Identification of $C_3H_6{\cdot}^+$ Structural Isomers by Ion Cyclotron Resonance Spectroscopy

Sir:

The determination of structures of gas-phase ions is important in the understanding of mass spectral fragmentation mechanisms, radiolysis mechanisms, and ionic solution mechanisms. Ion cyclotron resonance spectroscopy (icr)[1] appears to be a potentially powerful tool in such pursuits. Previous studies include the identification of $C_3H_6O{\cdot}^+$ structural isomers,[2] $C_2H_5O^+$ isomers,[3] and $C_8H_8{\cdot}^+$ isomers.[4] The ion–molecule reactions used to distinguish structural isomers in the above studies required deuterium-labeled ions or neutrals since the reactant neutral molecules employed also produced the ion under study by either ionization or subsequent fragmentation. Other structural information was gained from rather unselective ion–molecule reactions such as protonation or charge transfer. It is our hope that somewhat more selective distinguishing reactions can be found which do not depend on extensive labeling experiments and thus are more broadly applicable.[5]

We wish to report the first example of such an ion–molecule reaction and to show how conveniently it can be applied to the identification of C_3H_6 radical cations. Both thermochemical measurements[6] and ion–molecule reactions in a high-pressure mass spectrometer[7] indicate that, at the threshold, different structural isomers are formed in the ionization of cyclopropane and propene. Like the studies above, the bimolecular reactions of $C_3H_6^+$ required[7] a labeled neutral molecule (perdeuteriobutane). The structural information was gained from measurements of rate constants, and the study can only be conveniently made at sufficiently low ionizing energies such that competitive unimolecular and bimolecular reactions do not interfere.

If cyclopropane and ammonia are mixed in the icr spectrometer, abundant product ions are observed at *m/e* 30 and 31 (presumably CH_4N^+ and CH_5N^+). The sole origin of these product ions was determined to be *m/e* 42 ($C_3H_6{\cdot}^+$) by pulsed-double-resonance studies (irradiation of *m/e* 42 at *ca.* 0.04 V/cm produced a decrease in the abundance of both *m/e* 30 and 31). A plot of the corrected relative abundance *vs.* the partial pressure of NH_3 (Figure 1) indicates that the *m/e* 30

$$C_3H_6{\cdot}^+ + NH_3 \longrightarrow CH_4N^+ + C_2H_5 \qquad (1)$$

$$C_3H_6{\cdot}^+ + NH_3 \longrightarrow CH_5N{\cdot}^+ + C_2H_4 \qquad (2)$$

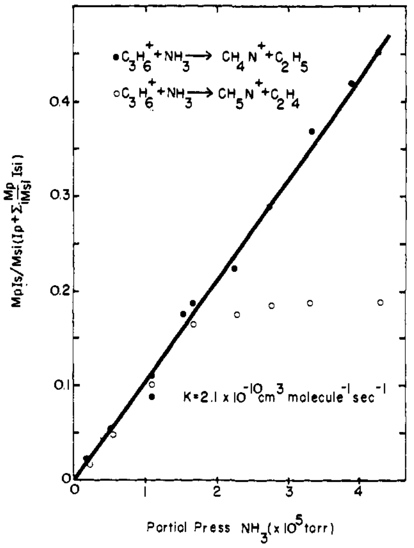
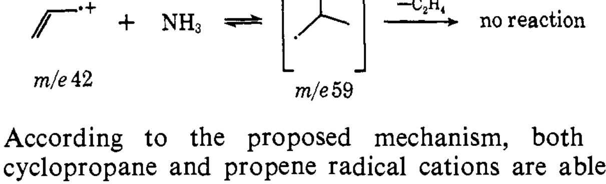


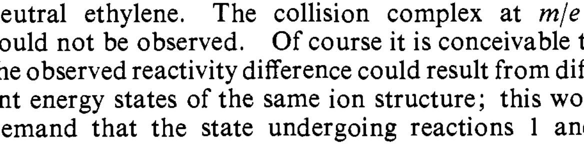
Figure 1. $M_pI_s[M_{si}(I_p + \Sigma_i(M_p/M_{si})I_{si})]^{-1}$ *vs.* the partial pressure of ammonia: electron energy 20 eV, emission current <0.1 μA, source and analyzer drift fields 0.24 V/cm, observing oscillation frequency 307 kHz, pressure determined from output current of ion pump. M_p and M_s are the masses of the primary and secondary (product) ions, respectively; I_p and I_s are the intensities of those ions.

ion is produced in a bimolecular reaction with a rate constant of approximately 2×10^{-10} cm^3 molecule^{-1} sec^{-1} at 20 eV.[8] The rate constant for reaction 2 is nearly equal to that for reaction 1, but the *m/e* 31 ion product apparently is consumed in a consecutive ion–molecule reaction causing its abundance to level off at higher pressures (Figure 1).

The unusual selectivity of this reaction was demonstrated by a study of a mixture of propene and ammonia by icr. No detectable *m/e* 30 or 31 was observed ($k < 10^{-12}$ cm^3 molecule^{-1} sec^{-1}). A possible rationalization for the differences in reactivity of $C_3H_6{\cdot}^+$ from cyclopropane and propene is given by eq 3 and 4.



(3)



(4)

According to the proposed mechanism, both the cyclopropane and propene radical cations are able to react with ammonia, but only the collision complex formed from cyclopropane is able to collapse by losing neutral ethylene. The collision complex at *m/e* 59 could not be observed. Of course it is conceivable that the observed reactivity difference could result from different energy states of the same ion structure; this would demand that the state undergoing reactions 1 and 2

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(8) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, 72, 4599 (1968).

would not be appreciably populated in cases in which the ion is formed from a variety of precursors using electrons of a broad energy range, however.

In order to demonstrate the ease of application of this reaction to structural problems, various compounds which produce abundant C_3H_6 radical cations in their mass spectra were studied. Examples undergoing reactions 1 and 2 are presented in Table I. The C_3H_6 ions produced by the ionization of cyclopropane and the fragmentation of tetrahydrofuran react identically with ammonia at both high and low ionizing energies. These results demonstrate the equivalence of the C_3H_6 ions, a fact consistent with thermochemical measurements.[9]

Table I. Relative Abundance of *m/e* 30 and 31 Produced in Reactions 1 and 2[a]

$V - E$, eV[b]	c-C_3H_6		THF		Cyclohexanone		Hexamethylene oxide	
10	0.075	0.065	0.079	0.070	0.052	0.040[c]	0.040	0.02
7	0.073	0.065	0.075	0.068	0.055	0.040	0.041	0.02
3	0.10	0.08	0.12	0.09				
1.1	0.18	0.12	0.16	0.10	0.16	0.08	0.19	0.05

[a] $P = 1 \times 10^{-5}$ Torr, mixture of 4:1 $NH_3:C_3H_6X$. Column 1 is $I_{30}/(I_{42} + I_{30} + I_{31})$, column 2 is $I_{31}/(I_{42} + I_{30} + I_{31})$. [b] V = electron energy. E = appearance potential of C_3H_6. [c] Corrected for trace of *m/e* 31 found in single-resonance spectrum of cyclohexanone.

The high-resolution mass spectrum of cyclohexanone shows that *m/e* 42 is approximately 70% $C_3H_6\cdot^+$,[10] consistent with the somewhat lower abundances of *m/e* 30 and 31 relative to the total *m/e* 42 ions. In hexamethylene oxide, metastable ions are found which indicate that $C_3H_6\cdot^+$ is produced from both *m/e* 72 ($C_4H_8O\cdot^+$) and *m/e* 70 ($C_5H_{10}\cdot^+$).[11] Since various C_5H_{10} ions (1-pentane and cyclopentene) produce C_3H_6 ions which are unreactive with ammonia (*vide infra*), the lower abundance of *m/e* 30 and 31 can be also understood.

The increased product-ion abundance of *m/e* 30 and 31 at lower ionizing energies (Table I) has been previously observed for other ion–molecule reactions[12] and is consistent with the intermediacy of a collision complex which decays relatively more rapidly to starting materials than to products at higher internal energies.

A variety of compounds produce $C_3H_6\cdot^+$ in their unimolecular fragmentation which are unreactive with ammonia. In addition to propene, these are 1-chloropropane, cyclopentane, 1-pentene, 2,5-dihydrofuran, and 2,3-dimethylbutane. The result for 1-chloropropane is in contrast to the behavior shown by 1-chlorobutane-*3,3-d*$_2$, in which 93% 1,3 elimination takes place.[13] However, in 1-chloropropane, the formation of cyclic $C_3H_6\cdot^+$ would involve the loss of a primary hydrogen atom, which is known to be less favored than loss of a secondary. It is also possible that rearrangement occurs during or after the production of a cyclic $C_3H_6\cdot^+$.

Of course all C_3H_6 ions exhibiting the same reactivity (or lack of reactivity) to NH_3 are not necessarily of identical structure. For example, $C_3H_6\cdot^+$ produced from the compounds in Table I could possess either a cyclic or an acyclic structure ($\cdot CH_2CH_2CH_2^+$), and some isomerization to produce a propene-like ion could have taken place. Further studies are underway to clarify these points and to test the generality of this reaction involving other cyclic hydrocarbons and other nucleophiles.

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Carbon-13 Chemical Shifts in 1-Substituted Bicyclo[2.2.2]octanes[1]

Sir:

The ideas of *field effects* and *through-space effects* have long been of interest in the study of substituent effects on reactivity[2] in organic chemistry. However, these ideas and their relationships to the concepts of *resonance effects* and *inductive effects* have been difficult to define precisely or to demonstrate clearly by experiments. Probably the most promising experimental approaches have employed bicyclic compounds.[3]

Chemical reactivity parameters and the language of organic substituent effects have been applied extensively in nmr interpretations, especially for the proton, ^{19}F, and ^{13}C nuclei.[4] Recent developments in the techniques, equipment,[5] and theory[6] of ^{13}C nmr guarantee

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[2] For reviews on substituent effects and reactivity relationships, see S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964); C. D. Ritchie and W. F. Sager, *ibid.*, **2**, 323 (1964).

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