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# Intrinsic (Gas Phase) Thermodynamic Stability of 2-Adamantyl Cation. Its Bearing on the Solvolysis Rates of 2-Adamantyl Derivatives

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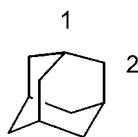
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The standard enthalpy of formation of gaseous 2-adamantyl chloride (2-Ad-Cl) was determined by calorimetric techniques. The standard Gibbs energy change for the chloride anion exchange between 1-adamantyl (1-Ad<sup>+</sup>) and 2-adamantyl (2-Ad<sup>+</sup>) cations in the gas phase was obtained by Fourier transform ion cyclotron resonance spectroscopy (FT ICR). Theoretical calculations at the G2(MP2) level were performed on these and other relevant species. This and data from the literature provided *three* highly consistent *independent* estimates of the relative stabilities of 2-Ad<sup>+</sup> and 1-Ad<sup>+</sup>. This difference in gas-phase stability was compared to the differential structural effects on the rates of solvolysis of the corresponding chlorides and tosylates, and it was shown that the thermodynamic stability of the secondary cation is the leading factor determining the solvolytic reactivity of the precursors in the absence of solvent effects. Thus, under these conditions, the previously established linear free energy correlation between carbenium ion stability and solvolytic reactivity of bridgehead derivatives applies also to secondary derivatives.

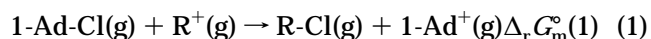
## 1. Introduction

The relevance of 2-adamantyl cation (2-Ad<sup>+</sup>) in physical organic chemistry essentially originates from the fact that solvolysis of the precursors of this secondary ion is an S<sub>N</sub>1 process free from effects of solvent participation.<sup>1</sup>



The concept that the thermodynamic stability of tertiary bridgehead carbocations is the predominant factor determining the reactivity of bridgehead derivatives in solvolytic S<sub>N</sub>1 processes was set forth years ago<sup>2</sup> and was experimentally confirmed in a number of cases. For instance, we were able to show the existence of an excellent linear relationship between log(*k/k*<sub>0</sub>), the logarithm of the ratio of the rate constants (*k*) for a standard process (the solvolysis of the corresponding tosylates, R-OTs at 70 °C in 80% ethanol) relative to the corresponding rate for the 1-adamantyl derivative (*k*<sub>0</sub>), and

the standard Gibbs energy changes for reaction 1, Δ<sub>r</sub>G<sub>m</sub><sup>°</sup> (1), the chloride exchange between the cations under investigation and the 1-adamantyl cation (1-Ad<sup>+</sup>).<sup>3</sup> These Gibbs energies were mostly determined by Fourier transform ion cyclotron resonance spectroscopy (FT ICR), using the dissociative proton attachment method (DPA).<sup>3,4</sup>



This linear relationship, eq 2, covers a range of ca. 50 kcal mol<sup>-1</sup> in Δ<sub>r</sub>G<sub>m</sub><sup>°</sup> and 18 log units in *k/k*<sub>0</sub> and its statistical quality (*n* = 8; *R*<sup>2</sup> = 0.987; sd = 0.7 log units) is very good. The slope of the straight line indicates that ca. 65% of the Gibbs energy change in the gas phase is expressed in the rates of solvolysis at 70 °C.

$$\log(k/k_0) = 0.414 (\pm 0.019) \Delta_r G_m^\circ(1) + 0.43 (\pm 0.25) \quad (2)$$

Furthermore, upon appropriate leaving group corrections, this correlation was shown to apply quite nicely to an even broader set of gas-phase bridgehead carbenium ion stabilities determined using bromides and alcohols as precursors.<sup>4</sup>

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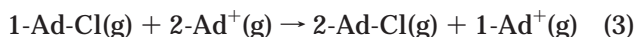
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We are presently involved in the extension of these studies to secondary carbenium ions. 2-Adamantyl cation (2-Ad<sup>+</sup>) appears as a benchmark species. Kinetic data are available for solvolytic processes of 2-adamantyl derivatives under a large variety of reaction conditions (see below). The determination of  $\Delta_f G_m^\circ(2\text{-Ad-Cl})$  requires both the standard enthalpy of formation of 2-Ad<sup>+</sup>(g),  $\Delta_f H_m^\circ(2\text{-Ad}^+, \text{g})$ , and its standard entropy  $S_m^\circ(2\text{-Ad}^+, \text{g})$ , respectively. Computational methods can provide reliable values for both magnitudes. It is obvious, however, that experimental values are highly desirable in the present context. At this point, mutually consistent experimental values for  $\Delta_f H_m^\circ(2\text{-Ad}^+, \text{g})$  are available from the adiabatic ionization energy of the 2-adamantyl radical, 2-Ad<sup>•</sup><sup>5a</sup> as well as from appearance energy experiments.<sup>5b</sup> Computations at the G2(MP2)<sup>6</sup> level are in good agreement with these data.<sup>7</sup> Following our previous study on 1-Ad<sup>+</sup>,<sup>8</sup> we sought further independent confirmation of these data, and for this reason we have undertaken this experimental study of the thermodynamic state functions of 2-Ad<sup>+</sup>(g) prior to exploring the applicability of eq 2 to this ion.

## 2. Methodology

**1. Method 1.** G2(MP2)<sup>6</sup> calculations were performed on 2-Ad-Cl. The results can be combined with data from previous calculations to yield  $\Delta_f H_m^\circ(3)$  and  $\Delta_f G_m^\circ(3)$ , magnitudes pertaining to reaction 3 (a particular case of reaction 1).



where 1-Ad-Cl stands for 1-adamantyl chloride.

**2. Method 2.** Experimental standard enthalpies of formation are available for gaseous 1-Ad-Cl,<sup>8</sup> 1-Ad<sup>+</sup>,<sup>8</sup> and 2-Ad<sup>+</sup>.<sup>5</sup> Here we determined  $\Delta_f H_m^\circ(2\text{-Ad-Cl, g})$  experimentally and combined these four values to obtain  $\Delta_f H_m^\circ(3)$ . Further combination of  $\Delta_f G_m^\circ(3)$  with the computed value of  $\Delta_f S_m^\circ(3)$  led to  $\Delta_f G_m^\circ(3)$ .<sup>9</sup>

**3. Method 3.** As in previous studies, the FT-ICR-based DPA method was used to directly determine  $\Delta_f G_m^\circ(3)$ .

## 3. Experimental Section

**3.1. Materials.** 2-Chloroadamantane (2-Ad-Cl), from Avocado Research Chemicals, of 98% nominal purity was sublimed twice. Differential scanning calorimetry (dsc) using the fractional fusion technique<sup>10</sup> indicated that the mole fraction of impurities in 2-Ad-Cl was less than 0.001. No impurities ( $\geq 0.001$  percent) could be detected by GLC.

**3.2. Kinetic Data.** The rate of solvolysis of 2-chloroadamantane (2-Ad-Cl) is very slow and, therefore, associated with an unusually large experimental error. The literature data are based on heavy extrapolations from other temperatures. For 80% EtOH, extrapolation of rate constants determined with 2-Ad-Br between 100 and 150 °C<sup>11</sup> gives  $5.3 \times 10^{-8} \text{ s}^{-1}$  at 70 °C. Assuming a Br/Cl ratio of 20<sup>12</sup> gives  $2.65 \times 10^{-9} \text{ s}^{-1}$  for

2-Ad-Cl, and interpolation of rate data for 1-Ad-Cl between 50 and 75 °C<sup>13</sup> results in  $2.7 \times 10^{-6} \text{ s}^{-1}$ . The final ratio of 2-Ad-Cl/1-Ad-Cl =  $9.8 \times 10^{-4}$  or  $\log(k/k_0) = -3.0$ . Similarly, the relative rate for 2-Ad-Cl/1-Ad-Cl in 80% acetone at 25 °C (extrapolated from other solvents) is  $4.8 \times 10^{-4} \text{ s}^{-1}$ .<sup>14</sup> Conversion to 70 °C by means of the Arrhenius equation assuming constant A-factors gives  $\log(k/k_0) = -2.9$ . The rate constant for 2-Ad-Br in 5% acetone at 75 °C is  $3.3 \times 10^{-4} \text{ s}^{-1}$ ,<sup>12</sup> that of 1-Ad-Cl extrapolates to 75 °C with  $7.43 \times 10^{-2} \text{ s}^{-1}$ .<sup>13</sup> Assuming the same ratio at 70 °C and a Br/Cl ratio of 20 gives a relative rate of  $2.2 \times 10^{-4} \text{ s}^{-1}$  and  $\log(k/k_0) = -3.65$ . In 97% HFIP the rate constant of 2-Ad-Cl at 70 °C, extrapolated from 71.5 °C is  $1.24 \times 10^{-5} \text{ s}^{-1}$ ,<sup>15</sup> and that of 1-Ad-Cl determined between 14 and 35 °C<sup>16</sup> extrapolates to 70 °C to give  $3.5 \times 10^{-2} \text{ s}^{-1}$ , thus  $\log(k/k_0) = -3.45$ . The lower rates in 5% acetone and HFIP are plausible and may be attributed to the high  $Y_{\text{Cl}}$  values of ca. five of these solvents. Nevertheless, in view of the experimental uncertainties, the average value of all of the data is used, hence  $\log(k/k_0) = -3.3$ . Owing to the higher nucleofugality of the tosylate group, the rate constants of OTs derivatives have less experimental variations: The 2-Ad-OTs/1-Ad-OTs rate ratios for 11 different solvents, including TFE and HFIP vary from  $3.2 \times 10^{-6}$  to  $12.2 \times 10^{-6} \text{ s}^{-1}$ , except that referring to 50% EtOH which deviates with  $5.1 \times 10^{-5}$  at 25 °C.<sup>17</sup> Conversion of the average of the 10 more consistent values to 70 °C as above gives  $\log(k/k_0) = -4.6$ .

**3.3. The Standard Enthalpy of Formation of Gaseous 2-Ad-Cl.**  $\Delta_f H_m^\circ(1\text{-Cl, g})$  was determined by combustion calorimetry, and the measurement of its vapor pressure was effected over a 16 K temperature interval. The energy of combustion was determined using a rotary-bomb calorimeter.<sup>18</sup> The vapor pressure of the compound was measured by means of the Knudsen-effusion technique,<sup>19</sup> and the enthalpy of sublimation was deduced from the temperature dependence of the vapor pressure (Clausius–Clapeyron).<sup>19</sup> Heat capacity measurements were also carried out by differential scanning calorimetry.<sup>20</sup>

**3.4. Ion Studies in the Gas Phase. 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 21. It has already been used in a number of studies.<sup>3,4</sup> The field strength of its superconducting 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.  $5 \times 10^{-4}$  mbar).

A summary of the experimental results is presented in Table 1, and full details are given as Supporting Information.

**B. The DPA Method.** The direct study of equilibrium 3 (with X = H, Cl, or Br) is a classical method.<sup>22</sup> Its usefulness is limited, however, to cases where the carbocations do not easily rearrange or appropriate reference compounds are

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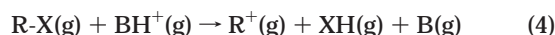
**Table 1. Experimentally Determined Standard Molar Energy of Combustion and Standard Molar Enthalpies of Combustion, Sublimation, and Formation in the Crystalline and Gaseous State at Temperature  $T = 298.15$  K for 2-Adamantyl Chloride (2-Ad-Cl).**

thermodynamic properties	experimental values <sup>a,b</sup>
$\Delta_c U_m^{\circ c}$	$-1402.03 \pm 0.55$
$\Delta_c H_m^{\circ d}$	$1404.09 \pm 0.55$
$\Delta_f H_m^{\circ}(\text{cr})^f$	$-54.44 \pm 0.65$
$\Delta_{\text{sub}} H_m^{\circ e}$	$14.7 \pm 0.2$
$\Delta_f H_m^{\circ}(\text{g})^g$	$-39.7 \pm 0.7$

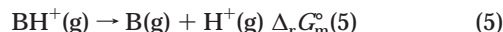
<sup>a</sup> All values in kcal mol<sup>-1</sup>. 1 kcal = 4.184 kJ. <sup>b</sup> This work. <sup>c</sup> Standard molar energy of combustion. <sup>d</sup> Standard molar enthalpy of combustion. <sup>e</sup> Standard molar enthalpy of sublimation. <sup>f</sup> Standard molar enthalpy of formation in the crystalline state. <sup>g</sup> Standard molar enthalpy of formation in the gaseous state.

available.<sup>3,4b,c</sup> This is why  $\Delta_r G_m^{\circ}(3)$  was obtained here by a different method, namely the dissociative proton attachment (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<sup>+</sup>(g) and neutral XH(g) molecules.<sup>3,4,23</sup> The DPA method allows one to find the base B such that its conjugate acid, BH<sup>+</sup>, is just able to transfer a proton to R-X (X = OH, halogen) according to eq 4. This defines the onset of DPA.



The gas-phase basicity of the base B, GB(B), is defined as the standard Gibbs energy change for reaction 5,  $\Delta_r G_m^{\circ}(5)$ .<sup>24</sup>



Let B<sub>1</sub> and B<sub>2</sub> stand for the two bases, respectively, defining the DPA onsets of R<sub>1</sub>X(g) and R<sub>2</sub>X(g) as determined under the same experimental conditions. Equation 6 holds:<sup>3,4</sup>

$$\Delta_r G_m^{\circ}(3) \approx \text{GB}(\text{B}_1) - \text{GB}(\text{B}_2) \quad (6)$$

Thanks to this expression, the experimental determination of the relative stabilities of R<sub>1</sub><sup>+</sup>(g) and R<sub>2</sub><sup>+</sup>(g) through the formal equilibrium 1 reduces to that of the DPA onsets for the corresponding precursors (eq 6).<sup>3,4,25</sup> In this work, the GB values of the reference bases are taken from the major critical compilation by Lias and Hunter.<sup>24</sup>

The experimental determination of these onsets involves a bracketing procedure. Therefore,  $\Delta_r G_m^{\circ}(3)$  values determined by this method are formally less precise (uncertainties estimated at ca. 2 kcal mol<sup>-1</sup>) than those obtained by direct equilibration. In practice, this inconvenience is largely offset by the facts that the carbocations are generated under extremely mild conditions and are much less prone to rearrange than in the standard equilibrium experiments.<sup>3,4,25</sup> and by the availability of over a thousand reliable GB values.<sup>24</sup>

**C. The DPA Experiments.** The technique used here is the same as in refs 3, 4, and 25. Full details are given as Supporting Information.

**Table 2. Computational Results at the G2(MP2) Level for Relevant Species<sup>a</sup>**

species	$H_{298}$	$G_{298}$
2-Ad-Cl	$-849.03403^b$	$-849.07665^b$
2-Ad <sup>+</sup>	$-388.97604^c$	$-389.016161^b$
1-Ad-Cl	$-849.03829^d$	$-849.07974^d$
1-Ad <sup>+</sup>	$-388.99432^d$	$-389.03284^d$

<sup>a</sup> All values in Hartree. <sup>b</sup> This work. <sup>c</sup> From ref 7. <sup>d</sup> From ref 8.

**Table 3. Thermodynamic State Functions for Relevant Species**

species	$\Delta_f H_m^{\circ}(\text{g})$	$S_m^{\circ}(\text{g})$
2-Ad-Cl	$-39.7 \pm 0.7^a$	$89.7 \pm 2.0^f$
1-Ad-Cl	$-42.45 \pm 0.60^b$	$87.2 \pm 2.0^f$
2-Ad <sup>+</sup>	$171 \pm 3^c$	$81.1 \pm 2.0^e$
	$171.9 \pm 1.1^d$	
1-Ad <sup>+</sup>	$162.0 \pm 2.0^b$	$84.5 \pm 2.0^f$

<sup>a</sup> Experimental value, this work. <sup>b</sup> Experimental value from ref 8. <sup>c</sup> Experimental value from ref 5a. <sup>d</sup> Experimental value from ref 5b. <sup>e</sup> Computed value, this work. <sup>f</sup> Computed value from ref 8.

**Table 4. Changes in Thermodynamic State Functions for Reaction 3<sup>a</sup>**

method <sup>b</sup>	$\Delta_f H_m^{\circ}(3)$	$\Delta_r G_m^{\circ}(3)$
1	-8.80	-8.53
2a	$-6.3 \pm 3.7$	$-6.0 \pm 3.8$
2b	$-7.2 \pm 2.5$	$-6.9 \pm 2.6$
3	$-7.9 \pm 2.9$	$-7.6 \pm 2.8$

<sup>a</sup> All values in kcal mol<sup>-1</sup>. <sup>b</sup> See text.

We found that the strongest base able to lead to the DPA of 2-Ada-Cl is *n*-propyl formate (GB = 186.93 kcal mol<sup>-1</sup>)<sup>24</sup> and the weakest base unable to lead to this DPA is acetone (GB = 184.97 kcal mol<sup>-1</sup>).<sup>24</sup> The DPA onset for 2-Ad-Cl is thus taken as the average value,  $186.0 \pm 2.0$  kcal mol<sup>-1</sup>. This result, combined with the DPA onset for 1-Ad-Cl,  $193.6 \pm 2.0$  kcal mol<sup>-1</sup>, leads to  $\Delta_r G_m^{\circ}(3) = -7.6 \pm 2.8$  kcal mol<sup>-1</sup>.

**3.5. Computational Methods.** Calculations were performed using the Gaussian 98 package of computer programs.<sup>26</sup> G2(MP2) results for the relevant species as obtained in this and previous studies are summarized in Table 2. The results of ancillary calculations at the HF/6-31G(d) level, discussed below, are given in Table S5 (Supporting Information).

## 4. Results and Discussion

**4.1. Thermodynamic Results.** The thermodynamic state functions for the relevant species are given in Table 3. Table 4 summarizes the results for reaction 3 obtained as indicated in sections 2 and 3. Notice that (i) G2(MP2) calculations show that the largest contributor to  $\Delta_r G_m^{\circ}(3)$  is by far  $\Delta_f H_m^{\circ}(3)$ . The computed  $\Delta_r S_m^{\circ}(3)$ ,  $(0.91 \pm 2.8)$  cal mol<sup>-1</sup> K<sup>-1</sup> is used throughout the subsequent discussion;<sup>9</sup> (ii) the average of the experimental  $\Delta_f H_m^{\circ}(2\text{-Ad}^+\text{g})$  values obtained from appearance energies<sup>5a</sup> and the ionization energy of 2-Ad<sup>5b</sup>,  $171.5 \pm 2.8$  kcal mol<sup>-1</sup> is used for the determination of  $\Delta_r G_m^{\circ}(3)$

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according to method 2. Results in Table 4 show that the value of  $\Delta_r G_m^\circ(3)$  obtained experimentally in this work agrees within 1 kcal mol<sup>-1</sup> with both the G2(MP2) datum and with the average of the experimental values (method 2), obtained from literature data.<sup>5,8</sup>

**4.2. Discussion.** Equation 2 links  $\log(k/k_0)$  for the rates of tosylate solvolysis with  $\Delta_r G_m^\circ(1)$ , pertaining to chloride exchange in the gas phase. The rate constants for bridgehead derivatives used in eq 2 have originally been determined with different leaving groups and in different solvents and are extrapolated to standard conditions (OTs leaving group, solvolysis in 80% EtOH at 70 °C), but it is generally accepted that in a first approximation, relative rates of bridgehead derivatives are independent of the leaving group and solvent.<sup>27</sup> Indeed, leaving group corrections as expressed by  $\Delta_r G_m^\circ(7)$  (defined in eq 7) for bridgehead derivatives are small (absolute values below 1 kcal mol<sup>-1</sup>) with respect to the overall range of ion stabilities. Since  $\Delta_r G_m^\circ(1)$  for bridgehead derivatives and for 2-Ad-Cl refer both to chlorides, the latter datum can be incorporated into eq 2. The average rate of solvolysis of 2-Ad-Cl relative to 1-Ad-Cl at 70 °C is  $\log(k/k_0) = -3.3$ . The calculated value according to eq 2 with  $\Delta_r G_m^\circ(3)$  (-7.6 kcal/mol) is -2.7 and, therefore, lies within the standard deviation for bridgehead derivatives (0.7 log units). The rate of 1-OTs may be fitted to eq 2 after application of the appropriate leaving group correction  $\Delta_r G_m^\circ(7)$ . This correction is not as small as those in the bridgehead series. From data given in Table S3 it was estimated at 3.7 kcal mol<sup>-1</sup> (using benzenesulfonates instead of tosylates). This is mainly due to an entropy effect: 2-Ad-OTs is more stable by ca. 1.5 kcal/mol than the 1-isomer although the enthalpies are about equal. Note that 1-Ad-Cl, in turn is mores stable than 2-AdCl by 2 kcal/mol.<sup>28</sup> Thus  $\Delta_r G_m^\circ(3)$  of 2-Ad-OTs becomes -11.3, and  $\log(k/k_0)_{\text{calcd}} = -4.2$ , while the experimental  $\log(k/k_0)$  is -4.7.

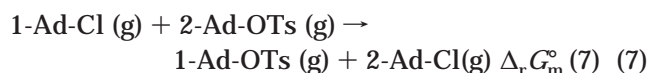
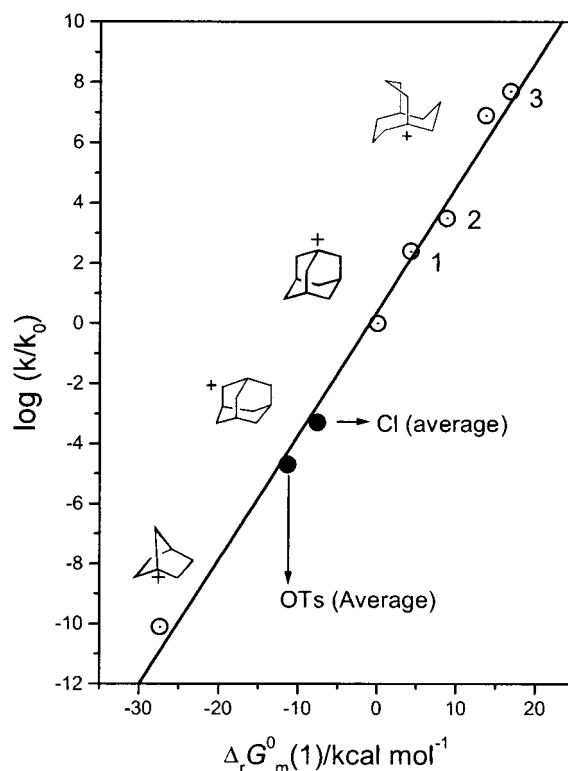


Figure 1 is a plot of the experimental  $\log(k/k_0)$  values for the solvolysis of the tertiary bridgehead chlorides in aqueous 80% EtOH at 70 °C, against  $\Delta_r G_m^\circ(1)$  (using data from ref 3b). As earlier indicated, they satisfy eq 2. Also shown are the data of 2-Ad-Cl and 2-Ad-OTs, the latter with the correction,  $\Delta_r G_m^\circ(7)$ , discussed above. As it can be seen, the points fall well within the uncertainty limits of the correlation. We conclude therefore that the correlation between thermodynamic stabilities of carbocations and solvolysis rates in S<sub>N</sub>1 reactions already established for tertiary bridgehead species applies also to secondary derivatives in the absence of solvent assistance.

Very recently, Takeuchi, Abboud, and co-workers<sup>25</sup> have applied the same methodology to the study of tertiary alkyl derivatives with increasingly bulkier substituents. They found that *tert*-butyl derivatives solvolyze faster than expected on the basis of this correlation (the largest departure was that for *tert*-butyl itself), and that increasing congestion around the cationic center brings the experimental data points closer to the bridgehead line. Indeed,  $\log(k/k_0)$  values for heavily substituted



**Figure 1.** Plot of  $\log k$  for bridgehead chlorides relative to 1-chloroadamantane vs experimental standard Gibbs energy change for chloride exchange in the gas phase,  $\Delta_r G_m^\circ(1)$ , with leaving group correction. Points 1 to 3 are, respectively, 3-homoadamantyl, 1-bicyclo[3.3.2]decy, and [1]diadamantyl.

species such as 4-ethyl-2,2-dimethylhexyl, do satisfy eq 2. Compounds reacting faster than expected on the grounds of this correlation are believed to profit from nucleophilic solvation. Our present results strongly support the hypothesis that in the absence of nucleophilic solvation, secondary derivatives should also satisfy eq 2. Nucleophilic solvation is the more appropriate term in the context of tertiary aliphatic derivatives for what was originally called nucleophilic solvent participation.<sup>29</sup>

## 5. Conclusions

1. Equation 2 also holds for secondary derivatives in the absence of nucleophilic solvation effects. This implies that when this condition holds, the thermodynamic stability of secondary carbocations is the leading factor determining the reactivity of their derivatives in the absence of solvent participation as is the case for tertiary bridgehead species.

2. Our results confirm that positive deviations from this behavior are measures of enhanced solvation effects.

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**Supporting Information Available:** Experimental details and tables of results for the determination of  $\Delta H_m^\circ(2\text{-Ad-Cl})$ , DPA experiments, and computation of the leaving group correction. This material is available free of charge via the Internet at <http://pubs.acs.org>

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