from ref. (31). [f] Value from ref. (32). [g] Value from $E_H(30)$ in ref. (33). [h] Value from ref. (34). [i] Value from ref. (35). [j] Value from $\Delta_v H$, at 25 °C, in ref. (36). [k] Value from $\Delta_v H$, at temperatures far below the boiling point, in ref. (37). [l] Estimated value from the structural comparison between butane-1,3-diol and butane-1,4-diol and propane-1,2-diol and propane-1,3-diol.

Table 3. Results of the single linear correlations of the solvent parameters shown in Table 2.

$$Y = a_0 + a_1 x \; (N = 23)^{a}$$

Y	x	a_0	a_1	r^{b}	σ^{c}
$f(\varepsilon)$	$g(\eta)$	0.469 81	−0.014 786	$—^{d}$	0.0123
$f(\varepsilon)$	E_T^N	0.406 01	0.092 835	0.85	0.0047
$f(\varepsilon)$	$10^{-3}C$	0.451 55	0.021 315	0.46	0.0090
$g(\eta)$	E_T^N	0.261 16	−0.020 906	$—^{d}$	0.0193
$g(\eta)$	$10^{-3}C$	0.263 35	−0.022 968	0.21	0.0173
E_T^N	$10^{-3}C$	0.470 04	0.259 53	0.69	0.0683

[a] Number of pairs of points. [b] Linear correlation coefficient. [c] Standard deviation of the fit. [d] r cannot be calculated on account of the close parallelism of the estimated straight line to the x axis.[38]

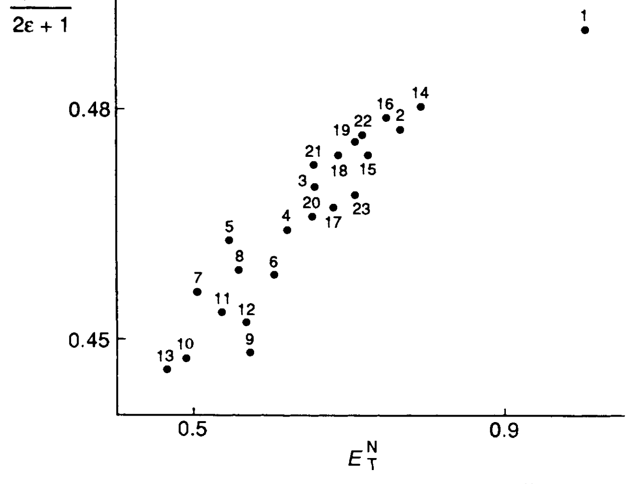

Figure. Correlation between the Kirkwood function and E_T^N.

interactions in our solvolytic systems are similar in nature to those in the reference system used to develop this particular solvent scale. This seems to confirm, therefore, that the blend of solvent–solute interactions as measured by $E_T(30)$ values represents a kind of 'mean solvent polarity,' as described by Reichardt[9] and Bentley *et al.*[40]

(*ii*) A comparison of the application of multiple solvent parameters shows that the best two- and three-parameter truncated versions of the general form, equations J and N, contain the cohesive pressure variable for both solvolytic systems. Thus, our reactions seem to be particularly sensitive to the solvent–solvent interactions which are related to the work of the creation of a cavity for the solute molecule. The importance of the C parameter has been tested by Abraham *et al.*[18] who found that the cavity term was statistically significant for t-butyl chloride and bromide solvolysis, even with a different set of solvents.

(*iii*) The apparent lack of statistical significance of the $f(\varepsilon)$ term coefficient, *i.e.* the dependence on solvent dipolarity, seems unusual and it is probably a consequence of the moderate collinearity among the variables E_T^N and $f(\varepsilon)$.

Application of Ehrenson's Criterion.—The final decision about the best fit, in strictly statistical terms, was achieved by reference to Ehrenson's criterion.[41] To perform this analysis, the f function [equation (7)], was calculated for the

$$f = \left[\frac{\sum_{i=1}^{n} (\log k_{\text{calc}} - \log k_{\text{obs}})^2}{\sum_{i=1}^{n} (\log k_{\text{obs}})^2} \right]^{\frac{1}{2}} \qquad (7)$$

complete and the best truncated versions of equation (6) (Table 5). Hence, to test the hypothesis that a parameter set provides as good a fit as another set obtained by the removal of one

Table 4. Correlations of Bu^{t}Cl and Bu^{t}Br solvolysis, at 25 °C.

$$\log k = a_0 + a_1 f(\varepsilon) + a_2 g(\eta) + a_3 E_T^N + a_4 \times 10^{-3} C \; (N = 23)^a$$

Reaction	a_0	a_1	a_2	a_3	a_4	r[b]	σ[c]
Bu^{t}Br							
A	−47.807	92.412	—	—	—	0.720	0.708
B	−3.1601	—	−6.3365	—	—	—[d]	1.333
C	−11.477	—	—	10.416	—	0.905	0.412
D	−6.8257	—	—	—	3.0604	0.798	0.602
E	−46.489	92.227	−4.9728	—	—	0.725	0.719
F	−2.3766	−22.414	—	12.497	—	0.912	0.408
G	−28.936	48.954	—	—	2.0184	0.907	0.418
H	−11.832	—	1.8187	10.294	—	0.902	0.430
I	−14.179	—	27.924	—	3.7018	0.927	0.369
J	−10.299	—	—	7.3884	1.1430	0.940	0.336
K	−1.7124	−26.607	3.9751	12.969	—	0.915	0.412
L	−26.515	31.588	20.604	—	2.8604	0.964	0.267
M	−10.017	−0.708 84	—	7.4709	1.1367	0.940	0.334
N	−13.886	—	17.644	5.1347	2.1331	0.979	0.206
O	−13.763	−0.331 56	17.686	5.1695	2.1325	0.979	0.211
Bu^{t}I							
A	−47.991	93.845	—	—	—	0.793	0.590
B	−3.4389	—	−3.2582	—	—	—[d]	1.294
C	−10.869	—	—	10.224	—	0.931	0.340
D	−6.1664	—	—	—	2.8039	0.715	0.692
E	−47.500	93.775	−1.8716	—	—	0.793	0.603
F	−15.597	12.553	—	8.6011	—	0.908	0.403
G	−34.102	61.865	—	—	1.4853	0.901	0.417
H	−12.245	—	5.2717	10.334	—	0.937	0.333
I	−13.756	—	28.818	—	3.4658	0.862	0.493
J	−10.372	—	—	8.9473	0.481 85	0.938	0.332
K	−9.6547	−6.6503	5.6902	10.960	—	0.938	0.340
L	−31.969	46.638	18.010	—	2.2235	0.947	0.312
M	−14.460	10.301	—	7.7485	0.573 41	0.939	0.337
N	−13.351	—	14.652	7.0758	1.3041	0.966	0.251
O	−17.598	10.598	14.670	5.8401	1.3993	0.967	0.253

[a] Number of pairs of points. [b] Simple or multiple linear correlation coefficient. [c] Standard deviation of the fit. [d] r cannot be calculated due to the close parallelism to the x axis of the estimated straight line.[38]

Table 5. The f values for equations C, J, N, and O shown in Table 4.

Substrate	Equation C	J	N	O
Bu^{t}Br	0.0803	0.0639	0.0382	0.0382
Bu^{t}I	0.0735	0.0699	0.0516	0.0514

parameter from the previous one, the ratio f_j/f_{j+1}, where j is the number of estimated parameters a, was compared with the distribution function for reference, $R_{1,n-(j+1),\alpha}$, where the confidence level was represented by α. The ratios for f_2/f_3 are 1.257 and 1.051, for f_3/f_4, 1.674 and 1.350 and for f_4/f_5, 1.000 and 1.005, for Bu^{t}Br and Bu^{t}I, respectively. Values over 1.05 mean that the hypothesis must be rejected at a confidence level $\geqslant 85\%$ (and over 1.30 at $\geqslant 99.9\%$), for $n = 23$; conversely, values less than 1.01 give $< 50\%$ and, consequently, the hypothesis must be accepted in these cases.

In conclusion, we consider that the three-parameter equations, equations N, are the statistically preferred correlations for both Bu^{t}Br and Bu^{t}I rate constants data [equations (8) and (9)].

$$\log k_{\mathrm{Bu^tBr}} = -13.886 + 17.644 g(\eta) + 5.1347 E_T^N + 2.1331 \times 10^{-3} C \qquad (8)$$

$$\log k_{\mathrm{Bu^tI}} = -13.351 + 14.652 g(\eta) + 7.0758 E_T^N + 1.3041 \times 10^{-3} C \qquad (9)$$

The Solvent–Solvent–Solute Interactions.—From the results of the linear solvation-energy relationships, we may describe the solvolytic reactions of t-butyl bromide and iodide as being dominated by the following solvent effects: (*i*) the non-specific solvent–solute interactions due to the polarizability of the solvent, represented by the $g(\eta)$ term; (*ii*) the non-specific dipolarity and the specific solvent hydrogen bond acidity interactions, both represented by the E_T^N term; (*iii*) the disruption and reorganization of solvent–solvent interactions in order to accommodate the solute, represented by the C term.

The comparison of the coefficients of both equations (equations N, Table 4) show that the dependence on solvent dipolarity–polarizability decreases from Bu^{t}Br to Bu^{t}I in accordance with the earlier findings of Abraham *et al.*[17] and at variance with the new order proposed by the same authors;[18] with respect to the C term, it is relevant for both substrates, although the dependence on the cavity term decreases from Bu^{t}Br to Bu^{t}I, as found earlier.[18] Further, the present work emphasizes the importance of solvent electrophilic assistance to the t-butyl halides in hydroxylic solvents, as stated before, using other sets of solvents and solvent parameters;[15,17,18] however, the assumption that E_T^N values are not only a measure of the solvent HBD acidity but also a blend of solvent dipolarity does not allow us to quantify separately both effects and to reach a conclusion about the comparative importance of electrophilic assistance to both solutes.

Finally, we discuss the physico-chemical interpretation of the independent parameter, a_0, in the general equation (6). The statistical quantity a_0 corresponds to the value of the solventdependent property log k, in the gas phase or in an inert solvent. Using the best relationships (equations N, Table 4), $a_0 = -13.89$ for Bu^{t}Br and $a_0 = -13.35$ for Bu^{t}I. These values are quite reasonable when compared with those experimentally obtained by Macoll[42] for the reactions in the gas phase, $\log k_g(\mathrm{Bu^tBr}) = -16.7$ and $\log k_g(\mathrm{Bu^tI}) = -14.3$, and by Abraham *et al.*,[18] using linear solvation-energy relationships, $\log k_0(\mathrm{Bu^tBr}) = -11.97$ and $\log k_0(\mathrm{Bu^tI}) = -9.80$.

Conclusions

In spite of the criticism of the method of linear solvation-energy relationships, on account of its empirical basis, this method is one of the most powerful procedures for predicting solvent effects on reaction rates, insofar as one understands how a particular process responds to a solvent change by choosing a suitable reference model.

With respect to the solvolytic reactions of t-butyl halides, significant improvements are, no doubt, achieved by the use of rigorous multiparameter approaches. The application of equation (6) to log k values for 23 hydroxylic solvents (water, mono- and di-alcohols) performed in this paper reveals important information on the solvent–solvent–solute interactions which dominate the reaction path.

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