An ICR Study of Ion-Molecules Reactions Relevant to Titan's Atmosphere: An Investigation of Binary Hydrocarbon Mixtures up to 1 Micron

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Results are reported for studies of binary mixtures of hydrocarbons exposed to low-energy electron impact ionization. A variety of experimental methods are used: conventional ICR mass spectrometry, the standard double resonance in an ICR for determination of the precursor ions, and the modulated double resonance ejection in an ICR for the determination of the daughter ions. A flowing afterglow-selected ion flow tube experiment (FA-SIFT) was used for validation and examination of termolecular reactions. An extensive database of reaction kinetics already exists for many of these reactions. The main point of this study was the determination of the accuracy of this database and the identification of missing reactions and reaction channels. An effort was made to extend the study to the highest pressures possible to determine if any important termolecular reaction channels were present that were not recognized in earlier investigations. A new approach was used here. In the binary mixtures of hydrocarbon gases, mass spectra were obtained as a function of independent pressure changes of both gases. All the mass peaks in the spectra were fitted using existing kinetic data as a starting point. A model of the ion abundances was then produced from the solution of the partial differential equations derived from the kinetics in terms of reaction rate coefficients and initial abundances. The model was fitted to the data for all of the pressures by a least-squares fit to the reaction rate coefficients and initial abundances. The kinetic parameters were then adjusted if required. (J Am Soc Mass Spectrom 2006, 17, 544–561) © 2006 American Society for Mass Spectrometry

This is the sixth in a series of articles on the ion-molecule chemistry that is expected to occur in the atmosphere of Saturn's satellite Titan. The first five articles described the reactions of the principal ions with the principal neutrals [1]; the structure of the association adducts of $HCNH^+$ with C_2H_2 and C_2H_4 [2]; the clustering of $HCNH^+$ with nitrogen [3]; the reactions in pure hydrocarbons at up to three consecutive reactions [4]; and the reactions of N^+, N_2^+, and HCN^+ with CH_4, C_2H_2, and C_2H_4 [5]. In this paper, we relate experimental results on the ion-molecule reaction of hydrocarbon ions with the *binary* mixtures of the hydrocarbons: CH_4, C_2H_2, C_2H_4, and C_3H_4 (propyne). In these results, we present several new channels for known reactions and identify several termolecular reactions that have significant effects on the ion abundances. It was necessary to include these termolecular reactions in the model describing the chemistry occurring in the ICR.

In previous studies, this same chemistry would usually have been examined under conditions in which the reactant ion was the predominant ion if not the only ion and conditions in the ion source would be optimized to achieve this. But in the studies we report here, all ions were present at significant partial pressures of the two different neutrals. In these cases, reaction rate coefficients and branching ratios were obtained through numerical modeling of the chemistry by adjusting the reaction rate coefficients and branching ratios to fit the data. In the extrapolation of the laboratory data to the actual environment of Titan it is apparent that many consecutive reactions take place after the initial ionization of the nitrogen occurs [6]. As the size of the ions increase, there is the question of which isomer or isomers are actually present. Since different isomers generally react differently, the ions in this study were generated under conditions similar to those present in Titan's atmosphere [7]. It is then expected that the isomers produced in our studies will better represent
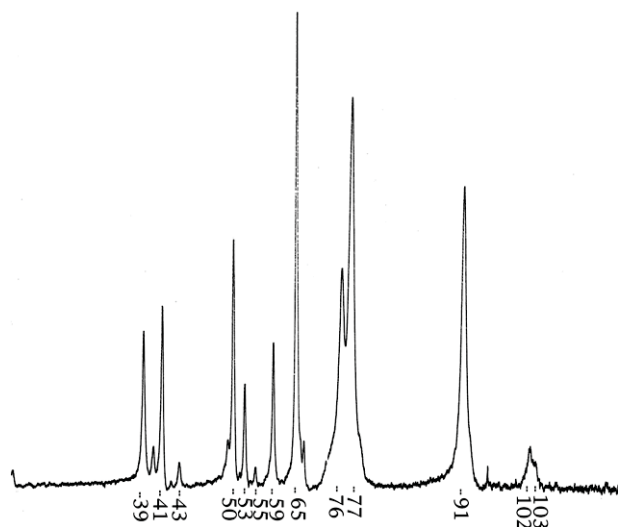
Figure 1. ICR mass spectrum of a methane-acetylene mixture, each at 2×10^{-4} Torr.

the ions present in Titan's atmosphere. Thus, by studying the chemistry through several consecutive reaction sequences, the results obtained should give an improved representation of Titan conditions compared with the results from more conventional low-pressure individual ion studies.

The present modeling of Titan's atmosphere shows that the ion chemistry is important in determining the neutral abundances of some of the trace species [8]. Also, the models show that up to the altitude where the electron density peaks, quite complex chemical structures may be produced. The existing laboratory data does not extend to these species or pressures. The following study will help in removing these deficiencies.

The following studies were made under room-temperature conditions. It is understood that the temperature in Titan's atmosphere never gets that warm. In Titan's ionosphere, the temperature is more like 180 K and it is not possible in our laboratories to study these reactions at that temperature. Does this mean that the room-temperature studies are of no value? We think not. The value of room-temperature studies comes from the fact that almost all exothermic ion-molecule reactions have reaction rate coefficients that are near the ion-molecule collision limit. The variation of these reaction rate coefficients with temperature can be modeled with the current theories of ion-molecule reactions. The difficulty in extrapolating room-temperature studies to low temperatures occurs in a few percent of reactions that have close to zero reaction energies or whose reaction rate coefficients are controlled by a barrier in the reaction pathway. In these cases, extrapolations from room-temperature may not be reliable and the reader should proceed with caution in using these results. The reactions that are problematic can easily be identified by rate coefficients that are less than the collision rate.

Experimental

In these studies, ion cyclotron resonance (ICR) mass spectrometry was the primary instrument used. The flowing afterglow-selected ion flow tube (FA-SIFT) was also used to examine those systems where differences between the two techniques occur and on occasions to provide complementary data. All experiments were made at room-temperature, about 298 K. The ionization in the ICR cell was done with the minimum amount of electron energy. The reactions of the parent ions proceeded at their collision rates. We were then able to examine the effect of any excess energy in those secondary ions that were formed from the primary ions shown by differences in product ion distributions. Ion formation in this way better represents the way ions are generated in Titan's atmosphere as they too, are formed in secondary reactions.

The ICR was at the Jet Propulsion Laboratory and has been described before [9]. The details needed for this paper are summarized next. The system uses a 12-inch electromagnet, which was normally set at 1.5 tesla for these experiments. The ICR cell was used in the drift mode in which the reaction time was ~1 ms. The cell has two sections; a source section and a resonance section. Ions were produced in the source section by means of an electron beam. Electron energies were kept at less than one electron volt above the ionization potential required to produce the desired ion. The ions drifted from the source to the resonance sections using the Lorentz force. A Wronka bridge detector [10] was attached to the drift plates of the resonance section for the detection of the relative ion abundances. Gas pres-

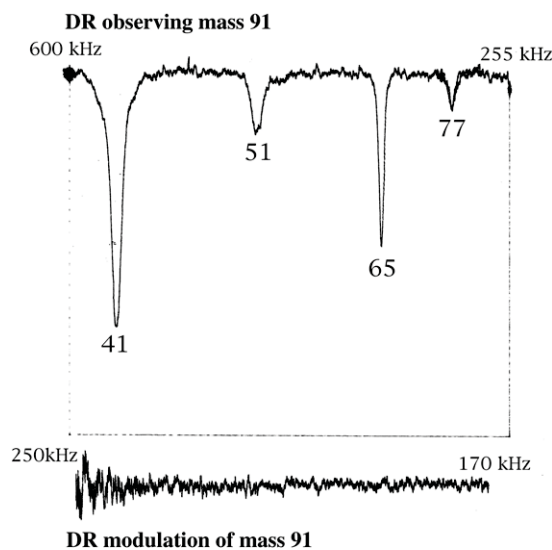**Figure 2.** ICR double resonance ejection and ICR modulated double resonance spectra of an methane-acetylene mixture, each at 2×10^{-4} Torr. The upper plot is the double resonance ejection spectrum and the lower plot is the modulated double resonance spectrum. Both spectrum are observing the m/e = 91 ion. The start and stop frequencies of each scan are noted at the ends of each trace.

Table 1. Summary of kinetic data for new reactions and existing reactions that have been modifed as a result of this investigation

Reaction				Br. ratio	Uncertainty Rate coefficient	% Mixture
$C_2H_2^+$	$+ CH_3CCH$	$\rightarrow C_3H_4^+$	$+ C_2H_2$	0.50	1.5×10^{-9}	a
		$C_3H_5^+$	$+ C_2H$	0.05		
		$C_5H_5^+$	$+ H$	0.45		
$C_2H_3^+$	$+ C_2H_2$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	b
$C_2H_3^+$	$+ C_2H_4$	$\rightarrow C_2H_5^+$	$+ C_2H_2$	1.00	1.0×10^{-9}	c
$C_2H_4^+$	$+ C_2H_4$	$\rightarrow C_3H_4^+$	$+ CH_4$	0.06	7.9×10^{-10}	c,d,e
		$C_3H_5^+$	$+ CH_3$	0.89		
		$C_4H_7^+$	$+ H$	0.06		
$C_2H_4^+$	$+ CH_3CCH$	$\rightarrow C_3H_4^+$	$+ C_2H_4$	0.00	2.3×10^{-9}	a
		$C_3H_6^+$	$+ C_2H_2$	0.05		
		$C_4H_5^+$	$+ CH_3$	0.22		
		$C_5H_7^+$	$+ H$	0.73		
$C_3H_4^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 2.0 \times 10^{-11}$	b,c
$C_3H_4^+$	$+ C_2H_2$	$\rightarrow C_5H_5^+$	$+ H$	1.00	4.2×10^{-10}	a,b,d
$C_3H_4^+$	$+ C_2H_4$	$\rightarrow C_4H_5^+$	$+ CH_3$	0.55	$\sim 3.3 \times 10^{-10}$	c,d,e
		$\rightarrow C_5H_7^+$	$+ H$	0.45		
$C_3H_5^{+*}$	$+ C_2H_4$	$\rightarrow C_5H_7^+$	$+ H_2$	1.00	8.9×10^{-11}	c,d,e
$C_3H_5^{+*}$	$+ C_2H_4 + M$	$\rightarrow C_5H_9^+$	$+ M$	1.00	$\sim 1.8 \times 10^{-23} \pm 99^f$	c,d,e
$C_3H_5^+$	$+ CH_3CCH$	$\rightarrow C_5H_5^+$	$+ CH_4$	0.04	7.4×10^{-10}	a,e
			$C_6H_7^+$	$+ H_2$	0.96	
$C_3H_6^+$	$+ C_2H_4$	$\rightarrow C_4H_7^+$	$+ CH_3$	1.00	1.8×10^{-10}	e
$C_4H_2^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	b
$C_4H_2^+$	$+ C_2H_2 + M$	$\rightarrow C_6H_4^+$	$+ M$		2.3×10^{-23}	b
$C_4H_2^+$	$+ C_2H_4$	$\rightarrow C_4H_4^+$	$+ C_2H_2$	0.47	1.5×10^{-9}	d
		$C_6H_4^+$	$+ H_2$	0.05		
		$C_6H_5^+$	$+ H$	0.48		
$C_4H_2^+$	$+ CH_3CCH$	$\rightarrow C_5H_4^+$	$+ C_2H_2$	0.16	2.3×10^{-9}	a
		$C_7H_5^+$	$+ H$	0.84		
$C_4H_3^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 2.0 \times 10^{-11}$	b
$C_4H_3^+$	$+ C_2H_2 + M$	$\rightarrow C_6H_5^+$	$+ M$		$9.5 \times 10^{-24} \pm 30$	a,d
$C_4H_3^+$	$+ C_2H_4$	$\rightarrow C_6H_5^+$	$+ H_2$		1.2×10^{-10}	d
$C_4H_3^+$	$+ CH_3CCH$	$\rightarrow C_5H_5^+$	$+ C_2H_2$	1.00	1.4×10^{-9}	a
$C_4H_5^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	b,c
$C_4H_5^+$	$+ C_2H_2$	$\rightarrow C_6H_5^+$	$+ H_2$	1.00	1.6×10^{-10}	b,d
$C_4H_5^+$	$+ C_2H_4$	$\rightarrow C_6H_7^+$	$+ H_2$	1.00	7.3×10^{-11}	c,d,e
$C_4H_5^+$	$+ CH_3CCH$	$\rightarrow C_6H_5^+$	$+ CH_4$	0.25	2.0×10^{-10}	e
		$C_7H_7^+$	$+ H_2$	0.75		
$C_4H_7^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	c
$C_4H_7^+$	$+ C_2H_2$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	d
$C_4H_7^+$	$+ C_2H_4$	$\rightarrow$ No reaction			$\leq 2.0 \times 10^{-11}$	c,e
$C_4H_7^+$	$+ CH_3CCH$	$\rightarrow C_7H_9^+$	$+ H_2$	1.00	1.5×10^{-10}	e
$C_5H_5^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	b
$a\text{-}C_5H_5^+$	$+ C_2H_2$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	a,b,d
$b\text{-}C_5H_5^+$	$+ C_2H_2$	$\rightarrow$ Association			1.7×10^{-10}	a,b,d
$C_5H_5^+$	$+ C_2H_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	e
$C_5H_5^+$	$+ CH_3CCH$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	a,e
$C_5H_7^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	c
$C_5H_7^+$	$+ C_2H_2$	$\rightarrow$ No Reaction			$\leq 2.0 \times 10^{-11}$	
$C_5H_7^+$	$+ C_2H_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	c
$C_5H_7^+$	$+ CH_3CCH$	$\rightarrow C_8H_{11}^+$		1.00	7.0×10^{-10}	e
$C_5H_9^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 2.0 \times 10^{-11}$	c
$C_5H_9^+$	$+ C_2H_2$	$\rightarrow$ No Reaction			$\leq 2.0 \times 10^{-11}$	
$C_5H_9^+$	$+ C_2H_4$	$\rightarrow$ No Reaction			$\leq 2.0 \times 10^{-11}$	c
$C_5H_9^+$	$+ CH_3CCH$	$\rightarrow$ No Reaction			$\leq 2.0 \times 10^{-11}$	
$C_6H_3^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	b
$C_6H_3^+$	$+ C_2H_2$	$\rightarrow C_8H_5^+$		1.00	2.3×10^{-10}	a,b,d
$C_6H_4^+$	$+ CH_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	a
$C_6H_4^+$	$+ C_2H_2$	$\rightarrow C_8H_6^+$		1.00	2.9×10^{-10}	a,b,d
$C_6H_5^+$	$+ CH_4$	$\rightarrow C_7H_7^+$	$+ H_2$	1.00	2.5×10^{-11}	b
$C_6H_5^+$	$+ C_2H_2$	$\rightarrow C_8H_7^+$		1.00	1.7×10^{-10}	a,b,d
$C_6H_5^+$	$+ C_2H_4$	$\rightarrow C_6H_7^+$	$+ C_2H_2$	0.60	1.2×10^{-10}	d,e
		$\rightarrow C_8H_7^+$	$+ H_2$	0.40		

Table 1. Continued

Reaction				Br. ratio	Uncertainty Rate coefficient	% Mixture
$C_6H_5^{+*}$	$+ CH_3CCH$	$\rightarrow C_7H_7^+$	$+ C_2H_2$	0.30	6.2×10^{-10}	a,e
		$\rightarrow C_9H_7^+$	$+ H_2$	0.70		
$C_6H_7^+$	$+ C_2H_4$	$\rightarrow$ No Reaction			$\leq 1.0 \times 10^{-11}$	a
$C_6H_7^+$	$+ CH_3CCH$	$\rightarrow C_7H_7^+$	$+ C_2H_4$	1.00	9.7×10^{-11}	a
$C_6H_7^+$	$+ CH_3CCH + M$	$\rightarrow C_9H_{11}^+$	$+ M$	1.00	3.0×10^{-25}	a
$C_7H_7^+$	$+ C_2H_4$	$\rightarrow C_9H_{11}^+$		1.00	2.0×10^{-10}	a
$C_7H_7^+$	$+ CH_3CCH$	$\rightarrow C_{10}H_{11}^+$		1.00	1.4×10^{-10}	a,e
$C_7H_7^+$	$+ CH_3CCH + M$	$\rightarrow C_{10}H_{11}^+$	$+ M$	1.00	7.9×10^{-24}	a
$C_9H_7^+$	$+ CH_3CCH$	$\rightarrow C_{12}H_{11}^+$		1.00	2.8×10^{-9}	a,e
$C_9H_7^+$	$+ CH_3CCH + M$	$\rightarrow C_{12}H_{11}^+$	$+ M$	1.00	7.9×10^{-24}	a

aFrom the C_2H_2-$HCCCH_3$ mixture
bFrom the CH_4-C_2H_2 mixture
cFrom the CH_4-C_2H_4 mixture
dFrom the C_2H_2-C_2H_4 mixture
eFrom the C_2H_4-$HCCCH_3$ mixture
f±99% actually means +100/−50%.

sures were measured using a Bayard-Alpert ionization gauge, which was calibrated against a 1 torr MKS Baratron capacitance manometer in the 10^{-5} torr pressure range. At pressures above 1×10^{-4} torr, the MKS Baratron manometer was used directly to measure the pressure. Mass spectra were obtained by scanning the cyclotron frequencies and the relative ion abundances were measured using the Wronka bridge detector. Phase sensitive detection was used to measure the signal from the bridge detector. Modulation of the ionizing electron beam was used for the mass spectra and the double resonance experiments [11]. A double resonance radio-frequency (rf) was used to search for precursor ions by observing individual ion peaks and radiating the double resonance rf in both the source and resonance regions of the drift cell. Double resonance coupling was identified when the parent ion was ejected at the cyclotron frequency of the parent ion and the accompanying loss of the product ion signal was noted using the Wronka bridge detector, which was set at the product ion cyclotron frequency. A modulated-ejection at the double resonance frequency of selected parent ions along with frequency scans of the Wronka bridge detector was used to identify the product ions formed from the selected parent ions. Between the direct double resonance ejection experiments and the modulated-ejection double resonance experiments it was felt that all significant reaction links between ions were determined.

In the analysis of the binary mixtures, two different sets of data were taken. In these two cases the partial pressure of one of the neutrals was kept constant while the other was varied. Both sets of data were analyzed together to provide a consistent set of kinetic parameters. In some cases specific kinetic parameters were combined from more than one set of binary mixtures to provide a unified correlation.

The flowing FA-SIFT has also been described previously. A summary follows for the understanding of this paper. The ions are formed in a flowing afterglow tube, mass selected and injected into the SIFT section through a Venturi injection port. Mass selection between the FA source and the SIFT is accomplished using a quadrupole mass spectrometer operated at a pressure of about 10^{-5} torr. The SIFT carrier gas was helium that was scrubbed by passing the gas over liquid nitrogen-cooled molecular sieve material. The pressure was about 0.48 torr in the SIFT and the flow times of an ion were about 3.5 millisecond from the reactant gas entrance to their exit at the skimmer-nosecone of the downstream quadrupole detector. Flows of reactant gases were added downstream of the Venturi injector and 50.4 cm upstream from the skimmer-nosecone. Ions were sampled in the SIFT using a skimmer at the end of the flow tube, behind which was a differentially pumped second quadrupole mass spectrometer and continuous dynode multiplier detector. The continuous dynode particle multiplier tube output was measured using pulse-counting technology. The ratio of ion counts of the different masses provided a measure of the relative ion abundances.

Gases were commercially obtained and purified using freeze-pump-thaw cycles.

Results and Discussion

The main experiments centered round the analysis of the five binary mixtures of CH_4/C_2H_2, CH_4/C_2H_4, C_2H_2/C_2H_4, $C_2H_2/HCCCH_3$, and $C_2H_4/HCCCH_3$. Example mass spectra of single pressure combinations are shown for the CH_4/C_2H_2 system in Figure 1, see Supplementary Material section (which can be found in the electronic version of the article) for other examples. This mass spectrum is representative of all the mass spectra obtained. In this binary mixture, the two parent gases when subjected to electron impact exhibited ion products at 39, 41, 43, 50, 53, 55, 59, 65, 76, 77, 91, 102, and 103 Da. Mass spectra were taken at many combi-

nations of pressures for each system. In addition to the conventional ICR mass spectrum, each binary mixture was analyzed using both the double resonance ejection technique and the modulated double resonance ejection technique to identify the precursor ions and product ions for the individual peaks in the mass spectra. A representative example of these double resonance and modulated double resonance ejection results are shown in Figure 2 for the CH_4/C_2H_2 system.

Each recorded mass spectrum was compared with a modeled mass spectrum based on the reported literature reactions for all reactant gas partial pressures. The objectives of the modeling were to achieve good fits between the observed ion density variations with parent gas pressure at all partial pressures and the modeled ion densities. The modeled mass spectrum was obtained by solving the partial differential equation for each individual reaction and the applicable set of equations for each binary system was solved providing an exact solution for each ion in the spectrum. The general solutions of the differential equations for three consecutive reactions have been given in an earlier paper [5]. Where differences between the model and the observations occurred, subsequent experiments were conducted to either validate or discard the existing kinetic data. If new branching ratios were required, they were measured carefully under specially designed conditions to maximize their accuracy. These conditions were obtained by monitoring the relevant partial pressures of the reactant gases to optimize product branching ratios. The resulting list of new kinetics determined in this study is presented in short tables through out the text and all new results have been summarized in Table 1.

A flow chart of the network of reactions occurring in the CH_4/C_2H_2 system is shown in Figure 3, for the CH_4/C_2H_4 system in Figure 4, for the C_2H_2/C_2H_4 system in Figure 5, for the $C_2H_2/HCCCH_3$ system in Figure 6, and for the $C_2H_4/HCCCH_3$ system in Figure 7.

It should be noted there were at times more than just the hydrocarbon parent ions present as primary ions from the initial electron impact. For example, in the model summarized in Figure 3, the primary ions produced by the electron beam acting on CH_4 and C_2H_2 were CH_3^+ ($m/z = 15$), CH_4^+ ($m/z = 16$), and $C_2H_2^+$ ($m/z = 26$). These primary ions then underwent reactions with both CH_4 and C_2H_2 to form *ten* new product ions of higher mass. These *ten* ions also reacted (with the exception of $C_3H_3^+$) to form *six* new product ions and *six* product ions seen previously. In the next set of ensuing reactions of these *twelve* ions with acetylene, *four* new product ions were produced. The exact solutions of only the first three sequential reactions of the initial ions were followed and these were effective in reproducing greater than 95% of the reactivity observed. All of the experimental mass spectra for each binary mixture were compared to the modeled data. Through least-squares fitting of each system, the individual reaction rate coefficients and branching ratios were determined relative to the reaction rate coefficient of one of the
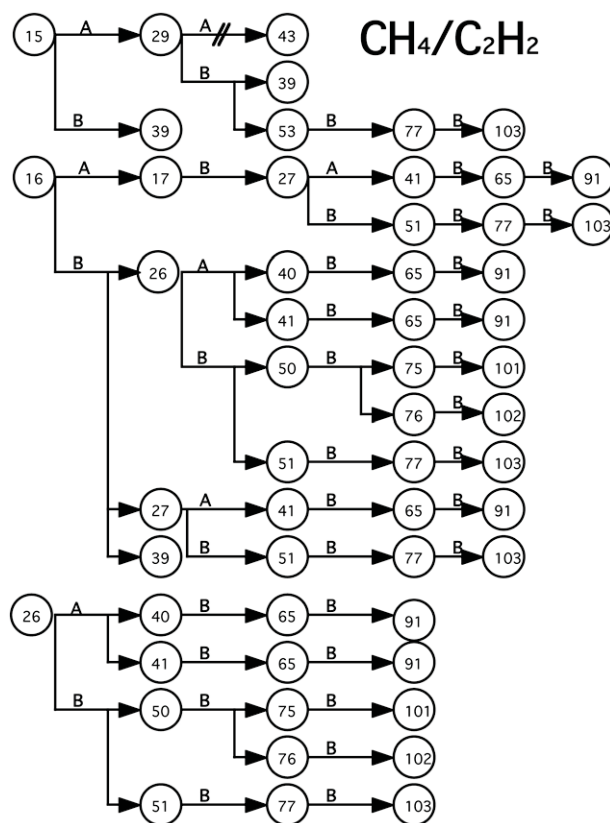

Figure 3. Flow chart of the reactions in a methane-acetylene mixture. A = CH_4 and B = C_2H_2.

reactions of the initial ions. Since the actual reaction time was not determined it was necessary to solve for the effective reaction time, by using a reference reaction rate coefficient in each system. These reference reaction rate coefficients were usually for the parent ion reacting with the parent neutral. In all cases these reactions have been studied extensively and their reaction rate coefficients have been well established [12].

We report next all the reactions observed in this work beginning with the CH_3^+ ion and their relevant kinetic parameters. We note that many reactions are common to more than one binary mixture. In these reactions, the enthalpy changes ΔH^0 are quoted in kJ mol^{-1}. In a few cases, some reactions with allene have also been included. The reactions with allene have been determined using the FA-SIFT instrument and are included here for comparison with propyne. A few of the reactions reported in the following discussion were reported in our earlier ICR study of pure hydrocarbons [4]. The results reported here for those reactions extend the earlier study to hydrocarbon *mixtures* and serve to provide corroborating data for the reactions common to both studies.

In the following results, the reaction rate coefficient is given the symbol k. To distinguish the differences between the bimolecular and termolecular reaction rate coefficients the termolecular reaction rate coefficient is given the symbol k_3.
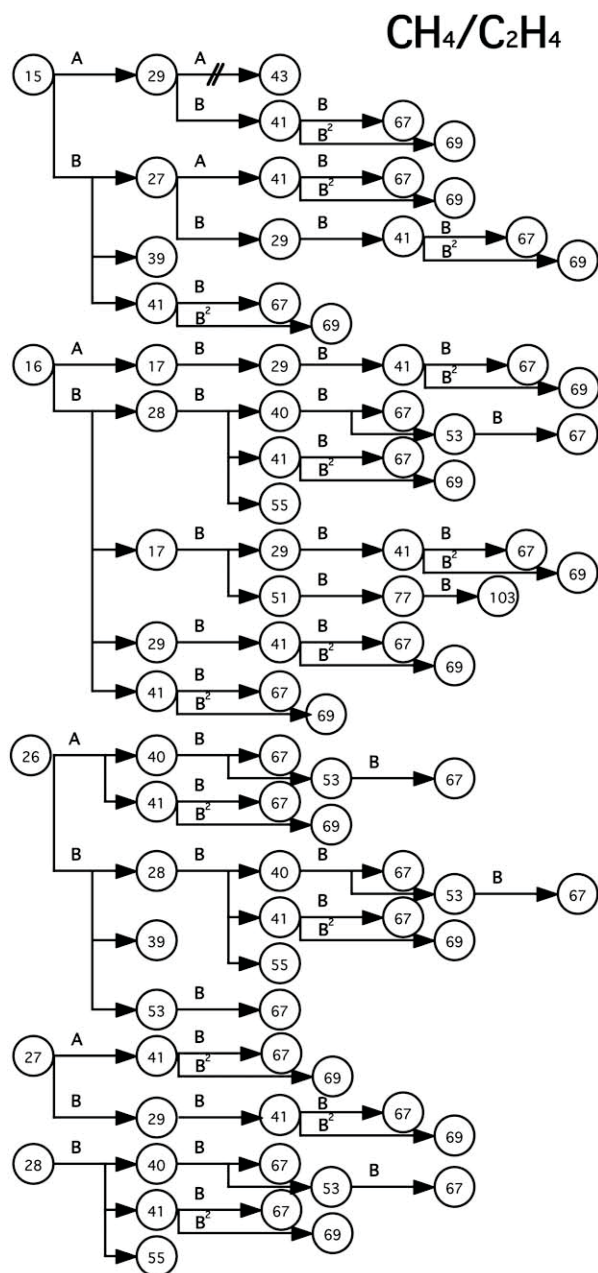
Figure 4. Flow chart of the reactions in a methane-ethylene mixture. A = CH_4 and B = C_2H_4.

Reactions of the CH_3^+ Ion

The reaction of CH_3^+ with methane has been widely studied and was used as a reference in the CH_4/C_2H_2 system. However, in the CH_4/C_2H_4 system, the best agreement between experiment and the model was found for a CH_3^+/CH_4 reaction rate coefficient of k = 8.11×10^{-10} $cm^3 s^{-1}$ instead of the accepted value of 1.15×10^{-9} $cm^3 s^{-1}$. This is probably indicative of the errors involved in the multistep analyses. We therefore consider the newly reported values in this work to be no more accurate that ±30%.

The reaction rate coefficients of CH_3^+ determined for acetylene and ethylene are consistent with the literature

values. The branching ratios found for the CH_3^+ reaction with ethylene were somewhat different from the literature. Here we determined that the products $C_2H_3^+$, $C_3H_3^+$, and $C_3H_5^+$ were in the ratio 0.78, 0.01, and 0.21. Since this ratio has only been reported twice previously, we add our measurement for statistical weighting.

Reactions of the CH_4^+ Ion

The established and well-studied reaction of CH_4^+ with methane was used as a reference in both the CH_4/C_2H_2 and the CH_4/C_2H_4 systems [12].

The branching ratios of CH_4^+ with acetylene and ethylene found in these studies are consistent with the literature values. The literature values of the reaction rate coefficients for these two reactions are significantly faster than the calculated Langevin collision rates. Our values are somewhat closer to the theoretical collision rates suggesting that the real values are probably the collision rate values. The measured reaction rate coefficients of CH_3^+, CH_4^+, and CH_5^+ with methane, acetylene, and ethylene are at or about the Langevin collision rates. It is expected that the reactions of CH_4^+ with acetylene and ethylene should not be any faster.

Reactions of the CH_5^+ Ion

The protonated methane ion proton transfers to both acetylene and ethylene at the collision limit as expected. CH_5^+ does not react with methane, except for the proton transfer reaction which is not detected because the product ions are the same as the reactant ions.

Reactions of the $C_2H_2^+$ Ion

1)

	ICR	SIFT	ΔH^0
$C_2H_2^+ + CH_4 \rightarrow C_3H_4^+ + H_2$	0.23		−126.1
$\rightarrow C_3H_5^+ + H$	0.78		−88.4

$$k \text{ (ICR)} = 6.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

2)

	ICR	SIFT	ΔH^0
$C_2H_2^+ + C_2H_4 \rightarrow C_2H_4^+ + C_2H_2$	0.30	0.45	−82.0
$\rightarrow C_3H_3^+ + CH_3$	0.48	0.25	−156.6
$\rightarrow C_4H_4^+ + H_2$	0.00	0.15	−170.1
$\rightarrow C_4H_5^+ + H$	0.23	0.15	−169.1

$$k \text{ (ICR)} = 1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

The ICR results come from the analysis of a mixture of ethylene with methane and also a mixture of ethylene with acetylene. The differences between the ICR and the SIFT experiments show the variability of the branching ratio in some cases and may also include some contribution from differences in the thermalization processes effecting both the reactant ion and the collision complex.
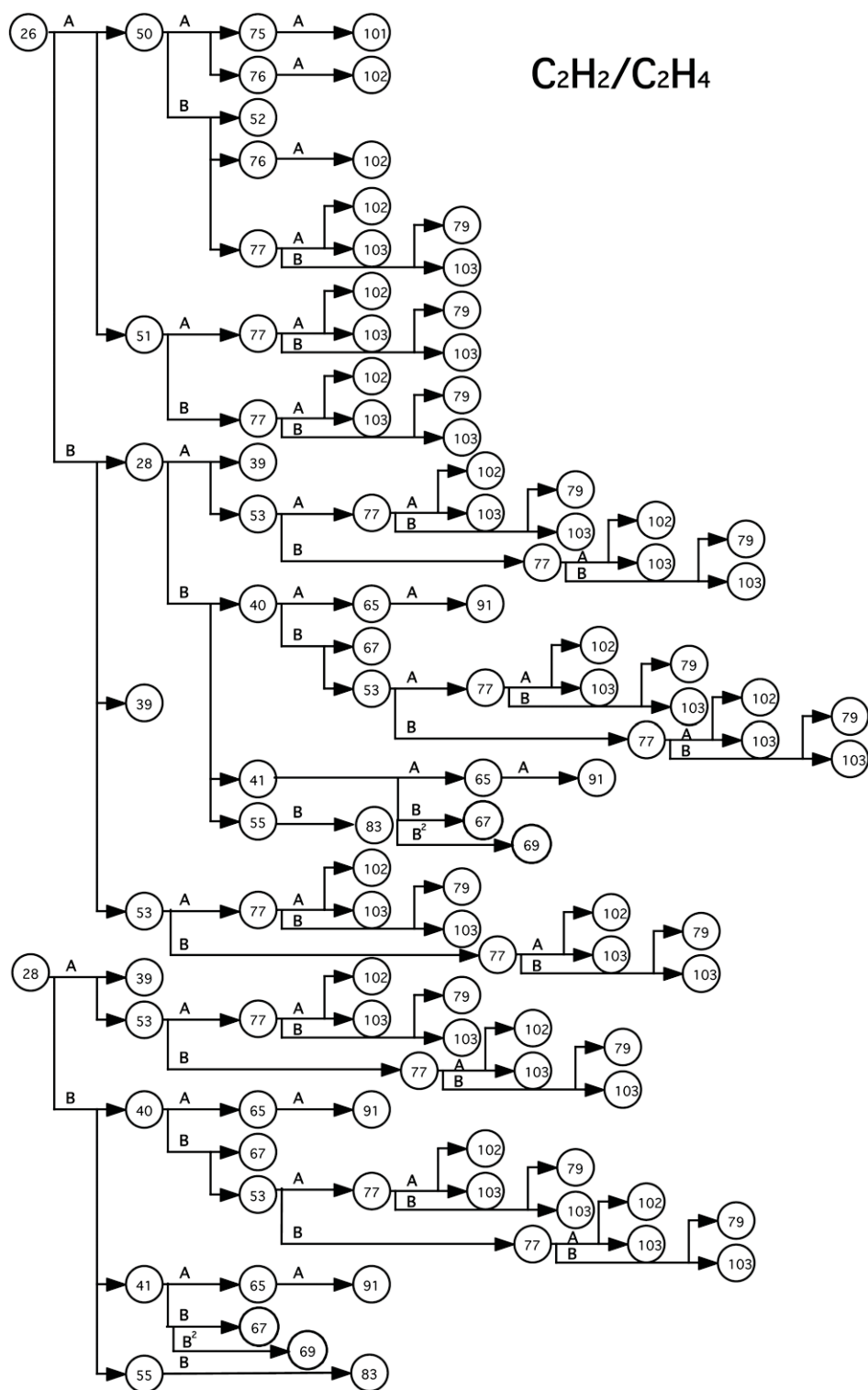
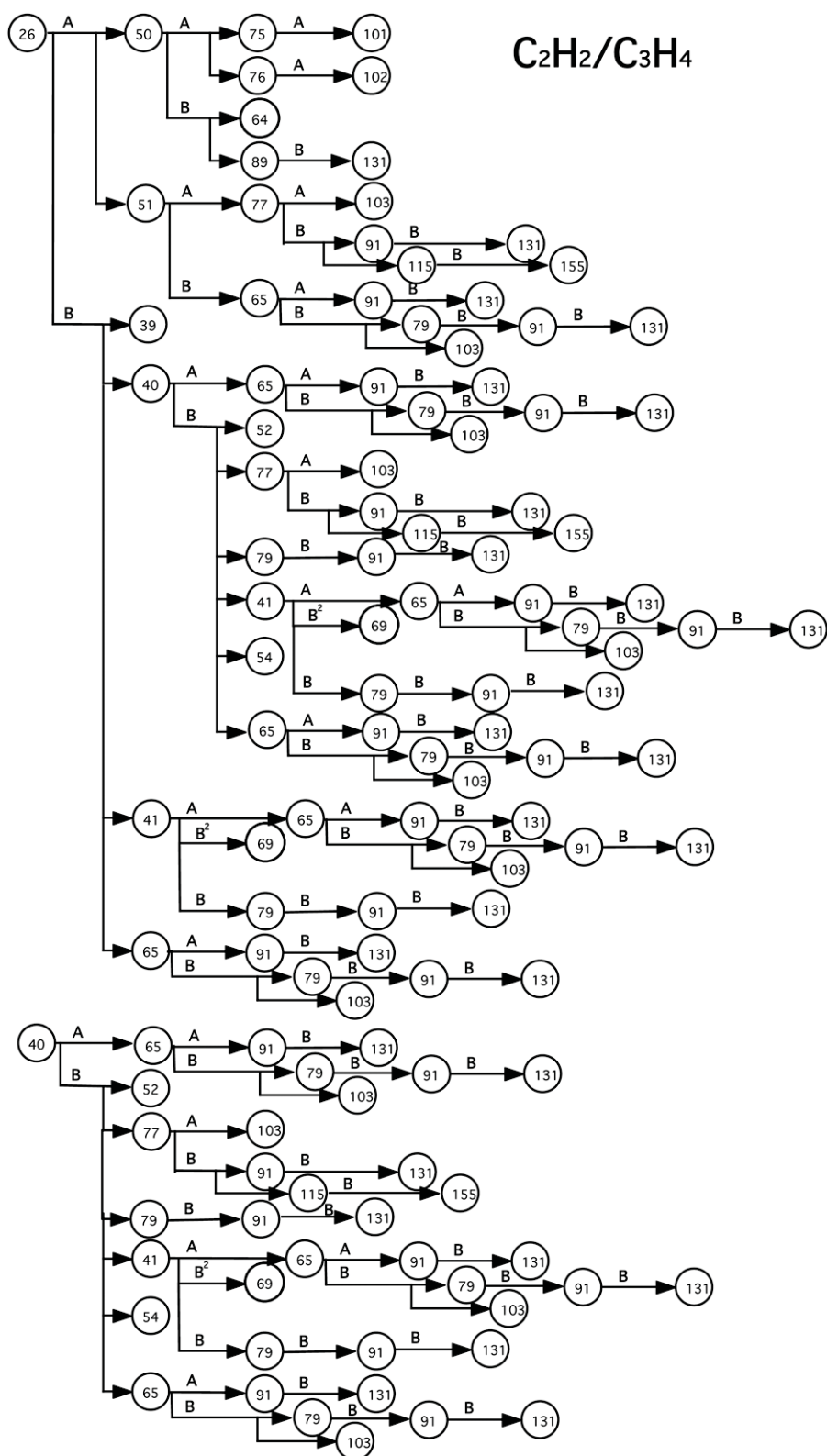**Figure 5.** Flow chart of the reactions in an acetylene-ethylene mixture. A = C_2H_2 and B = C_2H_4.

$$C_2H_2/C_3H_4$$

Figure 6. Flow chart of the reactions in an acetylene-propyne mixture. A = C_2H_2 and B = $HCCCH_3$.
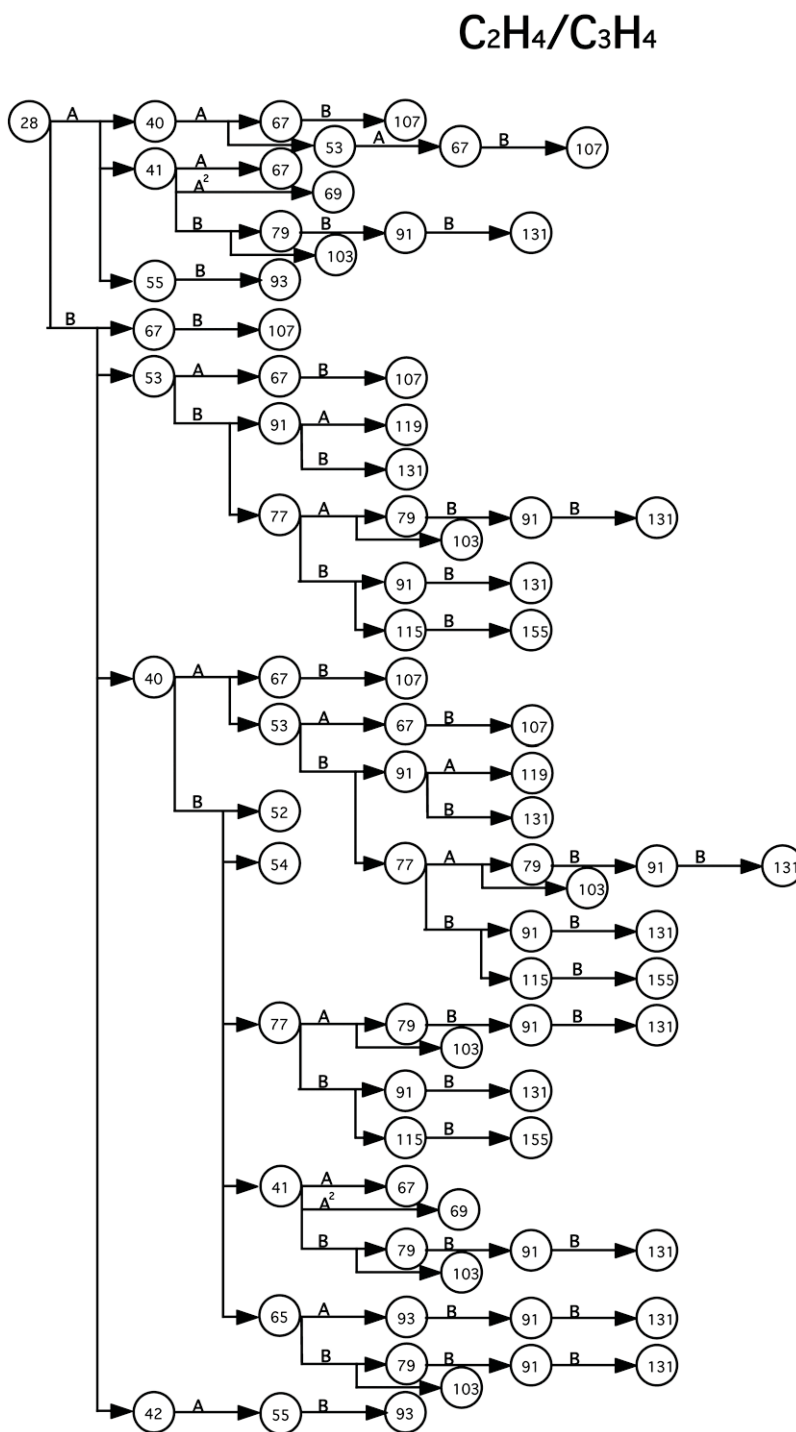
C₂H₄/C₃H₄

**Figure 7.**   Flow chart of the reactions in an ethylene-propyne mixture. A = C_2H_4 and B = $HCCCH_3$.

3)		ICR	SIFT	ΔH^0
$C_2H_2^+ + C_3H_4$	$\rightarrow C_3H_4^+ + C_2H_2$	0.50	0.65	-159.6
(propyne)	$\rightarrow C_3H_5^+ + C_2H$	0.05	0.10	-89.7
	$\rightarrow C_5H_5^+ + H$	0.45	0.25	-282.1

$$k\ (ICR) = 3.0 \times 10^{-9}\ cm^3\ s^{-1}$$
$$k\ (SIFT) = 1.5 \times 10^{-9}\ cm^3\ s^{-1}$$

These are new results. Here the ICR and SIFT results are considered to be consistent with each other. The ICR reaction rate coefficient is somewhat faster than the collision rate coefficient of 1.7×10^{-9} cm³ s⁻¹. However the model is not particularly sensitive to small changes in the rate coefficient. We therefore consider the rate of this reaction to be closer to that measured in the SIFT and the collision rate coefficient than the larger ICR result.

4)

			ICR	SIFT	ΔH^0
$C_2H_2^+ + C_3H_4$	$\rightarrow C_3H_4^+ + C_2H_2$			1.00	−105.5
(allene)					
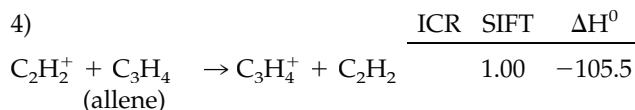
$$k \text{ (SIFT)} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

This is a new result. A comparison of the reaction of $C_2H_2^+$ with propyne and allene show the influence that different isomeric structures can have.

Reactions of the $C_2H_3^+$ Ion

1)

			ICR	SIFT	ΔH^0
$C_2H_3^+ + CH_4$	$\rightarrow C_3H_5^+ + H_2$		0.0	0.97	−95.2
$C_2H_3^+ + CH_4$	$\rightarrow$ association			0.03	−240.4
	+ M				

$$k \text{ (ICR)} \leq 1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
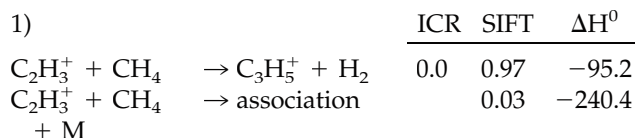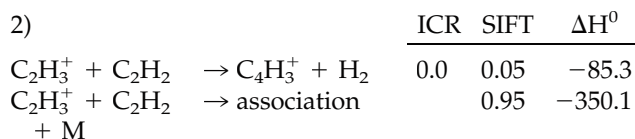$$k \text{ (SIFT)} = 1.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ at 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 3.0 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

The bimolecular reaction was studied in the ICR with both the CH_4/C_2H_2 and CH_4/C_2H_4 mixtures. In each case the reaction was not observed. The reaction rate coefficient for the ICR is reported here to be $\leq 1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, but the reaction scheme is not sensitive to the rate coefficient and statistically it could be as high as $1.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, as reported in Reference [12] without greatly influencing the result. Only $C_3H_5^+$ was previously reported as a product of reaction. In the SIFT this reaction proceeds rather slowly and has a detectable three-body association channel. The reason for the difference between the present ICR results and the previous results from 1977 [13] are not clear but most likely it is a consequence of not accounting completely for secondary ion chemistry.

2)

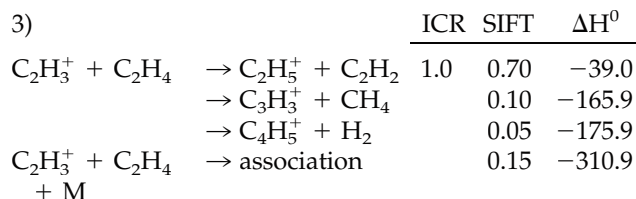|			ICR	SIFT	ΔH^0
$C_2H_3^+ + C_2H_2$	$\rightarrow C_4H_3^+ + H_2$		0.0	0.05	−85.3
$C_2H_3^+ + C_2H_2$	$\rightarrow$ association			0.95	−350.1
	+ M				

$$k \text{ (ICR)} \leq 1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 8.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ at 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 5.1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

Here again the ICR results showed no sign of reaction using a mixture of CH_4 and C_2H_2. The reaction rate coefficient for the ICR is reported here to be $\leq 1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, although the reaction scheme is not particularly sensitive to this reaction and statistically it could be as high as $1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. However, using modulated ICR double resonance no products were seen to originate from this reaction. The reaction in the ICR is therefore slow if it occurs at all. In the SIFT the bimolecular reaction rate was only about $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and the majority of the reaction went through the collision stabilization channel.

3)

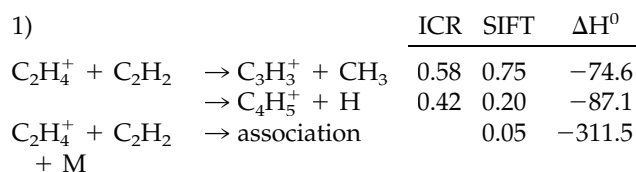|		ICR	SIFT	ΔH^0
$C_2H_3^+ + C_2H_4$	$\rightarrow C_2H_5^+ + C_2H_2$	1.0	0.70	−39.0
	$\rightarrow C_3H_3^+ + CH_4$		0.10	−165.9
	$\rightarrow C_4H_5^+ + H_2$		0.05	−175.9
$C_2H_3^+ + C_2H_4$	$\rightarrow$ association		0.15	−310.9
+ M				

$$k \text{ (ICR)} = 1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 9.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ at 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 8.9 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

The ICR results in this study are considered to be as accurate as that measured previously and so have been included in Table 1.

Reactions of the $C_2H_4^+$ Ion

1)

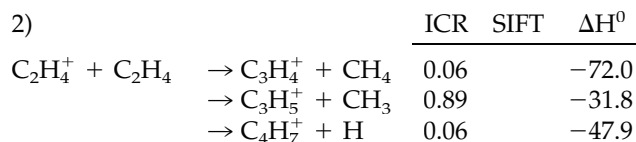|		ICR	SIFT	ΔH^0
$C_2H_4^+ + C_2H_2$	$\rightarrow C_3H_3^+ + CH_3$	0.58	0.75	−74.6
	$\rightarrow C_4H_5^+ + H$	0.42	0.20	−87.1
$C_2H_4^+ + C_2H_2$	$\rightarrow$ association		0.05	−311.5
+ M				

$$k \text{ (ICR)} = 7.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ at 0.5 Torr of He}$$
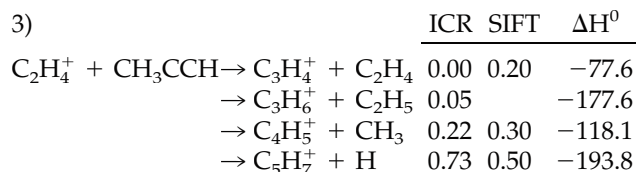$$k_3 \text{ (ICR)} < 1 \times 10^{-25} \text{ cm}^6 \text{ s}^{-1} \text{ (M = C}_2\text{H}_2)$$
$$k_3 \text{ (SIFT)} \geq 3.1 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

No adduct was seen in the ICR experiment. At Titan temperatures a 3-body rate coefficient of this magnitude needs to be considered in the models.

2)

		ICR	SIFT	ΔH^0
$C_2H_4^+ + C_2H_4$	$\rightarrow C_3H_4^+ + CH_4$	0.06		−72.0
	$\rightarrow C_3H_5^+ + CH_3$	0.89		−31.8
	$\rightarrow C_4H_7^+ + H$	0.06		−47.9

$$k \text{ (ICR)} = 7.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The rate coefficient for this reaction was used as a reference reaction rate coefficient in the analyses of the CH_4/C_2H_4, C_2H_2/C_2H_4, and C_2H_4/C_3H_4 systems. The additional channel forming $C_3H_4^+$ at 6% has not been reported previously.

3)

		ICR	SIFT	ΔH^0
$C_2H_4^+ + CH_3CCH$	$\rightarrow C_3H_4^+ + C_2H_4$	0.00	0.20	−77.6
	$\rightarrow C_3H_6^+ + C_2H_5$	0.05		−177.6
	$\rightarrow C_4H_5^+ + CH_3$	0.22	0.30	−118.1
	$\rightarrow C_5H_7^+ + H$	0.73	0.50	−193.8

$$k \text{ (ICR)} = 2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

Reactions of the $C_2H_5^+$ Ion

1)

		ICR	SIFT	ΔH^0
$C_2H_5^+ + C_2H_2$	$\rightarrow C_3H_3^+ + CH_4$	0.50	0.10	−126.9
	$\rightarrow C_4H_5^+ + H_2$	0.50		−136.8
$C_2H_5^+ + C_2H_2$	$\rightarrow$ association	(1.0)	0.90	−271.9
+ M				

$$k \text{ (ICR)} \sim 3.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 7.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ at 0.5 Torr of He}$$
$$k_3 \text{ (ICR)} = 2.5 \times 10^{-24} \text{ cm}^6 \text{ s}^{-1} \text{ (M = N}_2\text{)}$$
$$k_3 \text{ (SIFT)} \geq 4.1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

The $C_2H_5^+$ ion was formed from reactions in CH_4. The ICR reaction rate coefficient was determined in an analysis of the mixture of methane and acetylene. The reaction rate coefficient measured in the ICR is not considered to be as accurate as that reported in Reference [12]. The association reaction forming $C_4H_7^+$ needs to be considered in Titan models.

2)

		ICR	SIFT	ΔH^0
$C_2H_5^+ + C_2H_4$	$\rightarrow C_3H_5^+ + CH_4$	1.0	0.50	−84.1
$C_2H_5^+ + C_2H_4$	$\rightarrow$ association	0.0	0.50	−244.9
+ M				

$$k \text{ (ICR)} = 6.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k_3 \text{ (ICR)} < 1 \times 10^{-25} \text{ cm}^6 \text{ s}^{-1} \text{ (M = C}_2\text{H}_4\text{)}$$
$$k \text{ (SIFT)} = 6.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ at 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 1.8 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

An attempt was made to assess the extent of any adduct formation in the ICR. The problem encountered in this assessment is that $C_2H_5^+$ at $m/z = 29$ is made in C_2H_4 at the electron energy required to make CH_3^+ from CH_4, which also results in $m/z = 29$ formation. No direct evidence for $C_4H_9^+$ formation from association was found in the ICR. However, the observation of the occurrence of the association reaction forming $C_4H_9^+$ in the SIFT suggests that it should be included in Titan models. The reaction rate coefficient measured in the ICR is not considered to be as accurate as that reported in Reference [12].

Reactions of the $C_3H_4^+$ Ion

1)

		ICR	SIFT	ΔH^0
$C_3H_4^+ + CH_4$	$\rightarrow$ No Reaction	0.0	0.0	

$$k \text{ (ICR)} < 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} < 1.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

We note that $C_3H_4^+$ made from either allene or propyne had the same behavior.

2)

		ICR	SIFT	ΔH^0
$C_3H_4^+$ (propyne)	$\rightarrow C_5H_5^+ + H$	1.00		−122.5
+ C_2H_2				
$C_3H_4^+$ (propyne)	$\rightarrow$ association		1.0	−390.5
+ C_2H_2 + M				

$$k \text{ (ICR)} = 4.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 5.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ at 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} = 3.3 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

3)

		ICR	SIFT	ΔH^0
$C_3H_4^+$ (propyne)	$\rightarrow C_4H_5^+ + CH_3$	0.55	0.05	−40.5
+ C_2H_4				
	$\rightarrow C_5H_7^+ + H$	0.45	0.75	−116.2
$C_3H_4^+$ (propyne)	$\rightarrow$ association		0.20	−273.2
+ C_2H_4 + M				

$$k \text{ (ICR)} \sim 3.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 6.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ at 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 8.4 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

Reactions of the $C_3H_5^+$ Ion

1)

		ICR	SIFT	ΔH^0
$C_3H_5^+ + C_2H_4$	$\rightarrow C_5H_7^+ + H_2$	1.0		−153.8
$C_3H_5^+ + C_2H_4$	$\rightarrow$ association	(1.0)	1.0	−225.8
+ M				

$$k \text{ (ICR)} = 8.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$k_3 \text{ (ICR)} = 1.8 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1} \text{ (M = C}_2\text{H}_4\text{)}$$
$$k \text{ (SIFT)} = 5.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 3.3 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

We have noted in an earlier paper [4] that in some systems such as this one, it is only possible to fit the data by changing the product branching ratio as the pressure changes. This is a consequence of vibrational energy present in the reactant ion. The effect is most prevalent when the reactant ion is itself a product of an ion neutral reaction as we discussed in our earlier paper [4]. The results presented here are in good agreement with our earlier results obtained in a pure ethylene system. This reaction was observed in all mixtures containing ethylene. The ICR results in this study are considered to be as accurate as that measured previously and so this reaction has been included in Table 1.

2)

		ICR	SIFT	ΔH^0
$C_3H_5^+ + CH_3CCH$	$\rightarrow C_5H_5^+ + CH_4$	0.04		−193.6
	$\rightarrow C_6H_7^+ + H_2$	0.96	0.20	−268.2
$C_3H_5^+ + CH_3CCH$	$\rightarrow$ association		0.80	−335.8
+ M				

$$k \text{ (ICR)} = 7.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 6.0 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

The ICR results in this study are considered to be as accurate as that measured previously [4] and so has been included in Table 1. The additional channel forming the $C_5H_5^+$ ion has not been reported previously.

3)			ICR	SIFT	ΔH^0
$C_3H_5^+$ + C_3H_4(allene)	$\rightarrow C_6H_7^+$ + H_2		0.25		−273.4
$C_3H_5^+$ + C_3H_4(allene) + M	$\rightarrow$ association		0.75		−341.0

$$k \text{ (SIFT)} = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 5.1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

Reactions of the $C_3H_6^+$ Ion

1)			ICR	SIFT	ΔH^0
$C_3H_6^+$ + C_2H_4	$\rightarrow C_4H_7^+$ + CH_3		1.0	0.10	−20.7
$C_3H_6^+$ + C_2H_4	$\rightarrow$ association + M			0.90	−215.7

$$k \text{ (ICR)} \sim 1.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 7.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 4.4 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

Two other potential channels that are exothermic: $(C_5H_9^+ + H)$ $\Delta H^0 = -75.7$; $(C_4H_6^+ + CH_4)$ $\Delta H^0 = -101.3$, were not observed.

Reactions of the $C_4H_2^+$ Ion

1)			ICR	SIFT	ΔH^0
$C_4H_2^+$ + CH_4	$\rightarrow$ No reaction		0.0	0.0	

$$k \text{ (ICR)} < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} < 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

The $C_4H_2^+$ ion was made from the C_2H_2 sequence of reactions in the ICR.

2)			ICR	SIFT	ΔH^0
$C_4H_2^+$ + C_2H_2	$\rightarrow C_6H_3^+$ + H		0.25		−364.9
	$\rightarrow C_6H_4^+$		0.75		−361.9
$C_4H_2^+$ + C_2H_2	$\rightarrow$ association + M		(1.0)	1.0	−361.9

$$k_2 \text{ (ICR)} = 2.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k_3 \text{ (ICR)} = 2.3 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1} \text{ (M = C}_2\text{H}_2\text{)}$$
$$k \text{ (SIFT)} = 1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 6.2 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

These reactions with acetylene were previously reported from data recorded in a pure acetylene system [4]. Here the results allow us to extend that study with a mixture of methane and acetylene up to 1×10^{-2} torr. We noted in our earlier study that the $C_4H_2^+$ ions are made in an exothermic reaction and the ions do not have time in the ICR to lose their internal energy. The excess internal energy in the reactant ion slows the reactions and makes the association channel less probable. This reaction is another of those reactions in which the branching ratios are sensitive to the amount of energy in the reactant ion and to achieve a fit with the data it was necessary to vary the branching ratio between 0.17 at the lowest pressures for $C_6H_3^+$ up to 0.60 at 10^{-2} torr. The product ions of this reaction are both made in at least two different isomeric forms: one being reactive and the other apparently unreactive. About 50% of the $C_6H_3^+$ ions were found to be reactive and more than 80% of the $C_6H_4^+$ ions were found to be reactive. These results are in excellent agreement with the earlier study in pure acetylene [4].

3)			ICR	SIFT	ΔH^0
$C_4H_2^+$ + C_2H_4	$\rightarrow C_3H_3^+$ + C_3H_3		0.00	0.05	−82.9
	$\rightarrow C_4H_4^+$ + C_2H_2		0.47	0.10	−62.9
	$\rightarrow C_6H_4^+$ + H_2		0.05	0.05	−187.7
	$\rightarrow C_6H_5^+$ + H		0.48	0.25	−145.7
$C_4H_2^+$ + C_2H_4	$\rightarrow$ association + M			0.55	−523.7

$$k \text{ (ICR)} = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 3.4 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

A much earlier measurement [14] estimated a bimolecular rate coefficient of k $\sim 7 \times 10^{-10}$ cm^3 s^{-1} for this reaction. The ICR reaction rate coefficient and branching ratios presented here come from an analysis of a mixture of acetylene and ethylene. We note that other peaks also observed from the double resonance ejection of $m/z = 28$ ($C_2H_4^+$) were $m/z = 41, 55$ (both assumed from the reaction of ethylene with itself) and 65. It was assumed that the $m/z = 65$ peak came from $C_3H_5^+$ + C_2H_2.

4)			ICR	SIFT	ΔH^0
$C_4H_2^+$ + CH_3CCH	$\rightarrow C_5H_4^+$ + C_2H_2		0.16	0.05	−269.9
	$\rightarrow C_7H_5^+$ + H		0.84	0.95	−458.6

$$k \text{ (ICR)} = 2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$
$$k \text{ (SIFT)} = 1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

The ICR rate coefficient was found from the full analysis of the acetylene-propyne mixtures in the ICR cell.

Reactions of the $C_4H_3^+$ Ion

1)

	ICR	SIFT	ΔH^0
$C_4H_3^+ + CH_4 \rightarrow$ No reaction	0.0		

$$k\ (ICR) < 2 \times 10^{-11}\ cm^3\ s^{-1}$$

The reactions of $C_4H_3^+$ with C_2H_2 were reported earlier in the investigations of the pure C_2H_2 system. They are extended here to include a mixture of CH_4 and C_2H_2 up to a total pressure of 1×10^{-2} torr.

2)

	ICR	SIFT	ΔH^0
$C_4H_3^+ + C_2H_2 \rightarrow C_6H_5^+$	1.0		−348.6
$C_4H_3^+ + C_2H_2 \rightarrow$ association + M	1.0	1.0	−348.6

$$k\ (ICR) = 5.2 \times 10^{-12}\ cm^3\ s^{-1}$$
$$k_3\ (ICR) = 9.5 \times 10^{-24}\ cm^6\ s^{-1}\ (M = C_2H_2)$$
$$k\ (SIFT) = 8.3 \times 10^{-10}\ cm^3\ s^{-1}\ in\ 0.5\ Torr\ of\ He$$
$$k_3\ (SIFT) \geq 5.1 \times 10^{-26}\ cm^6\ s^{-1}\ (M = He)$$

As in our earlier study [4], the smaller rate coefficients reported here are a consequence of the $C_4H_3^+$ ions retaining internal energy from their formation reactions. The excess internal energy in the reactant ion slows the reactions and makes the association channel less probable. As with other reactions where excess vibrational energy is stored in the reactant ion, the branching ratio as noted in Ref. 4 changes over the pressure range of 10^{-5} torr to 10^{-2} torr from the reported value above at the lowest pressure (0.0) to 0.96 for the production of $C_6H_4^+$ at the highest pressure. Both products of this reaction ($C_6H_4^+$ and $C_6H_5^+$) are made in at least two different isomeric forms: one being reactive and the other apparently unreactive.

3)

	ICR	SIFT	ΔH^0
$C_4H_3^+ + C_2H_4 \rightarrow C_6H_5^+ + H_2$	1.0		−174.3
$C_4H_3^+ + C_2H_4 \rightarrow$ association + M		1.0	−446.7

$$k\ (ICR) = 1.2 \times 10^{-10}\ cm^3\ s^{-1}$$
$$k_3\ (ICR) = rate\ coefficent\ not\ measured$$
$$k\ (SIFT) = 7.0 \times 10^{-10}\ cm^3\ s^{-1}\ in\ 0.5\ Torr\ of\ He$$
$$k_3\ (SIFT) \geq 4.3 \times 10^{-26}\ cm^6\ s^{-1}\ (M = He)$$

The ICR results come from analyses of mixtures of acetylene and ethylene where $C_4H_3^+$ is formed. Herrod and Harrison have previously estimated the rate coefficient as $k = 2.6 \times 10^{-10}\ cm^3\ s^{-1}$ [14]. Even at the higher pressures of the current ICR studies a three body rate coefficient was not measurable.

4)

	ICR	SIFT	ΔH^0
$C_4H_3^+ + CH_3CCH \rightarrow C_5H_5^+ + C_2H_2$	1.0		−203.5

$$k\ (ICR) = 1.4 \times 10^{-9}\ cm^3\ s^{-1}$$

Reactions of the $C_4H_5^+$ Ion

1)

	ICR	SIFT	ΔH^0
$C_4H_5^+ + CH_4 \rightarrow$ No reaction	0.0		

$$k\ (ICR) < 1 \times 10^{-11}\ cm^3\ s^{-1}$$

2)

	ICR	SIFT	ΔH^0
$C_4H_5^+ + C_2H_2 \rightarrow C_6H_5^+ + H_2$	1.0	0.85	−83.7
$\rightarrow C_6H_6^+ + H$		0.10	−25.7
$C_4H_5^+ + C_2H_2 \rightarrow$ association + M		0.05	−356.1

$$k\ (ICR) = 1.6 \times 10^{-10}\ cm^3\ s^{-1}$$
$$k\ (SIFT) = 1.0 \times 10^{-10}\ cm^3\ s^{-1}\ in\ 0.5\ Torr\ of\ He$$

This is a new reaction. The ICR reaction rate coefficient was obtained from an analysis of a mixture of acetylene and the ethylene. In the SIFT the ion was made from ethylene with the reactive fraction of the $C_4H_5^+$ ions representing 20% of the total $C_4H_5^+$ ions present.

3)

	ICR	SIFT	ΔH^0
$C_4H_5^+ + C_2H_4 \rightarrow C_6H_7^+ + H_2$	1.0		−181.9

$$k\ (ICR) = 7.3 \times 10^{-11}\ cm^3\ s^{-1}$$

4)

	ICR	SIFT	ΔH^0
$C_4H_5^+ + CH_3CCH \rightarrow C_6H_5^+ + CH_4$	0.25		−117.3
$\rightarrow C_7H_7^+ + H_2$	0.75		−328.4

$$k\ (ICR) = 2.0 \times 10^{-10}\ cm^3\ s^{-1}$$

Reactions of the $C_4H_7^+$ Ion

The $C_4H_7^+$ ion was generated from the reaction between $C_2H_4^+ + C_2H_4$ and the results of this study can be compared with our earlier investigation in which $C_4H_7^+$ was formed in pure ethylene [4].

1)

	ICR	SIFT	ΔH^0
$C_4H_7^+ + CH_4 \rightarrow$ No reaction	0.0	0.0	

$$k\ (ICR) < 1 \times 10^{-11}\ cm^3\ s^{-1}$$
$$k\ (SIFT) < 1 \times 10^{-11}\ cm^3\ s^{-1}$$

2)

		ICR	SIFT	ΔH^0
$C_4H_7^+ + C_2H_2$	→ No reaction	0.0		

$$k \text{ (ICR)} < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

3)

		ICR	SIFT	ΔH^0
$C_4H_7^+ + C_2H_4$	→ No reaction	0.0		
$C_4H_7^+ + C_2H_4$	→ association + M	0.0	1.0	−199.4

$$k \text{ (ICR)} < 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$k_3 \text{ (ICR)} = 1.4 \times 10^{-24} \text{ cm}^6 \text{ s}^{-1} \text{ (M = C}_2H_4)$$
$$k \text{ (SIFT)} = 1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$k_3 \text{ (SIFT)} \geq 9.0 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

These reactions were reported in our study in pure ethylene with excellent agreement. Data obtained at much higher pressures (1×10^{-2} torr) in previous studies showed an association reaction between $C_4H_7^+ + C_2H_4$. In the current study of reactions in a mixture of methane and ethylene, no loss was seen of the $C_4H_7^+$ ion in 1×10^{-4} torr of ethylene. This is because at 1×10^{-4} torr the effective two body rate will still be only $5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, which is below the measurable limit in the current study.

4)

		ICR	SIFT	ΔH^0
$C_4H_7^+ +$ CH_3CCH	→ $C_7H_9^+ + H_2$	1.0		−246.4

$$k \text{ (ICR)} = 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

Reaction of the $C_5H_5^+$ Ion

At least two structures of the $C_5H_5^+$ ion could be distinguished in our study. These structures were not identified except that one was reactive and one was not. In the ICR the $C_5H_5^+$ ion was generated from the reaction $CH_3CCH^+ + C_2H_2 \rightarrow C_5H_5^+ + H$. In the SIFT studies, the $C_5H_5^+$ ion was made from C_5H_6 (1-methylbutene-3-yne) and also from a mixture of propyne and acetylene with similar results. In both cases more than 90% of the $C_5H_5^+$ ion was in the unreactive form and we designate this ion as a-$C_5H_5^+$. The reactive form amounting to a few percent of the total $C_5H_5^+$ signal, is designated b-$C_5H_5^+$

1)

		ICR	SIFT	ΔH^0
a-$C_5H_5^+ + CH_4$	→ No reaction	0.0	0.0	

$$\text{a-}k \text{ (ICR)} < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$\text{a-}k \text{ (SIFT)} < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

When $C_5H_5^+$ was formed from $HCCCH_3$ and C_2H_2 at

10.2 eV (i.e., no CH_4^+ ions present) and CH_4 was added to 3×10^{-4} torr, no products other than $m/z = 79$ were found and the $m/z = 79$ product ion did not appear to be made from CH_4. There is an exothermic pathway to $m/z = 79$ from $m/z = 65$ providing the lowest energy $C_6H_7^+$ ion is formed but there was no evidence for any reaction based on DR modulation of $m/z = 65$.

2)

		ICR	SIFT	ΔH^0
b-$C_5H_5^+ + C_2H_2$	→ association	1.0		−389.7
a-$C_5H_5^+ + C_2H_2$	→ No reaction	0.0	0.0	

$$\text{a-}k \text{ (ICR)} \leq 1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$\text{b-}k \text{ (ICR)} = 1.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The ICR reaction rate coefficient was obtained from a mixture of acetylene and ethylene. The data can be rationalized if only one of the structural isomers of $C_5H_5^+$ is reactive with C_2H_2. From the data, apparently only about 2% of the $C_5H_5^+$ is reactive and that it undergoes a rapid reaction with C_2H_2. More than 90% of the $C_5H_5^+$ generated is unreactive. Measurements in the SIFT confirmed this observation as a very small association peak at $m/z = 91$ was observed.

3)

		ICR	SIFT	ΔH^0
b-$C_5H_5^+ + C_2H_4$	→ association	0.0	1.0	−268.5
a-$C_5H_5^+ + C_2H_4$	→ No reaction	0.0	0.0	

$$\text{a-}k \text{ (ICR)} < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$\text{b-}k \text{ (ICR)} < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$\text{a-}k \text{ (SIFT)} \leq 1.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$\text{b-}k \text{ (SIFT)} \sim 1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$\text{b-}k_3 \text{ (SIFT)} \geq 6 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

For the reaction with C_2H_4, both structures of $C_5H_5^+$ showed no reactivity in the ICR. Association of b-$C_5H_5^+$ was observed at higher pressures in the SIFT.

4)

		ICR	SIFT	ΔH^0
$C_5H_5^+ +$ $HCCCH_3$	→ No reaction	0.0		
$C_5H_5^+ + C_3H_4$ (allene) + M	→ association		1.0	

$$\text{a-}k \text{ (ICR)} < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$\text{a-}k \text{ (SIFT)} < 5.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$\text{b-}k \text{ (SIFT)} \sim 5.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$\text{b-}k_3 \text{ (SIFT)} \geq 3.1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

This reaction is included for comparison only. The $C_5H_5^+$ ion was generated from a mixture of allene and C_2H_2. About 85% of the $C_5H_5^+$ ions were unreactive. An adduct was identified in the SIFT at $m/z = 105$.
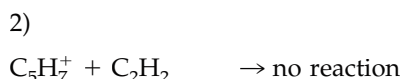
Reactions of the $C_5H_7^+$ Ion

In the ICR this ion was made from both mixtures of C_3H_4 (propyne) and C_2H_4 and mixtures of C_2H_4 and CH_4. In the SIFT the ion was made directly from C_5H_6 (1-methyl-butene-3-yne).

1)

$$C_5H_7^+ + CH_4 \qquad \rightarrow \text{no reaction}$$

k (ICR) < 1×10^{-11} cm³ s⁻¹
k (SIFT) ≤ 1.0×10^{-12} cm³ s⁻¹ in 0.5 Torr of He

2)

$$C_5H_7^+ + C_2H_2 \qquad \rightarrow \text{no reaction}$$

k (ICR) < 2×10^{-11} cm³ s⁻¹
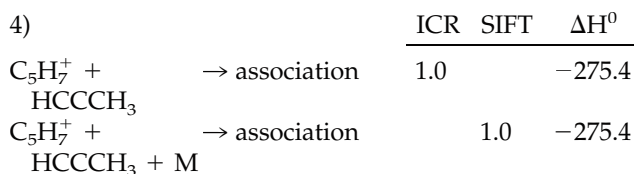**k (SIFT) ≤ 1.0×10^{-13} cm³ s⁻¹ in 0.5 Torr of He**

This reaction was studied in the ICR in special experiments in which we generated the $C_5H_7^+$ ion and then added acetylene. Sufficient acetylene was added to determine this minimum reaction rate coefficient. This reaction was not observed in the binary mixture studies.

3)

$$C_5H_7^+ + C_2H_4 \qquad \rightarrow \text{no reaction}$$

k (ICR) < 1×10^{-11} cm³ s⁻¹
k (SIFT) ≤ 1.0×10^{-13} cm³ s⁻¹ in 0.5 Torr of He

In a study of reactions in a mixture of methane and ehylene, no loss was seen of the $C_5H_7^+$ ion in 1×10^{-4} torr of ethylene.

4)

		ICR	SIFT	ΔH^0
$C_5H_7^+ +$ HCCCH$_3$	$\rightarrow$ association	1.0		−275.4
$C_5H_7^+ +$ HCCCH$_3$ + M	$\rightarrow$ association		1.0	−275.4

k (ICR) = 7.0×10^{-10} cm³ s⁻¹
k (SIFT) = 5.0×10^{-11} cm³ s⁻¹ in 0.5 Torr of He
k_3 (SIFT) ≥ 3.1×10^{-27} cm⁶ s⁻¹ (M = He)

Reactions of the $C_5H_9^+$ Ion

This ion is made from the association of $C_3H_5^+$ and C_2H_4 by a termolecular reaction. It was present in all mixtures containing ethylene. The $C_5H_9^+$ was found to be unreactive ($k < 2 \times 10^{-11}$ cm³ s⁻¹) with all of the neutrals (CH_4, C_2H_2, C_2H_4, and CH_3CCH) studied in this paper.

Reactions of the $C_6H_3^+$ Ion

The $C_6H_3^+$ was generated in binary mixtures of acetylene with methane, ethylene, and propyne at pressures up to 1×10^{-2} torr. The $C_6H_3^+$ ion was unreactive with CH_4 ($k < 1 \times 10^{-11}$ cm³ s⁻¹).
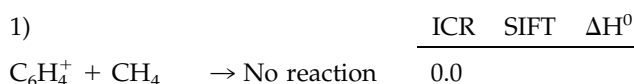
1)

		ICR	SIFT	ΔH^0
$C_6H_3^+ + C_2H_2$	$\rightarrow$ association	1.0		−361.7

k (ICR) = 2.3×10^{-10} cm³ s⁻¹

This result in the acetylene only system was reported in our earlier study of the ion chemistry of pure acetylene [4]. In that study as here, the $C_6H_3^+$ was formed by an exothermic reaction and the reaction rate coefficient was reduced by the excess internal energy resulting from the formation process. In the present mixture of methane and acetylene, the reaction rate coefficient was determined to be 3.1×10^{-10} cm³ s⁻¹. In the pure acetylene system the reaction rate coefficient was determined to be 4.6×10^{-10} cm³ s⁻¹ for the reactive part of the $C_6H_3^+$ products, which was about 50% of the total $C_6H_3^+$ ions produced.

Reactions of the $C_6H_4^+$ Ion

The $C_6H_4^+$ ion was generated in the ICR from a binary mixtures of acetylene with methane, ethylene, and propyne at total pressures up to 1×10^{-2} torr.

1)

		ICR	SIFT	ΔH^0
$C_6H_4^+ + CH_4$	$\rightarrow$ No reaction	0.0		

k (ICR) < 1×10^{-11} cm³ s⁻¹

2)

		ICR	SIFT	ΔH^0
$C_6H_4^+ + C_2H_2$	$\rightarrow$ association	1.0		−381.7

k = 2.9×10^{-10} cm³ s⁻¹

As the $C_6H_4^+$ was formed by an exothermic reaction, the reaction rate coefficient may be reduced by the excess internal energy resulting from the formation process.

Reactions of the $C_6H_5^+$ Ion

The $C_6H_5^+$ ion was generated in the ICR in a mixture of methane and acetylene, acetylene and ethylene or acetylene and propyne at total pressures up to 1×10^{-4} torr. Again there are two forms of this ion. A reactive component deemed to be cyclic [15] and a non reactive component [4].

1)

	ICR	SIFT	ΔH^0
$C_6H_5^+ + CH_4 \rightarrow C_7H_7^+ + H_2$	1.0		−211.1

$$k \text{ (ICR)} = 2.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

This value of the reaction rate coefficient is somewhat slower than the literature value [16]. It is not clear which is more accurate.

2)

	ICR	SIFT	ΔH^0
$C_6H_5^+ + C_2H_2 \rightarrow$ association	1.0		−357.7

$$k \text{ (ICR)} = 1.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The $C_6H_5^+$ was formed by an exothermic reaction and the reaction rate coefficient may be reduced by the excess internal energy resulting from the formation process. In the pure acetylene system the reaction rate coefficient was determined to be 2.5×10^{-11} cm³/s for the reactive part of the $C_6H_5^+$ products [4], which was about 50% of the total $C_6H_5^+$ ions produced from either the 3-body or the 2-body formation channel. This value of the reaction rate coefficient is greater than the literature value [16]. As noted above it is not clear which is more accurate.

3)

	ICR	SIFT	ΔH^0
$c\text{-}C_6H_5^+ + C_2H_4 \rightarrow C_6H_7^+ + C_2H_2$	0.60		−98.1
$\rightarrow C_8H_7^+ + H_2$	0.40		−183.4
$c\text{-}C_6H_5^+ + C_2H_4 \rightarrow$ association + M		1.0	−349.5
$ac\text{-}C_6H_5^+ + C_2H_4 \rightarrow$ association + M		1.0	−390.5

$$k \text{ (ICR)} = 1.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$c\text{-k (SIFT)} = 5.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$c\text{-}k_3 \text{ (SIFT)} \geq 3.4 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$
$$ac\text{-k (SIFT)} = 1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$ac\text{-}k_3 \text{ (SIFT)} \geq 6.2 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

This is a new reaction for measurements in the ICR. In the SIFT the two $C_6H_5^+$ isomers were made from bromobenzene where the reactive component represented 70% of the total ion count.

4)

	ICR	SIFT	ΔH^0
$c\text{-}C_6H_5^+ + C_3H_4 \rightarrow C_7H_7^+ + C_2H_2$ (propyne)	0.30		−244.7
$\rightarrow C_9H_7^+ + H_2$	0.70		−475.4
$c\text{-}C_6H_5^+ + HCCCH_3 + M \rightarrow$ association	(1.0)		—

$$k \text{ (ICR)} = 6.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
$$k_3 \text{ (ICR)} = 5.2 \times 10^{-24} \text{ cm}^6 \text{ s}^{-1} \text{ (M = C}_3\text{H}_4)$$

As noted above, there were two forms of the $C_6H_5^+$ ion. The results reported here are for the reactive cyclic component [15]. The termolecular reaction is from an earlier study. The conditions in the present study did not access sufficiently high pressures for this reaction to be observed.

Reactions of the $C_6H_7^+$ Ion

In the ICR the $C_6H_7^+$ ion was made in mixtures of ethylene and propyne. In the SIFT the $C_6H_7^+$ ion was generated from hexadiyne, from benzene and also from a propyne/ethylene mixture. In all cases, at least two forms of the ion were apparent: a reactive (a) and non-reactive component (b). In the SIFT, the more reactive component represented ~60% of the total ions. It is assumed that these two different forms constitute two difference isomeric structures. It is unlikely that different isomeric structures are produced in the different techniques as common source gas mixtures yielded similar results with both reactive and non-reactive forms generated.

1)

$$C_6H_7^+ + C_2H_4 \rightarrow \text{No reaction}$$

$$k \text{ (ICR)} < 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

2)

	ICR	SIFT	ΔH^0
$C_6H_7^+ + CH_3CCH \rightarrow C_7H_7^+ + C_2H_4$	1.0		−146.5
$C_6H_7^+ + CH_3CCH + M \rightarrow$ association		1.0	−271.0

$$k \text{ (ICR)} = 9.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$k_3 \text{ (ICR)} = 3.0 \times 10^{-25} \text{ cm}^6 \text{ s}^{-1} \text{ (M = C}_2\text{H}_2)$$

This value of the bimolecular reaction rate coefficient is some what faster than the literature value [4]. The termolecular reaction rate coefficient has not been reported previously.

3)

	ICR	SIFT	ΔH^0
$a\text{-}C_6H_7^+ + C_3H_4\text{(allene)} + M \rightarrow$ association		1.0	

$$a\text{-k (SIFT)} = 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ in 0.5 Torr of He}$$
$$a\text{-}k_3 \text{ (SIFT)} \geq 1.0 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} \text{ (M = He)}$$

In the SIFT the more reactive component represented 60% of the total ion count. The 40% component showed no reaction.

Reactions of the $C_7H_7^+$ Ion

In the ICR the $C_7H_7^+$ ion was made from mixtures of C_3H_4(propyne) and C_2H_2. In the SIFT the $C_7H_7^+$ was generated from cycloheptatriene.

1)		ICR	SIFT	ΔH^0
$C_7H_7^+ + CH_4$	$\rightarrow$ No reaction		0.0	

k (SIFT) $\leq 1.0 \times 10^{-13}$ cm^3 s^{-1} in 0.5 Torr of He

This reaction was studied in the SIFT in special experiments in which we generated only the $C_7H_7^+$ ion and then added methane. Sufficient methane was added to determine this minimum reaction rate coefficient. No product was observed in the binary mixture studies.

2)		ICR	SIFT	ΔH^0
$C_7H_7^+ + C_2H_2$	$\rightarrow$ No reaction		0.0	

k (SIFT) $\leq 1.0 \times 10^{-12}$ cm^3 s^{-1} in 0.5 Torr of He

This reaction was studied in the SIFT in special experiments in which we generated only the $C_7H_7^+$ ion and then added acetylene. Sufficient acetylene was added to determine this minimum reaction rate coefficient. This reaction was not observed in the binary mixture studies.

3)		ICR	SIFT	ΔH^0
$C_7H_7^+ + C_2H_4$	$\rightarrow C_9H_{11}^+$	1.0	0.0	−124.5

k (ICR) = 2.0 $\times 10^{-10}$ cm^3 s^{-1}

No reaction between $C_7H_7^+$ (from cycloheptatriene) and C_2H_4 was observed in the SIFT.

4)		ICR	SIFT	ΔH^0
$C_7H_7^+ +$ CH$_3$CCH	$\rightarrow C_{10}H_{11}^+$	1.0		−319.4
$C_7H_7^+ +$ CH$_3$CCH + M	$\rightarrow$ association	(1.0)	1.0	−319.4
b-$C_7H_7^+ +$ C$_3$H$_4$(allene) + M	$\rightarrow$ No reaction		0.0	
a-$C_7H_7^+ +$ C$_3$H$_4$(allene) + M	$\rightarrow$ association		1.0	

k (ICR) = 1.4 $\times 10^{-10}$ cm^3 s^{-1}
k$_3$ (ICR) = 7.9 $\times 10^{-24}$ cm^6 s^{-1} (M = CH$_3$CCH)
b-k (SIFT) $\leq 5.0 \times 10^{-13}$ cm^3 s^{-1} in 0.5 Torr of He
a-k (SIFT) = 7.0 $\times 10^{-10}$ cm^3 s^{-1} in 0.5 Torr of He
a-k$_3$ (SIFT) $\geq 4.3 \times 10^{-26}$ cm^6 s^{-1} (M = He)

In the SIFT the ion was made from cycloheptatriene. The primary signal in the reaction with allene was a mixture of two isomers: a reactive population (a) comprising 60% and an unreactive population (b) at 40%.

Reactions of the $C_9H_7^+$ Ion

In the ICR, the $C_9H_7^+$ ion was made from a mixture of HCCCH$_3$ and C_2H_4.

1)		ICR	SIFT	ΔH^0
$C_9H_7^+ +$ CH$_3$CCH	$\rightarrow$ association	1.0		−196.4
$C_9H_7^+ +$ CH$_3$CCH + M	$\rightarrow$ association	1.0		−196.4

k (ICR) = 2.8 $\times 10^{-9}$ cm^3 s^{-1}
k$_3$ (ICR) = 7.9 $\times 10^{-24}$ cm^6 s^{-1}

Conclusions

One of the primary objectives of this study was to provide a better understanding of the ion chemistry occurring in Titan's ionosphere. The principal ionization sources on Titan are solar photoionization and electron impact of nitrogen particularly when Titan resides within the magnetosphere of Saturn. Some of these ions are generated with excess energy [17], and the methods we have employed here have examined the effect of additional energy present in secondary hydrocarbon ions before collisional stabilization occurs. Of the neutral reactants, methane is the most abundant component for reaction with nitrogen ions where it forms a range of hydrocarbon and nitrile ions which then react with other hydrocarbons [18].

In our previous investigation [4] we reported the first application of the method used here in which we examined ion-molecule reactions occurring in pure hydrocarbons at pressure up to 1×10^{-3} torr. In this study we have extended the earlier measurements from single hydrocarbons to binary mixtures. We have examined all ions that are present in the binary mixtures and have modeled their mass and abundance according to existing kinetics. In a number of cases it was necessary to modify the kinetic database to achieve agreement between experiment and model.

An interesting comparison can be made between the ion chemistry of Earth and Titan. Both have significant nitrogen-based atmospheres but there the similarity stops. The positive ion-chemistry on earth is restricted to a modest number of reactions dominated by O^+, O_2^+ in the highest altitude region (F region), NO^+, O_2^+ in the intermediate E region, and water hydrates in the lower altitude D region [19]. The water ion hydrates are formed from association reactions of weakly bound clusters of other ions that are switched out by water [19]. Termolecular association reactions are pressure dependent. The higher the pressure (i.e., the lower is the

altitude) then the larger is their rate coefficient. The critical factors in evaluating the important association reactions are the termolecular rate coefficients, the temperature and the pressure. Most association reactions recorded in this investigation are sufficiently fast to warrant inclusion in models of Titan's ion chemistry. The role of association reactions is amplified in Titan's ionosphere compared to Earth because of two important factors. The ionosphere of Titan is considerably colder than Earth and also the binding energies of many hydrocarbon ions with hydrocarbons are much greater than $NO^+ \cdot H_2O$. It is therefore anticipated that association reactions play a much more important role in the ionosphere of Titan than they do on Earth. Of the ninety four reactions examined in this room-temperature investigation, over one third of them resulted in association. Furthermore, the interwoven chemistry resulting from the introduction of hydrocarbon ion reactions with hydrocarbon neutrals as occurs in Titan's ionosphere increases the matrix of reactions enormously.

Acknowledgments

References

1. Anicich, V. G.; Milligan, D. B.; Fairley, D. A.; McEwan, M. J. Termolecular Ion-Molecule Reactions in Titan's Atmosphere. I. Principal Ions with Principal Neutrals. *Icarus* **2000,** *146,* 118–124.
2. Milligan, D. B.; Freeman, C. G.; Maclagan, R. G. A. R.; McEwan, M. J.; Wilson, P. F.; Anicich, V. G. Termolecular Ion-Molecule Reactions in Titan's Atmosphere. II. The Structure of the Association Adducts of HCNH$^+$ with C_2H_2 and C_2H_4. *J. Am. Soc. Mass Spectrom.* **2001,** *12,* 557–564.
3. Anicich, V. G.; McEwan, M. J. Termolecular Ion-Molecule Reactions in Titan's Atmosphere. III. Clustering of Ions. *Icarus* **2001,** *154,* 522–530.
4. Anicich, V. G.; Wilson, P. F.; McEwan, M. J. Termolecular Ion-Molecule Reactions in Titan's Atmosphere. IV. A Search Made at up to 1 Micron in Pure Hydrocarbons. *J. Am. Soc. Mass Spectrom.* **2003,** *14,* 900–915.
5. Anicich, V. G.; Wilson, P. F.; McEwan, M. J. A SIFT Study of Some Reactions in Titan's Atmosphere. Reactions of N^+, N_2^+ and HCN^+ with CH_4, C_2H_2 and C_2H_4. *J. Am. Soc. Mass Spectrom.* **2004,** *15,* 1148–1155.
6. Keller, C. N.; Anicich, V. G.; Cravens, T. E. Model of Titan's Ionosphere with Detailed Hydrocarbon Ion Chemistry. *Planetary Space Sci.* **1998,** *46,* 1157–1174.
7. Toublanc, D.; Parisot, J. P.; Brillet, J.; Gautier, D.; Raulin, F.; McKay, C. P. Photochemical Modeling of Titan's Atmosphere. *Icarus* **1995,** *113,* 2–26.
8. Banaszkiewicz, M.; Lara, L. M.; Rodrigo, R.; Lopez-Moreno, J. J.; Molina-Cuberos, G. J. A Coupled Model of Titan's Atmosphere and Ionosphere. *Icarus* **2000,** *147,* 386–404.
9. McEwan, M. J.; Denison, A. B.; Anicich, V. G.; Huntress, W. T., Jr. Association Reactions at Low Pressure. I. Collision-Stabilized Association Below 1 Micron. *Int. J. Mass Spectrom. Ion Processes* **1987,** *81,* 247–257.
10. Wronka, J.; Ridge, D. P. Frequency-Swept Detector for Ion Cyclotron Resonance Mass Spectrometry. *Rev. Sci. Instrum.* **1982,** *53,* 491–498.
11. McMahon, T. B.; Beauchamp, J. L. Versatile Trapped Ion Cell for Ion-Cyclotron Resonance Spectroscopy. *Rev. Sci. Instrum.* **1972,** *43,* 509.
12. Anicich, V. G. Evaluated Bimolecular Ion-Molecule Gas Phase Kinetics of Positive Ions for Use in Modeling Planetary Atmospheres, Cometary Comae, and Interstellar Clouds. *J. Phys. Chem. Ref. Data* **1993,** *22,* 1469–1569.
13. Kim, J. K.; Anicich, V. G.; Huntress, W. T., Jr. Product distributions and rate constants for the reactions of CH_3^+, CH_4^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$ and $C_2H_6^+$ ions with CH_4, C_2H_2, C_2H_4 and C_2H_6. *J. Phys. Chem.* **1977,** *81,* 1798–1805.
14. Herod, A. A.; Harrison, A. G. *Int. J Mass Spectrom. Ion Phys.* **1970,** *4,* 415–431.
15. Scott, G. B. I.; Fairley, D. A.; Freeman, C. G.; McEwan, M. J.; Adams, N. G.; Babcock, L. M. $C_mH_n^+$ reactions with H and H_2: An experimental study. *J. Phys. Chem. A* **1997,** *101,* 4973–4978.
16. Ausloos, P.; Lias, S. G.; Buckley, T. J.; Rogers, E. E. Concerning the Formation and the Kinetics of Phenylium Ions. *Int. J. Mass Spectrom. Ion Processes* **1989,** *92,* 65–77.
17. Alcaraz, C.; Nicolas, C.; Thissen, R.; Zabka, J.; Dutuit, O. $^{15}N^+ + CD_4$ and $O^+ + ^{13}CO_2$ State Selected Ion-Molecule Reactions Relevant to the Chemistry of Planetary Atmospheres. *J. Phys. Chem. A* **2004,** *108,* 9998–10009.
18. Anicich, V. G.; McEwan, M. J. Ion-Molecule Chemistry in Titan's Ionosphere. *Planetary Space Sci.* **1997,** *45,* 897–921.
19. Ferguson, E. E. Ion Chemistry of Planetary Atmospheres. In *Int. Rev. Sciences. Phys. Chem. Ser. 2, Vol. XI*; Herschbach, MD. R., Ed., Butterworths: 1976; pp 93–125.