geometry as discerned from the effective capacitance, yielding interesting behavioral trends in cluster size and differences between clusters and surfaces.

Overall, then, there is reason to conclude that the exploration of the "ionizable metal cluster–electrode surface" analogy is capable of yielding substantial fresh insight into the behavior of both types of systems. We describe elsewhere an examination of the Pt carbonyl clusters in comparison with Pt/CO surfaces with regard to the issue of CO dipole coupling, as examined by means of $^{12}CO/^{13}CO$ substitution.[27] While the high-nuclearity platinum carbonyls offer redox properties that are so far unparalled for metal clusters, there are a wealth of other systems that can also be examined in this fashion to good effect. One such study, for nickel carbonyls, will be reported elsewhere.

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The Stability of Bridgehead and Rigid Tertiary Carbenium Ions in the Gas Phase and Their Rate of Formation in Solvolysis Reactions

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Abstract: The gas-phase stability of bridgehead and rigid tertiary carbenium ions has been measured by equilibria for bromide transfer and equilibria for protonation of olefins by ICR techniques. Combination of the experimental data with the MM2-calculated enthalpies of formation of the neutrals gives the enthalpy change associated with the ionization process. The rate constants for solvolysis of the corresponding tertiary halides and sulfonate esters correlate linearly with these enthalpy changes. However, simple acyclic and monocyclic tertiary derivatives exhibit higher solvolytic reactivities than expected on the grounds of the thermodynamics of the reaction.

Introduction

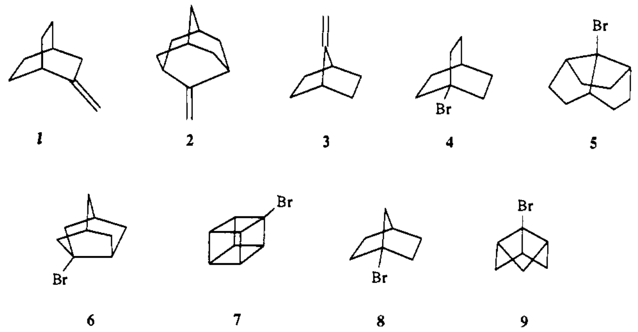
The interpretation of the rate constants of solvolysis of tertiary halides and sulfonate esters is a topic of long-standing interest in physical organic chemistry. Indeed, much of our present knowledge of the properties of carbenium ions is derived from solvolysis reactions.[1] For these reactions it is usually assumed that the transition state occurs late on the reaction coordinate so that, according to the Hammond postulate,[2] the intermediate carbenium ion may be assumed to be similar with respect to structure and energy. Based on this hypothesis, force field calculations have been performed to evaluate the strain difference between substrate and carbenium ion,[3] and the strain differences of some 50 bridgehead or other rigid tertiary substrates have been correlated with their rates of solvolysis. A satisfactory correlation over the entire rate range of ca. 25 log units was obtained.[4,5]

Since the force field calculations are empirical, and since the carbenium ion force field has been adjusted such as to achieve the best possible fit with the rate constants for solvolysis, the validity of the underlying hypothesis of geometric and energetic equivalency between transition state and intermediate in solvolysis reactions is not established by these strain–reactivity correlations. We have now determined the intrinsic stabilities of some strained tertiary carbenium ions in the gas phase in order to establish the thermodynamics of the ionization process.

Experimental Section

(a) Gas-Phase Experiments. Gas-phase stabilities were determined from equilibrium experiments from proton or bromide transfer reactions conducted in an ion cyclotron (ICR) spectrometer.[6] Proton transfer equilibrium reactions between olefins 2-methylenebicyclo[2.2.2]octane (**1**), 2-methyleneadamantane (**2**), and 7-methylenenorbornane (**3**) yielded the gas-phase basicity (GB) according to the reaction:

Scheme I



$$MH^+ + B \rightleftarrows M + BH^+ \qquad (1)$$

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Table I. Gas-Phase Basicity of Olefins Determined from Reaction 1

no.	alkene	base	GB(B)[a,b]	ΔG_r[a,c]	PA(M)[a]
1	2-methylene-bicyclo[2.2.2]-octane	diisopropyl ether	198.7	−0.2	206.3
2	2-methylene-adamantane	diisopropyl ether	198.7	0.3	
		acetylacetone	200.1	−0.8	206.9
		2-butanone	192.7	−0.3	
3	7-methylene-norbornane	diethyl ether	193.1	−0.6	200.2
		tetrahydropyran	192.9	−0.5	

[a] In kcal mol^{-1}. [b] Reference GB values from ref 17 based on GB(NH_3) = 196.4 kcal mol^{-1} and $T\Delta S$ = 8.1 kcal mol^{-1} at T = 313 K. [c] ±0.2 kcal mol^{-1}.

where M stands for the compound studied and B for reference bases. Measurement of the equilibrium constant for reaction 1 gives $\Delta G_r = -RT \ln K_{eq}$ from which GB(M) = GB(B) + ΔG_r can be deduced at the temperature T = 313 K. At least three independent measurements were carried out for each couple M/B with pressure ratios varying in about a 5-fold range and a total pressure of about 2–3 × 10^{-6} Torr. The concentrations of the neutrals were determined from the pressure measurements of an ionization gauge. The corrections for the gauge readings were estimated from the polarizability of the neutrals as explained in ref 6. After correction for the entropy factors associated with reaction 1, the proton affinity can be obtained as PA(M) = GB(M) + $T\Delta S$ from which the heat of formation of the carbenium ion is deduced as $\Delta H_f°(MH^+) = \Delta H_f°(M) + \Delta H_f°(H^+) - PA(M)$, with $\Delta H_f°(H^+)$ = 365.7 kcal/mol.

Alternatively, the stabilities of carbenium ions were determined from the equilibrium constant for bromide transfer, measured with the ICR instrument for the bromides **4**–**9** according to the reaction:

$$R_1Br + R_2^+ \rightleftarrows R_1^+ + R_2Br \qquad (2)$$

After correction for the entropy changes, the binding energy $D°(R^+{-}Br^-)$ is determined, from which the heat of formation of the carbenium ion is deduced as $\Delta H_f°(R^+) = \Delta H_f°(RBr) - \Delta H_f°(Br^-) + D°(R^+{-}Br^-)$, with $\Delta H_f°(Br^-)$ = 51 kcal/mol.[7]

(b) **Syntheses.** 2-Methylenebicyclo[2.2.2]octane (**1**) was prepared in ca. 33% yield from 2-bicyclo[2.2.2]octan-2-one[8] with a Wittig reaction[9] and purified by distillation [50 °C (20 Torr)]. 2-Methyleneadamantane (**2**) was synthesized via acid-catalyzed dehydration of 2-methyl-2-adamantanol,[10] and 7-methylenenorbornane (**3**) was obtained in 10% yield by base-induced elimination of 7-methyl-7-norbornyl-*p*-toluenesulfonate[11] with *t*-BuOK in DMSO.

The bromides were synthesized according to the procedures published in the literature; the procedure of Morita et al.[12] was used for the preparation of 1-bromobicyclo[2.2.2]octane (**4**). 10-Bromotricyclo-[5.2.1.$0^{4,10}$]decane (**5**) was obtained by reaction of the alcohol with thionyl bromide,[3a] and purified by column chromatography (silica gel, pentane–ether 9:1, followed by aluminum oxide, pentane–ether 9:1). 3-Bromonoradamantane (**6**), bromocubane (**7**), and 6-bromotricyclo-[3.1.1.$0^{3,6}$]heptane (**9**) were prepared by oxidative decarboxylation of the respective carboxylic acids.[13] 1-Bromonorbornane (**8**) was obtained from the 1-chloro derivative[14] via transhalogenation.[15] The purity of all compounds was verified by GC before equilibrium studies.

Table II. Heterolytic Bond Dissociation Energies $D°(R^+{-}Br^-)$ Determined from Reaction 2

no.	R_1^+	R_2^+	ΔG_r[a,b]	$D°(R^+{-}Br)$[c]
4	1-bicyclo[2.2.2]octyl	2-*exo*-norbornyl	−1.90	
		1-norbornyl	0.75	148.7
5	10-tricyclo-[5.2.1.$0^{4,10}$]decyl	1-norbornyl	−0.10	149.5
6	3-noradamantyl	1-bicyclo[2.2.2]octyl	−1.00	
		1-norbornyl	−0.12	149.6
7	1-cubyl	1-norbornyl	−0.30	
		tert-butyl	−1.00	149.7
8	1-norbornyl	1-bicyclo[2.2.2]octyl	−0.75	
		3-noradamantyl	0.12	149.5
9	6-tricyclo-[3.1.1.$0^{3,6}$]heptyl	10-tricyclo-[5.2.1.$0^{4,10}$]decyl	0.00	
		3-noradamantyl	0.00	149.6

[a] In kcal mol^{-1}. [b] ±0.4 kcal mol^{-1}. [c] Reference value $D°$(*exo*-2-bromonorbornane) = 146.8 kcal mol^{-1} (taken from ref 7).

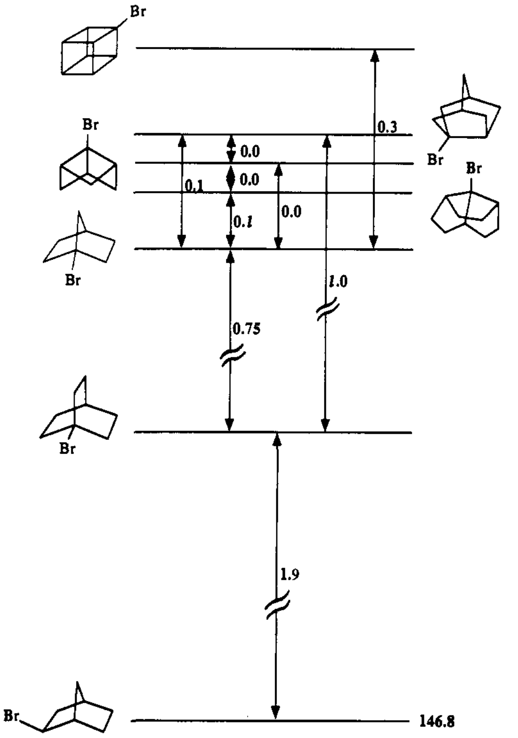

Figure 1. Multiple overlapping sequence for determination of heterolytic dissociation energy relative to 2-*exo*-bromonorbornane ($D°(R^+{-}Br^-)$ = 146.8 kcal mol^{-1}).

Results

Tables I and II report the experimentally determined ΔG_r for reactions 1 and 2. It was observed that the rate constants for proton transfer reactions, equilibrium 1, occurred with reaction efficiencies between 0.5 and 1, this being reflected in the rather small experimental uncertainty in the ΔG_r values. However, the efficiency for bromide anion transfer, reaction 2, occurred with an efficiency of a few percent only. This is reflected in the unusually larger experimental errors due to the difficulties found at distinguishing the contributions of reactive and unreactive (ion loss) processes on the time-dependent curves (in this respect, see the Appendix in ref 16). Figure 1 shows the overlapping sequence used to determine the relative $D°(R^+{-}Br^-)$ bond energies.

Table III summarizes the heats of formation of the carbenium ions derived from the data of Tables I and II. The required heats of formation of the neutrals M are from the literature in the case of 7-methylenenorbornane (14.4 kcal/mol).[18] The value of M for the 2-methyl-2-bicyclo[2.2.2]octyl cation is calculated from those of 2-methylenebicyclo[2.2.2]octane (−2.21 kcal/mol) and

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Table III. Heats of Formation of Tertiary Carbenium Ions and Rate Constants of Solvolysis of Tertiary Derivatives

no.	substrate	log k_{solv}-(R^+–RBr)[a]	ΔE_{st}-(R^+–RBr)[b]	ΔH°_f(RBr)[c,d]	D°(R^+–Br^-)[c,e]	ΔH°_f(R^+)[c]	ΔH°(R^+–RBr)[c]
1a	2-methyl-2-bicyclo[2.2.2]octyl	4.58	−4.28	−25.4	129.9[f]	155.5	180.9
2a	2-methyl-2-adamantyl	3.10	−3.47	−33.2	131.7[f]	149.5	182.7
3a	7-methyl-7-norbornyl	−2.50	10.56	−15.1	144.0[f]	179.9	195.0
4	1-bicyclo[2.2.2]octyl	−4.00	13.94	−21.9	148.7	177.8	199.7
5	10-tricyclo[5.2.1.$0^{4,10}$]	−6.16	15.42	−17.6	149.5	182.9	200.5
6	3-noradamantyl	−7.28	22.49	−11.5	149.6	189.1	200.6
7	1-cubyl	−7.39	20.98	157.4	149.7	358.1	200.7
8	1-norbornyl	−10.45	27.40	−11.7	149.5	188.8	200.5
9	6-tricyclo[3.1.1.$0^{3,6}$]		19.68	60.9	149.6	261.5	200.6

[a] Converted to 80% EtOH, 70 °C, TsO from other temperatures, solvents and leaving groups. [b] See ref 5. [c] In kcal mol^{-1}. [d] Calculated by MM2. [e] This work. [f] Derived from the gas-phase ΔH_f° of the carbenium ions and MM2 calculated ΔH_f° of the corresponding bromides.

Table IV. Heats of Formation of Carbenium Ions and Rate of Solvolysis of Tertiary Derivatives under Standard Conditions (Literature Data)

no.	substrate	log k_{solv}[a]	ΔE_{st}(R^+–RBr)[b]	ΔH°_f(RBr)[c,d]	D°(R^+–Br^-)[c,e]	ΔH°_f(R^+)[c,f]	ΔH°(R^+–RBr)[c]
10	2-methyl-2-*exo*-norbornyl	4.57	1.74	−16.0	136.0	171.0	187.0
11	1-methyl-1-cyclopentyl	3.25	3.04	−25.0	141.0	167.0	192.0
12	(methyl)(diethyl)methyl	3.17	−0.99	−38.9	139.9	152.0	190.9
13	(dimethyl)(ethyl)methyl	2.96	−0.25	−34.9	141.9	158.0	192.9
14	2-methyl-2-*endo*-norbornyl	2.49	0.92	−15.1	135.1	171.0	186.1
15	(*tert*-butyl)(dimethyl)methyl	2.45	−1.92	−45.5	139.0	144.5	190.0
16	*tert*-butyl	2.38	1.96	−31.3	146.1	165.8	197.1
17	1-methyl-1-cyclohexyl	2.05	0.59	−35.4	141.3	156.9	192.3
18	1-methyl-1-cyclobutyl	1.23	2.11	0.4	141.6	193.0	192.6
19	1-adamantyl	−0.41	7.44	−30.9	140.6	160.7	191.6

[a] Converted to 80% EtOH, 70 °C, TsO from other temperatures, solvents and leaving groups. [b] Reference 5. [c] In kcal mol^{-1}. [d] Calculated by MM2. [e] Derived from the gas-phase ΔH_f° of the carbenium ions and MM2 calculated ΔH_f° of the corresponding bromides. [f] Reference 22.

2-methylbicyclo[2.2.2]oct-2-ene (−4.45 kcal/mol)[19] present in the protonation equilibrium. The heats of formation of methyleneadamantane and of all of the bromides (RBr) were calculated by MM2.[20] The D°(R^+–Br^-) values of the bromides are from Table II; those of the olefins are derived from the ΔH_f° of the carbenium ions and ΔH_f° of the corresponding bromides, as calculated by MM2. The first column refers to the rate constants for solvolysis of halides and sulfonate esters converted to standard conditions (*p*-toluenesulfonate leaving group, solvolyzing in 80% aqueous EtOH at 70 °C)[21] and the second column to the MM2-calculated steric energy difference between the carbenium ions and the bromides.

Discussion

Table IV shows the enthalpies of formation of some other carbenium ions in the gas phase, available from the literature,[22] and the appropriate MM2 calculations and rate constants for solvolysis as in Table III. Figure 2 correlates the rate constants of solvolysis of the tertiary derivatives with the corresponding heterolytic bond dissociation energies D°(R^+–Br^-) from Tables III and IV.

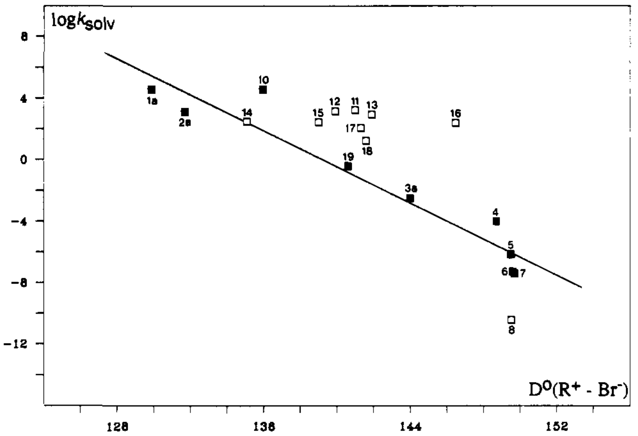

Figure 2. Plot of log *k* from solvolysis of tertiary derivatives versus D°(R^+–Br^-); data from Tables III and IV.

The following observations can be made. (i) For the bridgehead and rigid tertiary bicyclic compounds there exists a fairly good correlation between the kinetics (rate constants) in solution and the thermodynamics (in the gas phase). Since all of these compounds solvolyze with retention of the structure, the correlation suggests that the gas-phase measurements should refer to unrearranged species, with the exception of the 1-norbornyl system (see below). Particularly remarkable is the observation that the unexpectedly high reactivity in solvolysis of bromocubane (**7**)[23] is entirely consistent with the gas-phase stability of the cubyl cation. From the correlation the reactivity of 6-bromotricyclo[3.1.1.$0^{3,6}$]heptane (**9**) is extrapolated to ca. −6.3 ± 1.5 (log k_{solv}; standard conditions).

The plot covers a rate range of ca. 11 log units. The slope of the correlation is −0.588. (r = 0.959; σ = 1.481). If the rate constants are converted to free energies of activation, the slope increases to 0.923. This means that ca. 90% of the intrinsic energy difference between R–Br and R^+ is developed in the transition state of solvolysis. It follows that, in a first approximation, the solvolysis transition state may be considered similar with respect to structure and energy to the intermediate carbenium ion.

(ii) The 1-norbornyl cation deviates significantly from the correlation. Since this compound fits the strain–reactivity plot satisfactorily (see below), we believe that the deviation is due to rearrangement of the ion to another, more stable ion of unknown structure in the ICR spectrometer.

(iii) The monocyclic and acyclic tertiary derivatives solvolyze significantly faster than predicted on the grounds of the stability of their respective carbenium ions. This should at least in part be due to differential solvation effects during solvolysis. Backside solvation of the incipient carbenium ion is precluded for skeletal reasons in the series of bridgehead compounds, but may occur with the simple monocyclic and acyclic derivatives. In agreement with this hypothesis, the least hindered *tert*-butyl derivative shows

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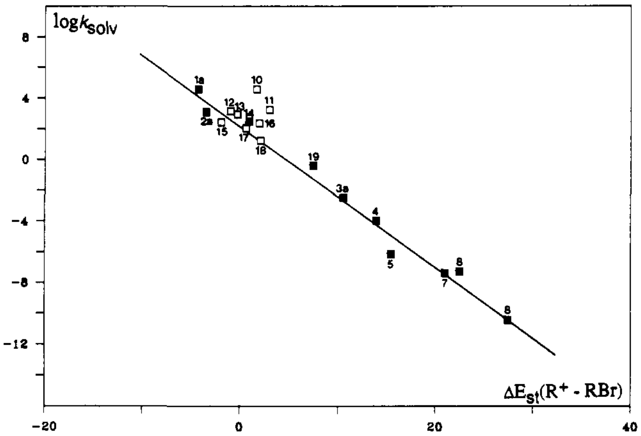

Figure 3. Plot of log *k* from solvolysis versus $E_{st}(R^+{-}RBr)$; data from Tables III and IV.

the strongest upward deviation from the plot. Thus the situation in the solvolysis appears to be substantially different from that encountered when carbenium ion stabilities in nonnucleophilic solvents, such as SO_2ClF, are considered.[24] In the latter, differential solvation effects on carbenium ion stabilities are weak. In other solvent systems, however, solvation effects are considerable and, for example, the *tert*-butyl cation, which is less stable than the 1-adamantyl cation in the gas phase, is considerably more stable in $SbF_5{-}FSO_3H{-}SO_2$.[25]

This explanation is, however, not entirely satisfactory. When log *k* for solvolysis is plotted against the previously calculated steric energy differences between bromides and carbenium ions, $\Delta E_{st}(R^+{-}RBr)$ for the same series of compounds (Figure 3), one finds that the mono- and acyclic compounds deviate much less from the straight line defined by the bridgehead derivatives than in Figure 2, while the slopes of the correlations are in the same order of magnitude.

If the deviations of the mono- and acyclic compounds in Figure 2 were due to solvation effects alone, then the same deviations should occur also in the strain–reactivity plot (Figure 3). Since this is not the case, there must be another contributing factor. We believe that the deviation of the *tert*-butyl system and that of the other acyclic and monocyclic compounds in Figure 2 is due to charge effects. Using the usual substituent corrections for β-branching of 1.5 kcal/mol per alkyl substituent,[26] the 1-adamantyl cation and the other bridgehead ions are stabilized by 4.5 kcal/mol or more with respect to the *tert*-butyl cation in the gas phase. The *tert*-butyl cation is the least strained tertiary carbenium ion, yet in the gas phase it is very unstable because it does not profit from this additional inductive stabilization. The same is true for the other aliphatic and monocyclic ions, albeit to a lesser degree. The rates of solvolysis of all these compounds are, however, little affected by this difference in inductive stabilization of the carbenium ion, and the compounds fit the strain–reactivity plot quite well. This suggests that stabilization of positive charge is much less important in the transition state of solvolysis than it is for the isolated ions in the gas phase. Irrespective of the detailed structure of the transition state, the proximity of the negatively charged leaving group must in part stabilize the positive charge of the incipient cation, and thereby reduce the demand for electronic internal stabilization of the latter.

(iv) The reactivity of the *exo*-2-norbornyl derivatives in solvolytic reactions has been the subject of much controversy in the past.[27] From all previous strain–reactivity correlations, we are accustomed to the fact that the secondary 2-*exo*-norbornyl derivatives react faster than predicted, because the solvolysis transition state should profit from nonclassical stabilization. The same tendencies, although considerably less dramatic, occur with the tertiary derivative (see also Figure 3). The bridged structure of the tertiary norbornyl cation is unequivocally established by X-ray methods.[28] However, in the correlation of log *k* versus $D°(R^+{-}Br^-)$, the 2-methyl-2-norbornyl derivative **10** is expected to be on the regression line, because contrary to the MM2 based strain calculations, the gas-phase measurements do take into account the intrinsic stability of the ion. If the ion is bridged, then the transition state is also bridged, and any stabilization due to bridging must lead to a proportionally enhanced rate. The endo isomer **14**, on the other hand, should react at a slower rate, because the extra stabilization due to bridging is not developed in the transition state of solvolysis. However, as Figure 2 shows, the exo isomer **10** is again above the correlation line, and the endo isomer **14** is exactly on it. We have at present no convincing explanation to account for this observation. We have considered the possibility that the discrepancy could be due to our mixing of experimentally determined ion stabilities with the empirical MM2 calculations for the enthalpies of formation of the neutrals. The bromide force field is not so widely tested, but if the calculations of the bromides are replaced by calculations for the corresponding hydrocarbons, the general picture does not change. Similarly, MM3 calculations produce the same result. Conceivably, the 2-norbornyl derivatives could both react at enhanced rates in solvolysis because of solvent participation as observed for the acyclic and monocyclic compounds. However, this seems unlikely considering the fact that the other bicyclic systems (7-methylnorbornyl, 2-methylbicyclo[2.2.2]octyl) do not show this effect. Alternatively, one could explain the apparent enhanced rate of the exo isomer by imbalance, i.e., bridging more developed at the transition state in comparison to strain. This view is, however, in contradiction with the observation that charge stabilization should play only a minor role in solvolysis as compared to the stability in the gas phase. In addition, the near energetic equivalency of solvolysis transition state and carbenium ion does not allow one to invoke imbalance as an important factor.

In the absence of a real convincing explanation, we tend to ascribe, at least for the moment, the deviation of the tertiary 2-norbornyl system to uncertainties in the experiments. The error in the rate constants is estimated to amount to ca. 0.5 log unit, which is a relatively optimistic estimate, considering the various extrapolations involved to convert the experimental data to standard conditions.[21,29] There is also considerable uncertainty in enthalpy of formation of the 2-methyl-2-norbornyl cation. The compilation of Lias et al.[22] recommends 171.0 kcal/mol, but the original communication[30] reports values of 170.0 ± 2.0 (from chloride transfer) and 171.3 ± 1.0 (from hydride affinity). Earlier authors reported 168 kcal/mol, however.[31] In view of these uncertainties, it appears premature to draw too subtle conclusions.

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