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(20) Data collection was carried out using a Princeton Applied Research (Princeton, N.J.) Model 131/SSA data acquisition system.
(21) D. W. Turner et al., ref 7, Chapter 11.
(22) B. Steiner, "Case Studies in Atomic Collision Physics 2", E. W. McDaniel and M. R. C. McDowell, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 483.
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Isomerization of Protonated Cyclopropane Cations[1]

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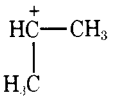
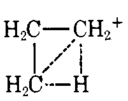
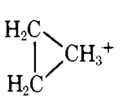
Abstract: The collisional activation (CA) spectra of gaseous ions formed by the protonation of cyclopropane and propene are identical, indicating that the isomerization c-$C_3H_7^+ \rightarrow$ *sec*-$C_3H_7^+$ occurs in $<10^{-5}$ s. However, ion-molecule reactions of $C_3H_7^+$ at $\sim 10^{-2}$ Torr indicate that c-$C_3H_7^+$ ions can have lifetimes of 10^{-7} s, supporting the results of equilibrium constant measurements by Chong and Franklin.[5] They derived ΔH_f(c-$C_3H_7^+$) − ΔH_f(*sec*-$C_3H_7^+$) = 8 kcal/mol, consistent with the prediction of MINDO/3 calculations;[3] however, the apparent low activation energy for c-$C_3H_7^+ \rightarrow$ *sec*-$C_3H_7^+$ indicated by the CA results is not consistent with the MINDO/3 value[3] of ΔH_f(*n*-$C_3H_7^+$) − ΔH_f(c-$C_3H_7^+$) if the transition state for this reaction is similar to the structure of the *n*-$C_3H_7^+$ ion.

The isomeric $C_3H_7^+$ ions I-IV have been the object of extensive experimental and theoretical studies; a number of these studies have resulted in conflicting conclusions.[2-6] Molecular orbital calculations of several types now predict[3,4] (Table I), in agreement with experiment,[5,6] that *sec*-propyl (I) is the most stable ion structure. Gaseous *n*-$C_3H_7^+$ ions have been shown experimentally to be unstable, isomerizing without hydrogen scrambling to *sec*-$C_3H_7^+$.[6] MINDO/3 calculations[3] predict the most stable form of the cyclic isomer to be the edge-protonated (IIa) cyclopropane structure, deriving a heat of formation value in close agreement with the experimental value determined by Chong and Franklin[5] (Table I) from equilibrium constant measurements of reactions 1 and 2 (Scheme I, A = HCOOH or CH_3OH) at 0.2-0.4 Torr total pressure, assuming the intrinsic entropy changes of these reactions to be zero.


I


IIa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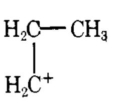
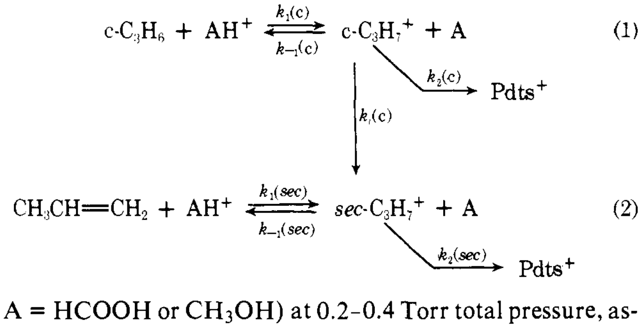

III

Scheme I



These theoretical calculations[3] also predict the lowest energy form of the cyclic $C_3H_7^+$ ion (IIa) to be 11 kcal/mol more stable than the *n*-propyl ion (III); if the latter structure resembles closely the transition state[7] for the rearrangement II → I, this reaction should exhibit a relatively high activation energy. However, interpretations of the experimental results[5,6] differ markedly in the stability indicated for the cyclic ion. In ion cyclotron resonance (ICR) experiments[6] (ion lifetimes of $\sim 10^{-3}$ s) ions formed by the protonation of cyclopropane were found to react with methanol in the same manner as *sec*-$C_3H_7^+$ ions react; it was concluded that either c-C_3H_6 and $CH_3CH{=}CH_2$ have nearly identical proton affinities, as postulated by Chong and Franklin, or that the c-$C_3H_7^+$ ions have isomerized to the *sec*-$C_3H_7^+$ structure before reacting (Scheme I). We report here evidence on the structures of these ions obtained from collisional activation (CA) spectra[8] (ion lifetimes of $\sim 10^{-5}$ s) utilizing a revised instrument with a higher pressure ion source, and from ion-molecule reaction studies at pressures $\sim 10^{-2}$ Torr with variation of the ion source residence time.

Experimental Section

Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer of reversed geometry,[9] with 7.8 kV ion accelerating potential and 70 eV ionizing electron energy. The instrument was modified with restricted electron entrance and ion exit slits on the ion source and a 1200 l./s diffusion pump on the source housing. Propene or cyclopropane was introduced at low pressure (10^{-6} Torr), and the ion source pressure was increased with CH_3OH, HCOOH, orH_2S, as well as with the C_3H_6 isomer itself, until the contribution of $C_3H_7^+$ to the *m/e* 43 peak in the normal mass spectrum was a factor of ~16 greater than that of $C_2{}^{13}CH_6^+$ ($\sim 10^{-2}$ Torr, source housing pressure $\sim 1 \times 10^{-4}$ Torr; higher pressures seriously degrade instrument performance). Helium was introduced into the collision chamber between the magnetic and electrostatic (ESA) analyzers at a pressure ($\sim 5 \times 10^{-3}$ Torr) selected so that the abundance of *m/e* 43 ions reaching the collector would be reduced to approximately 25% of its original value. The ionic products resulting from collisional activation (the CA spectrum) were then determined by multiple scanning of the ESA potential and averaging of the data under computer control; only the ions resulting from higher energy processes (those other than unimolecular metastable decompositions) were included.[8] Contributions from the CA spectrum of $C_2{}^{13}CH_6^+$ were subtracted, correcting for the experimental observation that the cross-section for the CA decomposition of $C_3H_7^+$ is 0.82 times that of $C_2{}^{13}CH_6^+$. The ion source repeller controls were modified (voltages adjustable from +90 to −90 V) to give limited ion trapping capabilities, both by direct trapping with negative voltages and by the negative space charge in the electron beam with positive repeller voltages.[10] Changing the repeller potential to more positive as well as more negative values increases the ion residence time in the source,[11] as shown by the increase in *m/e* 103 and 121 ion abundances produced by ion-molecule reactions of acetic acid at $\sim 10^{-2}$ Torr.

Results and Discussion

The CA spectra of the $C_3H_7^+$ ions obtained by protonation of propene and cyclopropane by methanol are given in Table

Table I. Relative Heats of Formation of $C_3H_7^+$ Isomers

	Heat of formation (kcal/mol) relative to that of *sec*-Pr^+		
Ion	MINDO/3[a]	6-31G*[b]	Exptl
sec-Pr^+ (I)	(0)	(0)	(0)
c-Pr^+ (edge) (IIa)	7.5	19.1	8[c]
c-Pr^+ (corner) (IIb)	12.3	13.0	
n-Pr^+ (III)	18.6	17[d]	16[e]

[a] Reference 3. [b] Reference 4; note that it is predicted that further refinements in geometry optimization and inclusion of p-type orbitals on hydrogen should substantially lower the relative energy of IIa and, to a lesser extent, that of IIb. [c] Reference 5. [d] Methyl-staggered form. [e] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

II. Within experimental error these spectra are identical for the abundances of all 13 peaks; these are also identical with the CA spectra (not shown) obtained by protonation with HCOOH or of C_3H_6 alone at higher pressure. No differences were noted in the CA spectra measured at longer ion source residence times (+90 or −90 V repeller potential) or using ionizing electrons of 15 eV energy, although the experimental reproducibility is substantially poorer under these conditions. These measurements constitute strong evidence for the isomerization of these two propyl ions to a common $C_3H_7^+$ structure in the 10^{-5} s time period of the experiment; this structure must be *sec*-$C_3H_7^+$, based on the stability demonstrated for this isomer over much longer lifetimes.[6] Because the CA spectrum of pure c-$C_3H_7^+$ ions has not been measured, no lower limit can be set on the amount of c-$C_3H_7^+$ which has not isomerized. However, for the analogous $C_2H_5O^+$ and $C_2H_5S^+$ isomers the CA spectra of the cyclic and linear forms are clearly distinguishable, the cyclic forms showing a much higher tendency to lose CH_2;[12] note that the $(C_3H_7 - CH_2)^+$ peak is negligible in the $C_3H_7^+$ spectra (Table II). Further, the CA spectra of the cyclic isomers of $C_4H_8\cdot^+$,[1] $C_2H_4O\cdot^+$,[13a] and $C_3H_6O\cdot^+$ [13b] are distinguishable from those of their open-chain isomers.

The identity of the CA spectra indicates that the activation energy of the c-$C_3H_7^+$ → *sec*-$C_3H_7^+$ isomerization is no greater than the excess energy present in the c-$C_3H_7^+$ ions at formation. This excess energy should average no more than a few kilocalories, as there was no appreciable change in the CA spectrum on protonation with higher pressures of c-C_3H_6 or with longer ion source residence times, conditions which should produce more efficient collisional stabilization of the initially formed c-$C_3H_7^+$ ions. Further, the protonation with CH_3OH as well as with C_3H_6 should not produce c-$C_3H_7^+$ ions with appreciable excess energy, as the proton affinity (PA) of c-C_3H_6 (and $CH_3CH{=}CH_2$) cannot be significantly greater than that of CH_3OH or HCOOH.[5,6] (If the heat of formation of c-$C_3H_7^+$ were actually 13 kcal/mol greater than that of *sec*-$C_3H_7^+$,[4] PA (c-C_3H_6) would be ~5 kcal/mol *less* than PA (CH_3OH) or PA ($CH_3CH{=}CH_2$).)

Barring experimental artifacts, the most probable explanation for these diverse experimental results is that the isomerization of gaseous c-$C_3H_7^+$ requires 10^{-5}–10^{-7} s; it is slow in comparison to the 10^{-7}–10^{-8} s between collisions in the high-pressure studies of Chong and Franklin[5] but fast in comparison to the time between collisions in the ICR experiments[6] and to the time before collisional activation in the CA experiments. To investigate this explanation further, the protonation of the C_3H_6 isomers with excess $HCOOH_2^+$ was examined under the CA experimental conditions of lower pressure (~10^{-2} Torr) and thus longer times between collisions (~10^{-6} s). Equilibrium is no longer achieved, with $[C_3H_7^+]/[HCOOH_2^+] = 0.09$ for c-C_3H_6 vs. 3.7 found[5] at higher pressures and 0.12 for $CH_3CH{=}CH_2$ vs. 2.1 found[5] at higher pressures. However, the total abundance of ions produced in other reactions of $C_3H_7^+$ [14] is lower than $[C_3H_7^+]$, so that $[C_3H_7^+]/[HCOOH_2^+]$ is not substantially affected by k_2 or k_{-1} (Scheme I); $[C_3H_7^+]$ should be determined primarily by k_1. Thus $k_1(\text{c})/k_1(\text{sec}) \sim 0.7$,[15] and, utilizing the high-pressure K_{eq} values,[5] $k_{-1}(\text{c})/k_{-1}(\text{sec}) \sim 0.4$. For the latter a value of unity would instead have been expected if the isomerization c-$C_3H_7^+$ → *sec*-$C_3H_7^+$ had been fast on the time scale of their experiment; further, if PA(c-C_3H_6) = PA($CH_3CH{=}CH_2$),[5] the $k_{-1}(\text{c})/k_{-1}(\text{sec})$ value corresponds to the relative reaction path degeneracy of 0.5 assumed by Chong and Franklin for their calculations.

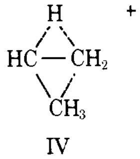
Table II. CA Spectra of $C_3H_7^+$ from the Protonation of Propene and Cyclopropane in Methanol[a]

m/e	Propene	Cyclopropane
14	<0.4	<0.4
15	1.7 ± 1.2	1.7 ± 1.1
24	0.5 ± 1.1	0.4 ± 1.0
25	1.7 ± 1.2	1.5 ± 0.8
26	6.4 ± 1.3	6.6 ± 1.2
27	19.7 ± 1.5	20.8 ± 1.5
28	1.8 ± 0.6	2.0 ± 0.8
29	<0.4	<0.4
36	2.0 ± 1.5	1.7 ± 1.0
37	9.0 ± 1.4	8.3 ± 1.3
38	12.3 ± 1.2	11.7 ± 1.3
39	39.9 ± 1.7	37.8 ± 1.7
40	4.5 ± 0.5[b]	6.3 ± 0.8[b]

[a] Mean and standard deviation of four separate runs; corrected for the presence of ~6% $C_2{}^{13}CH_6^+$ in the $C_3H_7^+$. [b] Value of lower reliability because the the *m/e* 40 peak accounts for 57% of the total ion abundance in the CA spectrum of $C_2{}^{13}CH_6^+$.

Increasing the ion source residence time of the ions by making the ion repeller values more negative decreases the abundances (relative to *m/e* 47) of ions such as *m/e* 43, 55, and 57 which must be formed by ion-molecule reactions but increases the abundances of ions such as *m/e* 27, 39, and 41.[14] Most of the latter should not arise directly from unimolecular decomposition of $C_3H_7^+$, as the required heats of reaction are high.[16] Although the reactivities of c-$C_3H_7^+$ and *sec*-$C_3H_7^+$ would not necessarily show substantial differences, the parallel behavior with increased ion source residence time of $C_3H_7^+$ ions from either c-C_3H_6 or $CH_3CH{=}CH_2$[14] is at least consistent with the postulation that the isomerization c-$C_3H_7^+$ → *sec*-$C_3H_7^+$ precedes these further reactions.

It is possible that the intrinsic entropy change of the reaction of HA with c-$C_3H_7^+$ is less than the zero value assumed by Chong and Franklin, especially if the ion is of structure IIb. If there is no offsetting entropy requirement for *sec*-$C_3H_7^+$ + HA, this would increase the value of $\Delta H_f(\text{c-}C_3H_7^+) - \Delta H_f(sec\text{-}C_3H_7^+)$ derived from the high-pressure equilibrium measurements to greater than the predicted[3] value of 8 kcal/mol but probably by no more than a few kilocalories per mole. Thus the ready isomerization of c-$C_3H_7^+$ → *sec*-$C_3H_7^+$ indicated by the CA spectra suggests that $\Delta H_f(n\text{-}C_3H_7^+)$ is lower than the calculated value or that the transition state for II → I has a substantially lower energy than that of III; the alternative IV has been suggested.[7]



IV

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Acknowledgments. We are grateful to R. Hoffmann, J. A. Pople, L. Radom, and M. J. S. Dewar for helpful discussions and to the National Institutes of Health (Grant GM 16609) for generous financial support.

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(14) The following ions are the most abundant which should be formed from $C_3H_7^+$ (the first two figures represent the abundances at 0 and 90 V repeller potential, respectively, relative to $[HCOOH_2^+]$ for reaction with c-C_3H_6 and the second two figures are the comparable values for the reaction with $CH_3CH{=}CH_2$): *m/e* 27 (0.0021, 0.017; 0.004, 0.031); *m/e* 39 (0.015, 0.04; 0.019, 0.067); *m/e* 41 (0.026, 0.061; 0.042, 0.105); *m/e* 43 (0.092, 0.016; 0.12, 0.031); *m/e* 55 (0.0043, <0.0008; 0.009, <0.0002). The *m/e* 42 abundances are 0.026, 0.068; 0.020, 0.07, but at zero repeller potential these should arise in substantial part from the direct ionization of C_3H_6. *M/e* 29, 61, and 65 product ions were also found, but the reaction of HCOOH alone under these conditions gives comparable amounts of these ions. Similar results were obtained when the repeller potential was made more positive.

(15) Approximately this same ratio is also obtained if $[C_3H_7^+]$ is corrected for the abundances of those ions which should arise from the decomposition of $C_3H_7^+$;[14] similar $[C_3H_7^+]/[HA^+]$ values were found in measurements made with H_3S^+ protonation and in connection with the previous ICR study.[6]

(16) $\Delta H(sec\text{-}C_3H_7^+ \rightarrow CH_3CH{=}CH_2^+) = 89$ kcal/mol; $\Delta H(sec\text{-}C_3H_7^+ \rightarrow C_3H_5^+) = 24$ kcal/mol; $\Delta H(sec\text{-}C_3H_7^+ \rightarrow C_3H_3^+) = 63$ kcal/mol; and $\Delta H(sec\text{-}C_3H_7^+ \rightarrow C_2H_3^+) = 59$ kcal/mol.[5,17]

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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. 25. Conformations of Methyl- and Fluoro-Substituted Cyclopentanes and Cyclohexanes

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Abstract: Ab initio molecular orbital theory is used to study the influence of single methyl and fluoro substituents on the conformational potential surface for cyclopentane and cyclohexane. The theory indicates that both substituents favor the envelope (E) form of cyclopentane leading to two separate potential minima for axial and equatorial substitution. The equatorial form of methylcyclopentane is more stable but the reverse is true for fluorocyclopentane. For the substituted cyclohexanes, both substituted molecules are more stable in the equatorial form. These theoretical results are in reasonable agreement with available experimental data. Comparison is also made with related 1-propanes.

In a previous paper,[1] we presented an ab initio molecular orbital study of the pseudorotational potential surface for cyclopentane. The results were in reasonable agreement with experimental data, indicating almost free pseudorotational motion interconverting among the various envelope (E) and twist (T) conformations and a significantly higher barrier for inversion through a form with a planar carbon skeleton. For cyclohexane, it is generally recognized that the lowest-energy conformation is a puckered chair form with a high barrier to inversion. An initial aim of this paper is to determine the puckering amplitude of cyclohexane by the same theoretical technique used previously for cyclopentane.

The main objective of the present work is to make a theoretical study of the influence of single methyl or fluoro substituents on the potential surfaces for these ring systems. For the cyclopentanes, the first aim of such a study is to find whether a substituent significantly hinders pseudorotational motion or changes the barrier to direct inversion. If a pseudorotational barrier is introduced, it should then be possible to determine the minima, corresponding to different pseudorotational conformers and their relative energies. For the E-type ring conformation, for example, the relative stabilities of axially and equatorially substituted forms can be compared. At the present time, there is only limited experimental information on these systems. For the substituted cyclohexanes, the ring is already locked in a chair-type arrangement, but this level of theory should again allow comparison of the energies of the axially and equatorially substituted conformations. Finally we shall give a comparative discussion of the interactions and their relation to similar interactions in substituted propanes.

Methods

Since the compounds considered in this study are relatively large, only simple quantum mechanical techniques can be used. Throughout we shall use single-determinant molecular orbital theory (restricted Hartree-Fock or RHF) in conjunction with two Gaussian-type basis sets. The simpler of these is the min-