Reversible Reactions of Gaseous Ions. X. The Intrinsic Stability of the Norbornyl Cation

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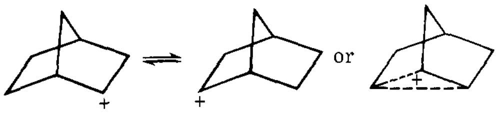
Abstract: The stabilities of cyclopentyl, methylcyclopentyl, norbornyl, and 2-methylnorbornyl cations have been determined by the technique of time-resolved high-pressure mass spectrometry. Equilibrium constants for hydride-transfer reactions involving these cyclic carbonium ions with *sec*-propyl and *tert*-butyl ions have been determined over the temperature range 310–648 K. From these measurements hydride affinities were determined which indicate that the norbornyl cation has 10 kcal/mol more stability than that which would be expected for a secondary species.

Introduction

The structure and stability of the norbornyl (bicyclo-[2.2.1]heptyl) cation has been the focal point of a lengthy controversy.[1] The heart of the debate is whether the structure of the norbornyl cation is a rapidly equilibrating pair of classical ions (I) or a σ-bridged nonclassical species (II).



I II

Most experiments related to this problem have been carried out in solution where complications due to solvent interactions may be present. For the past few years[2-4] we have been investigating hydride-transfer equilibria by high-pressure mass spectrometry in order to establish the relative gas-phase stabilities for various carbonium ions. We have extended these studies to include several cyclic and bicyclic paraffins to provide information useful in evaluating the extent of σ delocalization in the norbornyl system. The hydride-transfer reactions investigated are:

$$sec\text{-}C_3H_7^+ + CP \rightleftharpoons CP^+ + C_3H_8 \quad (1)$$

$$t\text{-}C_4H_9^+ + MCP \rightleftharpoons MCP^+ + i\text{-}C_4H_{10} \quad (2)$$

$$t\text{-}C_4H_9^+ + NB \rightleftharpoons NB^+ + i\text{-}C_4H_{10} \quad (3)$$

$$t\text{-}C_4H_9^+ + MNB \rightleftharpoons MNB^+ + i\text{-}C_4H_{10} \quad (4)$$

Throughout this paper the following abbreviations have been used: CP, cyclopentane; MCP, methylcyclopentane; NB, norbornane; and MNB, methylnorbornane.

Experimental Section

These experiments were carried out on the Rockefeller Chemical Physics mass spectrometer. The pulsed-electron beam high-pressure technique used has been described previously.[3,4] This method consists of the bombardment of a mixture of known composition (alkane/cyclic paraffin) with a 100-μsec pulse of 600-V electrons. Ion-molecule reactions take place in a field-free source, and ionic concentrations are monitored at variable reaction times. Two methods were used to measure the time dependence of the ion intensities. In one method, ions leaving the source were measured for the duration of the ion-focus pulse (100 μsec) which occurred at variable delay times (100–1800 μsec) after the electron-beam pulse. The other technique employed the use of a signal averager (Tracor NS 570). In a typical sequence using the multichannel-scaling mode, the electron beam pulsed on for 50 μsec at a repetition time of 1.0 msec. The mass-analyzed ion current was detected with an electron multiplier. The multiplier pulses were amplified, discriminated (Ortec 9301 preamplifier, 454 amplifier, and 436 discriminator), and counted with the multiscaler, whose sweep was triggered by the electron-beam pulse. The dwell time per channel was 10 μsec, and we typically counted for 6.6×10^4 sweeps. Experiments performed with both techniques gave identical results.

The reagents used were Matheson Instrument grade (99.5%) isobutane, Matheson Research grade (99.99%) propane, Chemical Samples Co. methylcyclopentane (99.9%) and norbornane (98%), and Matheson Coleman and Bell Spectroquality grade cyclopentane (93%). The 2-methylnorbornane was provided by Dr. H. C. Brown of Purdue University. Purities were checked by gas chromatography and found to be better than 99% for all compounds except cyclopentane and 2-methylnorbornane. These were purified by preparative-scale gas chromatography to give purities by gas chromatography of better than 99%.

Results and Discussion

The equilibrium constant for a general hydride transfer reaction $R_1^+ + R_2H \rightleftharpoons R_2^+ + R_1H$ is $K = (R_2^+/R_1^+)(R_1H/R_2H)$. By measuring the ion-intensity ratios ($I_{R_2^+}/I_{R_1^+}$) at various reaction times for a mixture of known composition (R_1H/R_2H), a plot of the apparent equilibrium constant (K_a) vs. reaction time can be obtained. Figure 1 shows such a plot for the reaction $t\text{-}C_4H_9^+(NB, i\text{-}C_4H_{10})NB^+$. K_a initially increases and after 500 μsec remains constant. Equilibrium is assumed to occur in the time-independent region of K_a. Hydride-transfer reactions are very slow, and the necessity of using time-resolved techniques to establish equilibrium in these systems has recently been demonstrated.[4] Plots analogous to Figure 1 were obtained at several temperatures.

The above technique was utilized for each of the reactions investigated. van't Hoff plots constructed from the temperature variation of the equilibrium constants are shown in Figure 2. The temperature and pressure ranges are 310–648 K and 0.9–2.99 Torr, respectively. For most measurements the total number density was maintained at $\sim 2 \times 10^{16}$ mol/cm^3, but for some experiments, where equilibrium was achieved only after a very long time, the number density was as high as 6×10^{16} mol/cm^3. The experimental points on the van't Hoff plot for the $t\text{-}C_4H_9^+(MCP, i\text{-}C_4H_{10})MCP^+$ system were obtained with mixtures whose neutral composition differed by a factor of 26.

Thermodynamic parameters were obtained from the least-squares lines shown in Figure 2. The experimental thermodynamic results are presented in Table I. The structures for the product ions drawn in Table I are only nominal, since we cannot preclude the possibility that rearrangement to other structures has occurred. Similarly, the names used in the text and tables are those appropriate to the nominal structures.

The experimental $\Delta H°$ values for reactions 1, 2, and 4 and the appearance of their van't Hoff plots are what would be expected for hydride-transfer reactions occurring be-

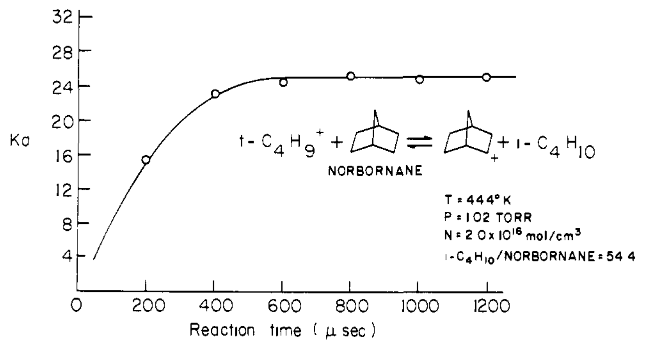
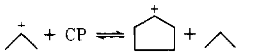
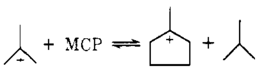
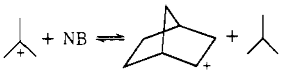
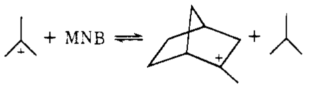


Figure 1. The apparent equilibrium constant vs. reaction time for reaction 3.

Table I. Experimental Thermodynamic Values

Reaction	$\Delta G°_{300}$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°_{300}$, eu
	−6.7	−5.9	+2.6
	−5.5	−6.4	−2.9
	−2.3	−1.5	+2.8
	−8.6	−7.5	+3.6

tween structurally similar carbonium ions (secondary → secondary, tertiary → tertiary). On the other hand, an exothermicity of 1.5 kcal/mol in reaction 3, the formation of a nominally secondary ion (NB$^+$) from a tertiary carbonium ion (t-$C_4H_9{}^+$), would normally be unexpected and indicates that extra stability is present in the norbornyl cation. By contrast, we have examined the reaction of *tert*-butyl ion with propane and cyclopentane and found that even at high temperatures (>600 K) no product ions are observed. Thus no perceptible reaction occurs between a tertiary ion and secondary hydrogens to produce an uncomplicated secondary ion.

The heats of formation of the product carbonium ions are given in Table II. These were obtained by combining the experimental values of $\Delta H°$ and the known heats of formation of the neutrals with resolved energy electron impact values[5] for *tert*-butyl and *sec*-propyl ions as starting reference points. Assuming we can ignore any uncertainty in the experimentally determined neutral heats of formation, the relative ionic heats of formation are believed to be accurate to within 0.3 kcal/mol. Lossing and Traeger[6] recently reported that $\Delta H_f°$(cyclopentyl ion) = 197 ± 3 kcal/mol. Our value of 192.6 ± 0.3 kcal/mol is lower by an amount we consider significant.

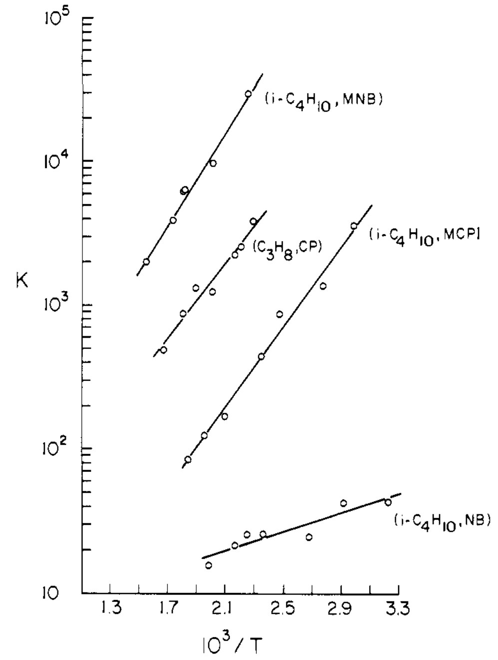
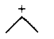
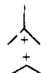
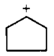
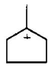
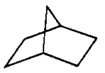
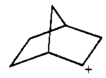
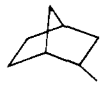
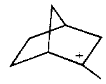


Figure 2. Comparison of van't Hoff plots for reactions 1-4.

Table II. Heats of Formation of Carbonium Ions and Neutrals[a]

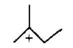
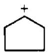
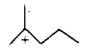
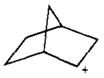
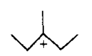
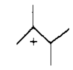
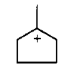
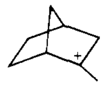
RH	$\Delta H°_f$ (RH)	R$^+$	$\Delta H°_f$ (R$^+$)
	−25.02[b]		192[f]
	−32.07[b]		169.1[f]
	−18.46[c]		192.6
	−25.0[c]		169.3
	−12.42[d]		187.3
	−19.6 ± 1.3[e]		~174[g]

[a] All values in kcal/mol. [b] D. W. Scott, *J. Chem. Phys.*, 60, 3166 (1974). [c] J. W. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 26 (1969). [d] R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany, and D. McNally, *J. Phys. Chem.*, 75, 1264 (1971). [e] Obtained from an empirical force field calculation: E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 95, 8005 (1973). [f] Arbitrary standard values from ref 5. [g] Estimated uncertainty is ±2 kcal/mol. This is a result of two factors: (1) the $\Delta H°_f$(MNB) is a calculated value; (2) there is a larger uncertainty in the experimental determination of $\Delta H°$ for reaction 4 due to the slowness of the reaction.

Relative carbonium ion stabilities can be evaluated by comparing hydride ion affinities (heterolytic bond-dissociation energies), which are obtained from the general reaction RH ⇌ R$^+$ + H$^-$; $\Delta H°$ = hydride affinity = D(R$^+$-H$^-$). Table III lists the hydride affinities for reasonably well-established secondary and tertiary carbonium ions. It is evident from the values for tertiary carbonium ions that the stability of MNB$^+$ fits in well with the trend of slightly increased stability with increasing molecular complexity for tertiary cations. By contrast, the nominally secondary norbornyl cation is much more stable (11.4 kcal/mol) than the cyclopentyl cation. Some of this stability may be attributed to the fact that the norbornyl cation has two more carbons, but the two-carbon difference between methylcyclopentane and methylnorbornane only produces a 1.1 kcal/mol stabilization. If we assume that a similar stabilization due to carbon number is operative between the cyclopentyl and norbornyl ions, then it appears that the norbornyl cation is ~10 kcal/mol more stable than would be expected for an uncomplicated secondary ion. These results are compatible with the stabilization to be expected from the occurrence of σ bridging in the norbornyl cation.

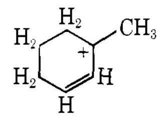
We have referred above to the possibility of rearrangement of the ions formed in the reactions studied, and this possibility is of particular importance to the norbornyl ion problem. Four comments pertinent to the possibility of rear-

Table III. Hydride Affinities of Secondary and Tertiary Carbonium Ions

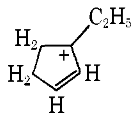
Tertiary		Secondary	
R^+	$D(R^+-H^-)$[a]	R^+	$D(R^+-H^-)$
	235.9		251.7
	232.5[b]		245.8
	232.1[b]		234.4
	231.1[b]		
	230.5[b]		
	229.5		
	228.4		

[a] All data in kcal/mol, $\Delta H^\circ_f(H^-) = 34.71$ kcal/mol. [b] Reference 4.

rangement of the ions can be made, although they do not permit one to draw an unequivocal conclusion about the probability of rearrangement or the lack thereof. (1) The reactions with which we are concerned are relatively gentle adiabatic processes with a maximum observed exothermicity of only 7.5 kcal/mol. (2) The values of ΔS°_{300} are consistent with the absence of rearrangement. ΔS°_{300} varies within only 3.6 eu of zero with an estimated uncertainty of ±2 eu. A negligible entropy change would be expected for the reaction of an acyclic ion with a cyclic neutral forming a cyclic product ion and an acyclic product neutral. An experimentally observed entropy change of small magnitude may be looked upon as a necessary, but not sufficient, condition for an absence of extensive rearrangement. (3) Ions with the same empirical formula as norbornyl ion ($C_7H_{11}^+$) but with different structures have approximately the same heats of formation as that found here for norbornyl (187.3 kcal/mol). Thus, using the group-equivalent method of calculating heats of formation and estimates of resonance energies, we obtain values of $\Delta H_f \simeq 182$ kcal/mol for A and $\Delta H_f \simeq 187$ kcal/mol for B. (4) Gas-phase hydrocarbon ions are known to undergo rearrangements, but virtually all of the reactions involve ion formation by vertical ionization processes, such as electron ionization or photon ionization. For practical purposes, little is known about the proclivity toward isomerization of ions formed by low-energy adiabatic processes such as H^- transfer or about the relative proclivities for such isomerization in gas phase and in solution.



A



B

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References and Notes

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Structure of Sarracenin. An Unusual Enol Diacetal Monoterpene from the Insectivorous Plant *Sarracenia flava*

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Abstract: The structure of an unusual enol diacetal monoterpene sarracenin ($C_{11}H_{14}O_5$, mp 127–128) from the insectivorous plant *Sarracenia flava* is reported. Confirmatory evidence includes x-ray crystallography and ^{13}C NMR data. A hypothesis is presented concerning the biogenetic role of sarracenin in the biosynthesis of monoterpenes and indole alkaloids.

Reports[2] that the ethanol (moonshine) extracts of the roots of *Sarracenia flava*[3] (golden trumpet) have been used as folk remedy by residents of the Okefenokee swamp region of Southeastern Georgia prompted the examination of this plant which entraps and digests insects.[4] We have recently confirmed the antitumor activity[5] of *S. flava* in the roots as well as the tops and reported[6] the presence of two amines which are responsible for paralyzing insects after they become entrapped in the pitcher. One of them, coniine,[7] is also one of the major alkaloids of the poisonous hemlock plant (*Conium maculatum*). We now wish to report the isolation and the structure of sarracenin as the

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