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Gas Phase Reactions of CH_3^+ with a Series of Homo- and Heterocyclic Molecules

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In gas phase ion chemistry, the growth of larger molecules is known to occur through association of ions and neutrals. Where the ion attaches to the neutral is important because it can influence the possibility of additional associations, effectively enabling or terminating further molecular growth. This was investigated by using a Selected Ion Flow Tube (SIFT) at 300 K to study the reactions of CH_3^+ with the following series of single-ring homocyclic and heterocyclic molecules: benzene (C_6H_6), cyclohexane (C_6H_{12}), pyridine (C_5H_5N), pyrimidine ($C_4H_4N_2$), piperidine ($C_5H_{11}N$), 1,4-dioxane ($C_4H_8O_2$), furan (C_4H_4O), pyrrole (C_4H_5N), and pyrrolidine (C_4H_9N). Most of the reactions, except for 1,4-dioxane, pyrrole, and pyrrolidine, proceed at the gas kinetic rate. In the ion product distributions, charge transfer, hydride ion abstraction, proton transfer, fragmentation, and association were observed. In particular, proton transfer is seen to be small in all cases even though these channels are energetically favorable. Association is appreciable when the molecules are aromatic (except for furan) and nonexistent when there are no π electrons in the ring. CH_3^+ ions are an important intermediate in molecular synthesis in interstellar clouds and in the Titan ionosphere and ring molecules have also been detected in these media. The significance of the studied reactions to these media is discussed.

Introduction

In gas phase ion chemistry, the growth of larger molecules occurs mainly through association of the ions and neutrals. Where the ion attaches to the neutral is important because it can affect the possibility of additional associations, effectively enabling or terminating further molecule growth. Association reactions are important in the interstellar medium (radiative association[1]) and the ionosphere of Titan (collisional association[2]) where ion-neutral associations are thought to lead to the formation of benzene and PAHs.[3−5]

There is a lack of experimental data exploring association reactions of larger hydrocarbons and because of this, the possible importance of association in models of Titan's atmosphere has been under exploration. In this work, a series of reactions of the methyl cation, CH_3^+, with homo- and heterocyclic neutral molecules is investigated. The structures of the neutral molecules are shown in Figure 1. The association product channel is explored as a function of the presence of π electrons and the type and/or amount of heterocyclic substitution. CH_3^+ is an important ion in Titan's ionosphere and the interstellar medium and reactions involving this ion figure significantly in ensuring the thorough modeling of the chemistry occurring in these regions. Association of CH_3^+ to any of these molecules would be of interest as a mechanism for creating more massive molecules.

Experimental Section

A selected ion flow tube (SIFT) was used to study this series of ion-neutral reactions between CH_3^+ and benzene (C_6H_6), cyclohexane (C_6H_{12}), pyridine (C_5H_5N), pyrimidine ($C_4H_4N_2$), piperidine ($C_5H_{11}N$), 1,4-dioxane ($C_4H_8O_2$), furan (C_4H_4O), pyrrole (C_4H_5N), and pyrrolidine (C_4H_9N). The SIFT method has been described extensively in the literature[6−8] and this will not be repeated here. Specific to this experiment, the CH_3^+ was formed by injecting methane into a low-pressure ionization source. After mass selection in a quadrupole mass filter, the ions were injected into the flow tube at an ion energy of ~20 eV to minimize fragmentation of the CH_3^+. Although a low ion injection energy was used it was not possible to completely eliminate further fragmentation of CH_3^+ and because of that the following ions were present in the flow tube at the average indicated percentage when compared to CH_3^+: C^+ (3%), CH^+ (5%), CH_2^+ (7%), and CH_4^+ (6%). Pyridine, pyrrole, pyrrolidine, furan, 1,4-dioxane, benzene, and cyclohexane were obtained from Sigma-Aldrich with purities of >99.9%, 98%, 99.5+%, 99+%, 99.5%, 99.5%, and 99%, respectively. Pyrimidine and piperidine were obtained from Alfa Aesar with manufactured purities of 99%. Benzene was obtained from Fisher Scientific with a purity of 99.5%. To eliminate dissolved gases, the liquids were further purified before use by several cycles of freeze−pump−thaw. The neat vapors proved difficult to work with due to condensation of the vapors in the neutral reactant system and on the flow tube walls, so a 1% mixture of the reactant neutral in helium was used. This dilution was accounted for when determining the rate coefficients. Ion product distributions and rate coefficients were determined in the usual way.[6,7,9] The ion product distributions are accurate to ±5 in the percentage and the rate coefficients are accurate to ±30% due to the sticky nature of these gases. All reactions were studied at 298 K. Mass discrimination in the detection quadrupole was corrected as before.[8]

Results

The rate coefficients for all reactions studied are given in Table 1. While it can be seen that most of the reactions occur within experimental error of the gas kinetic rate there is a tendency for the experimental rates to be less than gas kinetic. This feature has not been seen in reactions of other ions involving the same neutrals. The 1,4-dioxane and pyrrolidine

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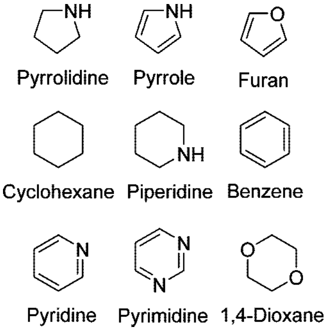

Figure 1. Structural diagrams of the cyclic neutrals used in this study.

TABLE 1: Experimental Rate Coefficients, k_{exp}, for the Reactions between CH_3^+ and the Indicated Neutrals Are Listed Followed by the Theoretical Rate Coefficients, k_{theor},[a] Calculated Using Combined Variational Transition State Theory and Classical Trajectory Theory[32]

neutral molecule	k_{exp} (10^{-9} cm^3 s^{-1})	k_{theor} (10^{-9} cm^3 s^{-1})	efficiency[b]
cyclohexane	1.87	2.18	0.86
piperidine	1.86	2.30	0.81
1,4-dioxane	1.73	3.44	0.50
pyrrolidine	1.60	2.97	0.54
benzene	1.88	2.12	0.89
pyridine	3.14	3.55	0.88
pyrimidine	2.71	3.76	0.72
pyrrole	2.23	3.21	0.70
furan	1.83	2.16	0.85

[a] Data needed to calculate the theoretical rate coefficients were obtained from the CRC Handbook and the literature.[33-36] [b] The reaction efficiency, k_{exp}/k_{theor}, is also included. All rate coefficients are expressed in units of 10^{-9} cm^3 s^{-1}.

reactions are significantly slower than the gas kinetic rate. The reason for this is not clear at present. A sample of the data is shown in Figure 2. Note that the decay of the primary ion is linear over 2 orders of magnitude. This provides increased confidence in the rate coefficients experimentally derived. Figure 2 will be discussed in more detail later.

The product distributions obtained for the reactions are listed in Table 2. The recombination energy for the methyl cation is given in the table together with the ionization energies and proton affinities for the reactant neutrals. All of the neutrals, with the exception of cyclohexane, have smaller ionization energies than the recombination energy of CH_3^+, therefore charge transfer is expected in these cases. Charge transfer is a product channel in all reactions studied.

The proton affinity of CH_2, 207 kcal/mol,[10] was used to determine if proton transfer was energetically favorable. For pyridine, pyrimidine, pyrrole, piperidine, and pyrrolidine, proton transfer is energetically possible and was seen as a product channel. Proton transfer is endothermic for furan, benzene, 1,4-dioxane, and cyclohexane and was not observed.

In all but two of the reactions, hydride abstraction was a significant product channel. The two neutrals that did not experience hydride abstraction were pyrrole and furan, the aromatic five-membered rings. By comparing the hydride ion affinities (HIA) of each species to that of CH_3^+ one can determine if the hydride abstraction channel is energetically favorable. The hydride ion affinity of CH_3^+ is well know in the literature[11] with a value of 313 kcal mol^{-1}. However, values for the species investigated in this study are not available. Since these values are unknown, it is logical to assume that the HIA of the species that have hydride abstraction as a product channel must be lower than that of CH_3^+, which indicates an exothermic reaction. In the case of pyrrole and furan, where no hydride abstraction is observed, an HIA value greater than CH_3^+ could explain the lack of this product channel. The HIA for furan was calculated[12] at the G3 level of theory and determined to be larger than 313 kcal mol^{-1} and therefore hydride abstraction is not energetically favorable for this reaction. Hydride abstraction for pyrrole was also calculated and is determined to be exothermic by 8.75 kcal mol^{-1}. Therefore, while hydride abstraction is energetically favorable it might not be seen due to competition from more favorable product channels.

An association product channel was observed in many of the reactions. Particularly, in the reactions involving pyridine and pyrimidine, it was surprising to see that association was very competitive with the other product channels such as proton transfer and charge transfer. There are some cases in the literature where this has occurred, for instance where association was competitive with charge transfer and hydride abstraction in reactions involving NO^+ [13] and where association was competitive with proton transfer in a reaction involving H_3O^+ [14] as the primary ion. However, it is generally known that when proton transfer is energetically favorable, it is a very efficient process and occurs rapidly.[15] Mechanistically, proton transfer must occur through a close encounter and usually it is only when proton transfer starts to become thermoneutral or endothermic that association is observed.[16] Because of this, it is not expected for proton transfer and association to be competitive product channels. The observation of association in this study suggests another process is taking place that can overcome or inhibit rapid proton transfer. Interestingly, for almost all of the neutral molecules that possess π electrons, association is a product channel while the neutral molecules without these π electrons show no association.

Discussion

Of the neutrals in this study, five (benzene, pyridine, pyrimidine, pyrrole, and furan) are aromatic and therefore possess π electrons. Association occurred with all these aromatic neutrals except furan. There was no association with saturated neutrals and thus the π electrons appear to promote association. This seems a natural conclusion considering CH_3^+ is an electron-deficient species and therefore will act as an electrophile and be strongly attracted to the concentrated density of negative charge that is easily accessible in aromatic molecules. Several theoretical studies have investigated the interaction between cations and aromatic compounds. The studies use species such as Na^+, Mg^+, Al^+, and other main group metal ions,[17] NH_4^+ and $CH_3NH_3^+$,[18] and it was determined how they interact with the π electrons. The conclusion was that the cation usually forms a π-complex with the aromatic molecule with the binding energy being dependent on several factors. In particular, one study looked at the differences in binding energies of a Na^+ cation with 11 cyclic molecules containing varying amounts of heteroatoms and substituents.[19] That study determined that the cation−π interaction most strongly depends on the electrostatic interaction and inspection of the electrostatic potential surface of the neutral molecule gives a good indication of the strength of cation−π bonding. In a further study, the number of cyclic molecules studied was expanded to include five-membered rings and several more polycyclic aromatic molecules.[20] The authors were able to conclude that they could use a lower level of theory to generate the electrostatic potential surfaces and still have the ability to predict the strength of the cation−π interaction. This enables the electrostatic maps of even large molecules to be generated with ease.

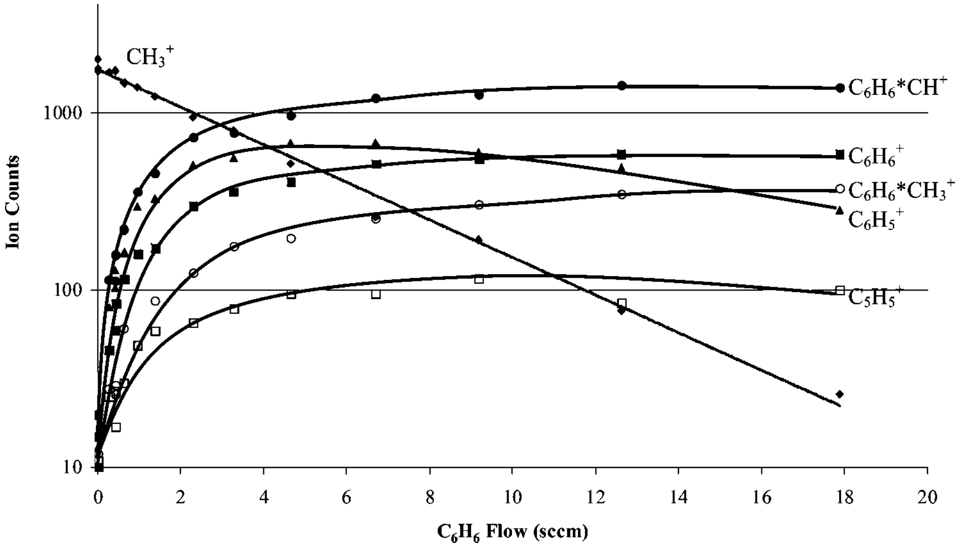

Figure 2. Decay of CH_3^+ and the rise of the product ions for the CH_3^+ reaction with benzene. Notice that the association product, $C_6H_6{\cdot}CH_3^+$ increases and shows no secondary reaction.

While the cation−π interaction is responsible for the increased association with aromatic molecules it is not an accurate way to describe the structure of the associated complex when dealing with CH_3^+ as the cation. Several theoretical calculations involving CH_3^+ with various aromatic molecules have been undertaken[21−24] and show that CH_3^+ does not have a long-lived π interaction with benzene; instead the σ interaction is more energetically favorable. A molecular dynamics study determined that the reactants were brought together by cation−π electron attraction; however, at a certain intermolecular separation, the CH_3^+, regardless of the initial approach, quickly forms a σ complex with a carbon in the ring.[23] This fast-forming complex rapidly isomerizes to give the final stable σ complex where the hydrogen attached to the same carbon as the newly attached methyl cation shifts to the para position. Miklis et al. explained the difference in reactivity of the CH_3^+ ion to ions that form π complexes (such as metal ions and the NH_4^+ ammonium ion) by pointing out that the unsaturated nature of the ion can promote different reactions.[22] It is likely that the interaction of an unsaturated species is not as strongly dependent on electrostatic forces as saturated species. Therefore, describing such interactions as cation−π is misleading. Hence, the term cation−π interaction will not be invoked and all associations of CH_3^+ with the aromatic neutrals studied in this paper are believed to result in a σ interaction.

Fragmentation product channels were also of great interest in this study. In an attempt to understand how each fragment was formed, it was necessary to study known fragmentation procedures in the literature. Rules governing unimolecular dissociation, used most widely in interpreting electron impact (EI), are well-known;[25] however, there is less information available on how the internal energy imparted during an ion−molecule reaction will be distributed and which bonds will break. One area of the literature where this is considered is chemical ionization mass spectrometry (CI). Fundamentally, CI occurs through ion−molecule reactions and though the reason CI is used differs from the reason ion−molecule reactions are investigated in this study, the basic principles are the same for both. If the reactions in this study are considered in terms of chemical ionization then information about fragmentation mechanisms becomes available.[11]

In these studies there are several product channels that do not involve fragmentation but might be the starting points for fragmentation. These are hydride abstraction, charge transfer, proton transfer, and association. By investigating the fragments formed, it is possible to identify the starting point as one of the four listed above. It is known in CI that if there is internal energy left over after a charge transfer reaction, then fragmentation reactions will resemble those observed in EI.[11] Some differences between the spectrums of CI versus EI relating to the relative abundances of the fragment ions formed are likely to occur. This arises because, in EI, a wide range of internal energy is imparted to the molecule upon ionization while in CI the energy imparted is restricted by the difference in the recombination energy of the primary ion and the ionization energy of the neutral. This allows for different fragmentation mechanisms to be favored in the two situations. Therefore, a major product ion in one process may only be a minor product ion in the other process. If the starting point for fragmentation is proton transfer then it is possible that the internal energy will be localized around the point of proton attachment; however, it is also possible for the internal energy to randomize throughout the molecule and break the weakest bond. It is likely that the fragmentation product of the proton transfer will be the result of the elimination of an even-electron stable molecule resulting in an even-electron product ion.[11] The fragmentation that occurs if the starting point is hydride abstraction or association is not well-known. In the case of hydride abstraction while it seems logical that the atom at which the H^- is lost will be the starting point for fragmentation, it is also possible for the internal energy to break the weakest bond just as with proton transfer.

The EI spectrum of each neutral, obtained from the NIST Web site, was compared to the fragments formed in each reaction. Fragmentation peaks seen in both spectra indicate that the fragment formed in our reactions could be initiated via charge transfer and if the peaks were not seen in both spectra then the fragment was not formed via charge transfer. In some cases, the fragments formed in our reactions, but not seen in the EI spectrum, only differ by an H-atom. It is possible that these fragments are created by unimolecular dissociation mechanisms, but with a starting point that has one extra hydrogen such as proton transfer, or a starting point with one less hydrogen such as hydride abstraction. In discussing each neutral in detail, an attempt has been made to determine the starting point of each fragmentation channel and how it was formed.

TABLE 2: Product Distributions (%) for the Reactions of CH_3^+ with the Listed Neutral Molecules[a]

neutral molecule	ion product	product channel[b]	yield (%)
cyclohexane	$C_4H_7^+$	F	7
C_6H_{12}	$C_4H_8^+$	F	7
9.88 eV	$C_6H_{11}^+$	HA	68
164.2 kcal/mol	$C_6H_{12}^+$	CT	18
piperidine	$C_2H_6N^+$	F	21
$C_5H_{11}N$	$C_4H_7^+$, $C_3H_5N^+$	F	6
8.03 eV	$C_5H_9^+$, $C_4H_7N^+$	F	7
228.0 kcal/mol	$C_5H_{10}^+$	F	6
	$C_5H_{10}N^+$	HA	34
	$C_5H_{11}N^+$	CT	22
	$C_5H_{11}NH^+$	PT	4
1,4-dioxane	$C_2H_5^+$, CHO^+	F	11
$C_4H_8O_2$	$C_2H_7^+$, CH_3O^+	F	18
9.19 eV	$C_3H_7^+$, $C_2H_3O^+$	F	5
190.6 kcal/mol	$C_2H_5O^+$,CHO_2^+	F	5
	$C_3H_7O^+$, $C_2H_3O_2^+$	F	28
	$C_4H_7O_2^+$	HA	14
	$C_4H_8O_2^+$	CT	19
pyrrolidine	$C_2H_6N^+$	F	46
C_4H_9N	$C_4H_8N^+$	HA	32
8.41 eV	$C_4H_9N^+$	CT	18
226.6 kcal/mol	$C_4H_9NH^+$	PT	4
benzene	$C_5H_5^+$	F	5
C_6H_6	$C_6H_5^+$	HA	31
9.24 eV	$C_6H_6^+$	CT	17
179.4 kcal/mol	$C_6H_6 \cdot CH^+$	AF	39
	$C_6H_6 \cdot CH_3^+$	A	8
pyridine	$C_5H_4N^+$	HA	20
C_5H_5N	$C_5H_5N^+$	CT	21
9.26 eV	$C_5H_5NH^+$	PT	9
222.3 kcal/mol	$C_5H_5N \cdot CH_3^+$	A	50
pyrimidine	$C_3H_3^+$, C_2HN^+	F	6
$C_4H_4N_2$	$C_3H_3N_2^+$	F	8
9.33 eV	$C_4H_2N_2^+$	F	9
211.7 kcal/mol	$C_4H_3N_2^+$	HA	19
	$C_4H_4N_2^+$	CT	25
	$C_4H_4N_2H^+$	PT	9
	$C_4H_4N_2 \cdot CH_3^+$	A	24
pyrrole	$C_3H_5^+$, $C_2H_3N^+$	F	3
C_4H_5N	$C_2H_4N^+$	F	5
8.21 eV	$C_3H_5N^+$	F	13
209.2 kcal/mol	$C_4H_5N^+$	CT	64
	$C_4H_5NH^+$	PT	7
	$C_4H_5N \cdot CH_3^+$	A	8
furan	HCO^+	F	9
C_4H_4O	$C_3H_3^+$	F	4
8.88 eV	$C_2H_3O^+$	F	5
194.0 kcal/mol	$C_3H_3O^+$	F	56
	$C_4H_4O^+$	CT	26

[a] Ionization energies (eV) and proton affinities (kcal/mol) are given below each neutral molecular species.[37] The recombination energy of CH_3^+ is given at 9.84 eV[37] and the proton affinity of CH_2 used is 207 kcal/mol.[10] [b] Product channels are indicated in the following manner: fragment (F), hydride abstraction (HA), charge transfer (CT), proton transfer (PT), association (A), and association with concerted fragmentation (AF).

Saturated Neutrals. ***Cyclohexane.*** The major product (68%) in the reaction with cyclohexane (C_6H_{12}) is hydride abstraction and it is much larger than in any other reactions. There is a small amount of charge transfer present although the reaction is slightly endothermic (0.04 eV endothermic at 298 K). However, when considering the errors associated with the ionization/recombination energies involved, the reaction could actually be thermoneutral or be driven by the fraction of the interactions that are energetically allowed by kinetic energy in a Maxwell−Boltzmann distribution and by internal energy in a Boltzmann distribution. Hence, the 18% charge transfer channel is not seem unreasonable. The two remaining product channels are fragmentations and each represents 7% of the product distribution. Both of the fragments, *m/z* 56 ($C_4H_8^+$) and *m/z* 55 ($C_4H_7^+$), are present in the EI spectrum of cyclohexane. It is most likely these fragments are from the dissociation of the charge transfer product. While $C_4H_7^+$ is a product of EI unimolecular dissociation, it is also possible it could be formed after hydride abstraction followed by two inductive cleavages (charge initiated bond dissociation) to give the loss of neutral C_2H_4.

Piperidine. Piperidine ($C_5H_{11}N$) has a significantly lower IE than cyclohexane; therefore more fragmentation is expected and is seen. The lone pair of electrons on the nitrogen in the piperidine ring provide an additional reaction site. In fact, this site would be an ideal place for CH_3^+ to associate because the availability of two electrons should be very attractive to the methyl cation. However, association was not a product of the reaction. Instead hydride abstraction was again the largest product channel followed closely by charge transfer. Several fragmentation products were observed along with a very small amount of proton transfer. Of the four fragmentation channels, three had the possibility of being assigned more than one unique molecular formula. By calculating the reaction enthalpies, ΔH_{rxn}, we were able to determine that the product at *m/z* 44 is $C_2H_6N^+$ ($\Delta H_{rxn} = -87.15$ kcal mol^{-1}) rather than $C_3H_8^+$ ($\Delta H_{rxn} = 122.75$) since the latter is very endothermic. Unfortunately, there was not enough information to give a definite assignment to the *m/z* at 55 or 69 so the two possible molecular formulas are listed in the table. In many of the reactions, the thermodynamic data were not available to make a distinction between two possible ions of the same mass. In these cases, the ions are not identified definitively. Identification by isotopic labeling was not within the scope of this study.

Of the four fragment products present, $C_2H_6N^+$, $C_4H_7^+$/$C_3H_5N^+$, and $C_5H_{10}^+$ are also present in the EI spectrum of piperidine. These fragments are likely formed from unimolecular decomposition of charged piperidine. The remaining fragment, $C_5H_9^+$/$C_4H_7N^+$, could originate from either the proton transfer by a loss of NH_3/CH_5 (unlikely) or from the hydride abstraction by a loss of NH/CH_3.

1,4-Dioxane. In 1,4-dioxane ($C_4H_8O_2$), the addition of two oxygen atoms compared to cyclohexane again provides two very reactive sites. The availability of two lone pairs of electrons on each oxygen would again suggest an ideal place for CH_3^+ to react. However, this reaction produced a large number of fragment ions and no association. The ionization energy of 1,4-dioxane is 9.19 eV. Upon ionization, only ~0.65 eV remains for bond dissociation so it was surprising to observe the large amount of fragmentation. Unfortunately, detailed thermodynamic information is not available for these channels. All five of the fragment ions are present in the EI spectrum of 1,4-dioxane and suggest these fragments originate from the charged parent ion. Charge transfer and hydride abstraction product channels are also present.

Pyrrolidine. Pyrrolidine (C_4H_9N), the only five-membered saturated ring studied, showed only one fragmentation product. The fragment is at *m/z* 44 and this was the major product with

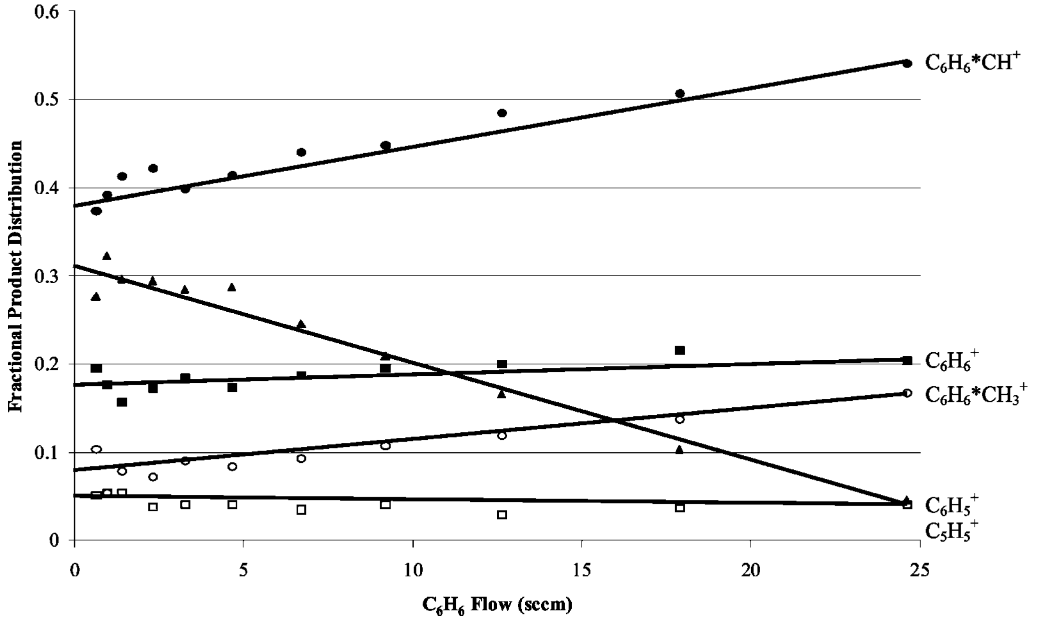

Figure 3. Fractional product distribution for the reaction of CH_3^+ with C_6H_6. If $C_6H_6{\cdot}CH^+$ were a secondary product it would be evident in this plot because the line going through those points would be zero at low flow and increase sharply as the flow increased. Points at flows less than 0.5 sccm have been omitted from the plot since with sticky gases, such as benzene, the time to equilibrate prevents accurate measurements.

a 46% abundance. This peak is identified as $C_2H_6N^+$ by thermodynamic consideration. The main peak in the EI spectrum of pyrrolidine is at *m/z* 43 but there is a small peak at *m/z* 44. This reversal in peak intensity can be explained by looking at the differences between EI and CI. When comparing the fragmentation of EI to CI, the major difference is in the relative abundances of the fragments.[11] This arises because, in EI, a wide range of internal energy is imparted to the molecule upon ionization, while in CI the energy imparted is restricted by the difference in the recombination energy of the primary ion and the ionization energy of the neutral. This allows for different fragmentation mechanisms to be favored in the two situations. Worth noting is the ability of $C_2H_6N^+$ to form from the protonated form of pyrrolidine. Assuming protonation happens on the carbon next to the nitrogen, as it does in pyrrole,[26] the ring can open by an inductive cleavage to the cation site and then an additional inductive cleavage to eliminate C_2H_4 leaving the $C_2H_6N^+$ product ion. Utilizing this mechanism in addition to the charge transfer mechanism might help explain why the $C_2H_6N^+$ is such a large product percentage.

Aromatic Neutrals. ***Benzene.*** The reaction of CH_3^+ with the prototype aromatic compound, benzene (C_6H_6) resulted in several product channels. As suggested by theory, and similar reactions, the association between the two species was observed; however, it is only an 8% product channel. This was a little unexpected since the association process for CH_3^+ and benzene is theoretically proven to be very rapid.[24] There is also a product at *m/z* 91, which can only correspond to the molecular formula $C_7H_7^+$. This is the dominant product of the reaction with a 39% product channel. It is not possible that this product is formed via association with injected CH^+ because CH^+ is not present in the flow tube in sufficient concentration to form such a major product. Nor can it be attributed to a secondary product where the first reaction is association of CH_3^+ with benzene and then a second reaction with another species in the flow tube to give rise to loss of H_2 from the association complex. Inspection of Figure 2 reveals that the product ion signal of $C_6H_6{\cdot}CH_3^+$ never decreases as the concentration of benzene increases, thereby indicating that the association ion product is not involved in any secondary reaction processes with benzene. Figure 3 confirms that, when plotting the product distribution, the behavior usually associated with a secondary reaction is not present for *m/z* 91. If it were a secondary product, the fraction would be zero at low neutral flow and increase as the flow increased. In light of this information, the product ion most likely is formed through a concerted reaction that adds CH_3^+ to the benzene ring and subsequently eliminates an H_2 molecule forming the $C_7H_7^+$ product. There has been much discussion in the literature concerning the structure of the $C_7H_7^+$ ion.[27−30] It is well-known that the lowest energy form is the tropylium ion, a seven-membered ring. In this study, the H_2 can be eliminated in several ways with the most likely eliminations coming from the ring to give $C_6H_4{\cdot}CH_2^+$, the tolyl ion, or from the ring and the CH_3^+ to give $C_6H_5{\cdot}CH_2^+$, the benzyl ion. The tolyl ion can isomerize to the benzyl ion providing the 26.3 kcal/mol[29] activation energy is overcome. Ultimately, the tropylium ion can be reached by the isomerization of the benzyl ion providing the activation energy of 32.7 kcal/mol[27] is surmounted. This reaction is energetically driven because the tropylium ion is 24.8 kcal/mol[27] lower in energy than the benzyl ion. While it is known that the benzyl ion reacts rapidly with aromatic compounds, the rate coefficient for the reaction of the benzyl ion with benzene is not known. If the aforementioned reaction was sufficiently slower than the gas kinetic rate of the CH_3^+ reaction then it would not be evident if *m/z* 91 reacted further from the data collected. Therefore, we are unable to say definitively that *m/z* 91 does not react further and therefore it is not clear whether the tolyl ion, benzyl ion, tropylium ion, or a mixture of these three are present.

Other products include a fragment at *m/z* 65, H-abstraction, and charge transfer. The fragment is assigned the molecular formula $C_5H_5^+$. This mass is not present in the EI spectrum of benzene and is not attributed to fragmentation of the charge transfer product. Intuitively, it seems unlikely to come from the hydride abstraction because it would require the loss of a bare carbon. It is more likely that it forms via dissociation of the association ion by the concerted loss of a C_2H_4 neutral to once again give a primary product ion.

Pyridine. The addition of nitrogen to the aromatic ring seems to have a large affect on the amount of association evident by the 50% association product channel. Since it has already been determined that CH_3^+ does not form π complexes, the CH_3^+ can interact either with a carbon on the ring or the nitrogen. Interaction with the nitrogen is more probable because the lone pair offers an attractive binding site. Also, theoretical calculations involving Na^+ and pyridine (C_5H_5N) showed that only binding to the nitrogen represented a minimum on the potential energy surface.[20]

Proton transfer is another product channel for this reaction. However, it is only present at 9%. Proton transfer is usually a very efficient and rapid process when energetically possible, as it is in this case. Since proton transfer, like association, must happen at very close intermolecular distances, it seems likely that the presence of π electrons stabilizes the initial complex long enough for CH_3^+ to form a strong interaction with the nitrogen lone pair. Without this stabilizing presence, the pyridine would quickly remove a proton from the CH_3^+ and any further interaction between the two species would cease. The other two products are charge transfer and hydride abstraction. There is no further fragmentation of the ring.

Pyrimidine. Reaction with pyrimidine resulted in three fragmentation products, as well as hydride abstraction, charge transfer, proton transfer, and association. The amount of association is only half of the amount observed in the pyridine reaction. This seems counterintuitive if the presence of nitrogen in the ring encourages a larger amount of association, as shown with pyridine. Having two sites at which association is possible should increase the amount of association. However, the fact that the opposite occurs indicates that the addition of a second nitrogen reduces the efficiency of the association channel. Once again there is only a 9% proton transfer channel even though the process is exothermic. The fragments observed are $C_3H_3^+$/C_2HN^+, $C_3H_3N_2^+$, and $C_4H_2N_2^+$. A peak at *m*/*z* 39 ($C_3H_3^+$/C_2HN^+) is present in the EI spectrum but only at a 1% intensity of the major peak. Also, in this study the product at *m*/*z* 39 is a minor product and it is likely it is formed via charge transfer dissociation. The other two fragments were not seen in the EI spectrum of pyrimidine and it is doubtful that these fragments were formed via the charge transfer product. They could be formed via dissociation of hydride abstraction, proton transfer, or association. If $C_3H_3N_2^+$ and $C_4H_2N_2^+$ were formed via proton transfer then neutral CH_2 and H_3 would have to be eliminated, respectively. If $C_3H_3N_2^+$ and $C_4H_2N_2^+$ were formed via hydride abstraction then neutral C (unlikely) and H would have to be eliminated, respectively. If $C_3H_3N^+$ and $C_4H_2N_2^+$ were formed via association then neutral C_2H_4 and CH_5 (unlikely) would have to be eliminated, respectively. It is not clear at this point which mechanisms created $C_3H_3N^+$ and $C_4H_2N_2^+$.

Pyrrole. Pyrrole is a five-membered heterocyclic molecule. Like the other heterocycles mentioned above it also has nitrogen in the ring. The nitrogen in pyrrole must donate the lone pair of electrons to the π system for the molecule to be aromatic so this lone pair is not as easily available for bonding as in pyridine and pyrimidine. Also, unlike the two species mentioned above, the nitrogen in pyrrole has a hydrogen atom attached, which uses the remaining electron. Because of these issues, it is not likely that the nitrogen atom will be as reactive as before. This is evident in the decreased amount of association. There is only an 8% product channel for association with pyrrole. Another reason for lower association might be attributed to the smaller ring size leading to more steric strain. Charge transfer is the major ion product with a channel of 64%. Since charge transfer can occur at a distance, it is possible that this occurs before CH_3^+ can get close enough to be stabilized by the π electrons and therefore decreasing the association product. Fragmentation accounts for 21% of the products and it is spread among three products. The smallest fragment, at *m*/*z* 41, can either be $C_3H_5^+$ or $C_2H_3N^+$ and is seen in the EI spectrum of pyrrole. $C_2H_4N^+$ is also a peak in the EI spectrum although it is very small. Therefore, these two ions are likely formed via dissociation of the charge transfer product. The remaining fragment, $C_3H_5N^+$, is not in the EI spectrum and must come from dissociation of either the proton transfer (by loss of a CH) or association (by a loss of C_2H_3) of pyrrole.

Furan. Furan is a five-membered ring that contains an oxygen atom. Oxygen has two lone pairs of electrons, one of which participates in the π system, allowing the molecule to be aromatic, and leaving the remaining lone pair available for reaction. This made the results of this reaction even more puzzling. Furan is the only aromatic molecule that does not undergo association with CH_3^+. The same stabilization of the ion by π electrons should occur and, once stabilized, the electrophilic nature of CH_3^+ should promote binding with the free electrons. In fact, association of the CH_3^+ to the lone pair on the oxygen does not require the loss of aromaticity like it does in pyrrole, the other five-membered ring. An IR study of the protonation site of furan showed that the proton is located on the carbon next to the heteroatom (C_α).[26] Using this information, and assuming that the CH_3^+ will also bind to the C_α, this situation closely resembles the intermediate in an electrophilic aromatic substitution (EAS) reaction that occurs with all aromatic species. In EAS reactions, pyrrole is more reactive than furan because the nitrogen atom has a lower electronegativity and is able to stabilize the cation more effectively.[31] Therefore the small amount of association seen in pyrrole is lost when going to furan because the more electronegative oxygen atom holds its electrons strongly and allows for less stabilization of the cation.

It is evident from the cases presented above that π electrons promote association by stabilizing the cation as it draws near the neutral molecule. In the case of furan, the σ complex is destabilized by the presence of the oxygen in the ring. Due to this, the complex can follow a number of reaction pathways such as fragmentation, hydride abstract, proton transfer, or charge transfer. Neither proton transfer nor hydride abstraction was energetically allowed nor were they observed as a product channel. Charge transfer was favorable and did occur. Fragmentation of the complex did occur to form the major product ion, $C_3H_3O^+$. This ion is not present in the EI spectrum of furan and thus cannot be attributed to the charge transfer, the only nonfragmented product ion. It is possible to envision $C_3H_3O^+$ being produced by several inductive cleavages of the unstable association complex ending with CH_3CH neutral eliminated from the ring. The three other fragments, HCO^+, $C_3H_3^+$, and $C_2H_3O^+$, are all present in the EI spectrum of furan and are most likely formed via dissociation of the charge transfer species.

Conclusion

The association of CH_3^+ to these nine simple cyclic molecules seems to depend strongly on the availability of π electrons. The substitution of nitrogen into the ring increases the amount of association when compared to benzene. Inclusion of two nitrogen atoms decreases the amount of association compared to pyridine but still gives more association than benzene. The aromatic five-membered rings showed little to no association even though π electrons are available to facilitate the association. Steric hindrance could be partially responsible along with the lack of availability of suitable association sites. The saturated ring compounds demonstrated no association.

Association is an important chemical process. The reactions of CH_3^+ also have a particular importance to the ionosphere of Titan. CH_3^+ is one of the major ions in this ionosphere and plays an important role in the chemistry. It is usually believed that when proton transfer can take place it will and CH_3^+ is largely considered to proton transfer in the reactions it is involved with in the ionosphere. However, these data suggest that proton transfer should not be the only product channel assumed to result from reactions with the methyl cation. Association products should also be included in chemical models of the Titan ionosphere and the importance of proton transfer should be diminished.

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