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# Properties of the *tert*-butyl halide solvolysis transition states†

Michael H. Abraham, [iD] *[a] Filomena Martins, [iD] *[b] Ruben Elvas-Leitão [iD] [bc] and Luís Moreira[bd]

We have obtained properties (or descriptors) of the transition states in the solvolysis of *tert*-butyl chloride, bromide and iodide. We show that all three transition states, in both protic and in aprotic solvents, are highly dipolar and are strong hydrogen bond acids and strong hydrogen bond bases, except for the *tert*-butyl iodide transition state in aprotic solvents, which has a rather low hydrogen bond acidity. Thus, the transition states are stabilized by solvents that are hydrogen bond bases (nucleophiles) and are hydrogen bond acids (electrophiles). We show also that the partition of the transition states between water and solvents is aided by both nucleophilic and electrophilic solvents and conclude that the rate of solvolysis of the three halides is increased by both nucleophilic and electrophilic solvents.

## 1 Introduction

Although the mechanism of solvolysis of *tert*-butyl chloride has been studied for the past 85 years,[1] questions about the mechanism still remain unsettled, especially whether or not there is nucleophilic assistance by solvents. Gajewski[2] has referred to this solvolysis as "...the most misunderstood reaction in organic chemistry" and has put forward arguments based on his multiple parameter equation[3] that there is no positive nucleophilic solvent participation in the solvolysis. Dvorko *et al.*[4–7] used the multi-parameter Koppel-Palm equation to reach a similar conclusion for the solvolysis of *tert*-butyl chloride, as did Ponomarev *et al.*[8] for the solvolysis of *tert*-butyl bromide and *tert*-butyl iodide.[9] Indeed, these workers[4–8] suggest that there is a small negative effect of nucleophilic solvation in the solvolysis of the three halides in protic solvents. However, it should be mentioned that Serebryakov[10] regards the various correlation analyses[4–8] to be unsound. Application of the multiparameter Kamlet–Taft equation to rate constants for the *tert*-butyl chloride solvolysis also indicated[11–13] that there was no, or little, positive nucleophilic assistance, as also suggested by Farcasiu

*et al.*[14] This is contrary to a long-established position[15–18] that the rate of solvolysis of the *tert*-butyl halides is increased by nucleophilic solvent participation, or by "nucleophilic assistance/cation solvation".

The *tert*-butyl halide transition states are generally regarded to be somewhere in between the relatively non-polar *tert*-butyl halides and the polar *tert*-butyl halide ion pairs, with the leaving halide atom in the transition state C···X bond carrying a partial negative charge. Then electrophilic solvents (hydrogen bond acids) can solvate the leaving halide, leading to a reduction in the energy of the transition state and to an increase in the rate constant. There will also be a corresponding partial positive charge on the carbon atom of the C···X bond – as shown in Scheme 1 for hydroxylic solvents. Then nucleophilic solvents (hydrogen bond bases) would be expected to solvate this area of the transition state, leading again to an increase in the rate constant. But according to various workers,[2–9,11–14] there is no rate enhancement due to nucleophilic solvents, and hence there must be no nucleophilic solvation of the transition state. Dvorko *et al.*[6] rationalized the lack of nucleophilic assistance as being due to an intermediate ion pair that they described as R⁻[O]X⁻ but this does not seem to make the cause of the lack of nucleophilic assistance any clearer.

We have set out a multi-parameter equation,[19–22] that we have used to obtain information on the properties of a large number

[a] *Department of Chemistry, University College London, 20 Gordon St, London WC1H 0AJ, UK. E-mail: m.h.abraham@ucl.ac.uk*

[b] *Centro de Química Estrutural (CQE), Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Edifício C8, 1749-016, Lisboa, Portugal. E-mail: filomena.martins@ciencias.ulisboa.pt*

[c] *Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, R. Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal*

[d] *Instituto Superior de Educação e Ciências (ISEC Lisboa), Alameda das Linhas de Torres, 174, 1750-142 Lisboa, Portugal*

† *In memoriam* of Professor Michael H. Abraham, who passed away on January 19th, 2021, during the revision of this manuscript.

Scheme 1

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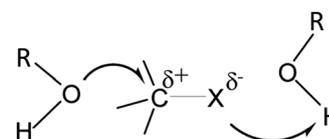
*Phys. Chem. Chem. Phys.*, 2021, **23**, 3311–3320 | **3311**

of neutral compounds from the effects of solvents on compound solubilities or on compound water–solvent partitions. More recently, we have extended the equations to ionic compounds such as permanent ions and ion-pairs.[23,24] Very relevant to the present study is the application to betaine[25] and to amino-acids.[26] In these cases, we found that the ionic form of the equation had to be used, in accordance with complete charge separation in these compounds. So application of our equations to the *tert*-butyl halide transition states may lead to information as to the extent of charge separation in the transition states, to the hydrogen-bond acidity (electrophilicity) and hydrogen-bond basicity (nucleophilicity) of the transition states, and hence to the role of solvent as a nucleophile (hydrogen bond base) and an electrophile (hydrogen bond acid).

## 2 Materials and Methods

### 2.1 Materials

For experiments carried out in this work, *tert*-butyl chloride and *tert*-butyl bromide were purchased from BDH (purity > 99%) and *tert*-butyl iodide was purchased from Aldrich (purity > 95%). *tert*-Butyl iodide was regularly purified by column chromatography (Silica gel 60). Solvents were obtained commercially and used without further purification from Aldrich, Merck and Koch-Light (>99% + purity) and their water content was always <2% v/v. Solvent mixtures were prepared by volume using pure solvents and freshly collected double deionized water, obtained with a Milli-Q system from Millipore (Bedford, MA, USA) with a resistivity of 18.2 MΩ.

### 2.2 Procedures

Kinetic curves were followed by conductimetry using an automated Wayne Kerr B905 conductance bridge. Temperature control was always better than ±0.01 K. Substrate concentration was 0.01 mol dm$^{-3}$ and, whenever deemed necessary, 0.02 mol dm$^{-3}$ of 2,6-lutidine (a weak base) was added to the solvent to capture the produced acid and prevent its further reactivity. In some cases, calibration curves were performed. Reactions were followed up to 90% of the apparent plateau. Mean $k$ values result from at least 3 different runs and showed a standard deviation better than 5%. All $k$ values were determined using a Microsoft Excel spreadsheet specifically designed by us for this purpose.[27,28]

### 2.3 Theory

Our method is based on eqn (1) and (2), set up for correlation of processes involving a given neutral solute in a variety of solvents.[19–22] The dependent variable is log $Ps$, where $Ps$ is a water–solvent partition coefficient

$$\text{Log } Ps = c + eE + sS + aA + bB + vV \tag{1}$$

$$\text{Log } Ps = c + eE + sS + aA + bB + lL \tag{2}$$

The independent variables, or descriptors, are properties of the neutral solutes as follows.[19–22] $E$ is the solute excess molar refraction in cm$^3$ mol$^{-1}$/10, $S$ is the solute dipolarity/polarizability,

$A$ is the overall solute hydrogen bond acidity, $B$ is the overall solute hydrogen bond basicity, $V$ is the McGowan's characteristic molecular volume in cm$^3$ mol$^{-1}$/100 and $L$ is the logarithm of the gas to hexadecane partition coefficient at 298 K.

In the extension of eqn (1)[23,24] to include permanent ions such as K$^+$ and Cl$^-$, ion pairs such as Me$_4$N$^+$Cl$^-$, deprotonated carboxylic acids, RCO$_2$$^-$, and protonated amines, the independent variables $E$, $S$, $A$, $B$ and $V$ were the same in eqn (1) and (3) so that only two extra variables were needed to incorporate the ionic solutes, $J^+$ for cationic solutes and $J^-$ for anionic solutes. Then eqn (1) becomes eqn (3), where $J^+ = 0$ for anions, $J^- = 0$ for cations and $J^+ = J^- = 0$ for neutral molecules.

$$\text{Log } Ps = c + eE + sS + aA + bB + vV + j^+J^+ + j^-J^- \tag{3}$$

The coefficients in eqn (1) and (3) for various solvents are given in Table 1.[19–24]

## 3 Results and discussion

Partition coefficients of the *tert*-butyl halide transition states, Tr, from water to solvents, as log $Ps$, were obtained from eqn (4), as described before[29,30]

$$\text{Log } Ps \text{ (Tr)} = \log Ps \text{ (}tert\text{-BuX)} + \log k(\text{S}) - \log k(\text{W}) \tag{4}$$

Here, $Ps$ (Tr) is the water (W) to solvent (S) partition coefficient of a *tert*-butyl halide transition state, log $Ps$ (*tert*-BuX) is the water to solvent partition coefficient of the corresponding halide, and $k(\text{S})$ and $k(\text{W})$ are the *tert*-butyl halide rate constants in the solvent S and in water.

Thermodynamic data on the initial states were available,[29–31] and these in turn were used to derive the descriptors for the *tert*-butyl halides in eqn (1) and in eqn (2), as set out in detail elsewhere.[21,22,30] The obtained values are in Table 2. In Table 3, $K_w$ is the gas to water partition coefficient. There is nothing exceptional about the descriptors for the *tert*-butyl halides. In particular, they have zero electrophilicity (hydrogen-bond acidity, $A$) and very little nucleophilicity (hydrogen-bond basicity, $B$).

### 3.1 *tert*-Butyl chloride

Several years ago we studied the structure of the *tert*-butyl chloride transition state using reaction field theory[36] Our results indicated that the transition state had decidedly different structures in protic and in aprotic solvents, and so it seems appropriate to apply our equations separately to data in protic and aprotic solvents. Rate constants at 298 K were obtained from various sources[4,5,12,29–37] and also in this work, and are given in Table 2 as log $k$ in s$^{-1}$. The corresponding values of the water to solvent partition coefficients as log $Ps$(Tr) were simply obtained through eqn (4).

Unfortunately, we only have 20 values of log $Ps$(Tr) in aprotic solvents to use in eqn (3), rather too small a number to analyse using six independent variables in an LFER (the term in eE was not significant). However, we give details of eqn (1) and (3)

**3312** | *Phys. Chem. Chem. Phys.*, 2021, **23**, 3311–3320

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**Table 1** Coefficients in eqn (1) and (3) for water–solvent partition coefficients, as log $P_s$

| Solvent | $c$ | $e$ | $s$ | $a$ | $b$ | $v$ | $j^+$ | $j^-$ |
|---|---|---|---|---|---|---|---|---|
| Perfluorooctane | 0.492 | −0.051 | −2.588 | −3.424 | −3.974 | 3.377 | | |
| Pentane | 0.369 | 0.386 | −1.568 | −3.535 | −5.215 | 4.514 | | |
| Heptane | 0.297 | 0.634 | −1.755 | −3.571 | −4.946 | 4.488 | | |
| Cyclohexane | 0.159 | 0.784 | −1.678 | −3.740 | −4.929 | 4.577 | | |
| Benzene | 0.142 | 0.464 | −0.588 | −3.099 | −4.625 | 4.491 | | |
| Dichloromethane | 0.319 | 0.102 | −0.187 | −3.058 | −4.090 | 4.324 | −3.984 | 0.086 |
| Trichloromethane | 0.191 | 0.105 | −0.403 | −3.112 | −3.514 | 4.395 | −3.155 | −3.705 |
| 1,2-Dichloroethane | 0.183 | 0.294 | −0.134 | −2.801 | −4.291 | 4.180 | 4.180 | −3.429 |
| tert-Butyl chloride (n-BuCl) | 0.222 | 0.273 | −0.569 | −2.918 | −4.883 | 4.456 | | |
| Diethyl ether | 0.350 | 0.358 | −0.820 | −0.588 | −4.956 | 4.350 | 0.434 | −10.124 |
| Dioxane | 0.123 | 0.347 | −0.033 | −0.582 | −4.810 | 4.110 | −5.883 | 4.649 |
| Tetrahydrofuran | 0.223 | 0.363 | −0.384 | −0.238 | −4.932 | 4.450 | −2.278 | −2.132 |
| Ethyl acetate | 0.328 | 0.369 | −0.446 | −0.700 | −4.904 | 4.150 | 4.243 | −2.232 |
| Propanone | 0.313 | 0.312 | −0.121 | −0.608 | −4.753 | 3.942 | −2.288 | 0.078 |
| Cyclohexanone | 0.077 | 0.249 | 0.028 | −0.891 | −4.917 | 4.283 | | |
| Acetonitrile | 0.413 | 0.077 | 0.326 | −1.566 | −4.391 | 3.364 | −2.234 | 0.101 |
| Nitromethane | 0.023 | −0.091 | 0.793 | −1.463 | −4.364 | 3.460 | −3.781 | −0.149 |
| N-Methylpyrrolidone | 0.147 | 0.532 | 0.225 | 0.840 | −4.794 | 3.674 | −1.797 | 0.105 |
| Dimethylsulfoxide | −0.194 | 0.327 | 0.791 | 1.260 | −4.540 | 3.361 | −3.387 | 0.132 |
| Dimethylfomamide | −0.305 | −0.058 | 0.343 | 0.358 | −4.865 | 4.486 | −3.605 | 0.415 |
| Dimethylacetamide | −0.271 | 0.084 | 0.209 | 0.915 | −5.003 | 4.557 | −2.125 | 0.286 |
| Propylene carbonate | 0.004 | 0.168 | 0.504 | −1.283 | −4.407 | 3.421 | −1.989 | 0.341 |
| Sulfolane | 0.000 | 0.147 | 0.601 | −0.318 | −4.541 | 3.290 | −1.200 | −0.792 |
| Chlorobenzene | 0.065 | 0.381 | −0.521 | −3.183 | −4.700 | 4.614 | −4.536 | −1.486 |
| Nitrobenzene | −0.152 | 0.525 | 0.081 | −2.332 | −4.494 | 4.187 | −3.373 | 0.777 |
| Benzonitrile | 0.097 | 0.285 | 0.059 | −1.605 | −4.562 | 4.028 | −2.729 | 0.136 |
| Acetophenone | 0.177 | 0.365 | 0.000 | −1.537 | −4.658 | 3.958 | | |
| Aniline | −0.156 | 0.325 | −0.006 | 1.289 | −3.512 | 3.841 | | |
| N-Methylpropanamide | | | | | | | | |
| N-Methylformamide | 0.114 | 0.407 | −0.287 | 0.542 | −4.085 | 3.471 | −3.733 | 3.869 |
| Formamide | −0.171 | 0.070 | 0.308 | 0.589 | −3.152 | 2.432 | −3.152 | 2.432 |
| Water | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Methanol | 0.276 | 0.334 | −0.714 | 0.243 | −3.320 | 3.549 | −2.609 | 3.027 |
| Ethanol | 0.222 | 0.471 | −1.035 | 0.326 | −3.596 | 3.857 | −3.172 | 3.146 |
| Propan-1-ol | 0.139 | 0.405 | −1.029 | 0.247 | −3.767 | 3.986 | −3.077 | 2.834 |
| Butan-1-ol | 0.165 | 0.401 | −1.011 | 0.056 | −3.958 | 4.044 | −3.605 | 2.685 |
| Pentan-1-ol | 0.150 | 0.536 | −1.229 | 0.141 | −3.864 | 4.077 | −3.387 | 2.816 |
| Hexan-1-ol | 0.115 | 0.492 | −1.164 | 0.054 | −3.978 | 4.131 | −3.100 | 2.940 |
| Heptan-1-ol | 0.035 | 0.398 | −1.063 | 0.002 | −4.342 | 4.317 | −3.318 | 2.751 |
| Octan-1-ol | −0.034 | 0.489 | −1.044 | −0.024 | −4.235 | 4.218 | −3.334 | 2.706 |
| Ethylene glycol | −0.270 | 0.578 | −0.511 | 0.715 | −2.619 | 2.729 | −1.300 | 2.363 |
| 1,2-Propylene glycol | −0.149 | 0.754 | −0.966 | 0.684 | −3.134 | 3.247 | −1.381 | 3.057 |
| Propan-2-ol | 0.099 | 0.344 | −1.049 | 0.406 | −3.827 | 4.033 | −3.896 | 2.889 |
| sec-Butanol | 0.127 | 0.253 | −0.976 | 0.158 | −3.882 | 4.114 | −3.700 | 2.700 |
| Isobutanol | 0.188 | 0.354 | −1.127 | 0.016 | −3.568 | 3.986 | −3.700 | 2.830 |
| tert-Butanol | 0.211 | 0.171 | −0.947 | 0.331 | −4.085 | 4.109 | −4.455 | 2.953 |
| 2-Methylbutan-1-ol | 0.104 | 0.400 | −1.185 | 0.187 | −3.921 | 4.151 | | |
| tert-Pentanol | 0.177 | 0.316 | −1.125 | 0.306 | −4.112 | 4.178 | | |
| 2-Methoxyethanol | 0.175 | 0.326 | −0.140 | 0.000 | −4.086 | 3.630 | −1.295 | 1.508 |
| Trifluoroethanol | 0.395 | −0.094 | −0.594 | −1.280 | −1.274 | 3.088 | −1.113 | 0.957 |
| HFIP | 0.533 | −0.901 | −0.535 | −0.539 | −0.832 | 3.080 | | |
| Acetic acid | 0.175 | 0.174 | −0.454 | −1.073 | −2.789 | 3.725 | | |
| 100% Ethanol[a] | 0.222 | 0.471 | −1.035 | 0.326 | −3.596 | 3.857 | −3.172 | 3.146 |
| 96 | 0.238 | 0.353 | −0.833 | 0.297 | −3.533 | 3.724 | | |
| 95 | 0.239 | 0.328 | −0.795 | 0.294 | −3.514 | 3.697 | −2.985 | 2.943 |
| 90 | 0.243 | 0.213 | −0.575 | 0.262 | −3.450 | 3.545 | −2.794 | 2.837 |
| 80 | 0.172 | 0.175 | −0.465 | 0.260 | −3.212 | 3.323 | −2.466 | 2.722 |
| 70 | 0.063 | 0.085 | −0.368 | 0.311 | −2.936 | 3.102 | −2.203 | 2.550 |
| 60 | −0.040 | 0.138 | −0.335 | 0.293 | −2.675 | 2.812 | −1.858 | 2.394 |
| 50 | −0.142 | 0.124 | −0.252 | 0.251 | −2.275 | 2.415 | −1.569 | 2.051 |
| 40 | −0.221 | 0.131 | −0.159 | 0.171 | −1.809 | 1.918 | −1.271 | 1.676 |
| 30 | −0.269 | 0.107 | −0.098 | 0.133 | −1.316 | 1.414 | −0.841 | 1.290 |
| 20 | −0.252 | 0.042 | −0.040 | 0.096 | −0.823 | 0.916 | −0.677 | 0.851 |
| 10 | −0.173 | −0.023 | −0.001 | 0.065 | −0.372 | 0.454 | −0.412 | 0.401 |
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 100% Methanol[a] | 0.276 | 0.334 | −0.714 | 0.000 | −3.320 | 3.549 | −2.609 | 3.027 |
| 95 | 0.270 | 0.278 | −0.520 | 0.230 | −3.368 | 3.365 | −2.661 | 2.909 |
| 90 | 0.258 | 0.250 | −0.452 | 0.229 | −3.206 | 3.175 | −2.629 | 2.707 |
| 80 | 0.172 | 0.197 | −0.319 | 0.241 | −2.912 | 2.842 | −2.540 | 2.421 |
| 70 | 0.098 | 0.192 | −0.260 | 0.266 | −2.558 | 2.474 | −2.267 | 2.164 |

Table 1 (*continued*)

| Solvent | $c$ | $e$ | $s$ | $a$ | $b$ | $v$ | $j^+$ | $j^-$ |
|---|---|---|---|---|---|---|---|---|
| 60 | 0.053 | 0.207 | −0.238 | 0.272 | −2.157 | 2.073 | −1.978 | 1.872 |
| 50 | 0.023 | 0.223 | −0.222 | 0.264 | −1.747 | 1.662 | −1.588 | 1.569 |
| 40 | 0.020 | 0.222 | −0.205 | 0.218 | −1.329 | 1.259 | −1.329 | 1.259 |
| 30 | 0.016 | 0.187 | −0.172 | 0.165 | −0.953 | 0.898 | −0.823 | 0.930 |
| 20 | 0.022 | 0.142 | −0.138 | 0.088 | −0.574 | 0.559 | −0.465 | 0.599 |
| 10% Methanol | 0.012 | 0.072 | −0.081 | 0.026 | −0.249 | 0.266 | −0.185 | 0.287 |

[a] Volume % alcohol.

applied to exactly the same data set, as eqn (5) and (6) in Table 4. In eqn (5) and (6) and subsequent equations, $N$ is the number of data points (solvents), SD is the regression standard deviation, $R^2$ is the determination coefficient and $F$ is the Fisher F-statistic. The leave-one-out statistics are PRESS, $Q^2$ and the predictive standard deviation, PSD. The errors on the coefficients are in parentheses.

The small values of $Q^2$ and the large values of PSD show that these equations are not well founded, but they indicate that the addition of the ionic descriptors in eqn (5) does not lead to any improvement over eqn (6).

More data are available for reactions in protic solvents and, in Table 5, we give equations that use exactly the same data set for eqn (1) and (3). Eqn (7) is marginally better statistically than eqn (8) but suffers from a set of chemically unreasonable coefficients. In particular, the $a$-coefficient is negative, which is technically impossible, and the $v$-coefficient is far too small to describe the solvent effect on a medium-sized species.

We conclude that the ionic eqn (3), when applied to the effect of protic solvents on the *tert*-butyl chloride transition state yields an inferior equation to the equation for 'neutral' compounds, eqn (1). Thus, in contrast to compounds such as betaine and the α-aminoacids, these results indicate that the *tert*-butyl chloride transition state does not possess a complete charge separation, in agreement with the reaction field calculations, and other studies,[36] which suggest a charge separation of about 0.80 units in protic solvents.

Dvorko *et al.*[4] have suggested that the solvolysis of *tert*-butyl chloride in aprotic and in protic solvents is determined by the ionization of the covalent C–Cl bond. This involves consecutive formation of three ion pairs, a contact ion pair, a loose ion pair and a solvent separated ion pair, as shown in eqn (9). Now if the transition state does not carry a unit charge separation, it cannot lie between any of the suggested ion pairs but must lie between the RX substrate and the first ion pair. Then as regards the nature of the transition state, the various subsequent ion pairs are irrelevant.

$$RX = R^+X^- = R^+\cdots X^- = R^+/Solv/X^- \rightarrow Products \tag{9}$$
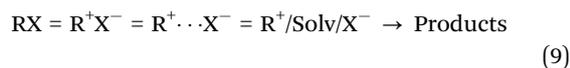
Another consequence is that we are no longer restricted to the set of equations of the form of eqn (3), but we can apply a much larger set of equations of the form of eqn (1) to solvent effects on the transition state. These equations are given in Table 6 as eqn (10) and (11) and include all the solvents for which we have the coefficients in eqn (1) and the corresponding rate constants.

As regards the effect of solvent hydrogen bond acidity, $a$, (solvent electrophilicity) and solvent hydrogen bond basicity, $b$, (nucleophilicity) on the partition of the transition state, eqn (10) and (11) are unambiguous. Solvent hydrogen bond basicity (nucleophilicity) greatly increases log$PsTr$. In both aprotic and protic solvents, the $b$-coefficient is very large. Solvent hydrogen bond acidity, $a$, (electrophilicity) also stabilizes the transition state, although now the effect is not so large ($a$ = 0.591 and 0.655). Both sets of solvents stabilize the transition state through transition state-solvent dipole–dipole and dipole-induced dipole interactions ($s$ = 2.338 and 3.295).

Eqn (10) and (11) can be interpreted in terms of properties or descriptors of the transition state, but we can employ our usual method[19–21,38] to obtain these directly. We construct a set of simultaneous equations with known values of $c$, $e$, $s$, $a$, $b$ and $v$, see Table 1, and with values of log$PsTr$ as the dependent variable. Then the set can be solved by trial-and-error to obtain the unknowns $E$, $S$, $A$, $B$ and $V$. It is useful to estimate $E$ as 0.20 (slightly larger than that for *tert*-butyl chloride) and $V$ as 0.8000 (again, slightly larger than $V$ for *tert*-butyl chloride at 0.7946), so that only $S$, $A$ and $B$ need to be determined. For aprotic solvents we have 26 simultaneous equations (we excluded *N*-methylformamide as a considerable outlier) that we solved with SD = 0.50 log units to give the descriptors in Table 7. For protic solvents we solved 41 simultaneous equations with SD = 0.61 log units to yield the descriptors in Table 7. In general, the descriptors for the *tert*-butyl chloride transition state are quite compatible with our descriptors for various ions and ion-pairs, as shown in Table 7.

It is of some interest that the Me$_4$N$^+$ ion is stabilized by solvents that are nucleophilic (hydrogen bond bases|), with $A$ = 0.68, see Table 7. This suggests that nucleophilic solvents can approach the central N$^+$ atom in spite of the adjacent four methyl groups. Thus, it is no surprise that the central carbon atom in the *tert*-butyl chloride transition state can also be approached and solvated by nucleophilic solvents, with $A$ = 0.66 and 0.45, Table 7. We can conclude that the *tert*-butyl chloride transition state in both protic and in aprotic solvents is very dipolar ($S$ = 2.27 and 2.63), has a significant hydrogen bond acidity ($A$ = 0.66 and 0.45) and a large hydrogen bond basicity ($B$ = 1.03 and 1.75), so that it will be stabilized by solvents that are hydrogen bond bases (nucleophiles) and that are hydrogen bond acids (electrophiles).

**3314** | *Phys. Chem. Chem. Phys.*, 2021, **23**, 3311–3320

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**Table 2** Rate constants, as $\log k/s^{-1}$, for solvolysis of the *tert*-butyl halides at 298 K

| Solvent | *tert*-Butyl chloride | | *tert*-Butyl bromide | | *tert*-Butyl iodide | |
|---|---|---|---|---|---|---|
| | Log k | Ref. | Log k | Ref. | Log k | Ref. |
| Perfluorooctane | −16.16 | 36 | | | | |
| Pentane | −16.00 | 29 | −13.30 | 11 | −11.20 | 11 |
| Heptane | −16.00 | 36 | | | | |
| Cyclohexane | −14.50 | 36 | | | | |
| Benzene | −12.16 | 12 | | | −6.56 | 6 |
| Toluene | | | | | −7.04 | 6 |
| Dichloromethane | −10.45 | 12 | −7.21 | 8 | −6.12 | 6 |
| Trichloromethane | −9.72 | 4 | −7.47 | 6 | | |
| 1,2-Dichloroethane | −9.54 | 12 | | | −6.15 | 6 |
| *tert*-Butyl chloride (*n*-BuCl) | −13.6 | 4 | | | | |
| Diethyl ether | −12.74 | 12 | −10.00 | 11 | −8.20 | 11 |
| Dioxane | −10.80 | 5 | −8.52 | 6 | −6.78 | 11 |
| Tetrahydrofuran | −11.00 | 12 | −8.30 | 11 | −6.57 | 11 |
| Ethyl acetate | −11.50 | 12 | −8.70 | 11 | −7.02 | 11 |
| Propanone | −9.90 | 12 | −7.13 | 6 | −5.21 | 11 |
| Cyclohexanone | −9.61 | 4 | | | | |
| Acetonitrile | −8.73 | 29 | −5.90 | 6 | −4.25 | *a* |
| Nitromethane | −8.13 | 4 | −5.51 | *a* | −3.89 | *a* |
| *N*-Methylpyrrolidone | −8.97 | 5 | −6.00 | 6 | −4.55 | 11 |
| Dimethylsulfoxide | −7.34 | 36 | −4.45 | *a* | −2.68 | *a* |
| Dimethylformamide | −8.55 | 12 | −5.56 | *a* | −3.70 | *a* |
| Dimethylacetamide | −9.30 | 5 | −5.92 | *a* | −5.00 | 11 |
| Propylene carbonate | −8.81 | 30 | −5.47 | *a* | −4.02 | 11 |
| Sulfolane | −7.91 | 4 | −5.18 | 6 | | |
| Fluorobenzene | | | | | −6.58 | 6 |
| Chlorobenzene | −11.34 | 12 | −9.44 | 6 | −6.58 | 6 |
| Bromobenzene | | | | | −6.59 | 6 |
| Iodobenzene | | | | | −6.51 | 6 |
| Nitrobenzene | −9.72 | 29 | −6.95 | 6 | −5.52 | 6 |
| Benzonitrile | −9.83 | 30 | −7.11 | 6 | −5.43 | 6 |
| Acetophenone | −10.13 | 4 | | | | |
| Aniline | −6.10 | *a* | −3.84 | *a* | −2.80 | *a* |
| *N*-Methylpropanamide | | | −5.54 | 8 | | |
| *N*-Methylformamide | −7.33 | 5 | | | | |
| Formamide | −4.40 | 12 | −2.85 | 6 | −1.98 | *a* |
| Water | −1.54 | 12 | −0.12 | 6 | 0.188 | 6 |
| Methanol | −6.10 | 12 | −4.46 | 34 | −3.910 | 34 |
| Ethanol | −7.07 | 12 | −5.24 | 37 | −4.650 | 34 |
| Propan-1-ol | −7.33 | 12 | −5.44 | 6 | −4.86 | 34 |
| Butan-1-ol | −7.52 | 12 | −5.61 | 6 | −4.95 | 34 |
| Pentan-1-ol | −7.45 | 32 | −5.64 | 32 | −5.29 | 32 |
| Hexan-1-ol | −7.45 | 4 | | | | |
| Octan-1-ol | −7.52 | 4 | | | | |
| Ethylene glycol | −4.60 | 5 | −3.03 | 34 | −2.55 | 34 |
| 1,2-Propylene glycol | −5.51 | 32 | −4.03 | 32 | −3.56 | 32 |
| Propan-2-ol | −7.74 | 29 | −5.67 | 34 | −5.05 | 6 |
| *sec*-Butanol | −8.10 | 31 | −5.78 | 6 | −5.40 | 34 |
| Isobutanol | −7.40 | *a* | −5.68 | 6 | −5.19 | 34 |
| *tert*-Butanol | −8.27 | 12 | −6.32 | 6 | −5.84 | 11 |
| 2-Methylbutan-1-ol | −7.60 | *c* | −5.71 | *a* | −5.40 | *a* |
| *tert*-Pentanol | −8.77 | 5 | | | | |
| 2-Methoxyethanol | −6.63 | *c* | −4.75 | *a* | −3.90 | *a* |
| Trifluoroethanol | −3.89 | *a* | −2.62 | 6 | | |
| HFIP | −2.70 | 12 | −1.45 | 6 and 12 | | |
| Acetic acid | −6.70 | 4 | −5.52 | 6 | | |
| 100% Ethanol*d* | −7.07 | 12 | −5.24 | 37 | −4.65 | 34 |
| 96 | −6.72 | 35 | −4.99 | *b* | −4.25 | *b* |
| 95 | −6.32 | 35 | −4.62 | *b* | −4.18 | *b* |
| 90 | −5.78 | 35 | −4.15 | 37 | −3.69 | *b* |
| 80 | −5.03 | 35 | −3.44 | 37 | −3.03 | *b* |
| 70 | −4.44 | 35 | −2.87 | *b* | −2.56 | *b* |
| 60 | −3.91 | 35 | −2.42 | 37 | −2.12 | *a* |
| 50 | −3.38 | 35 | −1.88 | *b* | −1.67 | *a* |
| 40 | −2.84 | 35 | −1.38 | *b* | −1.15 | *b* |
| 30 | −2.31 | 35 | −0.88 | *b* | −0.732 | *b* |
| 20 | −1.98 | 35 | −0.57 | *b* | −0.398 | *b* |
| 10 | −1.72 | 35 | −0.33 | *b* | −0.079 | *b* |

**Table 2** (*continued*)

| Solvent | *tert*-Butyl chloride | | *tert*-Butyl bromide | | *tert*-Butyl iodide | |
|---|---|---|---|---|---|---|
| | Log k | Ref. | Log k | Ref. | Log k | Ref. |
| 0 | −1.54 | 35 | −0.12 | 33 | 0.188 | 33 |
| 100% Methanol*d* | −6.10 | 12 | −4.46 | 34 | −3.903 | 34 |
| 95 | −5.530 | 33 | −4.05 | 33 | −3.553 | 33 |
| 90 | −4.859 | 33 | −3.67 | 33 | −3.221 | 33 |
| 80 | −4.032 | 33 | −3.00 | 33 | −2.627 | 33 |
| 70 | −3.412 | 33 | −2.48 | *a* | −2.107 | 33 |
| 60 | −2.964 | 33 | −2.00 | *a* | −1.653 | 33 |
| 50 | −2.598 | 33 | −1.56 | 33 | −1.254 | 33 |
| 40 | −2.304 | 33 | −1.20 | 33 | −0.900 | 33 |
| 30 | −2.060 | 33 | −0.88 | 33 | −0.582 | 33 |
| 20 | −1.859 | 33 | −0.60 | 33 | −0.299 | 33 |
| 10% Methanol | −1.685 | 33 | −0.34 | 33 | −0.044 | 33 |

*a* This work. *b* Values obtained by interpolation and by regression against $\log k$ values for *tert*-butyl chloride. *c* Values obtained by temperature extrapolation. *d* Volume % alcohol.

**Table 3** Descriptors for the *tert*-butyl halides

| Compound | E | S | A | B | V | L | Log $K_w$ |
|---|---|---|---|---|---|---|---|
| *tert*-Butyl chloride | 0.142 | 0.300 | 0.000 | 0.030 | 0.7946 | 2.286 | −0.80 |
| *tert*-Butyl bromide | 0.305 | 0.320 | 0.000 | 0.065 | 0.8427 | 2.563 | −0.40 |
| *tert*-Butyl iodide | 0.589 | 0.320 | 0.000 | 0.070 | 0.9304 | 3.350 | −0.39 |

These properties are quite consistent with the coefficients shown in eqn (10) and (11). The ground state is almost unaffected by nucleophilic and electrophilic solvents, see Table 3, where $A = 0.00$ and $B = 0.03$, and so the effect of nucleophilic solvents on stabilizing the transition state will inevitably lead to an increase in the rate constant.

Our conclusion is so contrary to the conclusions reached from the application of other multi-parameter equations to *tert*-butyl chloride rate constants, that we are obliged to discuss possible reasons. Gajewski[2,3] has used his linear free energy relationship to show that there is no positive nucleophilic solvent participation in the solvolysis and Dvorko et al.[4–7] used the multi-parameter Koppel–Palm linear free energy relationship with similar results. Use of the Kamlet–Taft equation also indicated[11–13] that there was little nucleophilic solvent participation. However, the Kamlet–Taft equation is not a linear free energy equation. The independent variables are calculated from solvatochromic measurements,[39] and are therefore spectroscopic energies and not free energies. Quite recently, Catalan and Reichardt[40] have applied an equation due to Catalan[41] to the solvolysis of *tert*-butyl chloride. The equation contains four independent variables, all of which are derived from solvatochromic measurements and hence, again, are related to spectroscopic energies. The equation is therefore not appropriate for the analysis of a dependent variable that is a free energy. We therefore concentrate only on the equations given by Gajewski and by Dvorko.

Gajewski applied his equation to Winstein–Fainberg *Y*-values for seven solvents and obtained eqn (12), Table 8. We recalculated his equation and obtained a slightly different

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*Phys. Chem. Chem. Phys.*, 2021, **23**, 3311–3320 | **3315**

**Table 4** Regression coefficients from the application of eqn (1) and (3) to the water−solvent partition coefficients of the *tert*-butyl chloride transition state, log $Ps$(Tr), in aprotic solvents

| Log $Ps$(Tr) | $c$ | $e$ | $s$ | $a$ | $b$ | $v$ | $j^+$ | $j^-$ | $N$ | SD | $R^2$ | $F$ | PRESS | $Q^2$ | PSD | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aprotic | 4.008 (1.920) | — | 1.621 (0.374) | 0.404 (0.115) | 2.182 (0.435) | 0.402 (0.387) | 0.0643 (0.0566) | 0.0918 (0.0513) | 20 | 0.494 | 0.882 | 16 | 14.204 | 0.472 | 1.045 | (5) |
| Aprotic | 4.191 (1.981) | — | 1.732 (0.361) | 0.423 (0.118) | 2.175 (0.438) | 0.302 (0.386) | — | — | 20 | 0.515 | 0.852 | 22 | 11.924 | 0.557 | 0.892 | (6) |

**Table 5** Regression coefficients from the application of eqn (1) and (3) to the water−solvent partition coefficients of the *tert*-butyl chloride transition state, log $Ps$(Tr), in protic solvents

| Log $Ps$(Tr) | $c$ | $e$ | $s$ | $a$ | $b$ | $v$ | $j^+$ | $j^-$ | $N$ | SD | $R^2$ | $F$ | PRESS | $Q^2$ | PSD | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Protic | 0.271 (0.169) | 1.161 (1.051) | 2.703 (0.599) | −1.354 (0.531) | 1.110 (0.461) | 0.116 (0.523) | 0.182 (0.212) | 1.333 (0.303) | 41 | 0.384 | 0.928 | 61 | 10.768 | 0.841 | 0.571 | (7) |
| Protic | 0.383 (0.198) | 1.589 (0.817) | 3.197 (0.478) | 0.453 (0.432) | 1.912 (0.393) | 1.675 (0.423) | — | — | 41 | 0.475 | 0.883 | 53 | 17.750 | 0.738 | 0.712 | (8) |

**Table 6** Regression coefficients from the application of eqn (1) to water−solvent partition coefficients of the *tert*-butyl chloride transition state, log $Ps$(Tr), in aprotic and protic solvents

| Log $Ps$(Tr) | $c$ | $e$ | $s$ | $a$ | $b$ | $v$ | $N$ | SD | $R^2$ | $F$ | PRESS | $Q^2$ | PSD | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aprotic | 2.513 (1.885) | 1.194 (0.741) | 2.338 (0.225) | 0.591 (0.127) | 2.472 (0.465) | 1.037 (0.373) | 28 | 0.673 | 0.940 | 69 | 19.684 | 0.882 | 0.945 | (10) |
| Protic | 0.372 (0.199) | 1.344 (0.606) | 3.295 (0.441) | 0.655 (0.366) | 2.178 (0.341) | 1.961 (0.367) | 44 | 0.477 | 0.901 | 69 | 17.134 | 0.803 | 0.671 | (11) |

**Table 7** Descriptors for the *tert*-butyl halide transition states

| Species | $E$ | $S$ | $A$ | $B$ | $V$ |
|---|---|---|---|---|---|
| *t*-BuCl(Tr) protic solvents | 0.20 | 2.27 | 0.66 | 1.03 | 0.8000 |
| *t*-BuCl(Tr) aprotic solvents | 0.20 | 2.63 | 0.45 | 1.75 | 0.8000 |
| Me$_4$N$^+$Cl$^-$ ion pair | 0.00 | 2.93 | 1.04 | 1.75 | 0.9913 |
| Me$_4$N$^+$ | −0.10 | 1.31 | 0.68 | 0.00 | 0.7635 |
| Cl$^-$ | 0.10 | 3.52 | 0.00 | 2.32 | 0.2278 |
| Acetate$^-$ | 0.42 | 2.19 | 0.00 | 2.93 | 0.4433 |
| *t*-BuBr(Tr) Protic solvents | 0.35 | 2.19 | 0.40 | 0.96 | 0.8500 |
| *t*-BuBr(Tr) Aprotic solvents | 0.35 | 3.06 | 0.40 | 1.49 | 0.8500 |
| Me$_4$N$^+$Br$^-$ ion pair | 0.07 | 2.11 | 0.89 | 2.18 | 1.0701 |
| Br$^-$ | 0.17 | 2.74 | 0.00 | 1.82 | 0.3066 |
| *t*-BuI(Tr) protic solvents | 0.65 | 2.47 | 0.35 | 0.85 | 0.9400 |
| *t*-BuI(Tr) aprotic solvents | 0.65 | 3.02 | 0.17 | 1.24 | 0.9400 |
| Me$_4$N$^+$I$^-$ ion pair | 0.28 | 2.51 | 0.75 | 1.48 | 1.1696 |
| I$^-$ | 0.38 | 3.55 | 0.00 | 1.34 | 0.4081 |

based on the partition of the chloride ion, and *CED* is the cohesive energy density.

Unfortunately, both eqn (12) and (13) are statistically invalid because they only have seven data points for four independent variables, as can be seen from the low value of $Q^2$ and the large value of PSD in eqn (13). Therefore, no valid information can be drawn in these circumstances.

In an interesting application, Gajewski[2] obtained values for the transfer of the *tert*-butyl chloride transition state itself and regressed these against the independent variables in eqn (12) to obtain eqn (14) for 23 protic and aprotic solvents. Again, we used the same *Y*-values and independent variables as listed by Gajewski with the corrected $\varepsilon$ value for HFIP and obtained eqn (15), as depicted in Table 9.

Results in Table 9, although statistically not very good, are in line with our own results presented in Table 6, with both solvent nucleophilicity ($b'$) and solvent electrophilicity ($a'$) stabilizing the transition state.

Koppel and Palm[9] applied their well-known equation to the solvolysis of *tert*-butyl chloride, with log $k$/s$^{-1}$ as the dependent variable, using 23 protic and aprotic solvents – Table 10 – where $Y_e$ is the dielectric constant function used by Gajewski, $P$ is the

equation, eqn (13), using a corrected $(\varepsilon - 1)/(2\varepsilon + 1)$ value from Marcus, for HFIP, as also shown in Table 8.[42] In these equations, $\varepsilon$ is the solvent dielectric constant, $a'$ is a descriptor based on the partition of the potassium ion, $b'$ is a descriptor

**Table 8** Regression coefficients from the application of Gajewski equation to seven solvents with uncorrected, eqn (12), and corrected, eqn (13), $\varepsilon$ value for HFIP

| Dependent variable | const | $\dfrac{(\varepsilon + 1)}{(2\varepsilon + 1)}$ | $a'$ | $b'$ | *CED* | $N$ | SD | $R^2$ | $F$ | PRESS | $Q^2$ | PSD | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.303$Y$ | −24.5 | 30.4 | 29.3 | −34.1 | 17.4 | 7 | 0.844 | 0.973 | — | — | — | — | (12) |
| 2.303$Y$ | −30.2 | 37.6 | 38.8 | −24.8 | 15.5 | 7 | 0.694 | 0.982 | 83 | 61.98 | 0.615 | 5.56 | (13) |

**Table 9** Regression coefficients from the application of Gajewski equation to 23 protic and aprotic solvents from ref. 2 with uncorrected, eqn (14), and corrected, eqn (15), $\varepsilon$ value for HFIP

| Dependent variable | const | $\dfrac{(\varepsilon+1)}{(2\varepsilon+1)}$ | $a'$ | $b'$ | CED | $N$ | SD | $R^2$ | $F$ | PRESS | $Q^2$ | PSD | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Log Tr(tranfer) | −11.2 | 11.9 | 43.2 | 10.6 | 1.1 | 23 | 1.02 | 0.925 | — | — | — | — | (14) |
| Log Tr(transfer) | −11.1 | 11.7 | 44.0 | 10.5 | 0.83 | 23 | 1.55 | 0.926 | 69 | 88.49 | 0.875 | 2.217 | (15) |

**Table 10** Coefficients from the application of the Koppel–Palm equation to solvents in ref. 9 and 5

| Ref. | log $k$ | const | $Y_e$ | $P$ | $E$ | $B$ | $\delta^2$ | $N$ | SD | $R^2$ | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Koppel–Palm[9] | Protic + aprotic | −19.89 | 13.39 | 13.46 | 0.378 | — | — | 23 | 4.8% | 0.964 | (16) |
| Dvorko et al.[5] | Protic + aprotic | −19.9 | 17.9 | 5.53 | 0.083 | — | — | 42 | 0.670 | 0.943 | (17) |
| Dvorko et al.[5] | Aprotic | −20.6 | 14.5 | 13.0 | 0.136 | — | — | 21 | 0.610 | 0.904 | (18) |
| Dvorko et al.[5] | Protic | −13.6 | 16.6 | — | 0.037 | −1.24 | 0.0014 | 20 | 0.630 | 0.929 | (19) |

refractive index function and $E$ is the solvent electrophilicity. In eqn (16) the solvent nucleophilicity, $B$, was not significant, and so this equation suggests the absence of any nucleophilic solvent participation. Dvorko et al.[5] also applied the Koppel–Palm equation to the solvolysis of tert-butyl chloride in a larger number of aprotic and protic solvents and obtained a similar equation, except that the coefficient of the electrophilicity descriptor is very small (0.083) so that neither solvent electrophilicity nor solvent nucleophilicity have any real effect on the reaction rate. These results are also presented in Table 10 together with the treatment for aprotic and protic solvents taken separately ($\delta^2$ stands for the cohesive energy density).

Based on these results, Dvorko et al.[5] concluded that in all solvents, the electrophilicity descriptor leads to an increase in the reaction rate, and that the nucleophilicity descriptor has no influence on reaction rate except in protic solvents where it actually leads to a small reduction in reaction rate.

Thus, of the linear free energy relationships applied to tert-butyl chloride rate constants or to transfers of the tert-butyl chloride transition state, our equations and Gajewski's (recalculated) equation indicate that both protic and aprotic solvents stabilize the transition state and lead to an increase in rate, but the Koppel–Palm equation suggests that there is no nucleophilic involvement of the solvent. Since both the $Me_4N^+$ ion and the $Me_4N^+Cl^-$ ion pair are stabilized by nucleophilic solvents, as seen in Table 7, the results of the Koppel–Palm equation appear to be incompatible with these solvent effects. It is possible that the differences between the outcomes of the various equations are due to our equation and Gajewski's equation using properties of the transition state as the dependent variable, whereas in the Koppel–Palm equation, rate constants, as log $k$, are used. We can check this by regressions of log $k$ – Table 11.

It is clear that our above conclusions about nucleophilic participation are not due to the use of transition state quantities as the dependent variable instead of log $k$. Eqn (20)–(22) show that solvent nucleophilic participation increases the rate, and eqns (10), (11) and (15) show that nucleophilic solvents stabilize the transition state. Our descriptors for the transition state itself show that the transition state exhibits considerable hydrogen bond acidity (electrophilicity) and considerable hydrogen bond basicity (nucleophilicity) in line with known properties of species such as $Me_4N^+$, $Cl^-$ and the $Me_4N^+Cl^-$ ion pair.

### 3.2 tert-Butyl bromide

We follow the same procedure as for tert-butyl chloride. Rate constants, as log $k$, that we used[6,8,11,33,37] and those from this work are in Table 2. We calculated the transition state partition coefficients through eqn (4). For the partition of the tert-butyl bromide transition state we obtain eqn (23) and (24) in Table 12, using aprotic and protic solvents, separately. In eqn (23) the point for dioxane was left out and in eqn (24) that for acetic acid was left out. Eqn (23) is only just statistically viable, with 19 data points for five independent variables, but suggests that there is stabilization of the transition state by electrophilic and nucleophilic aprotic solvents. Eqn (24), however, is statistically very good. We can thus conclude that hydrogen bond acids (electrophilic solvents) stabilize the transition state, and that hydrogen bond bases (nucleophilic solvents) greatly stabilize the transition state.

We can obtain descriptors for the tert-butyl bromide transition state by using our simultaneous equation method, as before. We took $E = 0.35$ and $V = 0.850$, by comparison to values for tert-butyl bromide and for the other species in Table 7 and obtained

**Table 11** Regressions of log $k$ (tert-butyl chloride) using coefficients from Table 1

| Log $k$ | $c$ | $e$ | $s$ | $a$ | $b$ | $v$ | $N$ | SD | $R^2$ | $F$ | PRESS | $Q^2$ | PSD | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| All solvents | −0.511 (0.278) | 1.653 (0.529) | 1.792 (0.202) | 1.081 (0.081) | 2.850 (0.204) | 1.202 (0.227) | 74 | 0.787 | 0.956 | 298 | 49.56 | 0.949 | 0.854 | (20) |
| Aprotic | 2.162 (1.415) | 1.407 (0.615) | 2.351 (0.193) | 0.560 (0.141) | 2.855 (0.328) | 0.555 (0.314) | 29 | 0.579 | 0.961 | 113 | 13.495 | 0.931 | 0.766 | (21) |
| Protic | −1.061 (0.204) | 1.026 (0.590) | 2.765 (0.428) | 1.341 (0.327) | 2.152 (0.350) | 1.023 (0.374) | 45 | 0.490 | 0.958 | 179 | 15.144 | 0.932 | 0.623 | (22) |

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Phys. Chem. Chem. Phys., 2021, **23**, 3311–3320 | **3317**

**Table 12** Regression coefficients from the application of eqn (1) to water–solvent partition coefficients of the *tert*-butyl bromide transition state, log $Ps$(Tr), in aprotic and protic solvents

| Log Ps(Tr) | c | e | s | a | b | v | N | SD | $R^2$ | F | PRESS | $Q^2$ | PSD | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aprotic | 3.583 (2.085) | 0.489 (0.747) | 2.510 (0.390) | 0.498 (0.116) | 2.242 (0.314) | 0.869 (0.357) | 19 | 0.469 | 0.961 | 95 | 8.039 | 0.890 | 0.786 | (23) |
| Protic | 0.199 (0.120) | 0.703 (0.377) | 2.600 (0.284) | 0.648 (0.253) | 1.718 (0.218) | 1.578 (0.233) | 41 | 0.287 | 0.935 | 101 | 5.910 | 0.867 | 0.410 | (24) |

**Table 13** Regression coefficients from the application of eqn (1) to water–solvent partition coefficients of the *tert*-butyl iodide transition state, log $Ps$(Tr), in aprotic and protic solvents

| Log Ps(Tr) | c | e | s | a | b | v | N | SD | $R^2$ | F | PRESS | $Q^2$ | PSD | Eqn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aprotic | 3.468 (2.011) | 1.247 (0.667) | 2.414 (0.354) | 0.315 (0.095) | 2.043 (0.376) | 1.012 (0.334) | 23 | 0.488 | 0.940 | 53 | 7.321 | 0.872 | 0.654 | (25) |
| Protic | 0.070 (0.099) | 1.835 (0.441) | 3.154 (0.324) | 0.099 (0.277) | 1.972 (0.338) | 2.071 (0.375) | 39 | 0.237 | 0.906 | 74 | 3.812 | 0.832 | 0.340 | (26) |

a set of 17 simultaneous equations for aprotic solvents. These were solved by trial-and-error to give the transition state descriptors in Table 7 with an SD of only 0.285 log units. We left out dioxane solvent which was a considerable outlier. For protic solvents we had 39 simultaneous equations (leaving out *tert*-butanol and acetic acid) which we solved with SD = 0.350 log units. The descriptors are in Table 7. In general, the transition state properties are in accord with the partition coefficient equations. The transition state is highly dipolar, is a very strong hydrogen bond base and a moderately strong hydrogen bond acid. It will therefore be stabilized by electrophilic and nucleophilic solvents.

### 3.3 *tert*-Butyl iodide

We could access a reasonable number of rate constants for *tert*-butyl iodide,[6,11,32–34] and from this work, as set out in Table 2. Equations for log $Ps$Tr(Aprotic) and log $Ps$Tr(Protic) are given as eqn (25) and (26) in Table 13.

We were also able to use our simultaneous equation method to obtain descriptors for the *tert*-butyl iodide transition state. By comparison to the various species in Table 7, we took $E$ = 0.65 and $V$ = 0.9400. Then for protic solvents we had a set of 36 equations (leaving out the equations for solvents *tert*-butyl alcohol and 2-methoxyethanol) which we solved to yield the descriptors in Table 7, with SD = 0.230 log units. For aprotic solvents we had 21 solvents that we solved with SD = 0.378 log units; the descriptors are also in Table 7. The transition state is thus stabilized by electrophilic solvents, although not to the same extent as are the *tert*-butyl chloride and *tert*-butyl bromide transition states. The transition state $A$-values are quite small (0.17, 0.35) which indicates that the transition state is weakly stabilized by solvents that are hydrogen bond bases (nucleophiles).

## 4 Conclusions

The descriptors for the three transition states are quite in line with descriptors for various other species given in Table 7. The three transition states are all moderately strong hydrogen bond acids, but not quite as strong as the corresponding ion pairs $Me_4N^+X^-$. Thus, the transition states are stabilized by nucleophilic solvents, just as are the ion pairs, with the stabilization

decreasing along the series Cl > Br > I. Since the ground states are unaffected by solvent nucleophilicity, Table 3, it follows that the reaction rates will be increased by nucleophilic solvents. If solvent nucleophilicity is unimportant,[4–9] then it follows that the transition states, with a substantial charge separation, must be unaffected by solvent nucleophilicity,[4–9] whereas the ion pairs are greatly stabilized by nucleophilic solvents – a conclusion that makes little sense. Our own conclusion is unambiguous. The three transition states are stabilized by nucleophilic solvents that consequently increase the rates of reaction.

The effect of electrophilic solvents is not in contention. They will greatly increase the rate of reaction through considerable stabilization of the transition states. The $B$-values of the transition states are all very large, just as are the $B$-values of the ion pairs. All these species are stabilized through interaction of the electrophilic solvents with the leaving halide in the transition states and the formed halide ion in the ion pairs.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

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3318 | *Phys. Chem. Chem. Phys.*, 2021, **23**, 3311–3320

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**3320** | *Phys. Chem. Chem. Phys.*, 2021, **23**, 3311–3320

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