

## Influence of Carbocation Stability in the Gas Phase on Solvolytic Reactivity: Beyond Bridgehead Derivatives

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The intrinsic gas-phase stability of bicyclic secondary carbocations has been determined by Dissociative Proton Attachment of chlorides and alcohols, respectively. From these data, Gibbs free energies for hydride transfer relative to 1-adamantyl ( $\Delta_r G^\circ(8, \text{exp})$ ) are derived after application of appropriate leaving group corrections, and good agreement with theoretical values, ( $\Delta_r G^\circ(8, \text{comp})$ ), calculated at the G2(MP2) or MP2/6-311G(d,p) level, is reached (Table 1). The relative rate constants for solvolysis ( $\log(k/k_0)$ ) of the bicyclic secondary derivatives correlate with the stabilities of the respective carbocations in the same manner as tertiary bridgehead derivatives, but simple monoderivatives and acyclic derivatives solvolyze faster than predicted on the grounds of the ion stabilities. The corresponding stabilities of cyclopropyl- and benzyl-substituted carbocations have been obtained by a combination of experimental and computational data available in the literature with computational methods. Correlation of the rate constants for solvolysis vs ion stabilities for these compounds reveals a trend similar to that observed for bridgehead derivatives, but with much more scatter, which is attributed to nucleophilic solvent participation and/or nucleophilic solvation.

### 1. Introduction

The  $S_N1$  solvolysis rates for a series of similar compounds under similar reaction conditions reflect directly the stability of their carbocationoid intermediates.<sup>1</sup> This hypothesis developed slowly over the last 50 years. It grew out of the observations of parallel reactivity profiles for solvolysis reactions and reactions involving  $sp^3$ – $sp^2$  interconversions at the reacting carbon atom, such as alcohol oxidation with chromic acid<sup>2</sup> or ketone reduction with sodium borohydride.<sup>3</sup> The lack of solvolytic reactivity of bridgehead derivatives of the 1-norbornyl and trypticene type<sup>4</sup> was taken as indicative for the preferentially planar structure of carbenium ions, long before the planar structure of the *tert*-butyl cation was experimentally determined by X-ray crystallography.<sup>5</sup> The first attempt to rationalize rate constants of solvolysis of secondary derivatives used strain estimates for carbenium ions, based on IR-stretching frequencies of carbonyl groups and nonbonded interactions.<sup>6</sup> These qualitative estimates were subsequently replaced by empirical force-field cal-

culations which were particularly successful in the context of bridgehead solvolysis,<sup>7</sup> but were also applied with various degrees of sophistication toward the solvolysis of secondary aliphatic derivatives.<sup>8</sup> However, owing to the empirical nature of these methods, the significance of the results could not be truly assessed. More recently, Arnett et al.<sup>1,9</sup> reported heats of ionization ( $\Delta H_i$ ) of secondary and tertiary alkyl and aralkyl chlorides to stable carbocations in  $\text{SbF}_5$ –solvent mixtures. Correlation of the heats of ionization with the respective free energies of activation for ethanolysis afforded a straight line over a range of 22 kcal/mol for  $\Delta H_i$ . These results established the near energetic equivalency of

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carbocations in solution and the transition state for solvolysis. Initial attempts to establish an analogous correlation between solvolytic reactivity of bridgehead and bridgehead-like halides and the stability of the respective carbocations in the gas phase by ion cyclotron resonance (ICR) met only limited success.<sup>10</sup> Although the majority of the ion stabilities could be correlated with the rate constants for solvolysis, some of the ions appeared to have rearranged under the conditions of the ICR experiments.

Some years ago, we developed the dissociative proton attachment method (DPA) based on Fourier Transform Ion Cyclotron Resonance Spectroscopy (FT ICR) to determine the stability of carbocations in the gas phase. Comparison of the experimental ion stabilities with ion stabilities calculated by ab initio methods at the MP2/6-311G\*\* level indicated the absence of rearrangements. In addition, correlation of the experimental ion stabilities with the rate constants for solvolysis under standard conditions<sup>11</sup> afforded a straight line covering the full rate range of bridgehead derivatives.<sup>12</sup> More recently, it was found that even 2-adamantyl derivatives which are typical representatives of secondary derivatives solvolyzing without nucleophilic solvent participation fit the correlation between ion stability and solvolytic reactivity, as established for bridgehead derivatives.<sup>13</sup> The same applies to tertiary aliphatic derivatives in the absence of nucleophilic solvent participation.<sup>14</sup>

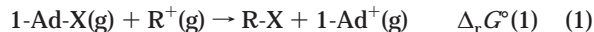
In the past, our investigations were essentially restricted to aliphatic tertiary derivatives and the respective carbocations. This restriction assured a certain mechanistic uniformity for the solvolysis, and ion stabilities were essentially determined by strain. However, several factors affecting carbocation stability have been identified, such as resonance, aromaticity, and homoaromaticity. In most cases, these effects were identified on the grounds of solvolytic reactivities, but the ion stabilities were not independently determined. We have now extended the DPA approach to carbocations of different structures with the hope of establishing a correlation between ion stabilities in the gas phase and solvolytic reactivity, analogous to that prevailing in the series of bridgehead derivatives. Some of the results are included in a forthcoming review.<sup>15</sup>

## 2. Experimental Section

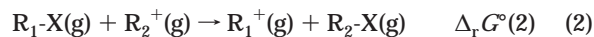
**2.1. Gas-Phase Studies. 2.1.1. The FT ICR Spectrometer.** The measurements were performed with a modified Bruker CMSD 47 FT ICR mass spectrometer,<sup>16</sup> which has been used in previous studies.<sup>12–14</sup> The field strength of the magnet, 4.7 T, allows the monitoring of ion–molecule reactions for relatively long periods of time and the performing of experi-

ments under “high” pressures (up to ca.  $5 \times 10^{-4}$  mbar). The temperature of the cell ( $331 \pm 2$  K) was determined by using a calibrated platinum thermometer (platinum resistor) located close to one of the repeller plates of the ICR cell. The experimental setup is similar to the one described by McMahon et al.<sup>17</sup>

**2.1.2. The DPA Method.** Consider reaction 1, the halide or hydroxide exchange between 1-adamantyl cation (1-Ad<sup>+</sup>) and a carbocation R<sup>+</sup> in the gas phase.

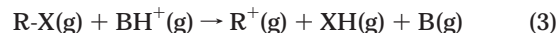


The process is a particular case of reaction 2, the latter providing [by means of  $\Delta_r G^\circ(2)$ ] a quantitative ranking of the intrinsic gas-phase stability of carbocations R<sub>1</sub><sup>+</sup> and R<sub>2</sub><sup>+</sup>:

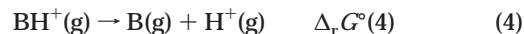


Conventionally, these reactions can be studied directly by means of ICR.<sup>18</sup> The method is limited, however, to cations which do not easily rearrange. Furthermore, the number of reference compounds allowing the direct determination of  $\Delta_r G^\circ(2)$  is very small. The DPA method allows the determination of the intrinsic gas-phase stability of carbocations R<sup>+</sup>(g) relative to the 1-adamantyl cation (1-Ad<sup>+</sup>) by means of the formal hydride transfer process (1).<sup>19</sup>

In the DPA approach  $\Delta_r G^\circ(2)$  is determined indirectly: Electron ionization of B in the spectrometer leads to the formation of BH<sup>+</sup> which, in turn, protonates the halide or alcohol precursor R–X. The protonation often leads to ion–molecule complexes that readily decompose to yield free ions R<sup>+</sup>(g) and neutral XH(g) molecules according to eq 3.



The gas-phase basicity of the base B, GB(B), is defined as the standard Gibbs energy change for reaction 4,  $\Delta_r G^\circ(4)$ :



The DPA method consists of determining the base B such that its conjugate acid is just able to transfer a proton to R–X (X = halide, OH). The DPA onset is defined by the average of the highest GB (GB<sub>1</sub>) where the ion is observed, and the lowest GB (GB<sub>2</sub>), where the ion is *not* observed, where GB is the gas-phase basicity of bases B<sub>1</sub> and B<sub>2</sub>, respectively. For example, in the case of 1-chloroadamantane (5-Cl), the conjugate acids of all bases weaker than and up to (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CO (GB = 193.08) transfer a proton to 5-Cl and the ion 5<sup>+</sup> is observed. However, with *t*-BuOMe (GB = 194.17), proton transfer to 5-Cl does no longer occur, and the ion is not observed.<sup>12</sup> If B<sub>(RX)</sub> and B<sub>(AdX)</sub> stand for the two bases defining the DPA onsets of RX(g) and

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**TABLE 1.** Relevant Thermodynamic Properties Pertaining to Reactions of Ions  $1^+$  to  $7^+$  <sup>a</sup>

species	$\Delta_r G^\circ(1,X)^b$	$\Delta_r G^\circ(7)^b$	$\Delta_r G^\circ(1,X=Cl)^b$	$\Delta_r G^\circ(9)^b$	$\Delta_r G^\circ(8,comp)^b$	$\Delta_r G^\circ(8,exp)^b$
1-Cl	-22.2 <sup>c</sup>	0.00	-22.2 <sup>c</sup>	-3.63	-27.40	-25.8
2-Cl	1.3 <sup>c</sup>	0.00	1.3 <sup>c</sup>	-3.18	-3.90	-1.9
2-OH	1.2 <sup>c</sup>	-0.10	1.1 <sup>d</sup>	-3.34	-3.90	-2.1
3-OH	4.3 <sup>c</sup>	2.60	6.9 <sup>d</sup>	-3.90	0.95	0.4
4-Cl	+1.6 <sup>c</sup>	0.00	1.6 <sup>c</sup>	-3.90	-3.4	-2.3
5-Cl	0.00	0.00	0.00	0.00	0.00	0.00
5-OH	0.00	0.00	0.00 <sup>d</sup>	0.00	0.00	0.00
6-OH	24.4 <sup>c</sup>	4.60	29.0 <sup>d</sup>	-1.07	24.6	23.3
7-Cl	-7.6 <sup>e</sup>	0.00	0.00	-1.94 <sup>e</sup>	-10.5 <sup>e</sup>	-9.5 <sup>e</sup>

<sup>a</sup> All values in kcal mol<sup>-1</sup>. <sup>b</sup> Defined in the text. <sup>c</sup> Experimental, this work. <sup>d</sup> Obtained from the experimental  $\Delta_r G^\circ(1,X=OH)$ , corrected by means of eq 7, see text. <sup>e</sup> In the particular case of  $7^+$ ,  $\Delta_r G^\circ(9)$  is simply the standard Gibbs energy change for the isomerization reaction 2-AdCl(g)  $\rightarrow$  1-AdCl(g).

AdX(g) as determined under identical experimental conditions, eq 5 holds:

$$\Delta_r G^\circ(1) \approx GB(B_{(RX)}) - GB(B_{(AdX)}) \quad (5)$$

Thus the determination of the relative stabilities of  $R_1^+(g)$  and  $R_2^+(g)$  through the formal equilibria 1 and 2 reduces to that of the DPA onsets of the corresponding precursors (reaction 3). The experimental determination of the onsets involves a bracketing procedure. The DPA onsets were probed with different reference bases having close GB values. The  $\Delta_r G^\circ(2)$  values determined by this method are formally less precise (uncertainties estimated to ca. 2 kcal mol<sup>-1</sup>) than those obtained by direct equilibration. This inconvenience is largely offset by the extremely mild conditions of the experiment and by the availability of over one thousand reliable GB values.<sup>20</sup> Ions generated by DPA are not vibrationally excited and, therefore, are less prone to undergo rearrangement than when generated by electron impact.

A table of the raw experimental results (Table S1) is given in the Supporting Information. Further experimental details are also given as Supporting Information.

**2.2. Computational Results.** Calculations were performed at the G2(MP2),<sup>21</sup> MP2/6-311(d,p),<sup>22</sup> and HF/6-31G(d)<sup>22</sup> levels, using the Gaussian 98 package of programs.<sup>23</sup> For the sake of consistency with the G2(MP2) calculations, harmonic vibrational frequencies were scaled with the factor 0.8929.

The detailed results of the calculations are summarized in the Supporting Information (Tables S2, S3, and S4.)

**2.3. Syntheses and Rate Constants for Solvolysis. 2.3.1. Synthesis of Halides and Alcohols.** Most of the neutrals used in this work are commercially available. The 7-norbornyl derivatives were synthesized from 7-*tert*-butoxynorbornadiene, which was converted to the acetate.<sup>24</sup> Hydrolysis of the acetate afforded 7-norbornadienol (3-OH), while reduction with LiAlH<sub>4</sub> led to *anti*-7-norborneol (2-OH). 7-*anti*-Norborneol (2-OH) was converted to the chloride (2-Cl) with SOCl<sub>2</sub>,<sup>25</sup> and the

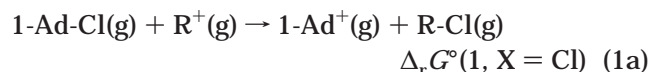
chloride was reduced to 7-chloronorbornane (1-Cl) via catalytic hydrogenation with Pd/C.<sup>26</sup> Tricyclopropylmethanol (6-OH) was obtained from dicyclopropyl ketone according to Hart and Sandri.<sup>27</sup>

4-Chlorohomoadamantane (4-cholortricyclo[4.3.2.2<sup>3,8</sup>]undecan, 4-Cl) was synthesized via ring expansion of 2-adamantanone with diazomethane, followed by reduction to the alcohol (4-OH),<sup>28</sup> which reacted in 54% yield to the chloride with SOCl<sub>2</sub>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.31–4.37, *m*, 1H), 1.42–2.78 (*m*, 16H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 26.6 (d), 26.8 (d), 30.4 (t), 30.9 (d), 34.7 (t), 36.2 (t), 38.4 (t), 40.6 (t), 41.5 (d), 46.0 (t), 67.5 (t). MS: 186 (1), 184 (5), 148 (100). HR MS: 184.0978 (C<sub>11</sub>H<sub>17</sub>Cl<sup>+</sup>; calcd 184.1019), 148.1248 (C<sub>11</sub>H<sub>16</sub><sup>+</sup>; calcd 148.1252).

**2.3.2. Rate Constants for Solvolysis.** The rate constants for solvolysis were extracted from the literature. They are expressed relative to the appropriate 1-adamantyl derivative reacting, whenever possible, under identical conditions (identical solvent and leaving group) or with use of appropriate conversion factors for solvents for which rate constants for adamantyl derivatives were not available. Since most of the data for bridgehead solvolysis have been determined at 70 °C, and since bridgehead solvolysis represents our reference system, all other rate constants are converted to 70 °C by means of the Arrhenius equation assuming constant A-factors. Details are given in the Supporting Information (Table S5), and the final results are included in Table 2.

### 3. The Database and Its Construction

$\Delta_r G^\circ(1,X=Cl)$ , the standard Gibbs energy change for reaction 1a, that is, reaction 1 with X = Cl, is quite convenient for obtaining a quantitative ranking of stabilities of carbenium ions in the gas phase



This property is used here again, the  $\Delta_r G^\circ(1,X=Cl)$  values being obtained (a) from a series of new DPA experiments, (b) from previous experimental data, and (c) computationally. In what follows, ions are numbered as shown in Tables 1 and 2.

**3.1. New Experimental Results.** New experimental values of  $\Delta_r G^\circ(1,X=Cl)$  and  $\Delta_r G^\circ(1,X=OH)$  were determined in this work for ions  $1^+$ ,  $2^+$ ,  $3^+$ ,  $4^+$ , and  $6^+$ . They are presented in Table 1. Raw experimental data are summarized as Supporting Information (Table S1). In

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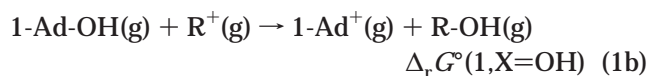
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**TABLE 2.** Relative Ion Stabilities,  $\Delta_r G^\circ(1, X=Cl)$ ,<sup>a</sup> for Ions  $1^+ - 29^+$  and Rate Constants for Solvolysis of Precursors Relative to 1-Adamantyl

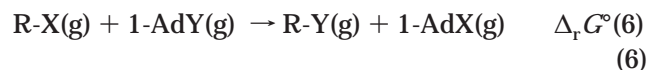
no.	ion	$\Delta_r G^\circ(1, X=Cl)^a$	method	$\log(k/k_0)^b$	$\log(k/k_0)^c$
1 <sup>+</sup>	norbornan-7-ylum (C <sub>7</sub> H <sub>11</sub> <sup>+</sup> )	-22.2 ± 2.8	A <sup>d</sup>	-9.5	
2 <sup>+</sup>	norbornen-7-ylum (C <sub>7</sub> H <sub>9</sub> <sup>+</sup> )	1.3 ± 2.8	A <sup>d</sup>	-0.1	
3 <sup>+</sup>	norbornadien-7-ylum (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> )	6.9 ± 3.0	A <sup>d</sup>	2.4	
4 <sup>+</sup>	homodamantan-4-ylum (C <sub>11</sub> H <sub>17</sub> <sup>+</sup> )	1.6 ± 2.8	A <sup>d</sup>	-1.4	
		-0.9 ± 3.0	B <sup>e</sup>		
5 <sup>+</sup>	adamantan-1-ylum (C <sub>10</sub> H <sub>15</sub> <sup>+</sup> )	(0.00)	C <sup>f</sup>	0.00	0.00
6 <sup>+</sup>	tricyclopropylmethylum [(c-C <sub>3</sub> H <sub>5</sub> ) <sub>3</sub> C <sup>+</sup> ]	29.0 ± 3.0	A <sup>d</sup>	12.2	
7 <sup>+</sup>	adamantan-2-ylum (C <sub>10</sub> H <sub>15</sub> <sup>+</sup> )	-7.6 ± 2.8	D <sup>g</sup>	-3.3	-4.80
		-11.3 ± 3.0	E <sup>h</sup>	-4.6	
8 <sup>+</sup>	benzylum (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> )	-5.8 ± 1.0	F <sup>i</sup>	-1.9	
9 <sup>+</sup>	1-phenylethan-1-ylum (C <sub>8</sub> H <sub>9</sub> <sup>+</sup> )	1.7 ± 1.0	F <sup>i</sup>	2.3	
10 <sup>+</sup>	2-phenylpropan-2-ylum (C <sub>9</sub> H <sub>11</sub> <sup>+</sup> )	6.4 ± 1.0	F <sup>i</sup>	5.1	
11 <sup>+</sup>	diphenylmethanylium (C <sub>13</sub> H <sub>11</sub> <sup>+</sup> )	13.4 ± 3.0	G <sup>j</sup>	3.8	
12 <sup>+</sup>	1,1-diphenylethan-1-ylum (C <sub>14</sub> H <sub>13</sub> <sup>+</sup> )	23.5 ± 3.0	G <sup>j</sup>	7.7	
13 <sup>+</sup>	triphenylmethanylium (C <sub>9</sub> H <sub>15</sub> <sup>+</sup> )	28.4 ± 3.0	G <sup>j</sup>	9.0	
14 <sup>+</sup>	cyclopropylmethylum (c-C <sub>3</sub> H <sub>5</sub> -CH <sub>2</sub> <sup>+</sup> )	-7.1 ± 2.0	H <sup>k</sup>	-0.3	
15 <sup>+</sup>	1-cyclopropylethan-1-ylum (c-C <sub>3</sub> H <sub>5</sub> -CHCH <sub>3</sub> <sup>+</sup> )	2.0 ± 2.0	H <sup>k</sup>	2.6	
16 <sup>+</sup>	2-cyclopropylpropan-2-ylum [c-C <sub>3</sub> H <sub>5</sub> -C(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup> ]	14.2 ± 2.0	H <sup>k</sup>	7.5	
17 <sup>+</sup>	dicyclopropylmethylum [(c-C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> -CH <sup>+</sup> ]	12.0 ± 2.0	H <sup>k</sup>	6.9	
18 <sup>+</sup>	1,1-dicyclopropylethan-1-ylum [(c-C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> CCH <sub>3</sub> <sup>+</sup> ]	22.1 ± 2.0	H <sup>k</sup>	8.8	
19 <sup>+</sup>	propan-2-ylum ( <i>iso</i> -C <sub>3</sub> H <sub>7</sub> <sup>+</sup> )	-22.7 ± 2.6	I <sup>l</sup>	-3.3	-6.65
20 <sup>+</sup>	butan-2-ylum ( <i>sec</i> -C <sub>4</sub> H <sub>9</sub> <sup>+</sup> )	-18.9 ± 3.0	I <sup>l</sup>	-3.1	-5.65
21 <sup>+</sup>	2-methylpropan-2-ylum ( <i>tert</i> -C <sub>4</sub> H <sub>9</sub> <sup>+</sup> )	-6.0 ± 1.0	J <sup>m</sup>	1.76	0.36
22 <sup>+</sup>	cyclopentylum (c-C <sub>5</sub> H <sub>9</sub> <sup>+</sup> )	-13.6 ± 1.5	I <sup>l</sup>	-2.2	-4.41
23 <sup>+</sup>	norbornan-2-ylum	-3.0	K <sup>n</sup>	-1.1 <sup>o</sup>	-1.10
24 <sup>+</sup>	bicyclo[2.2.2]octan-1-ylum	-7.4	K <sup>n</sup>	-3.6 <sup>o</sup>	-3.69
25 <sup>+</sup>	homoadamant-3-ylum	4.2	K <sup>n</sup>	1.9 <sup>o</sup>	2.48
26 <sup>+</sup>	[1]diadamantan-1-ylum	16.7	K <sup>n</sup>	7.7 <sup>o</sup>	
27 <sup>+</sup>	bicyclo[3.3.3]undecan-1-ylum	13.6	K <sup>n</sup>	6.9 <sup>o</sup>	
28 <sup>+</sup>	bicyclo[3.3.2]decan-1-ylum	8.7	K <sup>n</sup>	3.5 <sup>o</sup>	
29 <sup>+</sup>	norbornan-1-ylum	-27.3	K <sup>n</sup>	-10.1 <sup>o</sup>	

<sup>a</sup> All values in kcal/mol. <sup>b</sup> Data from Table S5. <sup>c</sup> In HFIP, data from Table S6. <sup>d</sup> Experimental, this work (Table S1). <sup>e</sup> Experimental, this work, with leaving group correction (OTs) at the HF/6-31G(d) level, see text. <sup>f</sup> Experimental value from ref 12, taken as reference. <sup>g</sup> Experimental value from ref 13. <sup>h</sup> Experimental value with leaving group correction (OTs), from ref 13. <sup>i</sup> Experimental value from ref 28. <sup>j</sup> Computational value from ref 33, see text. <sup>k</sup> Computational value at the G2(MP2) level, this work. <sup>l</sup> Based on the experimental standard enthalpies of formation of the ion and the relevant neutral species, see text. <sup>m</sup> Experimental value from ref 29. <sup>n</sup> Experimental value from ref 12a. <sup>o</sup> From ref 12.

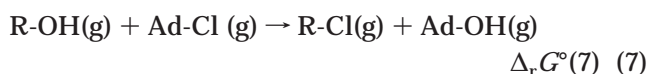
some cases, the experiments only involved the chlorides of the relevant species and the experimental values were used directly. For highly reactive ions, the DPA onsets for the alcohols, R-OH, were determined experimentally. These experiments lead to  $\Delta_r G^\circ(1, X=OH)$ , the standard Gibbs energy change for reaction 1b:



The general problem of linking the experimental data obtained from the DPA of different precursors, say R-X and R-Y can be solved through the use of  $\Delta_r G^\circ(6)$ , the standard Gibbs energy change for reaction 6:



For instance, in previous studies,  $\Delta_r G^\circ(1, X=OH)$  data were converted into  $\Delta_r G^\circ(1, X=Cl)$  values by means of  $\Delta_r G^\circ(7)$ , the standard Gibbs energy change for reaction 7:



since  $\Delta_r G^\circ(1, X=Cl) = \Delta_r G^\circ(1, X=OH) + \Delta_r G^\circ(7)$ .

Notice that  $\Delta_r G^\circ(7)$  refers to an isodesmic process involving neutral species, its physical meaning being that of a leaving group correction that quantitatively links relative stabilities based on the DPA of chlorides and alcohols. Of course, similar corrections can be applied to other leaving groups. As before,<sup>12-14</sup> they were determined computationally, generally at the HF/6-31G(d) level, a moderate level sufficient for this purpose. Values for  $\Delta_r G^\circ(7)$  are given in Table 1.

Notice that we have two different values for  $\Delta_r G^\circ(1, X=Cl)$  for **2**<sup>+</sup>; one, 1.3 kcal mol<sup>-1</sup>, was determined directly from the DPA of **2-Cl**, while the other, 1.1 kcal mol<sup>-1</sup>, obtains from the experimental DPA of **2-OH** and the  $\Delta_r G^\circ(7)$  term. The fact that these two values agree within 0.2 kcal mol<sup>-1</sup> further confirms the self-consistency of our database (see also ref 12b).

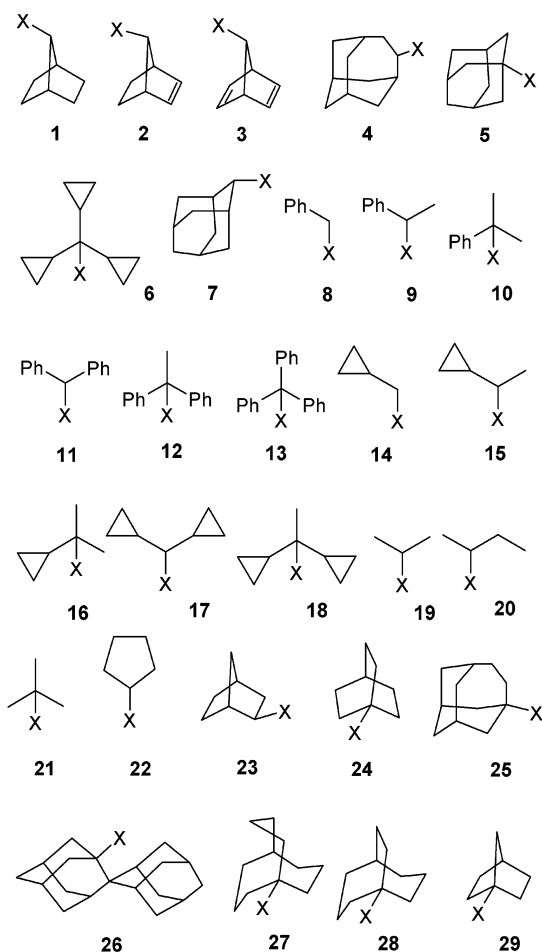
**3.2. Experimental Results from the Literature.** Experimentally based values of  $\Delta_r G^\circ(1, X=Cl)$  values are available for **7**<sup>+</sup>,<sup>13</sup> **8**<sup>+</sup>,<sup>29</sup> **9**<sup>+</sup>,<sup>29</sup> **10**<sup>+</sup>,<sup>29</sup> **21**<sup>+</sup>,<sup>30</sup> and **23**<sup>+</sup> to **29**<sup>+</sup>.<sup>12</sup> In the cases of **19**<sup>+</sup> ( $\Delta_r H^\circ_m = 193.4 \pm 0.36$  kcal mol<sup>-1</sup>),<sup>31</sup> **20**<sup>+</sup> ( $\Delta_r H^\circ_m = 182.4 \pm 1.1$  kcal mol<sup>-1</sup>, from the gas-phase

(29) Mishima, A.; Arima, K.; Inoue, H.; Usui, S.; Fujio, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3199-3206.

(30) Flores, H.; Dávalos, J. Z.; Abboud, J.-L. M.; Castaño, O.; Gomperts, R.; Jiménez, P.; Notario, R.; Roux, M. V. *J. Phys. Chem. A* **1999**, *103*, 7555-7557.

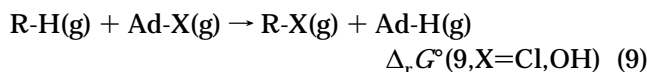
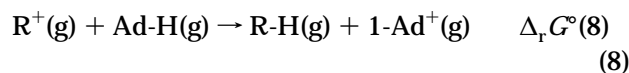
(31) Baer, T.; Song, Y.; Ng, C.; Liu, J.; Chen, W. *J. Phys. Chem. A* **2000**, *104*, 1959-1964.

CHART 1



basicity of  $E\text{-C}_4\text{H}_8$ ,  $-172.5 \pm 1.0 \text{ kcal mol}^{-1}$ ,<sup>20,32</sup> together with  $\Delta_f H_m^\circ(E\text{-C}_4\text{H}_8)$  and  $S_m^\circ(E\text{-C}_4\text{H}_8)$ <sup>33a</sup> and the computed entropies (this work) for the two equilibrating forms of this ion,<sup>32b</sup> ( $69.8 \pm 2.0$  and  $71.2 \pm 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ ), and **22**<sup>+,20,33</sup> reliable values of their standard enthalpies of formation,  $\Delta_f H_m^\circ$ , exist. When combined with the  $\Delta_f H_m^\circ$  values for the relevant neutral species<sup>33</sup> and 1-adamantyl cation,<sup>30</sup> they provide purely experimental values of  $\Delta_f H_m^\circ(1, X=\text{Cl})$ . Application of the entropy correction leads to  $\Delta_r G^\circ(1, X=\text{Cl})$ .

**3.3. Computational Results.** Whenever experimental data were not available, or standard DPA, direct halide exchange, or protonation of an ethylenic precursor would not lead to ions of unequivocally defined structures,  $\Delta_r G^\circ(1, X=\text{Cl})$  values were obtained either directly at the G2(MP2) level or by combining  $\Delta_r G^\circ(1, X=\text{H})$ , the standard Gibbs energy change for the hydride transfer reaction 8 as computed at the G2(MP2) level, with the corresponding leaving group correction,  $\Delta_r G^\circ(9, X=\text{Cl})$ , according to  $\Delta_r G^\circ(1, X=\text{Cl}) = \Delta_r G^\circ(8) + \Delta_r G^\circ(9, X=\text{Cl})$ .



In this work,  $\Delta_r G^\circ(1, X=\text{Cl})$  values for **14**<sup>+</sup>, **15**<sup>+</sup>, **16**<sup>+</sup>, **17**<sup>+</sup>, and **18**<sup>+</sup> were calculated at the G2(MP2) level. In the case of small species, calculations were performed on the carbocations and the corresponding chlorides. For large ones,  $\Delta_r G^\circ(8)$  was calculated at this level and corrected with the corresponding  $\Delta_r G^\circ(9, X=\text{Cl})$  values. Raw computational results for these species are summarized in Table S2 of the Supporting Information.

$\Delta_r H^\circ(8)$  values for **11**<sup>+</sup>, **12**<sup>+</sup>, and **13**<sup>+</sup> were obtained from the published standard enthalpies of formation of these ions<sup>34</sup> and the experimental values for the other relevant enthalpies. They led to  $\Delta_r G^\circ(1, X=\text{Cl})$  values upon the corresponding entropy and leaving group correction.

The database used in this work is summarized in Table 2, and full details are given in the following sections.

## 4. Discussion

**4.1. Energetics for Hydride Transfer. 4.1.1. Experiment and Theory.** The experimental values of  $\Delta_r G^\circ(1, X=\text{Cl})$  and  $\Delta_r G^\circ(1, X=\text{OH})$  given in section 3.1 were subject to the leaving group corrections  $\Delta_r G^\circ(9, X=\text{Cl})$  or  $\Delta_r G^\circ(9, X=\text{OH})$  as appropriate. This provided the corresponding “experimental” values of the standard Gibbs energy change for the hydride exchange reactions,  $\Delta_r G^\circ(8, \text{exp})$ . Calculations at the G2(MP2) or MP2/6-311G(d,p) levels led to purely computational values of this property,  $\Delta_r G^\circ(8, \text{comp})$ . These results are also given in Table 1. (Raw data are given in Tables S2 and S3 of the Supporting Information.) As we discuss below, the agreement between  $\Delta_r G^\circ(8, \text{exp})$  and  $\Delta_r G^\circ(8, \text{comp})$  is very good.

Furthermore, in some cases, the new computational data,  $\Delta_r H^\circ(8, \text{comp})$ , and experimental results available from the literature for  $\Delta_r H^\circ(8, \text{exp})$  can be directly compared. Thus, (i) in the case of 2-cyclopropylpropan-2-yl cation (**16**<sup>+</sup>), a value of  $\Delta_r H^\circ(8, \text{exp}) = 10.0 \pm 2.8 \text{ kcal mol}^{-1}$  results from the standard enthalpies of formation of the various species involved in the reaction.<sup>32,35,36</sup> At the G2(MP2) level,  $\Delta_r H^\circ(8, \text{comp}) = 7.4 \text{ kcal mol}^{-1}$  with an estimated accuracy of  $2.0 \text{ kcal mol}^{-1}$ .<sup>30</sup> (ii) The experimental GB and PA of 1,1-dicyclopropylethylene amount to  $209.3 \pm 1.0$  and  $216.2 \pm 1.1 \text{ kcal mol}^{-1}$ , respectively.<sup>20</sup> Here we find values of  $210.0$  and  $218.1 \text{ kcal mol}^{-1}$  at the G2(MP2) level, respectively. For 1,1-dicyclopropylethan-1-yl cation (**18**<sup>+</sup>), the experimental  $\Delta_f H_m^\circ(\text{g})$  for 1,1-dicyclopropylethylene and 1,1-dicyclopropylethane (**18-H**) have not been determined. From the corresponding values calculated at the G2(MP2) level, using the bond separation method<sup>37</sup> we obtain  $\Delta_f H_m^\circ(\text{g})$  values of

(32) (a) Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540–2548. (b) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; de Carneiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 259–270.

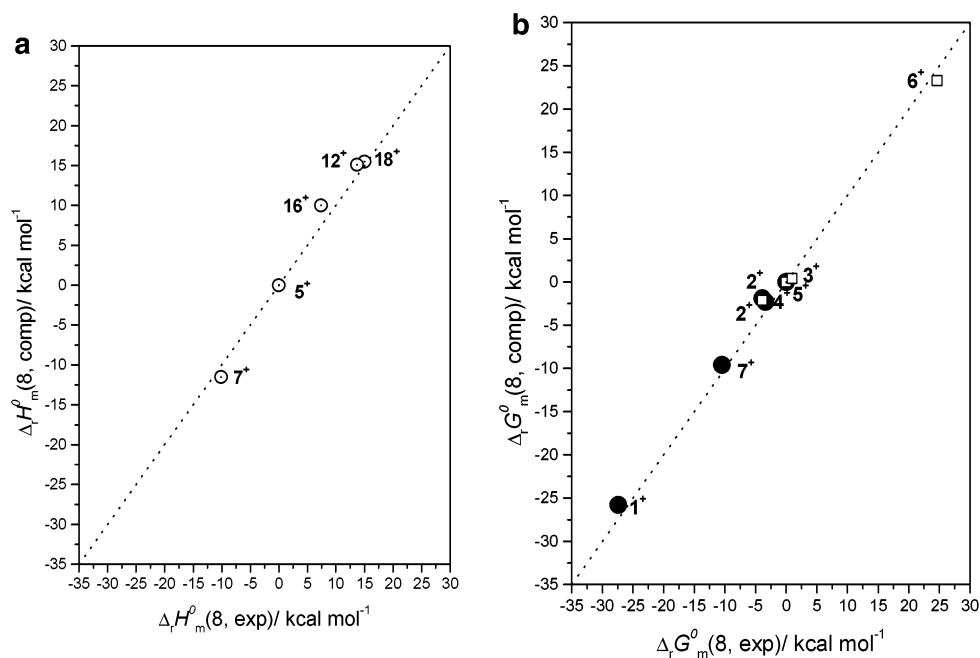
(33) (a) *TRC Thermodynamic Tables*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1997. (b) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; NIST Standard Reference Database No. 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, July 2001 (<http://webbook.nist.gov>).

(34) Reindl, B.; Clark, T.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8953–8963.

(35) Abboud, J.-L. M.; Castaño, O.; Dávalos, J. Z.; Gomperts, R. *Chem. Phys. Lett.* **2001**, *337*, 327–330.

(36) (a)  $\Delta_f H_m^\circ$  values for adamantane (**5-H**): ref 29. (b)  $\Delta_f H_m^\circ$  for 2-cyclopropylpropene (**16-H**),  $22 \pm 1 \text{ kcal mol}^{-1}$ , and **16**<sup>+</sup>,  $179.8 \pm 1.5 \text{ kcal mol}^{-1}$ ; refs 19 and 37.

(37) Raghavachari, K.; Stefanov, B. B.; Curtiss, L. A. *J. Chem. Phys.* **1991**, *94*, 7221–7230.

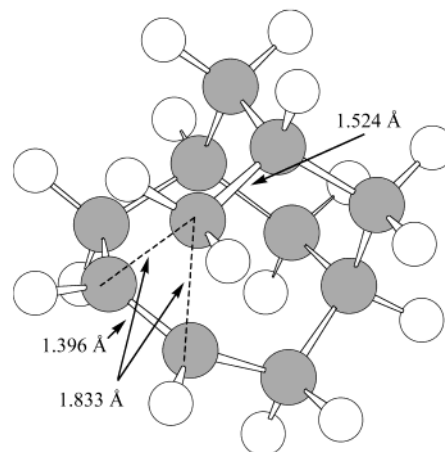


**FIGURE 1.** (a) Calculated vs experimental standard enthalpy changes for hydride transfer, reaction 8. Data from text, Section 4.1. For numbering, see Table 2. (b) Calculated vs experimental standard Gibbs energy changes for hydride transfer, reaction 8. Filled circles, values for X = Cl; open squares, values from X = OH. Data from Table 1 and text, Section 4.1. For numbering, see Table 2.

$49.4 \pm 2.0$  and  $20.7 \pm 2.0$  kcal mol<sup>-1</sup>, respectively, from which we derive  $\Delta_r H^\circ(8, \text{exp}) = 15.5 \pm 2.8$  kcal mol<sup>-1</sup>, while  $\Delta_r H^\circ(\mathbf{18}^+, \text{comp}) = 15.0 \pm 2.0$  kcal mol<sup>-1</sup>. (iii) Two values of  $\Delta_f H^\circ_m(\text{g})$  for 1,1-diphenylethan-1-ylum ( $\mathbf{12}^+$ ) are available,  $212.7 \pm 2.0$  and  $214.1 \pm 2.3$  kcal mol<sup>-1</sup>. The first one is purely experimental and is obtained from the PA<sup>20</sup> and  $\Delta_f H^\circ_m(\text{g})$  of 1,1-diphenylethylene ( $58.7 \pm 1$  kcal mol<sup>-1</sup>).<sup>38</sup> The latter is purely computational, from MMP2 and MP4(SDQ)//MP2(Full)/6-31G(d) calculations by Reindl and co-workers.<sup>33</sup> When combined with the experimental  $\Delta_f H^\circ_m(\text{g})$  for the various relevant species, they lead to  $\Delta_r H^\circ(8)$  values of respectively 15.1 and 13.7 kcal mol<sup>-1</sup>. (iv) Using data just published,<sup>13</sup> we obtained  $\Delta_r G^\circ(8, \text{exp}) = -9.6 \pm 3.0$  (from DPA) and  $\Delta_r G^\circ(8, \text{comp}) = -10.5 \pm 3.0$  kcal mol<sup>-1</sup> (at the G2(MP2) level) for adamantan-2-ylum ( $\mathbf{7}^+$ ).

We have plotted in Figure 1, parts a and b, respectively,  $\Delta_r H^\circ(8, \text{comp})$  vs  $\Delta_r H^\circ(8, \text{exp})$  and  $\Delta_r G^\circ(8, \text{comp})$  vs  $\Delta_r G^\circ(8, \text{exp})$  for the species examined above. The straight line is drawn for better visualization, and has no physical significance. That the agreement is excellent between the *primary experimental data* and the calculated values is confirmed by the size of the average unsigned difference between their values, which amounts to 1.5 kcal mol<sup>-1</sup>, well within the estimated uncertainties of the experimental and calculated data (irrespective of the thermodynamic state function being considered). The variety of structures and the range of effects (some 50 kcal mol<sup>-1</sup>) lend considerable support to our experimental and computational methodologies.

**4.1.2. Note on Some Structures Calculated in This Work.** Most of the structures examined in this work have been the subject of high-level computational studies.<sup>15</sup>



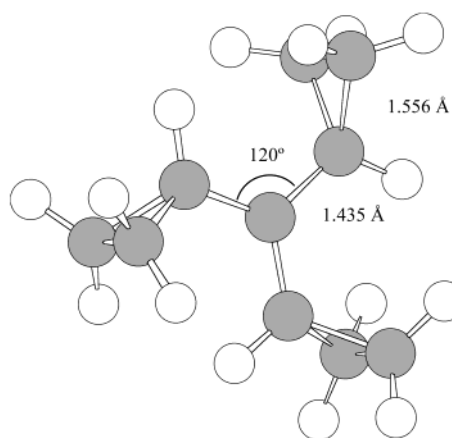
**FIGURE 2.** Fully optimized [MP2/6-311G(d,p)] level structure of cation  $\mathbf{4}^+$ .

This is why we only focus attention on the following species: homoadamantan-4-ylum ( $\mathbf{4}^+$ ). The structure of this ion (of  $C_s$  symmetry), Figure 2, was fully optimized at the MP2/6-311G(d,p) level and shows a simultaneous lengthening of the C(3)–C(11) and C(4)–C(11) bonds to 1.833 Å, as well as a substantial shortening of the C(3)–C(4) bond to 1.396 Å. The electron density of  $\mathbf{4}^+$  was analyzed with the Atoms in Molecules (AIM)<sup>39</sup> methodology and the AIMPAC set of programs.<sup>40</sup> This study shows a “catastrophic configuration” due to the simultaneous interaction of the CH<sub>2</sub> group with the CH–CH bond. That is, any small change that distorts the symmetry, induces

(39) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: New York, 1990.

(40) Biegler-König, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317–328.

(38) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.



**FIGURE 3.** Fully optimized [MP2/6.311G(d,p)] level structure of cation **6**<sup>+</sup>.

the formation of a unique bond between the C(11) atom and C(3) or C(4) (Figure 2). Thus the *effective* electron density map of this system shows a tetracoordinated carbocation. Similar catastrophic electron density maps have been described for hydrogen-bonded complexes where  $\pi$  systems act as acceptors.<sup>41</sup> The small value of the electron density and the Laplacian with a negative value in this region indicate that it is within the limits of what is considered as a shared-shell interaction similar to standard covalent bonds.

It is interesting that previous studies with Molecular Mechanics<sup>42</sup> showed that the strain in **4-Cl** is some 5 kcal mol<sup>-1</sup> higher than that in 2-chloroadamantane (**7-Cl**). In terms of chloride exchange, we find that **4**<sup>+</sup> is 9.2 kcal mol<sup>-1</sup> more stable than **7**<sup>+</sup> (see Table 2). This is surprising at first sight, because both are large ions formally differing only in one methylene group. Actually, this is rationalized by the fact that the nonclassical structure of **4**<sup>+</sup> provides an energetically efficient means to release the strain of the neutral precursor.

The fully optimized [MP2/6-311G(d,p)] structure of tricyclopropylmethyl cation (**6**<sup>+</sup>), of  $C_{3h}$ -symmetry, is shown in Figure 3. A significant feature is the short C–C distance between the central carbon and the  $\alpha$ -carbons in the cyclopropyl rings (1.435 Å), indicative of significant conjugation.<sup>15</sup> We observe that, starting from cyclopropylmethyl cation (**14**<sup>+</sup>), an increase in the number of cyclopropyl groups increases this C<sup>+</sup>–C( $\alpha$ ) distance (Table 3). The same effect is found for phenyl-substituted cations.

Interestingly, the ion stabilizing effects  $\Delta_r G^\circ(1, X \text{ Cl})$  (eq 1a) from Table 2 are the same (within experimental error) for cyclopropyl and phenyl substitution with the one exception of the couple **10-Cl/16-Cl**, where we find a deviation of 7.8 kcal mol<sup>-1</sup>. Inspection of the calculated structures reveals that the H–H distance between the methyl hydrogens and the closest hydrogens in the phenyl or cyclopropyl ring, respectively, is almost 0.3 Å shorter in the case of the cumyl cation **10**<sup>+</sup>. This increased repulsion is reflected in part by the twisting of the phenyl group in the case of **10**<sup>+</sup>.

(41) Rozas, I.; Alkorta, I.; Elguero, J. *J. Phys. Chem.* **1997**, *101*, 9457–9463.

(42) Müller, P.; Mareda, J.; Milin, D. *J. Phys. Org. Chem.* **1995**, *8*, 507–528.

**TABLE 3.** Cyclopropyl- and Phenyl-Substituent Effects on Selected Bond Lengths<sup>a</sup>

no.	ion	$L_1^b$	no.	ion	$L_2^c$
<b>14</b> <sup>+</sup>	<i>c</i> -C <sub>3</sub> H <sub>5</sub> -CH <sub>2</sub> <sup>+</sup>	1.357	<b>8</b> <sup>+</sup>	Ph-CH <sub>2</sub> <sup>+</sup>	1.372
<b>15</b> <sup>+</sup>	<i>c</i> -C <sub>3</sub> H <sub>5</sub> -CH <sup>+</sup> CH <sub>3</sub>	1.372	<b>9</b> <sup>+</sup>	Ph-CH <sup>+</sup> CH <sub>3</sub>	1.389
<b>16</b> <sup>+</sup>	<i>c</i> -C <sub>3</sub> H <sub>5</sub> -C <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub>	1.387	<b>10</b> <sup>+</sup>	Ph-C <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub>	1.408
<b>17</b> <sup>+</sup>	( <i>c</i> -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> CH <sup>+</sup>	1.409	<b>11</b> <sup>+</sup>	Ph <sub>2</sub> CH <sup>+</sup>	1.411
<b>18</b> <sup>+</sup>	( <i>c</i> -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> C <sup>+</sup> CH <sub>3</sub>	1.419	<b>12</b> <sup>+</sup>	Ph <sub>2</sub> C <sup>+</sup> CH <sub>3</sub>	1.428
<b>6</b> <sup>+</sup>	( <i>c</i> -C <sub>3</sub> H <sub>5</sub> ) <sub>3</sub> C <sup>+</sup>	1.433	<b>24</b> <sup>+</sup>	Ph <sub>3</sub> C <sup>+</sup>	1.437

<sup>a</sup> All values in Å computed at the MP2(FU)/6-31G(d) level.

<sup>b</sup> Distance between the central carbon atom and the carbon of a cyclopropyl ring. <sup>c</sup> Distance between the central carbon atom and the  $\alpha$  carbon of a phenyl ring.

## 4.2. Rate Constants of Solvolysis and Carbocation

**Stabilities. 4.2.1. Rate Constants.** In our previous work we have established a linear correlation between solvolytic reactivity and carbocation stability for bridgehead derivatives as determined by DPA experiments with chlorides, bromides, and alcohols. Leaving group corrections, as calculated by ab initio methods (HF/6-31G(d)) for interconversion of data for chlorides, bromides, and alcohols, allowed the establishment of a single correlation covering the entire rate range of some 20 log units. In the bridgehead series, these leaving group corrections are relatively small, i.e., on the order of 1 kcal mol<sup>-1</sup>.

Owing to their cage-type structure, which inhibits backside interaction by the solvent with the reacting center, the bridgehead derivatives represent a series of compounds particularly well suited for such investigations. They all react via an S<sub>N</sub>1 mechanism, and their relative rates of solvolysis are practically independent of leaving group and solvent.<sup>11</sup> In addition, according to the traditional interpretation,<sup>7</sup> release or build up of steric strain is the only dominant feature governing solvolytic reactivity throughout the series. This interpretation is fully consistent with our theoretical calculations, which show no anomalies which could be ascribed to nonclassical behavior of bridgehead carbocations. The situation is less favorable for solvolysis in general. Rate constants are available in a temperature range between 0 and 200 °C, according to the reactivity and the leaving group of the compound under investigation. The temperature dependency of the rate constants was very often not established with the necessary degree of reliability, and relative rate constants were obtained, often at 25 °C, by extrapolation. The rate constants may be affected by nucleophilic solvent participation (NSP)<sup>43</sup> or front-strain,<sup>44</sup> and even relative rates may vary upon changing leaving group and/or solvent. In addition, it is not established whether the different mechanism for stabilization or destabilization of positive charge in the transition state, such as strain, resonance, or polar effects, etc., develops synchronously along the reaction coordinate.

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The problem may be exemplified in the case of cumyl solvolysis. Rate constants have been measured in several systems, and  $\log k$  relative to 1-adamantyl at 70 °C varied from 5.1 for **10**-OPNB in 80% acetone to 6.3 for **10**-Cl in EtOH,<sup>45</sup> 6.1 in MeOH,<sup>46</sup> 5.5 in 80% EtOH,<sup>47</sup> and 5.4 in 80% acetone.<sup>48</sup> In general, for the compounds of the present investigations, rate constants are available for only a limited number of systems and a choice had to be made. To minimize NSP contributions, rate constants determined in acetic acid were given preference over those from other systems (Table S5). In light of the results from cumyl solvolysis, the uncertainty in the relative rates is estimated at ca. 1 log unit. This seems acceptable considering the uncertainties in the DPA data (ca. 2 kcal mol<sup>-1</sup>).

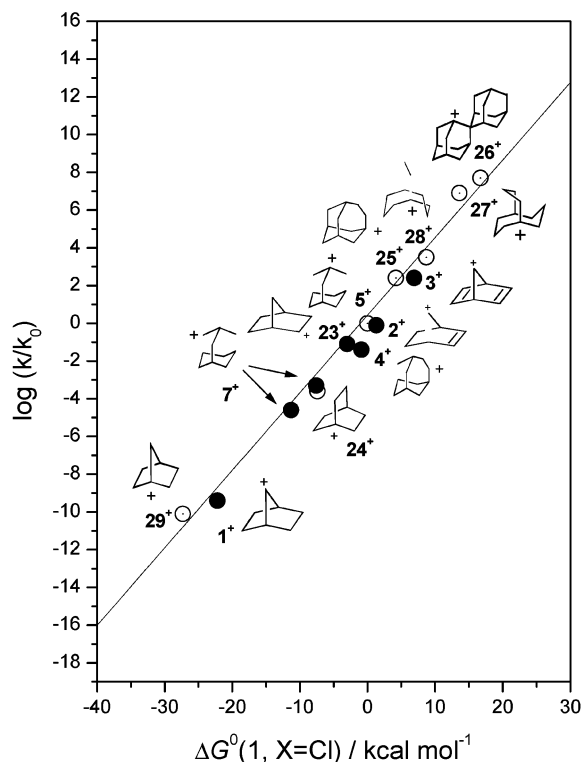
**4.2.2. Solvolysis of Bicyclic Secondary Derivatives.** The relative ion stabilities  $\Delta_r G^\circ(1, X=Cl)$  (eq 1a) for bicyclic secondary chlorides and alcohols and the appropriate rate constants for solvolysis ( $\log k$ ) are summarized in Table 2, and details are given in Table S5. Combination of the data from Table 2 of compounds **1–4** and **6** with those for the previously reported bridgehead chlorides<sup>12</sup> and incorporating the recently published results for 2-adamantyl derivatives **7–X**<sup>13</sup> results in correlation (10):

$$\log(k/k_0) = (0.417 \times 0.016)\Delta_r G^\circ(1, X=Cl) + (0.08 \times 0.19) \quad (10)$$

where  $n = 14$ ,  $r^2 = 0.9849$ , and  $\sigma = 0.71$ .

The correlation uses purely experimental data, except in the case of the alcohols **2**-OH and **3**-OH, to which a leaving group correction  $\Delta_r G^\circ(7)$  was applied. These corrections amount to  $-0.1$  and  $2.6$  kcal mol<sup>-1</sup>, respectively. The plot spans almost 50 kcal mol<sup>-1</sup> in  $\Delta_r G^\circ$  and over 17 orders of magnitude in rates. Figure 4 shows the overwhelming bridgehead-like behavior of the bicyclic compounds. The plot is almost identical with that for the bridgehead chlorides alone [ $\log(k/k_0) = (0.414 \times 0.019)\Delta_r G^\circ(1, X=Cl) + (0.43 \times 0.25)$  ( $n = 8$ ,  $r^2 = 0.9875$ , and  $\sigma = 0.70$ )].<sup>12</sup> Although the bicyclic cations **1**<sup>+</sup>–**4**<sup>+</sup>, **7**<sup>+</sup>, and **23**<sup>+</sup> are all secondary, they differ significantly in the way they stabilize charge. Thus the 7-norbornyl- (**1**<sup>+</sup>) and the 4-homoadamantyl (**4**<sup>+</sup>) cations are nonclassical, while the 7-norbornenyl- and 7-norbornadienyl cations (**2**<sup>+</sup> and **3**<sup>+</sup>, respectively) are homoaromatic. The common feature of these compounds is, that owing to their bicyclic structure, the backside of the reacting center is efficiently shielded from interaction with solvent so that nucleophilic solvent participation (NSP)<sup>43</sup> may not intervene. The 2-adamantyl system **7** is the model *par excellence* for a secondary compound solvolyzing via a clean  $k_c$  mechanism, i.e., without NSP. The structural analogy of the other bicyclic compounds used in this study suggests that the same mechanism should apply to them.

Note that the plot also contains 2-*exo*-chloronorbornane (**23**-Cl), which, although not a bridgehead derivative, fits



**FIGURE 4.** Plot of  $\log(k/k_0)$  for solvolysis of bridgehead and tri- and bicyclic secondary derivatives vs  $\Delta_r G^\circ(1, X=Cl)$ , eq 10. Data from Table 2.

eq 10. As mentioned previously, the experimentally determined stability of the 2-norbornyl cation agrees with its computational stability, and this stability is reflected in the solvolytic reactivity.<sup>12a</sup> The *endo*-norbornyl isomer is, however, not included in this series. Theoretical calculations show the *exo*-transition state 1.3 kcal mol<sup>-1</sup> higher in energy than the nonclassical 2-norbornyl cation, but the *endo*-transition state is 8.8 kcal mol<sup>-1</sup> higher.<sup>49</sup>

**4.2.3. Phenyl- and Cyclopropyl-Substituted Derivatives.** Combination of the data for phenyl- and cyclopropyl-substituted derivatives (Table 2) with those used for eq 10 results in eq 11:

$$\log(k/k_0) = (0.409 \times 0.017)\Delta_r G^\circ(1, X=Cl) + (0.27 \times 0.24) \quad (11)$$

where  $n = 24$ ,  $r^2 = 0.962$ , and  $\sigma = 1.1$ .

In contrast to the almost perfect bridgehead behavior of bicyclic derivatives, the correlation between solvolytic reactivity and carbenium ions stability for phenyl- and cyclopropyl-substituted compounds is somewhat less satisfactory (Figure 5). The correlation line was obtained by first plotting all of the pertinent data for  $\log k$  vs  $\Delta_r G^\circ(1, X=Cl)$ . Compounds deviating more than 2 standard deviations from the regression line, i.e., **13** and **14**, were eliminated and the final correlation resulted from the remaining 24 data points. Although diphenylethyl (**12**) deviates slightly more than 2 standard deviations (2.25 log units), it is considered borderline and retained in eq 11. It is noteworthy that only 8 data points used for eq 11 are from bridgehead derivatives, but nevertheless the

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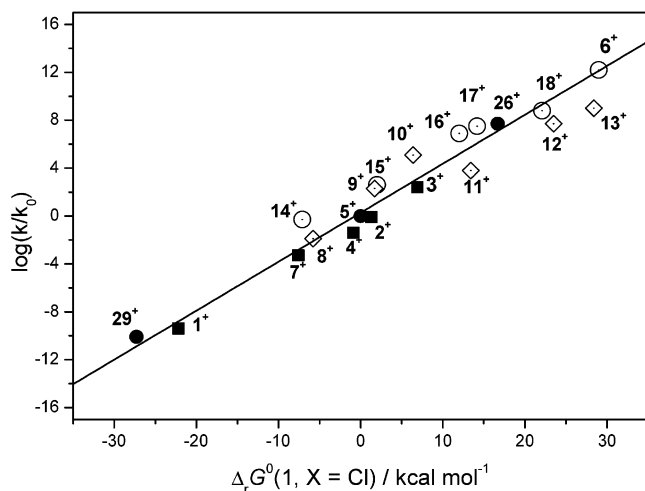
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**FIGURE 5.** Plot of  $\log(k/k_0)$  for solvolysis of bridgehead chlorides (filled circles) and bi- and tricyclic secondary (filled squares) benzyl- (dot-centered diamonds) and cyclopropyl-substituted (dot-centered circles) derivatives vs  $\Delta_r G^\circ(1, X=Cl)$ , eq 11. Data from Table 2.

slope of the regression line is practically identical with that of eq 10. The scatter is, however, somewhat higher. The increase of the standard deviation from 0.71 for eq 10 to 1.1 in eq 11 should be appreciated in light of the 60 kcal mol<sup>-1</sup> range of ion stabilities and the 23 orders of magnitude of the rate constants. Inclusion of **13** and **14** in the correlation leads only to a slight deterioration of the fit [ $\log(k/k_0) = (0.38 \times 0.019)\Delta G^\circ + (0.38 \times 0.27)$ ] ( $n = 26$ ,  $r^2 = 0.948$ , and  $\sigma = 1.3$ ). Even though the value of  $\sigma$  is 1.3 log units, the equation allows useful predictions of the order of magnitude of solvolysis rates.

In a first approximation, the correlation confirms the dominance of carbocation stability for the determination of solvolytic reactivity and confirms the long-held hypothesis of structural and energetic similarity of carbenium ions and the transition states for solvolysis. In addition, it provides quantitative justification of the various qualitative mechanisms for charge stabilization in carbocations which have been developed intuitively over many years on the grounds of solvolytic reactivity.

Conversion of  $\log(k/k_0)$  in units of free energies of activation results in a slope of  $-0.69$ , in reasonable agreement with the slope reported by Arnett for correlation of  $\Delta G^\ddagger$  for solvolysis vs ion stabilities,  $\Delta H_i^\ddagger$  in the condensed phase ( $-0.89$  in  $\text{SO}_2\text{ClF}$ ,  $-1.02$  in  $\text{CH}_2\text{Cl}_2$ , and  $-0.95$  in  $\text{SO}_2$ ).<sup>1</sup> The lower value of the slope for the gas phase may be attributed to the absence of cation stabilization by solvent. In a first approximation, and with the exceptions discussed below, solvation affects all the ions (and transition states for solvolysis) to the same degree and there are no differential effects.

Closer inspection of Figure 5 reveals that the phenyl-substituted compounds **8**–**13** exhibit scatter in both directions from the straight line in the range of  $\pm(0.8$ – $2.25)$  log units, except **13**, which deviates by 3.0. The possibility that these discrepancies might originate from a leaving group effect on the rate constants was ruled out on the grounds of comparison of the relative rates for chlorides and OPNB's of the series. The variations are within 1 log unit and they do not produce a trend. We also considered that the deviations could be due to a

computational artifact originating from the leaving group corrections. However, no significant change appeared, when the corrections calculated for chlorides were replaced by corrections for benzenesulfonates. It appears, therefore, that the scatter in Figure 5 may not be attributed to the methodology used, but should perhaps be mechanistically significant. Conceivably, differential solvation effects could be responsible for some of the scatter, but other subtle mechanistic changes<sup>50</sup> may further complicate the situation. Unfortunately, the experimental error inherent in our approach prohibits a more detailed analysis.

Some scatter also occurs within the cyclopropyl-substituted compounds, but it is at the limits of statistical significance, except in the case of the primary cyclopropylmethyl derivative **14-X**, which deviates upward by 2.3 log units and, therefore, falls out of the correlation. This behavior parallels that of the small, acyclic secondary or tertiary compounds, and will be discussed below.

**4.2.4. Acyclic and Monocyclic Compounds.** The remarkable mechanistic homogeneity observed for bicyclic secondary, benzylic, and cyclopropyl-substituted derivatives does not apply to the solvolysis of simple mono- or acyclic secondary or tertiary substrates. Attempted correlation of the acetolysis rates of 2-propyl (**19-OTs**), 2-butyl (**20-OTs**), and cyclopentyl (**22-OTs**), as well as *tert*-butyl (**21-OTs**) and cyclopropylmethyl (**14-OTs**) tosylates, with  $\Delta_r G^\circ(1, X=Cl)$  values shows that these compounds solvolyze significantly faster than predicted on the grounds of the gas-phase stability of the respective carbenium ions. These deviations are traditionally attributed to nucleophilic solvent participation (NSP). NSP is the effect on the rate constant for solvolysis of a substrate relative to that of the corresponding 1-adamantyl derivative upon solvent change from trifluoroacetic acid to the solvent of interest.<sup>43</sup> It occurs in solvolysis reactions that lead to small, undelocalized carbocations. Initially, the effect was ascribed to a direct interaction of the solvent with the reacting center in an  $\text{S}_{\text{N}}2$ -type process and to Brønsted-type interactions of the solvent,<sup>51</sup> in particular, with  $\beta$ -hydrogens.<sup>52</sup> However, recent investigations show that NSP has a more general significance. Kevill et al. introduced "nucleophilic solvation" of the incipient carbocation, as opposed to intervention of the solvent concerted with departure of the leaving group, to rationalize the rate of solvolysis of cyclopropylmethyl derivatives.<sup>53</sup> The involvement of NSP in tertiary solvolysis including *tert*-butyl has been discussed extensively. According to Richard, only "nucleophilic solvation", which implies stabilization of the carbocation by the dipoles of the solvent, is significant in *tert*-butyl solvolysis,<sup>54</sup> while in secondary solvolysis, "nucleophilic solvation", as well as participation of the solvent in a concerted  $\text{S}_{\text{N}}2$  process, may be involved.

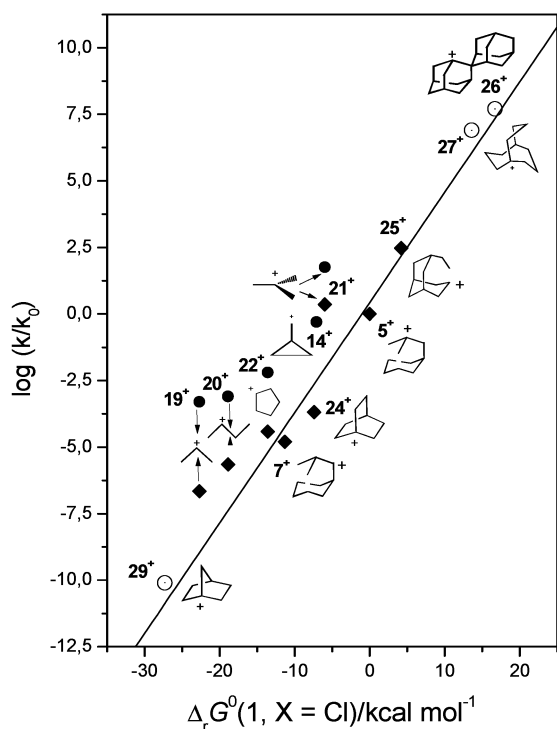
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**FIGURE 6.** Plot of  $\log(k/k_0)$  for solvolysis of bridgehead (dot-centered circles) and secondary and tertiary aliphatic (filled circles) derivatives in acetic acid vs  $\Delta_r G^\circ(1, X = \text{Cl})$ , eq 11. Data from Table 2. Diamonds are for values in HFIP (data from Table S6, Supporting Information).

The magnitude of NSP decreases in strongly dissociating (nonnucleophilic) solvents, parallel to decreasing solvent nucleophilicity  $N$ , which changes from 0.00 (80% EtOH) to  $-2.05$  (AcOH),  $-4.74$  (trifluoro acetic acid, TFA), and  $-3.93$  (97% hexafluoro-2-propanol, HFIP).<sup>55</sup> TFA and HFIP are considered nonnucleophilic, and solvolysis reactions of secondary tosylates are believed to proceed without or at least with very little NSP in these solvents. One would therefore expect that HFIP rates for simple aliphatic derivatives should be accommodated by a correlation of  $\log(k/k_0)$  vs the  $\Delta_r G^\circ$  values defined for bridgehead derivatives. The limited number of data available at present does not allow rigorous testing of this hypothesis. However, some data for bridgehead solvolysis and for secondary  $k_c$  substrates in HFIP, such as 1- and 2-adamantyl ( $5^+$  and  $7^+$ ), bicyclo-[2.2.2]-octyl ( $24^+$ ), and 3-homoadamantyl ( $25^+$ ), are available (Table 2 and Table S6, Supporting Information). As expected, these compounds are well accommodated by the plot for bridgehead derivatives in conventional solvents (Figure 6), demonstrating again the insensitivity of bridgehead solvolysis to solvent effects. The HFIP rates for 2-propyl ( $19$ ), 2-butyl ( $20$ ), and *tert*-butyl ( $21$ ) deviate again significantly upward from the regression line. The deviations are smaller than those in acetic acid (also shown in the plot), indicating less NSP, and cyclopentyl solvolysis appears approximately normal. However, even in nonnucleophilic HFIP, the intrinsic gas-phase stability of the small carbocations is still not entirely reflected in

the solvolytic reactivity of their precursors. This contrasts with the situation encountered with highly crowded tertiary derivatives which approach bridgehead behavior in HFIP.<sup>14</sup> However, the deviations shown in Figure 6 disappear if ion stabilities in solution are correlated rather than gas-phase stabilities: Arnett has shown that rates of solvolysis for a large variety of compounds, including 2-propyl, *tert*-butyl, and cyclopentyl derivatives, correlate well with ion stabilities ( $\Delta H_i$ ) in  $\text{CH}_2\text{Cl}_2/\text{SbF}_5$ .<sup>1</sup> This is consistent with the suggestion of Richard<sup>54</sup> that the enhanced rate of *tert*-butyl derivatives is due to enhanced solvation of the *tert*-butyl cation and the transition state leading to this ion. Small ions, which are unable to provide sufficient charge stabilization, and the respective transition states profit from preferential solvation relative to the more delocalized ions, or relative to ions which, for skeletal reasons, are inefficiently solvated. Whether NSP in the traditional sense is involved in secondary solvolysis may not be assessed on the grounds of the gas-phase data alone. The reaction in the condensed phase leads to solvated ions or ion pairs rather than free ions, and this process is a more appropriate model for the solvolysis reaction than the formation of free ions in the gas phase. However, as shown above, gas-phase data provide a unique vantage point from which it is possible to unravel the contributions from intrinsic reactivity and medium effects.

## 5. Epilogue

Bridgehead solvolysis has been proposed as the mechanistic model for unimolecular solvolytic processes proceeding via carbenium ions or ion pairs without backside intervention of the solvent and was rationalized by empirical molecular mechanics calculations. In our approach, we have defined the bridgehead line for solvolysis on the grounds of experimental gas-phase stabilities of carbenium ions, as determined by Dissociative Proton Attachment (DPA). The stability of these ions is well reproduced by high-level ab initio calculations. Using the bridgehead line as reference, we find that secondary bicyclic derivatives exhibit bridgehead-like solvolytic reactivity, and the same applies to benzyl- and cyclopropyl-substituted derivatives, although with more scatter.

To our knowledge, this is the most comprehensive comparison ever reported of kinetic reactivity vs thermodynamic stability of carbocations. Figure 6 shows clearly that solvolytic reactivity reflects the ranking of carbocation stability over the entire rate range, and affects of leaving groups and reaction medium, although not negligible, are of secondary importance.

Acyclic, monocyclic, and *tert*-butyl derivatives solvolyze faster than expected on the grounds of the stabilities of the respective carbenium ions. This enhanced solvolytic reactivity is ascribed to a combination of nucleophilic cation solvation in comparison to that of bridgehead derivatives, and nucleophilic solvent participation in an  $\text{S}_\text{N}2$ -type process. Thus, the bridgehead line, as defined from ion stabilities in the gas phase, provides insight in the reaction mechanism for solvolysis in solution, and further allows the discussion of effects such as NSP in a broader context.

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**Supporting Information Available:** Tables of computational results for the species investigated and tables for

conversion of rate constants of solvolysis to standard conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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