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Experimental and Theoretical Evaluation of Energetics for Nucleophilic Solvent Participation in the Solvolysis of Tertiary Alkyl Chlorides on the Basis of Gas Phase Bridgehead Carbocation Stabilities

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Abstract: The specific rates of solvolysis in 80% ethanol and 97% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) for various tertiary alkyl chlorides having different steric requirement and experimental (FT ICR) gas-phase stabilities of the corresponding carbocations were determined. The experimental gas-phase stabilities were in good agreement with theoretical values computed at the MP2/6-311G(d,p) or the MP2/6-311G(d,p)//MP2/6-31G(d) level. The relation of differential activation Gibbs energy changes for solvolysis [$\delta\Delta G^{\ddagger} = -RT \ln(k/k_o)$] (relative to 1-chloroadamantane) vs the experimental gas-phase cation-stabilities $\Delta G°$ (relative to 1-adamantyl cation) was compared with the previously established similar relation for bridgehead systems. It was revealed that the solvolysis of *tert*-butyl chloride in 80% ethanol is nucleophilically assisted by 4−8 kcal mol^{-1}. The $\delta\Delta G^{\ddagger}$ vs $\Delta G°$ relation for heavily crowded 4-chloro-2,2,4,6,6-pentamethylheptane was found to be comparable to that of bridgehead compounds. The reversal of the ranking of stabilities of the *tert*-butyl cation and 1-adamantyl cation on going from the gas phase to aqueous solution was computationally assessed. The results agree with the fact that larger substituents around a cationic center increase the stability of the ion in the gas phase thanks to their larger polarizability, and that this effect is either offset or even dramatically reversed in solution.

1. Introduction

Detailed understanding of substrate−solvent interactions at the molecular level is one of the most important problems in physical organic chemistry. Among a large number of organic reactions, the S_N1 solvolysis is perhaps the most studied in this respect since the historic work by Hughes and Ingold in the 1930s.[1] Nevertheless, interaction between solvent molecules and substrate in the transition state, and even in the ground state, has not necessarily been well understood. Nucleophilic solvent participation (NSP) in the solvolysis of *tertiary* alkyl compounds may be one of such typical examples.[2a−c]

Recent studies on the Grunwald−Winstein relations in the solvolysis of a series of congested tertiary alkyl halides showed that NSP essentially vanishes in extremely congested systems.[3] However, no energetic information has been obtained regarding the magnitude of the NSP in the solvolysis rates of even the simplest tertiary substrate, *tert*-butyl chloride (**1**Cl). Statistical analysis of solvolysis rates of **1**Cl by means of the extended Grunwald−Winstein model, eq 1, succeeded in evaluating the magnitude of NSP in terms of the *l* coefficient.[2b,4]

$$\log(k/k_o) = lN + mY_X \qquad (1)$$

In eq 1 N is a nucleophilic parameter such as N_{OTs}[2d] or N_T[2b] while Y_X is a measure of the ionizing power of the solvent in the absence of NSP effects.[2a,d,5,6] The NSP as measured by using eq 1 is considered to involve the interactions with both the reacting carbon atom and the hydrogen atoms, in particular the β-hydrogens.[7] However, it is still an open question how much the transition state for the ionization of **1**Cl is stabilized by NSP.

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[6] In the pioneering work by Grunwald and Winstein (Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846−854) the solvent ionizing power of a given solvent was defined by $\log(k/k_o)$ based on the rate constants of *tert*-butyl chloride solvolysis at 25 °C, where k is the specific rate in a given solvent and k_o in 80% ethanol−20% water (V/V at 25 °C). Later, Schleyer, Bentley, and their co-workers redefined Y values based on the solvolysis rates of 2-adamantyl or 1-adamantyl substrates that are essentially free from NSP.[2a,d,5]

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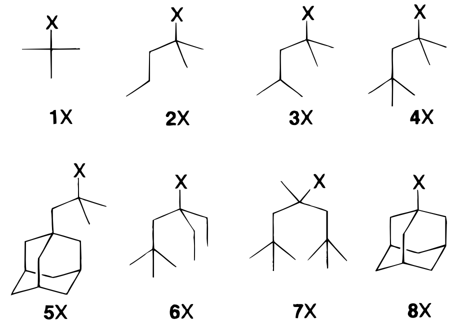
Chart 1



Jorgensen and co-workers calculated stabilization energies by hydration for *t*-Bu$^+$ Cl$^-$ ion pairs by using Monte Carlo simulations and extended RISM methodology, but the computational results have not been supported so far by experimental data.[8a] Very recently, Fãrcaşiu and Lukinskas carried out ab initio calculations on the structure of the *tert*-butyl cation ion-paired with BH_3F^- or BF_4^- at various interatomic distances.[8b] One of the results was that the anion interacts strongly with only one of the hydrogen atoms, suggesting the importance of solvation at β-hydrogen atoms to stabilize the ion pair.[8b]

Here we address the problem of the quantitative assessment of structural effects on the thermodynamics of NSP in the solvolysis of tertiary alkyl halides. We believe that the information thus obtained facilitates a better understanding of this phenomenon.

In their classical studies[9] Schleyer and co-workers succeeded in rationalizing the rates of solvolysis of bridgehead derivatives, RX, in terms of the strain changes between the corresponding hydrocarbons (RH) and carbocations (R^+). These strain changes are fundamental contributors to the difference in thermodynamic stabilities between these species.[10]

More recently,[10a] Fourier Transform Ion Cyclotron Resonance Spectroscopy[11] (FT ICR) was used to determine the intrinsic (gas-phase) stabilities of a number of bridgehead carbocations $R^+(g)$ relative to 1-adamantyl cation (1-Ad$^+$, **8**$^+$) by means of the formal bromide exchange process (2, X = Br):

$$\text{1-Ad}^+(g) + RX(g) \rightleftharpoons \text{1-AdX}(g) + R^+(g) \qquad \Delta G^\circ_{(2)} \quad (2)$$

The range of structural effects on the stabilities of these cations spans some 50 kcal mol^{-1}.[10a] Moreover, it was found that the relative stabilities of these ions [as measured by $\Delta G^\circ_{(2)}$] and the corresponding logarithmic solvolysis rates relative to 1-bromoadamantane (**8**Br), $\Delta \log k_{\text{solv}}$, show an excellent linear relationship [correlation coefficient = 0.9957, standard deviation (σ of 0.77 on $\Delta \log k_{\text{solv}}$)]. This work was later extended[12] to the study of the chlorides of the same bridgehead species and it was found by means of experimental and computational methods that ΔG°(2,X=Cl) is essentially the same as ΔG°(2,X=Br). Inasmuch as their $\Delta \log k_{\text{solv}}$ are also extremely close,[12,13] a nice linear relationship (hereafter called "bridgehead line") between $\Delta \log k_{\text{solv}}$ for chlorides and ΔG°(2,X=Cl) follows. Since NSP from the backside is precluded in the cage-shaped compounds, the "bridgehead line" permits, as a first approximation, the quantitative estimation of the energetics of NSP in the solvolysis of open chain, tertiary alkyl substrates.

In what follows we use the tool of the "bridgehead line" for the comparison of the solvolysis rates for compounds **1**Cl–**7**Cl in 80% ethanol and 97% HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) with their ΔG°(2,X=Cl) values, determined by means of FT ICR using the Dissociative Proton Attachment (DPA) method. This study is complemented with and supported by a series of ab initio calculations of substantial level and several ancillary experiments.

2. Experimental Section

2.1. Gas-Phase Studies. A. The FT ICR Spectrometer. In this work, use was made of a modified Bruker CMS 47 FT ICR mass spectrometer. A detailed description of the original instrument is given in ref 14. It has already been used in a number of studies.[10a,12,15] The field strength of its supraconducting magnet, 4.7 T, allows the monitoring of ion–molecule reactions for relatively long periods of time and the performing of experiments under "high" pressures (up to ca. 5 × 10^{-4} mbar).

B. The DPA Method. Reaction 3 is a particular case of reaction 2, in which R_1^+ and R_2^+ are two carbocations and X = H, halogen.

$$R_1^+(g) + R_2X(g) \rightleftharpoons R_1X(g) + R_2^+(g) \qquad \Delta G^\circ_{(3)} \qquad (3)$$

The direct study of equilibrium 3 has been carried out (with X = H, Cl, or Br) in a number of instances.[16] Its usefulness is limited, however, to cases wherein the carbocations do not easily rearrange.[10a,12,17] This is why we obtain here $\Delta G^\circ_{(3)}$ by a different method, namely the DPA technique, summarized as follows:

The gas-phase protonation of a halide or an alcohol, R–X, often leads to ion–molecule complexes that readily decompose to yield free ions $R^+(g)$ and neutral XH(g) molecules.[10a,12,17] The DPA method allows one to find the base B such that its conjugate acid, BH^+, is just able to transfer a proton to R–X (X = OH, halogen) according to eq 4. This

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defines the onset of DPA.

$$R{-}X(g) + BH^+(g) \rightarrow R^+(g) + XH(g) + B(g) \qquad (4)$$

The gas-phase basicity of the base B, GB(B), is defined as the standard Gibbs energy change for reaction 5, $\Delta G^\circ_{(5)}$.

$$BH^+(g) \rightarrow B(g) + H^+(g) \qquad \Delta G^\circ_{(5)} \qquad (5)$$

Let B_1 and B_2 stand for the two bases respectively defining the DPA onsets of $R_1X(g)$ and $R_2X(g)$ as determined under the same experimental conditions. Equation 6 holds:[10a,12,17]

$$\Delta G^\circ_{(6)} \approx GB(B_1) - GB(B_2) \qquad (6)$$

Thanks to this expression, the experimental determination of the relative stabilities of $R_1^+(g)$ and $R_2^+(g)$ through the formal equilibria 2 and 3 reduces to that of the DPA onsets for the corresponding precursors [reaction 4].[10a,12,17] In this work, the GB values of the reference bases are taken from the recent, major critical compilation by Lias and Hunter.[18]

The experimental determination of these onsets involves a bracketing procedure. Therefore, $\Delta G^\circ_{(6)}$ values determined by this method are formally less precise (uncertainties estimated at ca. 2 kcal mol^{-1}) than those obtained by direct equilibration. In practice, this inconvenience is largely offset by the fact that the carbocations are generated under extremely mild conditions and have much less tendency to rearrange than in the standard equilibrium experiments.[10a,12,17]

C. The DPA Experiments. The experimental technique is quite similar to that used in refs10a, 12, and 17. As in ref 17b, some minor changes were introduced to specifically avoid the deprotonation of $R^+(g)$ by B(g). Full details, as well as the table of raw experimental results (Table S1), are given as Supporting Information.

Compounds **5**Cl and particularly **5**OH have very low vapor pressures. This has prevented us from obtaining reliable data for these materials.

2.2. Solution Studies. A. Rate Studies. The solvent 80% ethanol was prepared as described previously.[19] 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was distilled from Molecular Sieves 3 A and mixed with 3.0 wt % water. The rates of solvolysis in 80% ethanol were determined titrimetrically or conductometrically in the presence of 0.025 mol L^{-1} 2,6-lutidine following previously reported procedures.[19] The rates of solvolysis in 97% HFIP for **2**Cl, **3**Cl, and **9**Cl were determined conductometrically in this study by using 3−5 mL of solvent in the absence of 2,6-lutidine, whereas those for **1**Cl and **8**Cl were taken from the literature and that for **4**Cl was obtained by extrapolation of the Grunwald−Winstein plot.[3a] The first-order plots were satisfactorily linear until 80−90% conversion in all measurements. The rates of **5**Cl, **6**Cl, and **7**Cl in 97% HFIP were estimated from the Grunwald−Winstein relationship for nonaqueous solvents (see Supporting Information). The experimental solvolysis rates are summarized in Table S2.

B. Materials. The synthesis of alcohols and chlorides for **2**,[20a] **3**,[20a] **4**,[20b] and **7**[20c] was reported previously. The new chlorides **5**Cl and **6**Cl were prepared as follows.

1-(2-Chloro-2-methylpropyl)adamantane (**5**Cl). The known precursor alcohol, 1-(1-adamantyl)-2-methyl-2-propanol (**5**OH), was prepared from 1-(bromomagnesiomethyl)adamantane and acetone in diethyl ether: mp 57.5−58.5 °C (from hexane). Although the melting point was about 20 °C lower than the reported values [76−78 °C,[21] 79−81 °C[22]], the ^{13}C NMR spectrum showed a purity higher than 99%: ^{13}C NMR ($CDCl_3$, 67.94 MHz) δ 28.8 (CH), 32.0 (CH_3), 33.6 (C), 37.0 (CH_2), 43.8 (CH_2), 57.3 (CH_2), 72.5 (C). The alcohol was hydrochlorinated with HCl in a mixture of pentane and CH_2Cl_2 at 0 °C until HCl absorption ceased.The reaction mixture containing small amounts of white crystals was dried ($CaCl_2$) and the solvent was evaporated to give a pale yellow solid, which was recrystallized from pentane at dry ice temperature to give **5**Cl as white needles: mp 53−54 °C: ^{13}C NMR ($CDCl_3$, 67.94 MHz) δ 28.8 (CH), 34.6 (C), 35.1 (CH_3), 36.9 (CH_2), 43.6 (CH_2), 59.3 (CH_2), 71.7 (C). Anal. Calcd for $C_{14}H_{23}Cl$: C, 74.15; H, 10.22. Found: C, 73.98; H, 10.22.

4-Chloro-4-ethyl-2,2-dimethylhexane (**6**Cl). The precursor alcohol, 3-ethyl-5,5-dimethylhexan-3-ol (**6**OH),[23] was prepared from 3-pentanone and neopentyllithium. The crude product was purified by medium-pressure liquid chromatography (SiO_2, hexane−ether 3:1) and then distilled to give a colorless liquid: bp 67.5−68.5 °C/13 mmHg: ^{13}C NMR ($CDCl_3$, 67.94 MHz) δ 8.1(CH_3), 31.4 (C), 31.8 (CH_3), 32.3 (CH_2), 50.3 (CH_2), 76.4 (C). The alcohol was hydrochlorinated with dry HCl in CH_2Cl_2 at 0 °C until HCl absorption ceased. The reaction mixture was dried ($CaCl_2$) and then distilled to give a colorless liquid: bp 51.5−52 °C/10 mmHg: ^{13}C NMR ($CDCl_3$, 67.94 MHz) δ 9.2 (CH_3), 31.7 (CH_3), 32.3 (C), 34.8 (CH_2), 51.9 (CH_2), 80.3 (C). Since **6**Cl was unstable and contaminated by small amounts of olefins, the crude product was used without further purification.

3. Computational Methods

All calculations were performed using the Gaussian 98 package of computer programs.[24]

3.1. Standard Calculations. In all cases, a careful search of the most stable conformers was performed. All derivatives (cations, hydrocarbons, alcohols, and chlorides) from species **1**−**4**, **6**, and **8** were studied at the MP2/6-311G(d,p) level. Because of their very large size, derivatives of **5** and **7** were studied at the MP2/6-311G(d,p)//MP2/6-31G(d) level. It was established in the case of **8** and its derivatives that the differences between MP2/6-311G(d,p) and MP2/6-311G(d,p)//MP2/6-31G(d) energetic results are very small.

For all species, harmonic frequencies were computed at the HF/6-31G(d) level. These calculations were used to generate the zero-point energies (ZPE), thermal corrections to enthalpy (TCE), and entropies (*S*). ZPE values were scaled by the factor 0.9135.[25a] The vibrational contributions to enthalpy (excluding ZPE) and entropy were also corrected according to ref 25a. To this end, the computed harmonic vibrational frequencies were respectively multiplied by the factors 0.8905 and 0.8978 and the corresponding contributions calculated by means of standard equations.[25b]

These computational results are summarized in Table S3 of the Supporting Information Section.

3.2. Medium Effects. The medium effects were explored in the case of **1**H, **1**Cl, $\mathbf{1}^+$, **8**H, **8**Cl, and $\mathbf{8}^{+\cdot}$. In all cases, use was made of the PCM (polarizable continuum model) of Tomasi and colleagues[26] as implemented in the Gaussian 98 package of programs. This program performs the self-consistent computation of the electrostatic interaction between the polarizable solute and the reaction field of the solvent. It also calculates the cavitation, dispersive, and repulsive solvent−solute contributions to the energetics of the system. The medium was considered to be water (relative permittivity = 78.39). Symmetry constraints were lifted and the condition **opt = (nonlinear)** was applied.

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Table 1. Experimental and Computational Data for Reaction 2[a,b]

compd	ΔG°(2, X=Cl,exp)	ΔG°(2, X=Cl,th)	ΔG°(2, X=OH, exp)	ΔG°(2, X=OH,th)	$\Delta G^\circ_{(7)}$	ΔG°(2, X=Cl, calcdOH)
1X	5.3[c]	6.2		7.5	−1.3	
2X	1.1	1.8		3.3	−1.5	
3X	−1.9	−0.7		0.7	−1.4	
4X	−4.9	−3.9	−2.0	−1.6	−2.3	−4.3
5X	(−5.0)[d]	−7.1		−4.9	−2.2	
6X	−7.6	−8.0	−4.3	−5.4	−2.6	−6.9
7X	−13.3	−13.0	−8.9	−9.8	−3.2	−12.1
8X	0.0	0.0	0.0	0.0	0.0	0.0
9X[e]	−4.2	−4.2	−4.3	−3.3	−0.9	−5.2
10X[e]	−13.6	−12.4	−11.9	−11.1	−1.3	−13.2

[a] All values in kcal mol^{-1}. [b] All magnitudes defined in the text. [c] From ref 10a. [d] Less reliable value, see text. [e] Taken from ref 12.

Calculations of this sort are quite heavy. Thus, a rather modest level was used, HF/6-31G(d). Frequencies were computed numerically because analytical calculations for the solvation model were not available. Raw computational data were corrected as indicated in section 3.1.

The results are summarized in Table S4 of the Supporting Information Section.

4. Discussion

4.1. Relative Stabilities of Carbocations 1^+ to 8^+ in the Gas Phase. The results given in Table S1 are used to determine the ranking of carbocation stabilities relative to 1-adamantyl cation according to reaction 2. $\Delta G^\circ_{(2)}$ is given by the difference between the DPA onsets for 1-AdX(g) and the corresponding RX(g). The experimental values of $\Delta G^\circ_{(2)}$ are summarized in Table 1. Two sets of values, ΔG°(2,X=Cl) and ΔG°(2,X=OH), are obtained, corresponding respectively to the formal chloride and hydroxide exchanges, reactions 2a and 2b:

$$\text{1-Ad}^+(\text{g}) + \text{RCl(g)} \rightleftharpoons \text{1-AdCl(g)} + \text{R}^+(\text{g}) \qquad \Delta G^\circ(2,\text{X}{=}\text{Cl}) \quad (2a)$$

$$\text{1-Ad}^+(\text{g}) + \text{ROH(g)} \rightleftharpoons \text{1-AdOH(g)} + \text{R}^+(\text{g}) \qquad \Delta G^\circ(2,\text{X}{=}\text{OH}) \quad (2b)$$

These processes can be combined to yield reaction 7:

$$\text{1-AdOH(g)} + \text{RCl(g)} \rightleftharpoons \text{1-AdCl(g)} + \text{ROH(g)} \qquad \Delta G^\circ_{(7)} \quad (7)$$

where

$$\Delta G^\circ_{(7)} = \Delta G^\circ(2,\text{X}{=}\text{Cl}) - \Delta G^\circ(2,\text{X}{=}\text{OH}) \qquad (8)$$

$\Delta G^\circ_{(7)}$ is a "leaving group correction" that quantitatively links the scales of carbocation stabilities obtained through the experimental study of alcohols and chlorides. In principle, this magnitude can be determined experimentally. In practice, thermodynamic data for the relevant neutral species are seldom available. Fortunately, reaction 7 is an isodesmic process involving neutral species and reliable values of the corresponding changes in thermodynamic state functions can be obtained by means of ab initio calculations of even moderate level.[10a,12,17a]

We present in Table 1 the experimental values of ΔG°(2,X=Cl) and ΔG°(2,X=OH) for compounds **1**X to **8**X as well as the values of these magnitudes obtained by purely computational means (using data from Table S3). Also given are the values of ΔG°(2,X=Cl,calcdOH), that is, ΔG°(2,X=Cl) obtained from the experimental ΔG°(2,X=OH) and the corresponding correction through eq 7. For comparison purposes we report similar data for compounds **9**X (3-homoadamantyl derivatives) and **10**X (manxyl derivatives), taken from ref 12.

Table 2. Thermodynamics of Hydride Transfer Reactions[a,b]

compd	G°(9,th)	G°(10, X=Cl)	G°(9, calcdCl)	G°(10, X=OH)	G°(9, calcdOH)
1X	10.3	4.1	9.4	2.8	
2X	5.9	4.0	5.1	2.6	
3X	4.8	5.4	3.5	4.1	
4X	3.1	7.0	2.1	4.8	2.8
5X	−0.2	6.9		4.7	
6X	−0.1	8.0	0.4	5.4	1.1
7X	−3.0	9.9	−3.4	6.8	−2.1
8X	0.00	0.00	0.00	0.00	0.00
9X[c]	−1.8	2.4	−1.8	1.5	−2.8
10X[c]	−8.5	3.9	−9.7	2.6	−9.3

[a] All values in kcal mol^{-1}. [b] Magnitudes defined in the text. [c] From ref 12.

In a large study involving 16 different carbocations[12] (mostly bridgehead species) obtained from chlorides, bromides, and alcohols it was firmly established that the quantitative experimental rankings of stabilities determined from these different precursors were in remarkably good agreement, provided the appropriate "leaving group corrections" (such as the one indicated above) were applied. Our present results seem equally satisfactory. Thus, the experimental values of ΔG°(2,X=Cl) and ΔG°(2,X=Cl,calcdOH) are seen to agree within an average of 0.7 kcal mol^{-1}. The agreement between the experimental and ab initio values of ΔG°(2,X=Cl) is also excellent.[27]

4.2. Hydride Exchange Processes. A conceptually convenient, alternative way of ranking the thermodynamic stabilities of carbocations is through the hydride-transfer process, reaction 9:[10a,12,17a]

$$\text{R}{-}\text{H(g)} + \text{1-Ad}^+(\text{g}) \rightleftharpoons \text{R}^+(\text{g}) + \text{Ad-H(g)} \qquad \Delta G^\circ_{(9)} \quad (9)$$

$\Delta G^\circ_{(9)}$ can be obtained from the experimental values of ΔG°(2,X=Cl) and ΔG°(2,X=OH) and the appropriate leaving group correction, $\Delta G^\circ_{(10)}$, pertaining to reaction 10. As in the case of $\Delta G^\circ_{(7)}$, $\Delta G^\circ_{(10)}$ is obtained computationally.

$$\text{R}{-}\text{H(g)} + \text{1-Ad-X(g)} \rightleftharpoons \text{R}{-}\text{X(g)} + \text{Ad-H(g)} \qquad \Delta G^\circ_{(10)} \quad (10)$$

where X = Cl, OH.

We present in Table 2 the values of $\Delta G^\circ_{(9)}$ based on the experimental data for ΔG°(2,X=Cl) and ΔG°(2,X=OH), corrected through combination with $\Delta G^\circ_{(10)}$ as well as the purely computational value ΔG°(9,th), obtained from the data given in Table S3. Data for **9**X and **10**X are reported for comparison.

The agreement between the computed and experimental values of $\Delta G^\circ_{(9)}$ is quite satisfactory because, for the set of 11 data, the values agree within an unsigned average of 0.6 kcal mol^{-1}. This can be considered to substantiate the self-consistency of our approach.

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(26) (a) Miertu, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117−129. (b) Miertu, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1982**, *65*, 239−245. (c) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327−331.

(27) The following correlation equation holds: $\Delta G^\circ(2,\text{X}{=}\text{Cl,th}) = 0.64(\pm 0.25) + [1.038(\pm 0.039)]\Delta G^\circ(2,\text{X}{=}\text{Cl,exp})$. In kcal mol^{-1}, $R^2 = 0.993$ with $n = 7$ and sd = 0.6 kcal mol^{-1}. This correlation includes data for compounds **1**Cl to **4**Cl and **6**Cl to **8**Cl. The less reliable datum for **5**Cl was not included.

Table 3. Experimental Differential Gibbs Activation Energies for the Solvolysis of Compounds **1**Cl−**10**Cl[a,b]

compd	$-\delta\Delta G^{\ddagger}$(80% EtOH,70 °C)	$-\delta\Delta G^{\ddagger}$(97% HFIP,25 °C)
1Cl	4.3	0.6
2Cl	4.5	1.8
3Cl	5.2	3.0
4Cl	6.3	4.3
5Cl	6.6	4.6
6Cl	6.7	5.2
7Cl	8.1	7.0
8Cl	(0.0)	(0.0)
9Cl	3.8[c]	3.9
10Cl	10.8[c]	

[a] All values in kcal mol^{-1}. See Table S2 for rate data. [b] Defined through eq 11. [c] Based on data from ref 12.

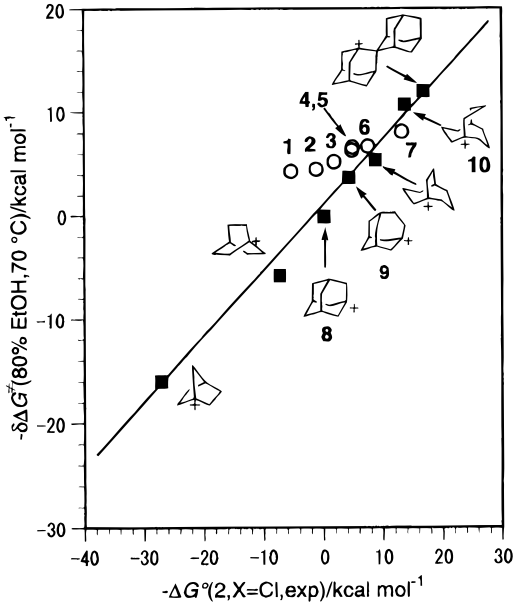

Figure 1. Plot of $-\delta\Delta G^{\ddagger}$(80% EtOH, 70 °C) vs $-\Delta G°$(2,X=Cl,exp) for **1**Cl−**7**Cl, open circles, with reference to "bridgehead line", filled squares. For the data for the "bridgehead line" see Tables 1 and 2 and refs 10a and 12.

$\Delta G°_{(10)}$ has an interesting meaning, as it includes differential strain effects relative to hydrogen. In the case of bridgehead compounds, absolute values of this magnitude are generally smaller. Here, they are substantial. Thus, on the basis of $\Delta G°_{(9)}$, the only cation significantly more stable than 1-Ad$^+$ is **7**$^+$, the difference being about 3 kcal mol^{-1}. The difference for this same couple, in terms of $\Delta G°$(2,X=Cl), amounts to 13.3 kcal mol^{-1}. This suggests that the structural effects on solvolysis rates observed in this study are very largely affected by the release of strain attending the loosening of the C−Cl bond.

4.3. Structural Effects on Solvolysis Rates. Differential activation Gibbs energy changes for the solvolysis of compounds **1**Cl to **7**Cl relative to **8**Cl, $\delta\Delta G^{\ddagger}$, are given by eq 11:

$$\delta\Delta G^{\ddagger} = -RT\ln(k/k_{o}) \tag{11}$$

Values of $\delta\Delta G^{\ddagger}$ for these reactions in 80% EtOH at 70 °C and 97% HFIP at 25 °C are collected in Table 3 and are plotted against $\Delta G°_{(2)}$ in Figures 1 and 2.

The plot for the chlorides **1**Cl to **7**Cl in 80% EtOH in Figure 1 utilizes 70 °C data since the bridgehead line has been defined for data at 70 °C;[10a,12] however, the use of 25 °C data only shifts the points upward by ca. 0.6 kcal mol^{-1}. It is also remarkable that the bridgehead line is almost unchanged for the solvolysis in HFIP at 25 °C: the $\delta\Delta G^{\ddagger}$ value for bicyclo[2.2.2]oct-1-yl tosylate[28] vs 1-adamantyl tosylate[29] under these conditions is 5.7 kcal mol^{-1},[30] very close to 5.6 kcal mol^{-1} for the corresponding bromides in 80% EtOH.[10a] Similarly, the $\delta\Delta G^{\ddagger}$ value for 3-chlorohomoadamantane (**9**Cl) and **8**Cl in 97% HFIP at 25 °C is −4.0,[31] which is again close to −3.6 kcal mol^{-1} in 80% ethanol at 70 °C.[32]

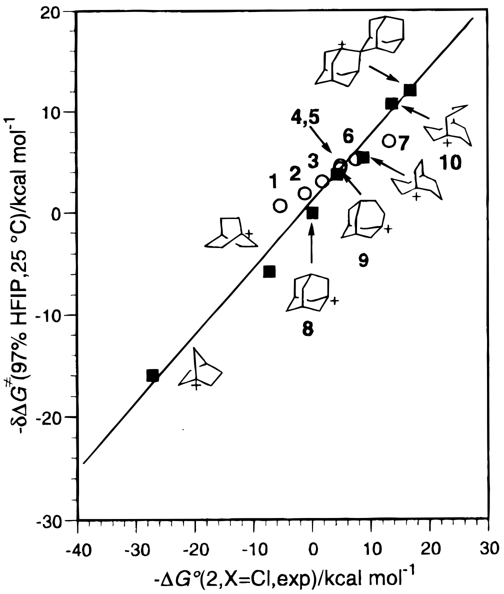

Figure 2. Plot of $-\delta\Delta G^{\ddagger}$(97% HFIP, 25 °C) vs $-\Delta G°$(2,X=Cl,exp) for **1**Cl−**7**Cl, open circles, with reference to "bridgehead line", filled squares, defined for the solvolysis data in 80% EtOH at 70 °C. For the data for the "bridgehead line" see Tables 1 and 2 and refs 10a and 12.

The following characteristic features are noted. First, the data points in 80% ethanol for **1**Cl−**5**Cl deviate significantly upward from the bridgehead line, but the deviation decreases as the steric crowding increases, and finally the points for **6**Cl and **7**Cl essentially fall on the bridgehead line.[33] The deviation for **1**Cl from the line amounts to 7.4 kcal mol^{-1}. Second, the data points for 97% HFIP, a solvent having a very low nucleophilicity,[2b] approach more closely to the line, but there still is a difference of 3.1 kcal mol^{-1} for **1**Cl.[35] Notably, the $\delta\Delta G^{\ddagger}$ values for **7**Cl in 80% ethanol and 97% HFIP are essentially the same, indicating that *the protection of the backside of the open chain, tertiary alkyl system by steric congestion can change the behavior of the system to that of a bridgehead one with respect to NSP*.[36] Therefore, the major portion in the deviation of 7.4 kcal mol^{-1} for **1**Cl in 80% ethanol (Figure 1) would most

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[28] Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466−5475

[29] Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 4821−4828.

[30] Specific rates in 97% HFIP at 25 °C for bicyclo[2.2.2]oct-1-yl tosylate (1.52 × 10^{-3} s^{-1})[28] and for 1-adamantyl tosylate (27 s^{-1})[29] were used.

[31] Based on the conductometrically determined specific rates of solvolysis of **9**Cl in 97% HFIP: 0.0687 s^{-1} (0.0 °C), 0.179 s^{-1} (10.0 °C), and 0.294 s^{-1} (15.0 °C), which give an extrapolated specific rate of 0.705 s^{-1} at 25.0 °C.

[32] $\Delta G°$(2,X=Cl) for 3-chlorohomoadamantane (**9**Cl) has been determined to be −4.3 kcal mol^{-1}.[12] The rate ratio between **9**Cl and **8**Cl has been reported as 211 in 80% ethanol at 70 °C: Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189−3199.

[33] Recently, the dispersion of data points that is found in the Grunwald−Winstein type relation in the solvolysis of **7**Cl[3b,c] has been ascribed to possible mechanistic change to concerted elimination[34a] or differential ion-pair return.[34b] However, the essential agreements of the $\delta\Delta G^{\ddagger}$ data for **7**Cl with the bridgehead line suggest the discrete formation of an ion-pair intermediate that is usually the case in the solvolysis of bridgehead substrates.

probably be ascribed to NSP to the carbenium carbon in the transition state for ionization.

According to Jorgensen's theoretical calculations on t-Bu$^+$Cl$^-$ ion pairs in water, the Lewis base type hydration toward the carbenium carbon contributes to stabilization of a contact ion pair at 2.75 Å separation by 7.8 kcal mol^{-1}. The present results that the data points for the highly congested **7**Cl fall on the bridgehead line and that the difference in $\delta\Delta G^\ddagger$ for **1**Cl between 80% ethanol and 97% HFIP corresponds to 4.3 kcal mol^{-1} suggest that NSP amounts to at least 4.3 kcal mol^{-1} in the solvolysis of **1**Cl in 80% ethanol. If NSP is not important in 97% HFIP, the acceleration of solvolysis amounting to ca. 3 kcal mol^{-1} for **1**Cl in this solvent would be attributed to other effects. A more efficient dielectric stabilization of the relatively small t-Bu$^+$ Cl$^-$ ion pair than bridgehead and bulky open-chain compounds might be a responsible factor.

We have carried out a preliminary exploration of the solvation problem by quantum-mechanical methods. From the information available at this point[37] a treatment of medium effects on the transition states for the solvolysis of the systems studied herein seems well beyond our computational capabilities. Thus, we have simply explored the effect of the solvent on the energetics of reactions 12 and 13:

$$t\text{-C}_4\text{H}_9{}^+ + 1\text{-AdCl} \rightleftharpoons t\text{-C}_4\text{H}_9\text{Cl} + 1\text{-Ad}^+ \qquad \Delta G^\circ{}_{(12)} \quad (12)$$

$$t\text{-C}_4\text{H}_9{}^+ + 1\text{-AdH} \rightleftharpoons i\text{-C}_4\text{H}_{10} + 1\text{-Ad}^+ \qquad \Delta G^\circ{}_{(13)} \quad (13)$$

Using the data given in Table S4, we obtain values of respectively -1.7 and -4.3 kcal mol^{-1} for ΔG°(12,g) and ΔG°(13,g) at the HF/6-31+G(d) level. Modeling of the same reactions in water (at the same level) leads to values for ΔG°(12,aq) and ΔG°(13,aq) of 3.7 and 1.7 kcal mol^{-1}, respectively.

The level of calculation used for these comparisons is admittedly low and this explains the modest quality of the agreement between ΔG°(12,g) and ΔG°(13,g) obtained here and the corresponding values reported in previous sections. This notwithstanding, *these results show the reversal of the ranking of stabilities of* ***1***$^+$ *and* ***8***$^+$ *on going from the gas phase to aqueous solution.* While we believe that this is the first time this result has been arrived at computationally, the existence of this reversal on going from the gas phase to solution has been known for some time. Thus, Arnett and Petro[38] have reported enthalpies of ionization of t-C$_4$H$_9$Cl and 1-AdCl in SbF$_5$/SO$_2$-ClF solutions of -25.4 and -21.6 kcal mol^{-1}. This leads to an approximate value of ΔH°(13,SO$_2$ClF) of 3.8 kcal mol^{-1}. A value of ΔH°(13,CH$_2$C$_2$) of 4.4 kcal mol^{-1} was obtained for the same process in SbF$_5$/CH$_2$Cl$_2$.[39] While all these results are known to be affected by medium effects, ion-pairing, etc.,[40] it is rewarding that *the magnitude* of our results compares nicely with these data. In any case, all this agrees with the fact that larger substituents around a cationic center increase the stability of the ion in the gas phase thanks to their larger polarizability, and that this effect is either offset[41] or even dramatically reversed in solution.[42] These results seem to reflect the importance of the thermodynamics of the process examined in this work and the role played by the nonspecific, largely dielectric effect of the solvent. However, the direct extension of these results to the analysis of the experimental kinetic effects is not warranted.

5. Conclusions

(1) The experimental indexes of gas-phase stability of open-chain *tertiary*-alkyl carbocations from **1**X$-$**7**X relative to the 1-adamantyl cation (**8**$^+$) from **8**X, ΔG°(2,X=Cl) and ΔG°(2,X=OH), were obtained by means of FT ICR techniques. These values are in very good agreement with the corresponding computational values obtained at the MP2/6-311G(d,p) or MP2/6-311G(d,p)//MP2/6-31G(d) levels.

(2) The differential activation Gibbs energy changes, $\delta\Delta G^\ddagger$ (eq 11) for the solvolysis of **1**Cl to **7**Cl relative to **8**X were plotted against $\Delta G^\circ{}_{(2)}$ and compared with the case for bridgehead compounds, the so-called "bridgehead line". For the solvolysis in 80% ethanol the data point for **1**Cl deviates upward by 7.4 kcal mol^{-1}, whereas the deviation decreases with increasing steric crowding, and the points for **6**Cl and **7**Cl finally fall on the bridgehead line. A similar plot for the solvolysis in 97% HFIP (1,1,1,3,3,3-hexafluoro-2-propanol), a solvent having a very low nucleophilicity, shows closer approach to the "bridgehead line", but there still exists the difference of 3.1 kcal mol^{-1} for **1**Cl. The discrepancy of 4.3 kcal mol^{-1} between the two solvents, 80% ethanol and HFIP, would reasonably be ascribed to the minimum value of nucleophilic solvent participation for the solvolysis of **1**Cl in 80% ethanol.

(3) The faster rate of solvolysis of **1**Cl than **8**Cl corresponding to $\delta\Delta G^\ddagger \approx 0.6$ kcal mol^{-1} even in 97% HFIP is not in harmony with the greater value of ΔG°(2,X=Cl) (5.3 kcal mol^{-1}) favoring 8$^+$ over 1$^+$ in the gas phase. Computation for t-Bu$^+$ + 1-AdCl $\rightleftharpoons$ t-BuCl + 1-Ad$^+$ (eq 12) and t-Bu$^+$ + 1-AdH $\rightleftharpoons$ t-BuH + 1-Ad$^+$ (eq 13) in the gas phase and in water at the HF/6-31G(d) level (using the polarizable continuum model in water) gave negative values for ΔG°(12,g) and ΔG°(13,g) and positive values for ΔG°(12,aq) and ΔG°(13,aq). This shows the reversal of the ranking of stabilities of **1**$^+$ and **8**$^+$ on going from the gas phase to aqueous solution. The results agree with the fact that larger substituents around a cationic center increase the stability of the ion in the gas phase thanks to their larger polarizability, and that this effect is either offset or even dramatically reversed in solution.

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[35] It has been reported that the $\delta\Delta G^\ddagger$ value for **1**Cl in 97% HFIP changes only to an extent of ±0.3 kcal mol^{-1} for several kinds of leaving group.[2c]

[36] Evaluation of the data points for **1**Cl$-$**7**Cl in terms of the 95% confidence level bands of the bridgehead line[10a,12] indicates that the points for **6**Cl and **7**Cl in 97% HFIP fall well within the line. For 80% ethanol solvent, the point for **6**Cl is on the borderline and that for **7**Cl is well within the line.

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[39] Arnett, E. M.; Petro, S. C. *J. Am. Chem. Soc.* **1978**, *100*, 5408$-$5415.

[40] Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 3522$-$3524.

[41] Abboud, J.-L. M.; Catalán, J.; Elguero, J.; Taft, R. W. *J. Org. Chem.* **1988**, *53*, 1137$-$1140 and references therein.

[42] Arnett, E. M.; Abboud, J.-L. M. *J. Am. Chem. Soc.* **1975**, *97*, 3865$-$3867.

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Supporting Information Available: The DPA experiments, data for the onset for reaction 4, solvolysis rate data, results of theoretical calculations for species in the gas phase and in solution, ^{13}C NMR spectra for **5**Cl and **6**Cl, and specific rates and the Grunwald−Winstein type plots for **5**Cl−**7**Cl in nonaqueous solvents (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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