

Correlation of Gas-Phase Stability of Bridgehead Carbocations with Rates of Solvolysis and *ab Initio* Calculations

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Abstract: The stability of bridgehead carbocations has been determined by Fourier transform ion cyclotron resonance spectroscopy (FT ICR) based on dissociative proton attachment (DPA) of bromides and alcohols. The stability of the ions correlates with the solvolytic reactivity of bridgehead derivatives over a rate range of 23 log units, and with theoretical calculations for hydride transfer of bridgehead hydrocarbons at the MP2/6-311G** level.

I. Introduction

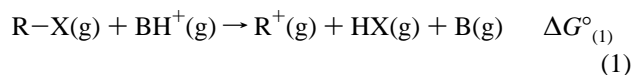
Experimental insight into the structures of tertiary aliphatic carbenium ions has become available through NMR studies¹ and X-ray crystallography.² Much less information exists, however, with respect to their energies. Although some data have been determined in the gas³ and in the condensed phase,⁴ much of our knowledge on carbenium ion stabilities is derived from solvolytic studies.⁵ The early empirical force-field calculations of Schleyer *et al.*⁶ correlating solvolytic reactivity with strain changes between bridgehead derivatives and the corresponding carbenium ions suggest that the transition state for solvolysis should occur late on the reaction coordinate and resemble the carbenium ion with respect to structure and energy.

However, lack of reliable experimental data on the stability of carbenium ions in the bridgehead series made it impossible to verify this hypothesis. Until very recently adamantane was the only bridgehead derivative for which the stability of the cation had been determined.³ An attempt was made to determine the heterolytic bond dissociation energies $D(\text{R}^+ - \text{X}^-)$ of bridgehead bromides in the gas phase by ICR methods,

but the experimentally accessible range of ion stabilities was limited owing to apparent rearrangements of the highly strained ions under the conditions of the experiments.⁷

The observation of rearrangements upon generation of strained carbenium ions in the gas phase is, in part, due to the methods of ionization. In the past, most bridgehead cations, and also simple tertiary ions, were generated in the gas phase by electron ionization of halogen derivatives with ionization energies in the range of 9–12 eV (213–276 kcal/mol). Ions thus obtained were then subject to halide exchange reactions, and the equilibrium constants were determined by ICR and high pressure mass spectrometry (HPMS).⁷ The energies used in the ionization process are large enough to break not only the carbon–halogen bond, but also other bonds, as shown by the extensive fragmentation often observed, and the frequently low yields of the ions of interest. Under these conditions, rearrangements of such ions are to be expected.

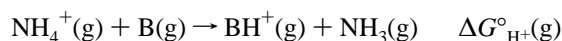
Recently, one of us⁸ used Fourier transform ion cyclotron resonance spectroscopy (FT ICR) to develop a method for determination of ion stabilities based on dissociative proton attachment (DPA) of halides. Protonation of halides $\text{R}-\text{X}$ produces weakly associated complexes which decay almost without activation to free ions and HX . The FT ICR experiments allow one to determine the bases B such that their conjugate acids BH^+ are just able to transfer a proton to $\text{R}-\text{X}$, according to reaction 1:



$\text{X} = \text{OH}, \text{halogen}$

For such a base, $\Delta G^\circ_{(1)} \approx 0$ (see ref 8).

The gas-phase basicity of B is expressed with respect to NH_3 , according to:



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$\Delta G^\circ_{\text{H}^+}(\text{g})$ is the basicity of the base B, relative to ammonia, which leads to the DPA embodied in eq 1.⁹ In the DPA method, ionization is effected essentially under thermal conditions, so that the ions have much less opportunity to rearrange than when generated upon electron impact as in the standard ICR approach. We have now applied the method to a series of highly strained bridgehead bromides. In addition, the method was extended to alcohols, and this allowed the determination of ion stabilities for structures where the bromo derivatives were not isolable.

II. Experimental Section

A. Synthesis of Alcohols and Bromides. The compounds used in this study were either purchased or synthesized according to procedures reported in the literature. Thus 2-*tert*-butyladamantan-2-ol (**1a**) and 9-*tert*-butylbicyclo[3.3.1]nonan-9-ol (**2b**) were obtained by reaction of *tert*-butyllithium with 2-adamantanone and 9-bicyclo[3.3.1]nonan-2-one, respectively.¹⁰ 1-Bromobicyclo[2.2.2]octane (**4**) was synthesized according to the procedure of Morita *et al.*¹¹ Bromocubane (**6**), 6-bromotricyclo[3.2.1.0^{3,6}]octane (**10**), homocubane-4-carboxylic acid, and 1-bromohomocubane (**8**) were prepared as described.¹² 3-Bromonoradamantane (**7**) was synthesized in 94% yield by oxidative decarboxylation of 3-noradamantanecarboxylic acid.¹³ 1-Bromonorbornane (**9**)¹⁴ was accessible from the chloride by halide exchange.¹⁵

4-Bromohomocubane (5). Homocubane-4-carboxylic acid (0.30 g, 1.85 mmol) and 1-hydroxypyridine-1(*H*)-thione (0.24 g, 1.85 mmol) were dissolved in dichloromethane (15 mL); the solution was cooled to 0 °C under an atmosphere of nitrogen. Dicyclohexylcarbodiimide (0.40 g) was added in one portion, and the mixture was stirred for 2 h. Dicyclohexylurea was filtered off and washed with dichloromethane (2 mL) and the washings combined with the filtrate and evaporated at room temperature. The residue was dissolved in 1-chloro-2,2,2-trifluoroethane (4 mL) and the solution irradiated with a tungsten lamp (300 W) for 1 h. The solution was cooled, washed successively with cold concentrated HCl (3 mL) and saturated sodium bicarbonate solution (3 mL), and then dried (MgSO₄). Careful removal of the solvent and distillation (Kugelrohr: 90 °C/0.1 mm) of the residue gave 4-bromohomocubane (0.26 g, 71%), which had identical properties with those reported.¹⁶

B. The FT ICR Spectrometer. The study was carried out on a modified Bruker CMS-47 FT ICR mass spectrometer¹⁷ used in previous studies.^{8,18} A detailed description is given in refs 10 and 11. Some modifications have been introduced with respect to the standard instrument. They are described in ref 18. The substantial field strength

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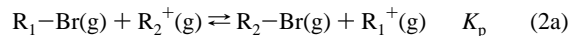
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of its supraconducting magnet, 4.7 T, allows the monitoring of ion molecule reactions for relatively long periods of time.

C. Bromide Exchange Experiments. The equilibrium constant K_p for reaction 2a, the exchange of bromide between the carbenium ions R_1^+ and R_2^+ in the gas phase, has been determined directly in some instances, by means of the standard experimental technique already used by a number of workers, including Beauchamp,¹⁹ Taft,²⁰ Kebarle²¹ (the latter used high pressure mass spectrometry instead of ICR) and ourselves.^{7a}



K_p values defined through eq 2b were obtained by combining the ratio of the intensities of R_1^+ to R_2^+ (taken as a measure of the ratio of the partial pressures of these ions) with the ratio of the partial pressures of the neutral reagents.

$$K_p = [P(R_2\text{Br})/P(R_1\text{Br})][P(R_1^+)/P(R_2^+)] \quad (2b)$$

The standard Gibbs energy change for reaction 2a, $\Delta G^\circ_{(2a)}$ is given by the equation

$$\Delta G^\circ_{(2a)} = -RT \ln K_p$$

D. Dissociative Proton Attachment Method (DPA). The basic concepts of the method and its thermodynamic implications have been developed in ref 8 and are summarized in the Introduction. The general procedure for the generation of a carbenium ion $R^+(\text{g})$ starting from $R\text{-X}(\text{g})$ ($X = \text{Br}, \text{OH}$) is as follows. A mixture of known composition of $R\text{-X}(\text{g})$ and a base ($B(\text{g})$) is prepared. The mixture is introduced into the high-vacuum section of the instrument and subjected to electron ionization (generally using nominal energies of 10–13 eV). Nominal pressures of $R\text{-X}(\text{g})$ are in the range of 1–2 10^{-7} mbar. Pressures of B are some 3 to 20 times larger, depending on the system. Charged fragments (mostly from B) act as primary ion sources. In general, after 1–2 s, the main ions present are $BH^+(\text{g})$ and $R^+(\text{g})$. Then, depending on the system, one of the following series of experiments was performed.

1. Determination of DPA Thresholds. This is carried out according to the procedure described in ref 8: First, the system is allowed to evolve for at least 5 s, and all ions, with the exception of $BH^+(\text{g})$, are ejected off the ICR cell²² by means of radiofrequency ejection “chirps” (broad band). Great care is taken in order to avoid the excitation of this ion, and so use is made of an “ejection safety belt” (a feature of the Bruker software that strictly prevents the irradiation of a preselected frequency range around the resonance energy of BH^+ in order to avoid its accidental excitation). $BH^+(\text{g})$ is then allowed to react for times of up to 100 s. During this period of time, the main reactions observed are, first the formation of $R^+(\text{g})$, and later on that of the hydrogen-bonded dimers of B, $B_2H^+(\text{g})$, and, eventually, variable amounts of $(B\text{-R})^+(\text{g})$. The formation of $B_2H^+(\text{g})$ is frequently met in proton-exchange studies. The formation of $(B\text{-R})^+(\text{g})$ is a consequence of both the electrophilicity of $R^+(\text{g})$ and the stability of this ion with respect to proton donation to B(g).

Given the very low working pressures prevailing in the experiments, reaction 1 is essentially irreversible (the partial pressure of XH is extremely small), and so, while a true equilibrium is not reached, the onset of this process can be clearly determined.

2. DPA–Bromide Exchange Experiments. Here, features of both methods are combined. It is useful when one of the halides, say $R_2\text{-Br}$, is likely to lead to secondary reactions. This is the case of the cubyl derivatives (particularly **6** and **8**) (this may be related to the fact

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Table 1. Experimentally Determined Gibbs Energy Changes for Reaction 2a, $\Delta G^\circ_{(2a)}$ ^a

R ₁ Br	R ₂ ⁺	$\Delta G^\circ_{(2a)}$	R ₁ Br	R ₂ ⁺	$\Delta G^\circ_{(2a)}$
1-bromoadamantane	2-norbornyl	-2.3 (0.3) ^b	4-bromohomocubane	bicyclo[2.2.2]octyl ^c	2.5 (0.3) ^d
2-bromo-2-methylpropane	2-norbornyl	3.0 (0.3) ^b	1-bromohomocubane	1-norbornyl ^c	-0.6 (0.3) ^d
bromocubane	3-noradamantyl ^c	0.5 (0.3) ^d			

^a All values in kcal mol⁻¹. Estimated uncertainties are given in parentheses. ^b Values obtained by the standard bromide exchange method. ^c Ions generated by the DPA technique. ^d Values obtained by combining DPA and bromide exchange. See text.

Table 2. Experimentally Determined DPA Thresholds for Reaction 1^a

compound	reference ^b (Δ GB) ^c	reference ^d (Δ GB) ^a	$\Delta G^\circ_{H^+(g)}$ ^e
1a 2- <i>tert</i> -butyl-2-adamantanol	<i>n</i> -BuNH ₂ (-15.6)	EtC(O)NMe ₂ (-16.6)	-16.1
2a 9- <i>tert</i> -butyl-9-bicyclo[3.3.1]nonanol	<i>n</i> -PrNH ₂ (-15.1)	<i>n</i> -BuNH ₂ (-15.6)	-15.4
3a 1-adamantanol	<i>n</i> -Bu ₂ S (-5.6)	pyrazine (-6.1)	-5.9
3b 1-bromoadamantane	Et ₂ CO (2.8)	<i>t</i> -BuOMe (2.2)	2.5
4 1-bromobicyclo[2.2.2]octane	Me ₂ CHCN (10.6)	HCO ₂ <i>n</i> -Pr (10.5)	10.6
7 3-bromonoradamantane	MeCHO (18.0)	MeSH (16.9)	17.5
9 1-bromonorbornane	Cl ₃ CCN (27.5)	Cl ₃ CCH ₂ OH (26.0)	26.8
10 6-bromotricyclo[3.2.1.0 ^{3,6}]octane	(CF ₃ CH ₂) ₂ O (33.3)	H ₂ CO (30.8)	32.1

^a All values in kcal mol⁻¹. ^b Strongest base able to lead to DPA. ^c Gas-phase basicities of the reference bases, relative to ammonia (see text). ^d Weakest base not leading to DPA. ^e Average of two (Δ GB) values. that cubane has a high gas-phase basicity, well above the DPA thresholds of all the bromides studied in this work²³).

The study is carried out with a mixture of known amounts of R₁-Br(g) and R₂-Br(g) and B(g) under conditions similar to those given above. The gas-phase basicity of B is close to, but lower than the DPA threshold of R₁-Br(g), the "well-behaved halide". Some 5 s after electron ionization of the mixture, BH⁺(G) is selected and allowed to react with R₁-Br(g) and R₂-Br(g). Of the various ions formed, R₁⁺(g) is selected and its reaction monitored. The relevant process taking place under these conditions is reaction 2a. After reaction time of up to 20 s, *K_p* values are determined by means of eq 2b as in the standard halide exchange method.

The experimental uncertainties on $\Delta G^\circ_{(2a)}$ are estimated to be at least 0.3 kcal mol⁻¹. This is the usual size of uncertainties affecting relative gas-phase basicities studied by means of proton-exchange reactions. Here, the situation is less favorable because of (a) the absence of appropriate references to carry out multiple overlap studies and (b) the fact that some of the *K_p* values are large. As indicated above, uncertainties on $\Delta G^\circ_{H^+(g)}$, the DPA thresholds, are estimated to 2 kcal mol⁻¹.

Tables 1 and 2 summarize the experimental results obtained in this work.

III. Computational Details

All the structures studied in this work were fully optimized at the HF/6-31G* level.²⁴ The harmonic vibrational frequencies were determined analytically and used to compute the corresponding zero-point energies (scaled by a factor of 0.9135),²⁵ thermal corrections, and entropies. The structures of the carbenium ions R⁺ having between 4 and 10 carbon atoms as well as those of the corresponding hydrocarbons, R-H, were further subject to a complete optimization at the MP2/6-311** level. All calculations were performed on a Silicon Graphics "Challenge" Computer, using the Gaussian 94 (Revision B.3)²⁶ program. The results of these calculations are collected in Table 3.

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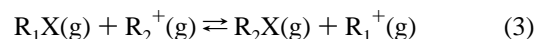
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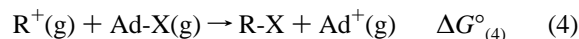
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IV. Discussion

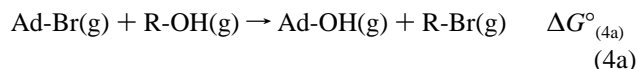
Consider two compounds, R₁X and R₂X. It can be easily shown that the difference of their DPA thresholds equals the standard Gibbs energy change for reaction 3:



This important fact allows us to unify the results obtained by halide exchange and DPA (see Experimental Section). The results are summarized as $\Delta G^\circ_{H^+(g)}$ values in Table 4. Also given are the ion stabilities expressed relative to the 1-adamantyl cation (Ad⁺) by means of $\Delta G^\circ_{(4)}$, the standard Gibbs energy change for reaction 4:



The $\Delta G^\circ_{(4)}$ values for 2-bromo-2-*tert*-butyladamantane (**1b**) and 9-bromo-9-*tert*-butylbicyclo[3.3.1]nonane (**2b**) were determined by combining the experimental $\Delta G^\circ_{(4)}$ values of the corresponding alcohols **1a** and **2a**, respectively, relative to 1-adamantanol (Ad-OH, **3a**) with the standard Gibbs energy changes for the isodesmic reactions 4a:



The $\Delta G^\circ_{(4a)}$ values for **1b** and **2b** amount to 5.68 and 5.64 kcal/mol, respectively, at the 6-31G* level.²⁴ It should be emphasized that the ranking of stabilities of carbenium ions is independent of the nature of X. Results to be published elsewhere obtained with chlorides, bromides and alcohols are in remarkably good agreement.

In Figure 1 $\Delta G^\circ_{(4)}$ values are plotted against the standardized rates of solvolysis (log *k* for solvolysis with OTs leaving groups, in 80% EtOH at 70°, relative to 1-adamantyl-*p*-toluenesulfonate).^{27,28} The correlation spans about 23 log units for *k*. Taking into account that at 70° one order of magnitude in rate constants corresponds to 1.57 kcal mol⁻¹ in Gibbs energy of activation, this amounts to 36.1 kcal mol⁻¹ and almost 50 kcal/mol in Gibbs energies for bromide exchange. It covers practically the full experimental rate range for solvolytic bridgehead reactivities, including the previously not accessible 1-homocubyl (**8**⁺), 1-norbornyl (**9**⁺), and 6-tricyclo[3.2.1.0^{3,6}]-

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Table 3. Total Energies^a at HF/6-31G* and MP2/6-311G** Levels, Zero-Point Vibrational Energies (ZPE)^a Thermal Correction to Enthalpies (TCE)^a and Total Entropy Values (S)^b for the Species Studied in this Work

compound	HF/6-31G*	MP2/6-311G**	ZPE ^{a,d}	TCE ^a	S ^d
2-tert-butyladamantane	-544.143 796		0.349 717	0.354 133	102.08
2-tert-butyl-2-adamantanol	-618.988 536		0.354 724	0.359 711	103.48
9-tert-butylbicyclo[3.3.1]nonane	-506.257 855		0.342 348	0.347 478	104.25
9-tert-butylbicyclo[3.3.1]nonanol	-581.102 266		0.347 479	0.353 159	106.15
adamantane	-388.026 478	-389.592 731	0.238 762	0.239 823	79.86
1-adamantyl	-387.180 304	-388.705 010	0.226 767	0.228 254	80.27
adamantanol	-462.882 909		0.242 844	0.245 876	84.58
1-bromoadamantane	-295.345 085		0.229 210	0.232 853	88.80
bicyclo[2.2.2]octane	-311.103 599	-312.388 487	0.202 363	0.204 244	81.85
bicyclo[2.2.2]oct-1-yl	-310.246 490	-311.464 498	0.190 446	0.192 716	80.73
1-bromobicyclo[2.2.2]octane	-2880.421 136		0.192 931	0.197 301	90.07
homocubane	-346.504 487	-347.859 363	0.162 206	0.163 174	72.43
1-homocubyl	-345.615 165	-346.924 581	0.149 358	0.150 943	73.41
1-bromohomocubane	-2915.819 435		0.152 663	0.156 227	81.89
4-homocubyl	-345.623 485	-346.947 954	0.148 791	0.150 585	74.28
4-bromohomocubane	-2915.821 215		0.152 729	0.156 351	82.37
cubane	-307.393 906	-308.580 611	0.132 288	0.133 396	69.62
cubyl	-306.507 589	-307.665 563	0.118 599	0.120 335	70.45
bromocubane	-2876.710 581		0.122 858	0.126 558	79.55
noradamantane	-348.970 068	-350.376 567	0.209 766	0.215 414	76.38
3-noradamantyl	-348.101 166	-349.461 809	0.197 097	0.198 642	77.62
3-bromonoradamantane	-2918.285 595		0.200 176	0.203 675	85.55
norbornane	-272.061 201	-273.164 341	0.173 604	0.174 930	73.79
1-norbornyl	-271.181 170	-272.235 168	0.161 343	0.163 263	74.92
1-bromonorbornane	-2841.376 669		0.164 133	0.167 951	82.99
2-norbornyl	-271.200 613	-272.269 098	0.160 967	0.163 067	76.84
2-bromonorbornane	-2841.375 277		0.164 463	0.168 159	83.14
tricyclo[3.2.1.0 ^{3,6}]octane	-309.903 129	-311.146 170	0.179 783	0.180 847	73.68
6-tricyclo[3.3.1.0 ^{3,6}]octyl	-309.011 188	-310.205 790	0.167 197	0.168 928	74.88
6-bromotricyclo[3.2.1.0 ^{3,6}]octane	-2879.217 708		0.170 292	0.173 921	83.05
2-methylpropane	-157.298 978	-157.964 175	0.128 600	0.131 140	71.18
tert-butyl	-156.442 549	-157.056 582	0.107 725	0.111 480	75.65
2-bromo-2-methylpropane	-2726.614 852		0.119 514	0.124 134	77.15

^a In hartree. ^b In kcal mol⁻¹ K⁻¹. ^c Evaluated at HF/6-31G* level. ^d ZPE values corrected by the factor 0.9135.²⁵

Table 4. Experimental and Theoretical Data for Gas-Phase and Solution Reactions^a

compound	$\Delta G^\circ_{\text{H}^+}(\text{g})$	$\Delta G^\circ_{(4)}$	$\Delta G^\circ_{(5)}$	$\Delta G^\circ_{(6)}$	$\Delta G^\circ_{(6)}(\text{th})$	$\Delta \log k_{\text{sol}}$
1a 2-tert-butyl-2-adamantanol	-16.1	10.2 ^b	-8.0	2.2		
1b 2-tert-butyl-2-bromoadamantane		15.9 ^{c,d}		2.2		8.8
2a 9-tert-butyl-9-bicyclo[3.3.1]nonanol	-15.4	9.5 ^b	-8.1	1.4		
2b 9-tert-butyl-9-bromobicyclo[3.3.1]nonane		15.1 ^{c,d}		1.4		8.6
3a 1-adamantanol	-5.9	0.0 ^b		0.0		
3b 1-bromoadamantane	2.5	0.0 ^d	0.0 ^d	0.0	0.0	0.0
4 1-bromobicyclo[2.2.2]octane	10.6	-8.1 ^d	-0.9	-9.0	8.5	-3.6
5 4-bromohomocubane		-10.6 ^{d,e}	-1.0	-11.6	-14.7	-5.9 ^h
6 bromocubane		14.5 ^{d,e}	-0.6	-15.1	-16.3	-7.3
7 3-bromonoradamantane	17.5	-15.0 ^d	-1.8	-16.8	-16.9	-6.9
8 1-bromohomocubane		-23.7 ^{d,e}	-2.1	-25.8	-29.3	-11.0 ^h
9 1-bromonorbornane	26.8	-24.3 ^d	-2.0	-26.3	-26.2	-10.1
10 6-bromotricyclo[3.2.1.0 ^{3,6}]octane	32.1	-29.6 ^d	-2.5	-32.1	-33.1	-13.9 ^h
11 2-bromonorbornane		-2.3 ^{d,f}	-2.9	-5.2 (-5.9) ^g	-5.3	
12 2-bromo-2-methylpropane		-5.9 ^{d,f}	-2.6	-8.5 (-8.2) ^g	-8.6	

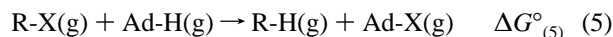
^a All Gibbs energies in kcal mol⁻¹. ^b Relative to **3a**. ^c Calculated as indicated in the text. ^d Relative to **3b**. ^e Determined as indicated in the text. ^f Determined by the standard bromide method. See text and Table 1. ^g Experimental value from Kebarle and co-workers.²¹ ^h Extrapolated from triflate solvolysis.²⁸

octyl (**10**⁺) cations. To our knowledge, this is the widest range ever reported for correlation of gas-phase data and solution kinetics. Correlation coefficient ($r = 0.9957$) and standard deviation ($\sigma = 0.77$ on $\log k$) are very satisfactory. The slope of the correlation between $\log k$ and the ion stabilities (-0.49) implies that 77% of the energy difference between the bromides and the respective cations are expressed in the rates of solvolysis. This slope compares favorably with that of -0.39 relating $\log k$ with strain changes between R^+ and $\text{R}-\text{Br}$.⁵⁻⁷ The consistency between the two sets of experimental data supports fully the basic mechanistic concepts on bridgehead solvolysis.

Comparison of the present set of cation stabilities with the previous one, determined by ICR,^{7a} reveals discrepancies for

ions more strained than bicyclo[2.2.2]octyl (**4**⁺). The rearrangement of the norbornyl cation (**9**⁺) under ICR conditions has been noted previously.^{7a} It now appears, that, in addition, the cubyl (**6**⁺) and 3-noradamantyl (**7**⁺) cations might also have undergone rearrangement in the ICR spectrometer and are slightly less stable than previously suggested.

Since the ion stabilities in the gas phase are free of solvation effects, they represent intrinsic properties and are, therefore, amenable to rigorous quantum chemical calculations. Since no experimental data are available for the energy of the majority of the neutral species, a leaving group correction ($\Delta G^\circ_{(5)}$) was applied to the $\Delta G^\circ_{(4)}$ values as defined by eq 5:



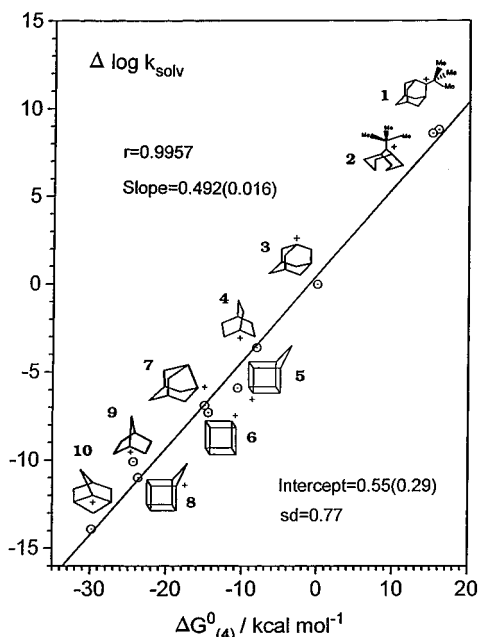
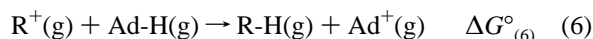


Figure 1. Log k_{solv} values relative to 1-adamantyl *vs* experimental standard Gibbs energy changes ($\Delta G^\circ_{(4)}$) for bromide exchange in the gas phase (reaction 4). Values in parentheses are standard deviations. Data from Table 4.

Owing to the large number of atoms in these molecules, and since only neutral species are involved, this corrective term ($\Delta G^\circ_{(5)}$) was computed only at the HF 6-31G**//6-31G* level, but, nevertheless, with full energy optimization (see Experimental Details). In the bridgehead series, $\Delta G^\circ_{(5)}$ varies in a rather narrow range from -0.9 to -2.6 kcal/mol; however, in the case of **1a** and **2a** the values are -8.0 and -8.1 , respectively. This suggests that the high solvolytic reactivity of **1a** and **2a**, as well as that of the corresponding bromides, is due to a front-strain effect,²⁹ and not to some particular stabilization of the carbenium ions. Although this F-strain effect is treated adequately by force-field calculations of **1a,b** and **2a,b**, respectively, it was not recognized as such in the past.²⁷

Combination of eqs 4 and 5 leads to eq 6 for hydride exchange between R^+ and adamantane (Ad-H):



Kebarle *et al.* have used high-pressure mass spectrometry to directly determine $\Delta G^\circ_{(4)}$ for the 2-norbornyl (**11**⁺) and *tert*-butyl (**12**⁺) cations.²¹ Their experimental values, which are also included in Table 4, are in excellent agreement with the values reported here.

In order to secure completely independent evidence for the absence of rearrangements for the systems studied in this work, thermodynamic Gibbs energy changes for the relevant reactions, $\Delta G^\circ_{(6)}(\text{th})$, were determined by means of high-level *ab initio* calculations (see Experimental Details) for compounds having up to 10 carbon atoms. The calculated values for $\Delta G^\circ_{(6)}(\text{th})$ are given in Table 4. Figure 2 shows a plot of $\Delta G^\circ_{(6)}(\text{th})$ in function of the experimental values for hydride transfer $\Delta G^\circ_{(6)}(\text{exp})$, after leaving group correction according to eq 4a and eq 5.

As Figure 2 shows, the two sets of data correspond almost perfectly. The agreement between theoretical and experimental values provides strong support for the experimental method and

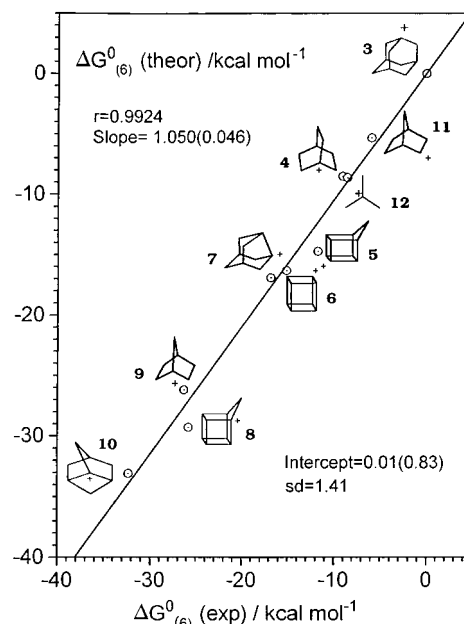


Figure 2. Calculated (MP2/6-311G**) *vs* experimental standard Gibbs energy changes for reaction 6. Values in parentheses are standard deviations.

confirms that no rearrangements took place in the DPA experiments. It also lends credibility to the empirical force-field calculations which predicted the same trends with much simpler means.⁷

The unusually high stability of the 2-norbornyl cation (**11**⁺) has been the subject of much controversy in the past.³⁰ It is of interest to note that the secondary **11**⁺ lies nicely on the correlation line in Figure 2, although the latter is defined by tertiary ions. The stability of the 2-norbornyl cation (**11**⁺) is close to that of the 1-adamantyl cation (**3**⁺). It is much more stable than simple "classical" secondary or strained tertiary carbenium ions (see below). Our MP2/6-311G** calculations lead to a structure of **11**⁺ in which the carbon-carbon bond lengths agree within 0.04 Å or better with that reported by Jorgensen, Schleyer, Schaefer, and co-workers³¹ in a recent high-level theoretical study on the stability of this ion in the gas phase and in solution. All these results are obviously in agreement with the nonclassical structure of **11**⁺.

Our results demonstrate the overwhelming significance of strain on the stability of tertiary carbenium ions, which may be destabilized to such a degree that they lie in the range of secondary ions. Chloride exchange reactions in the gas phase reveal an enthalpy difference of 14.6 kcal/mol between the *tert*-butyl and the 2-propyl cation.²¹ With the same difference we assign a $\Delta G^\circ_{(6)}$ value of about -20.6 kcal/mol to the 2-propyl cation, which would place it between the 3-noradamantyl (**7**⁺) and 1-homocubyl (**8**⁺) cations, but almost 10 kcal/mol above **10**⁺ (6-tricyclo[3.2.1.0^{3,6}]octyl cation), the least stable of the tertiary cations of this series.

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