porphyrin IX in ethanol–water solutions.[4] They found with ferriprotoporphyrin IX that imidazolium was much more reactive than imidazole. It appears that by changing the charge on the peripheral side chains significant effects can be produced on the metal substitution reactions.

A comparison of the rate constants k'_{12} and k'_{34} shows that the rates of formation of the two imidazole complexes are approximately equal. This is consistent with the proposed mechanism if one assumes that the statistical difference of a factor of 2 in the loss of water from the diaquo- and monaquomonohydroxy complexes is compensated for by an increased rate of water loss from the monohydroxy complex.

The hydrolysis behavior of iron(III) is modified considerably when the iron is complexed to a porphyrin as evidenced by a change in the first hydrolysis constant from $10^{-2.2}$ to $10^{-4.8}$.[15] This occurs despite the fact that charge neutralization should be more important in the case of the positively charged ferriporphyrin.

The use of the ethylenediamine-substituted protoporphyrin IX has thus enabled a more extensive study of the hydrolysis behavior of an iron(III) porphyrin and has given valuable insight into some of the effects of side chains on the substitution behavior of metalloporphyrins. Indeed, the effect of the charge on the side chains has been to give specificity to the heme in reactions with charged and uncharged substrates.

[15] L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17, 53 (1964).

An Ion Cyclotron Resonance Study of the Structure of $C_3H_6^+$ and the Mechanism of Its Reaction with Ammonia

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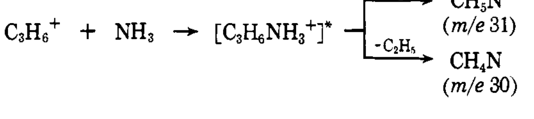
Abstract: The reactions of ammonia and ammonia-d_3 and the C_3H_6 radical cation, produced in the ionization of cyclopropane and in the unimolecular fragmentation of tetrahydrofuran, and the $C_3H_4D_2$ radical cation from tetrahydrofuran-2,2,5,5-d_4 were investigated in detail. The $C_3H_6^+$ ion reacts with ND_3, and the elements of C_2H_5 are lost as C_2H_4D indicating no scrambling of hydrogen among the carbon and nitrogen atoms of the collision complex. Furthermore, the label distributions in the product ions produced by $C_3H_4D_2^+$ and NH_3 or ND_3 demonstrate that the structure of $C_3H_4D_2^+$ is one in which the three carbon atoms have become equivalent. The results also show that there is essentially no randomization of hydrogen atoms in the primary $C_3H_4D_2^+$ or in the intermediate complex formed in the reaction with ammonia.

To aid in the interpretation of mass spectra of cyclic hydrocarbons, it has been suggested that ionization removes an electron from a C–C bond, effectively opening the ring.[1] This ring scission is followed by subsequent fragmentation. Supporting evidence for this hypothesis is found in labeling experiments of cyclopentane[2] and methylcyclopentane[3] and in energetic measurements for the fragmentation of methylcyclopentane.[4] The nondecomposing or stable molecular ions from cyclobutane have been shown to be open structures by photoionization followed by product analysis[5] and by ion–molecule reaction studies.[6] In fact, a more recent comparison of the bimolecular reactivities of the molecular ions of cyclobutane, 1-butene, 2-butene, and 2-methylpropene indicates that two or more different open-ring structures occur in the ionization of cyclobutane.[7] Radiolysis of cyclopropane seems to produce a propene ion;[8] however, recent studies of the ion–molecule reactions of $C_3H_6^+$ from cyclopropane indicate that it does not possess this structure.[9,10] These latter results do not exclude the possibility of an unisomerized acyclic ion, *i.e.*, the trimethylene radical cation.

The purpose of the research reported here is twofold. By employing suitably labeled reagents in the previously reported reaction of $C_3H_6^+$ with ammonia (reaction 1),[10] we hope to be able to answer whether the



$$C_3H_6^+ + NH_3 \rightarrow [C_3H_6NH_3^+]^* \begin{cases} \xrightarrow{-C_2H_4} CH_5N \ (m/e\ 31) \\ \xrightarrow{-C_2H_5} CH_4N \ (m/e\ 30) \end{cases} \quad (1)$$

first member of the saturated cyclic hydrocarbon ion series is better represented as an acyclic ion. A second, but equally important, purpose is to test whether randomization of hydrogen atoms occurs in the intermediate complex of reaction 1. Such randomization is

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[1] See, for example, J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier, Amsterdam, 1968, p 109.

[2] B. J. Millard and D. F. Shaw, *J. Chem. Soc. B*, 664 (1966).

[3] D. P. Stevenson, *J. Amer. Chem. Soc.*, **80**, 1571 (1958); S. Meyerson, T. D. Nevitt, and P. N. Rylander, *Advan. Mass Spectrom.*, **2**, 313 (1963).

[4] R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 3204 (1961).

[5] R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **43**, 3814 (1965).

[6] B. M. Hughes and T. O. Tiernan, *ibid.*, **51**, 4373 (1969).

[7] L. W. Sieck, S. K. Searles, and P. Ausloos, *J. Amer. Chem. Soc.*, **91**, 7627 (1969).

[8] P. Ausloos and S. G. Lias, *J. Chem. Phys.*, **43**, 127 (1965).

[9] L. W. Sieck and J. H. Futrell, *ibid.*, **45**, 560 (1966).

[10] M. L. Gross and F. W. McLafferty, *J. Amer. Chem. Soc.*, **93**, 1267 (1971).

extensive in the ion–molecule reactions in methane,[11] acetylene,[12] and ethane.[13] However, in larger hydrocarbons such as allene and propyne,[14] butenes through hexenes,[15] and styrene,[16] the reactions proceed with less randomization. Introduction of a heteroatom as in the reactions of CH_3^+ with ammonia[17] and in H_2S and ethene[18] also minimizes the hydrogen equilibration presumably because of localization of charge.[18] Lack of randomization in ion–molecule collision complexes is desirable for labeling studies of ion–molecule reaction mechanisms and structure determinations of gas-phase ions. Therefore, it is important to know under what conditions randomization will be important.

Experimental Section

Materials. The cyclopropane, ammonia, and methylamine were obtained from Matheson Gas Products; the tetrahydrofuran was certified grade from Fisher Scientific Co. The ND_3 was supplied by Merck Sharp and Dohme of Canada, 99 atom % grade. We found 10% ND_2H by icr and gas-phase ir studies. The tetrahydrofuran-2,2,5,5-d_4 was prepared by the lithium aluminum deuteride (Alfa Inorganics) reduction of diethyl succinate followed by dehydration according to the method of Bissell and Finger.[19] This material was 95% d_4 by icr and conventional mass spectrometry. The nmr spectrum of a 20% solution of this compound in CCl_4 showed only a singlet at δ 0.63. All of the compounds were thoroughly degassed on a vacuum line prior to the icr studies.

Apparatus and Procedure. The icr spectrometer was a Varian ICR-9 equipped with a dual inlet system. The standard flat cell (cross section 1.27 × 2.5 cm) was used for all measurements. The ionizing energies reported in the text are nominal values and were set by use of a digital voltmeter. The emission current was less than 0.2 μA. The source and analyzer drift fields were 0.28 V/cm, and a trapping voltage of 0.60 V was employed. Single resonance spectra were obtained in a field modulation mode (amplitude = 20 G) with a marginal oscillator frequency of 307 kHz and a level which did not produce a change in the total ion current at resonance.

Typically, the source of $C_3H_6^+$ was admitted to the icr cell at a pressure of 2×10^{-6} Torr (from the ion pump current monitor). Ammonia or ND_3 was added *via* the second inlet. At various points during additions of ammonia, the source of $C_3H_6^+$ was pumped away, and the partial pressure of NH_3 was determined by use of reaction 2. A rate constant of 1.5×10^{-9} cm^3 molecule^{-1} sec^{-1}, an

$$NH_3^+ + NH_3 \longrightarrow NH_4^+ + NH_2 \qquad (2)$$

average value taken from literature reports[20] for low kinetic energy studies, was used for an ionizing energy of 15 eV. Pressure measurements at other partial pressures of NH_3 were made by callibrating the total ion current monitor.

Results and Discussion

The first question to be answered is the origin of the hydrogen atom lost in the formation of CH_4N^+ (*m/e* 30). When mixtures of cyclopropane and ND_3 are studied in the icr at partial pressures of ND_3 between 0.5 and 3.0×10^{-5} Torr, two major peaks are observed at *m/e* 32 and 34 indicating the hydrogen lost is primarily from the ammonia molecule (reaction 3). A small peak (6 ± 2% of the peak at *m/e* 32) is found at *m/e* 33.[21] At pressures of $ND_3(NH_3)$ where subsequent

$$C_3H_6^+ + ND_3 \longrightarrow \left\{ \begin{array}{l} CH_2D_3N^+ + C_2H_4 \\ \quad (m/e\ 34) \\ CH_2D_2N^+ + C_2H_4D \\ \quad (m/e\ 32) \end{array} \right. \qquad (3)$$

reaction of $CH_2ND_3^+$ ($CH_2NH_3^+$) is unimportant, the cross section for production of $CH_2ND_3^+$ is definitely smaller than for $CH_2NH_3^+$, demonstrating a secondary isotope effect ($k_H/k_D = 1.1$). In addition, the loss of D from $CH_2ND_3^+$ is less favorable than loss of H from CH_2NH_3 ($k_H/k_D = 1.4 \pm 0.1$). Similar effects are found in the reaction of $C_3H_6^+$ from tetrahydrofuran (THF) and ND_3. Nearly exclusive formation of *m/e* 34 and 32 is observed (with 4 ± 2% formation of *m/e* 33) along with small regular isotope effects.

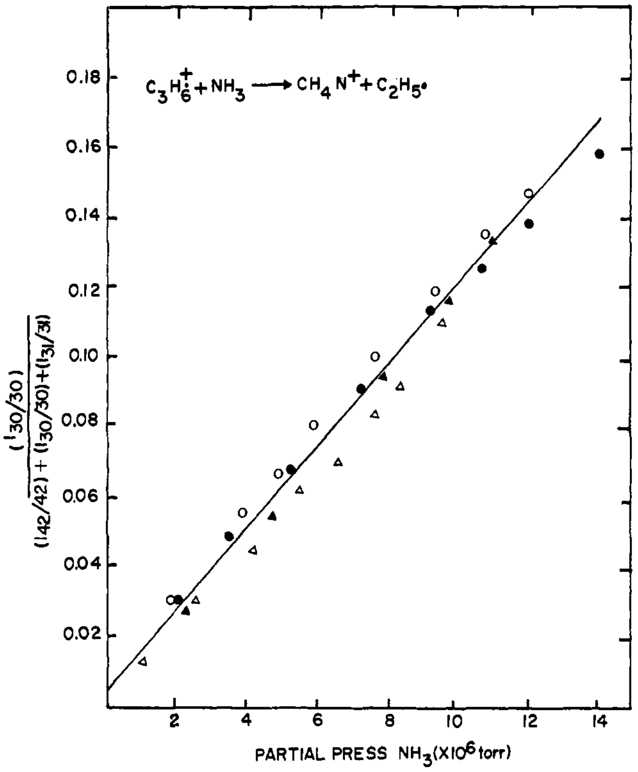

Figure 1. Relative abundance of CH_4N (*m/e* 30) as a function of the partial pressure of NH_3. Source of $C_3H_6^+$: (●) cyclopropane at 20 eV; (○) cyclopropane at 15 eV; (▲) THF at 20 eV; (△) THF at 15 eV.

The above results indicate very little randomization of hydrogen atoms between the nitrogen atom and the three carbon atoms in the intermediate complex. These labeling data are in accord with either a one-step loss of C_2H_5 from the intermediate complex or a loss of H (D in the case of ND_3) from the CH_5N (CH_2D_3N) radical cation. The data of Figure 1 suggest that CH_4N^+ is formed directly from the intermediate since the pressure plot is linear over the entire pressure range studied for this ion (see also Figure 1 in ref 10). Consideration of energetic data leads to the same conclusion (reactions 4–6).[22] As can be seen, production of CH_5N^+

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(12) J. H. Futrell and T. O. Tiernan, *J. Phys. Chem.*, 72, 158 (1968).

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(15) F. P. Abramson and J. H. Futrell, *ibid.*, 72, 1994 (1968); J. M. S. Henis, *J. Chem. Phys.*, **52**, 282 (1970).

(16) C. L. Wilkins and M. L. Gross, *J. Amer. Chem. Soc.*, **93**, 895 (1971).

(17) W. T. Huntress and D. D. Elleman, *ibid.*, **92**, 3565 (1970).

(18) S. E. Buttrill, Jr., *ibid.*, **92**, 3560 (1970).

(19) E. R. Bissell and M. Finger, *J. Org. Chem.*, **24**, 1259 (1959).

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(21) The abundance at *m/e* 33 was corrected for the reaction of $C_3H_6^+$ with ND_2H.

$$C_3H_6^+ + NH_3 \longrightarrow CH_5N^+ + C_2H_4 \qquad (4)$$
$$\Delta H = -20 \text{ kcal mol}^{-1}$$

$$C_3H_6^+ + NH_3 \longrightarrow CH_4N^+ + C_2H_5 \qquad (5)$$
$$\Delta H = -31 \text{ kcal mol}^{-1}$$

$$C_3H_6^+ + NH_3 \longrightarrow CH_4N^+ + C_2H_4 + H \qquad (6)$$
$$\Delta H = +9 \text{ kcal mol}^{-1}$$

and CH_4N^+ is exothermic provided the elements of C_2H_5 are lost in one step as an ethyl radical for the CH_4N^+ case.

The abundance of CH_5N (*m*/*e* 31) does not increase linearly with pressure but rather begins to level off as the partial pressure of ammonia is increased (see Figure 1, ref 10). Presumably this ion is being consumed in a consecutive ion–molecule reaction with neutral ammonia. The possibility for this reaction to produce NH_4^+ (reaction 7) was checked by pulsed double resonance. No change in the abundance of NH_4^+ could be observed with irradiation of CH_5N^+ probably because of the relatively small abundance of the CH_5N^+ species. Using a value of 154 kcal mol^{-1} for the heat of formation of NH_4^+,[23] the heat of reaction for reaction 7 is -1 kcal mol^{-1}. This reaction pathway is thermodynamically plausible. Thus, a study of the reactions of CH_5N^+ (*m*/*e* 31) and CH_4N^+ (*m*/*e* 30) formed from methylamine with neutral ammonia was initiated. The measurements of interest would involve the fate of *m*/*e* 30 and 31 as the partial pressure of ammonia is increased. The molecular ion of methylamine (*m*/*e* 31) was observed to decrease as the partial pressure of NH_3 was increased, whereas the abundance of CH_4N^+ (*m*/*e* 30) remained constant (see Table I). A pulsed double resonance experiment could now be carried out because of the larger abundances of *m*/*e* 30 and 31, and a decrease in NH_4^+ was observed as CH_5N^+ (*m*/*e* 31) was irradiated. These data provide support for the argument that CH_5N^+ abundance levels off because of a consecutive reaction with ammonia to produce NH_4^+. Table I also provides a comparison of the rate of decrease of *m*/*e* 31 formed in the bimolecular reaction of $C_3H_6^+$ from cyclopropane and the molecular ion of methylamine. Even though the CH_5N^+ is produced in a bimolecular reaction in the case of cyclopropane and ammonia, this ion disappears more rapidly than CH_5N^+ from methylamine. The rate constant for reaction 7, CH_5N^+ produced from cyclopropane, must be significantly larger than for the methylamine molecular ion. There are two reasons for this enhanced reactivity. Either CH_5N^+ from $C_3H_6^+$ and NH_3 possesses a different structure than the molecular ion of methylamine, *e.g.*, $\dot{C}H_2N^+H_3$, or it is of the same structure but less internally excited (since an increase in vibrational energy decreases the rate constant of ion–molecule reactions proceeding through an intermediate complex[24]).

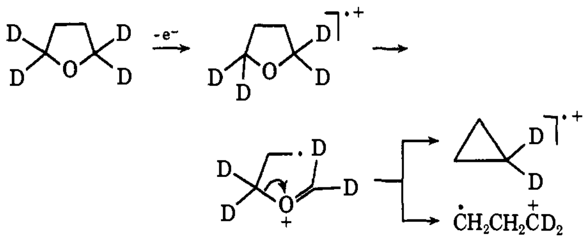
$$CH_5N^+ + NH_3 \longrightarrow CH_4N + NH_4^+ \qquad (7)$$

Table I. Abundance of CH_5N^+ (*m*/*e* 31) Relative to CH_4N^+ (*m*/*e* 30) as a Function of the Partial Pressure of Ammonia (Ionizing Energy = 20 V)

Pressure, NH_3 ($\times 10^6$ Torr)	I_{31}/I_{30} Methylamine	I_{31}/I_{30} Cyclopropane
0	1.00	1.00
2	0.94	1.00
4	0.90	0.94
8	0.84	0.86
10	0.81	0.83
12	0.80	0.78
14	0.76	0.71
16	0.71	0.65

Now that the origin of the hydrogen atom lost in the formation of CH_4N (*m*/*e* 30) and the consecutive reaction of CH_5N^+ (*m*/*e* 31) have been uncovered, we now wish to examine whether randomization of hydrogen among the three carbon atoms has occurred, either in the primary $C_3H_6^+$ ion or in the collision complex. If such randomization is minimal, we should be able to determine the structure of the "stable" C_3H_6 radical cation.

It is immediately apparent that labeling neutral cyclopropane will not provide an answer in regard to the structure of $C_3H_6^+$. A cyclic ion will yield identical label distributions in the products formed in the reaction with ammonia as does an acyclic ion since there is equal probability of opening the ring at any of the C–C bonds. For this reason, we chose to generate a labeled $C_3H_6^+$ from tetrahydrofuran-2,2,5,5-*d*$_4$[25] (reaction 8). We feel if the ring-open structure is preferred for $C_3H_4D_2^+$, this species will be formed in the unimolecular fragmentation of THF-*d*$_4$ with a CD_2 moiety at the terminus, either as a positively charged or radical site (see reaction 8). Referring back to Figure 1, it can be seen that the rate constant for reaction of $C_3H_6^+$ from cyclopropane with ammonia is essentially identical with that of $C_3H_6^+$ from THF since all the data lie along a straight line. Thus, a study of $C_3H_6^+$ from THF should serve as a means of obtaining structural information about ionized cyclopropane.



(8)

The possibilities are outlined in Schemes I and II for either a cyclic or acyclic $C_3H_4D_2$ radical cation, respectively. No equilibration of hydrogen over the three carbon atoms in either the initial C_3H_6 radical cation or the collision complex is assumed. A cyclic ion will produce product ions **1** and **3** and **2** and **4** in ratios of 1:2. The abundances of ions **2** and **4** relative to **1** and **3** will depend on the pressure of NR_3 since CH_5N participates in a consecutive reaction with NH_3(ND_3), and these abundances are obtained by an experiment with unlabeled THF and NR_3 at partial pressures of NR_3 identical with that used with the labeled THF. An acyclic ion, on the other hand, will produce

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[22] The relevant thermodynamic data are taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, 26 (1969).

[23] A. P. Altshuller, *J. Amer. Chem. Soc.*, 77, 3480 (1955).

[24] A. Weingartshofer and E. M. Clarke, *Phys. Rev. Lett.*, **12**, 591 (1964); W. A. Chupka, M. E. Russell, and K. Refaey, *J. Chem. Phys.*, **48**, 1518 (1968); M. L. Gross and J. Norbeck, *ibid.*, **54**, 3651 (1971).

[25] Like A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 2920 (1965), we found the *m*/*e* 42 species ($C_3H_6^+$) to be quantitively shifted to *m*/*e* 44 ($C_3H_4D_2$).

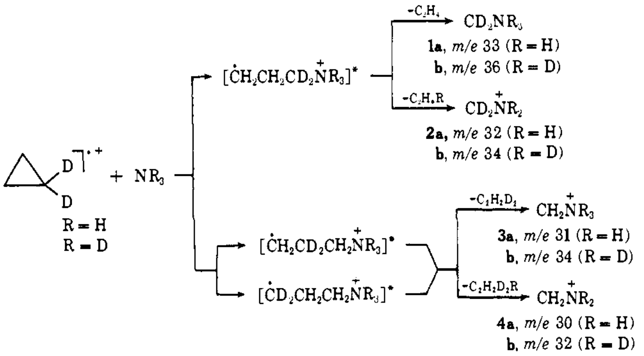
Table II. Distribution of Product Ions for Reaction of $C_3H_4D_2^+$ and NH_3 or ND_3 Using 19-eV Electrons

Pressure ($\times 10^5$ Torr)	NH_3 $I_{30}:I_{31}:I_{32}:I_{33}$ Calcd[a]	Obsd[b]	ND_3 $I_{36}:I_{34}:I_{32}$ Calcd[c]	Obsd[b]
0.7	2.2:2.0:1.1:1.0	2.5:2.0:1.6:1.0		
0.9	2.6:2.0:1.3:1.0	2.7:1.9:1.4:1.0	2.1:3.0:1.0	2.5:3.1:1.0
1.4			2.4:3.2:1.0	2.4:3.2:1.0
1.8	3.8:2.0:1.9:1.0	3.6:2.1:1.8:1.0	2.5:3.2:1.0	2.7:3.4:1.0
2.9	4.2:2.0:2.1:1.0	4.4:2.1:2.1:1.0		
0.7	2.40:2.00:1.20:1.00	2.50:1.75:1.30:1.00[d]		
1.0	2.64:2.00:1.32:1.00	2.85:1.95:1.59:1.00[d]		
2.0	3.70:2.00:1.85:1.00	3.60:2.25:1.87:1.00[d]		

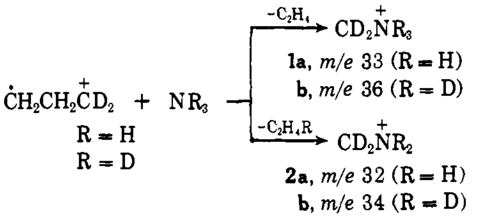
[a] Calculated ratio assuming a cyclic $C_3H_4D_2^+$ and using I_{30}/I_{31} in THF–NH_3 at identical pressure of NH_3 to measure the extent of loss of H. [b] Corrected by dividing the abundances by the mass of the respective ion. Also corrected for ^{13}C and ^{15}N. [c] I_{34}/I_{32} in THF–ND_3 at identical pressure of ND_3 was used to measure the extent of loss of D. [d] At 14.9 eV.

only ions **1** and **2**, or ions **3** and **4** if the positive charge is located on the other terminus.

Scheme I



Scheme II



The results are tabulated in Table II. The data in the first half of Table II were obtained by holding the pressure of THF (THF-d_4) constant while varying the partial pressure of NR_3. The data in the second half represent a better experimental approach. Here, the NH_3 pressure was held constant and THF was added *via* the second inlet until a large signal was generated for the product ions. After measurement, the THF was pumped away followed by introduction of THF-d_4 without modification of the NH_3 pressure. In this way an additional significant figure could be obtained. These latter data were obtained at 14.9 eV, a sufficiently low ionizing energy that no *m/e* 31 was found in the mass spectrum of THF (*m/e* 33 and 34 for THF-d_4). The results at higher ionizing energy (first half of Table I) were corrected for these ions.

The results demonstrate that the stable configuration for $C_3H_6^+$ from THF and, therefore, from cyclopropane is a form possessing three equivalent carbon atoms, and the best representation of this fact is a cyclic structure. This is in accord with recent molecular orbital calculations which show that the low energy form is an isosceles triangle.[26] However, the data do not rule out the possibility of ring opening prior to reaction with ammonia. Thus, it is possible that $C_3H_6^+$ from cyclopropane and THF ultimately becomes a trimethylene radical cation which then participates in the bimolecular reaction with ammonia. What is clear, however, is the fact that the three carbon atoms in $C_3H_6^+$ must be equivalent at some point in its history. The driving force for production of this cyclic form must be its inherent stability. It is well to point out that these experiments do not give information concerning all of the C_3H_6 ions formed in the icr cell. At the highest partial pressures of NH_3 investigated here, only 15% of the ions have reacted with ammonia. We can only extrapolate to the reactivity of the remaining 85%.

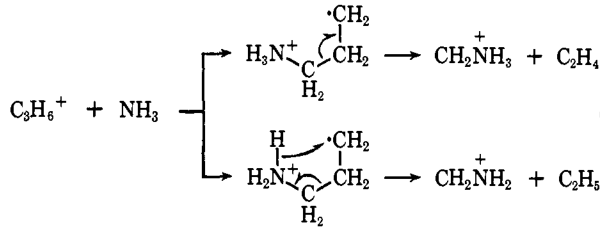
The second objective of this study has been realized as well. There is no significant randomization of the hydrogen atoms in $C_3H_6^+$ or in the collision complex. A model involving complete randomization would give rise to an abundance ratio of 1:5 for the product ions **5** and **6** in reaction 9 and ions **7** and **8** in reaction 10.

$$C_3H_4D_2^+ + NH_3 \longrightarrow \underset{\mathbf{5}}{CD_2NH_3^+} \text{ and } \underset{\mathbf{6}}{CH(D)NH_3^+} \qquad (9)$$

$$C_3H_4D_2^+ + ND_3 \longrightarrow \underset{\substack{m/e\ 36\\ \mathbf{7}}}{CD_2ND_3^+} \text{ and } \underset{\substack{m/e\ 35\\ \mathbf{8}}}{CH(D)ND_3^+} \qquad (10)$$

These possibilities are significantly different from the results observed in this work. In fact, a randomized $C_3H_4D_2^+$ would produce an ion at *m/e* 35 in reaction 10, a peak which is not observed in the studies with ND_3.

We are now in a position to write a rather detailed mechanism for the reaction of $C_3H_6^+$ with ammonia (reaction 11), a mechanism which proceeds with essentially no randomization of hydrogen over the three carbon atoms and the nitrogen atom. This lack of randomization is very encouraging, for not only can



(11)

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(26) E. Haselbach, *Chem. Phys. Lett.*, 7, 428 (1970). Preliminary *ab initio* SCF calculations using Gaussian lobe orbitals on the doublet $C_3H_6^+$ state show that the cyclic structure as an isosceles triangle with an apex angle around 68° is more stable than the ring-open structure by about 30 kcal mol^{-1}. Private communication, Professor G. A. Gallup.

reaction intermediates be elucidated for small systems,[18] but also these reactions should prove extremely useful in structural determinations of gas-phase ions.

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Ion Cyclotron Resonance Study of the Mechanism of Chemical Ionization. Mass Spectroscopy of Selected Hydrocarbons Using Methane Reagent Gas

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Abstract: A four-section ion cyclotron resonance (icr) cell with independent trapping capabilities in the source and the reaction-analyzer regions has been used to study mechanisms of chemical ionization (CI) processes. A pressure dependence study on pure methane (a frequently used reagent gas) has shown that CI conditions approximating those of conventional high source pressure mass spectrometers can be obtained at a pressure of around 1×10^{-4} Torr using icr techniques. Through the use of trapping field ejection, the role of the principal reagent ions in methane, CH_5^+ and $C_2H_5^+$, in producing the various CI products from some C_6 hydrocarbons has been ascertained and mechanisms for such processes have been deduced. Results indicate that, with minor exceptions, only those CI reactions which are exothermic for ground state ion energetics actually occur. With the C_6 paraffins, $C_5H_{11}^+$ is a major CI product and is produced exclusively from CH_5^+ reagent ion; the other CI products, in the order of decreasing intensities, are $C_6H_{13}^+$, $C_4H_9^+$, $C_3H_7^+$, and $C_4H_8^+$ or $C_3H_6^+$, which have varying but systematic contributions from both CH_5^+ and $C_2H_5^+$. The CI of cyclohexane produced primarily $C_6H_{11}^+$, having both CH_5^+ and $C_2H_5^+$ as reagent ions, but the fragments $C_3H_7^+$, $C_4H_8^+$, and $C_4H_9^+$ came exclusively from CH_5^+. The CI of benzene produces primarily $C_6H_7^+$ with minor amounts of $C_7H_7^+$. The former had mostly CH_5^+ as progenitor ion while $C_7H_7^+$ had the third reagent ion in methane, $C_3H_5^+$, as its primary precursor. The results of this study are compared with related work and generally acceptable agreement was found despite widely variant experimental parameters.

A survey of recent literature[2] reveals that the ion cyclotron resonance (icr) technique has played an ever increasing part in the study of gas phase ion–molecule reactions. It has proven its value by elucidating complex reaction mechanism and by determining the endothermicity or exothermicity of ion–molecule reactions through ion cyclotron double resonance. More recently, quantitative determinations of reaction rate constants and energy dependence of some ion–molecule reactions have been reported. In this paper, we will present another extension of icr spectroscopic techniques to elucidate the mechanism of chemical ionization (CI) mass spectroscopy of selected C_6 hydrocarbons.

Even though chemical ionization studies in conventional high pressure source mass spectrometers are done in the 0.5–1 Torr range, comparable studies can be performed in the icr at around 1×10^{-4} Torr. This is possible because of the long ion residence times associated with weak electric and strong magnetic fields of an ion cyclotron resonance mass spectrometer. For the drift parameters used in this investigation, for example, the ion residence time at the magnetic field to detect m/e 85 is 14 msec.[3] Since this is about five orders of magnitude higher than the ion residence times in a conventional high pressure source, chemical ionization experiments can be readily performed at a pressure of around 1×10^{-4} Torr in an icr instrument.

In this study, methane was used as the reagent gas. It was chosen for this investigation both because ion–molecule reaction products for this system have been well characterized and because it has been used most extensively as the reagent gas in chemical ionization studies. It has, however, been impossible to determine which one of the two major ion–molecule products in methane (CH_5^+ and $C_2H_5^+$) are responsible for the various chemical ionization products. The technique of ion cyclotron resonance using trapping field ion ejection was used to resolve individual contributions from these principal secondary ions in high pressure methane.

The ion-ejection technique used in this research was developed by Beauchamp and Armstrong.[4a] The principles of ion ejection have been discussed and its

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(1) Alfred P. Sloan Fellow, 1968–1972.

(2) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, 4, 114 (1971), and references cited therein.

(3) Techniques recently developed for the experimental measurement of residence times (R. P. Clow and J. H. Futrell, *Int. J. Mass Spectrom. Ion Phys.*, **8**, 119 (1972)) have demonstrated that residence times are somewhat less than 14 msec under these conditions. The general conclusion of this paragraph nevertheless applies.

(4) (a) J. L. Beauchamp and J. T. Armstrong, *J. Rev. Sci. Instrum.*, **40**, 123 (1969); (b) M. T. Bowers, D. D. Ellemen, and J. King, *J. Chem. Phys.*, **50**, 4787 (1969).