Diagnosis of a CH_4/N_2 Microwave Discharge: Ionic and Neutral Species

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The neutral and ionic products in CH_4/N_2 plasmas were studied as a function of the nitrogen partial pressure in a microwave (MW) flow tube with 2.465 MHz, 30 W, and 0.6 Torr total pressure. Mass spectrometry, coupled with Li^+ ion attachment techniques, was used to identify the products. Our study clearly showed the presence of various polymer compounds of hydrocarbons, nitriles, amines, and possibly hydrazines, as well as their ionized species. Possible reaction schemes, which may account for the observed profiles, are considered for some of these products, particularly with regard to the role of radical and ionic condensation reaction processes. An attempt was made to link both the ionic and neutral species to a proposed mechanism. It is apparent from a comparison with the neutral species in this plasma that the proton transfer reaction plays a significant role in the ion chemistry of the CH_4/N_2 plasma.

Introduction

Microwave discharge methods[1,2] have been used to form various kinds of chemical substances. Among them, the use of CH_4/N_2 plasma formed in an electric discharge first received attention in the synthesis of HCN.[3] Yields of HCN have been rather extensively studied in both dc and rf thermal plasmas. A glow discharge of a mixture of CH_4 and N_2 has been used to generate the HNCN radical.[4]

More recently, there has been much interest in the deposition of carbon nitride film because of the existence of the superhard phase predicted theoretically by Liu and Cohen.[5] CH_4/N_2 discharge plasma has been studied with a view to obtain such carbon nitride films,[6] but its diagnosis is hindered by the major experimental problem of explaining the chemical reactions in the MW plasma. A tool to accurately characterize the CH_4/N_2 discharge plasma would be desirable.

Considerable effort has been expended in recent years in attempting to describe the chemistry of the atmosphere of Titan.[7−11] Since the major constituents in the atmosphere of Titan are CH_4 and N_2, a CH_4/N_2 discharge was employed in a recent set of experiments to simulate the upper altitudes of Titan's atmosphere. Only in the past few years have these experiments approached a minimum set of products that might acceptably model Titan's atmosphere.[7] Much of the matter in the universe is ionized, and the corresponding ionized chain compounds[12] are also expected to abound. The mass spectrometry of these ionized chain compounds is of considerable interest.

The understanding of reactions in plasmas is largely impeded due to the complex nature of plasmas. The most difficult task is to determine the relative importance of ions and neutral species in these reactions. During the past 40 years, several reports of mass spectrometric sampling of electric discharges have appeared, but few attempts have been made to obtain correlations between the ions and neutral species, and the extent of their participation is still unclear.

We recently reported the detection of various neutral polymer hydrocarbon (HC) radicals.[13,14] This was followed by a second report on the CH_4/O_2 plasma,[15,16] demonstrating (a) the complete Li^+ adduct mass spectrum for identification of the products, (b) evidence that many O-containing neutral chemical species are generated in the plasma, and (c) that the identified species include alcohols, aldehydes, and possibly organic peroxides. The present investigation continues this work and deals with the ionic species as well as the neutral species.

The aims of this paper are (a) to report both the ionic and neutral products in CH_4/N_2 MW discharge plasmas as measured by mass spectrometric diagnosis, (b) to present dependencies of the distributions of the species as functions of gas composition, (c) to use the product analysis to comment on the degree to which neutral products contribute to the formation of some ionic products, and (d) to gain a better understanding of the chemistry involved in the system by considering plausible reactions.

Experimental Section

Detailed descriptions of the experimental setup can be found elsewhere.[13,17,18] We shall briefly review the main points here. The formation and involvement of products (M) in the MW plasma were directly confirmed through their Li^+ ion attachments. Lithium ions are produced by heating a glass bead containing lithium oxide in an aluminosilicate matrix (Li^+ emitter). The experimental setup was such that, in the process of termolecular association reactions, Li^+ ions attached to the chemical species (M) to produce $(M + Li)^+$ ions. The Li^+ adduct ions were transferred to a quadrupole mass spectrometer through a skimmer, and the spectrum was recorded. The apparatus can sample the ionic and neutral species that effuse through the discharge tube.

The MW source was constructed from a straight quartz tube (4 mm inner diameter, 6 mm outer diameter, 30 cm long). A mixture of dry N_2 and CH_4 is formed in a dynamic dilution system and metered into the flow tube. The MW plasma was created by connecting a cavity to a 2.465 MHz MW generator through a matching network.

Mass spectra were obtained with plasma activation in 2 modes: Mode I, in the presence of Li^+, and Mode II, in the absence of Li^+. The intensity of any mass peak in Mode II was

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TABLE 1: Assignment of Neutral and Ionic Products Formed by CH_4/N_2 MW Discharge

m/*z*	neutral species N-containing/hydrocarbon[a]	ionic species N-containing/hydrocarbon
17		NH_3^+/CH_4H^+
18		NH_3H^+/H_2O^+
23	...../CH_4Li^+	
24	$NH_3Li^+/OHLi^+$	
25	...../H_2OLi^+	
28		$HCNH^+/C_2H_3H^+$
29		...../$C_2H_4H^+$
30		$CH_2{=}NHH^+/C_2H_5H^+$
31		...../$C_2H_6H^+$
32		$CH_3NH_2H^+$/.....
34	$HCNLi^+/C_2H_3Li^+$	
36	$CH_2{=}NHLi^+/C_2H_5Li^+$	
38	$CH_3NH_2Li^+$/.....	...../C_3HH^+
39		...../$C_3H_2H^+$
40		...../$C_3H_3H^+$
41		...../$C_3H_4H^+$
42		$CH_3CNH^+/C_3H_5H^+$
43		$H_2NCNH^+/C_3H_6H^+$
44		$C_2H_3NH_2H^+/C_3H_7H^+$
45		$CH_3N{=}NHH^+/C_3H_8H^+$
46	...../$C_3H_3Li^+$	$C_2H_5NH_2H^+$/.......
48	$CH_3CNLi^+/C_3H_5Li^+$	
49	$H_2NCNLi^+/C_3H_6Li^+$	
50	$C_2H_3NH_2Li^+/C_3H_7Li^+$	
51	$CH_3N{=}NHLi^+/C_3H_8Li^+$ [b]	
52	$C_2H_5NH_2Li^+$/.......	$HCCCNH^+/C_4H_3H^+$
54		$C_2H_3CNH^+/C_4H_5H^+$
56		$C_2H_5CNH^+/C_4H_7H^+$
57		$C_2H_3N{=}NHH^+/C_4H_8H^+$
58	$HCCCNLi^+/C_4H_3Li^+$	$C_3H_5NH_2H^+$/.......
59	$NCCNLi^+/C_4H_4Li^+$	$C_2H_5N{=}NHH^+$/.......
60	$C_2H_3CNLi^+/C_4H_5Li^+$	$C_3H_7NH_2H^+$/.....
62	$C_2H_5CNLi^+/C_4H_7Li^+$	
63	$C_2H_3N{=}NHLi^+/C_4H_8Li^+$	
64	$C_3H_5NH_2Li^+/C_4H_9Li^+$	...../$C_5H_3H^+$
65	$C_2H_5N{=}NHLi^+/C_4H_{10}Li^+$	
66	$C_3H_7NH_2Li^+$/.....	$CH_3CCCNH^+/C_5H_5H^+$
67		$NC{-}CH_2{-}CNH^+$/.....
68		$C_3H_5CNH^+/C_5H_7H^+$
69		$C_3H_3N{=}NHH^+$/.....
70		$C_3H_7CNH^+/C_5H_9H^+$
72	$CH_3CCCNLi^+/C_5H_5Li^+$	$C_4H_7NH_2H^+$/.....
73	$NC{-}CH_2{-}CNLi^+$/.....	
74	$C_3H_5CNLi^+/C_5H_7Li^+$	
75	$C_3H_3N{=}NHLi^+/C_5H_8Li^+$	
76	$C_3H_7CNLi^+/C_5H_9Li^+$	
77	$C_3H_5N{=}NHLi^+$/.....	
78	$C_4H_7NH_2Li^+/C_5H_{11}Li^+$	
79	$C_3H_7N{=}NHLi^+/C_5H_{12}Li^+$	$NC{-}(CH)_2{-}CNH^+$/.....
80	$C_4H_9NH_2Li^+$/.....	
82		$C_4H_7CNH^+$/.....
83	...../$C_6H_4Li^+$	
85	...../$C_6H_6Li^+$	
87	$NC{-}(CH_2)_2{-}CNLi^+$/.....	
88	$C_4H_7CNLi^+$/.....	
89	$C_4H_5N{=}NHLi^+$/.....	
90	$C_4H_9CNLi^+$/.....	
91	$C_4H_7N{=}NHLi^+$/.....	
92	$C_5H_9NH_2Li^+$/.....	
93	$C_4H_9N{=}NHLi^+$/.....	
94	$C_5H_{11}NH_2Li^+$/.....	
101	$NC{-}(CH_2)_3{-}CNLi^+$/.....	
102	$C_5H_9CNLi^+$/.....	
103	$C_5H_7N{=}NHLi^+$/.....	
104	$C_5H_{11}CNLi^+$/.....	
105	$C_5H_9N{=}NHLi^+$/.....	
106	$C_6H_{11}NH_2Li^+$/.....	
107	$C_5H_{11}N{=}NHLi^+$/.....	
115	$NC{-}(CH_2)_4{-}CNLi^+$/.....	
116	$C_6N_{11}CNLi^+$/.....	
117	$C_6H_9N{=}NHLi^+$/.....	
118	$C_6H_{13}CNLi^+$/.....	
119	$C_6H_{11}N{=}NHLi^+$/.....	
120	$C_7H_{13}NH_2Li^+$/.....	
121	$C_6H_{13}N{=}NHLi^+$/.....	
129	$NC{-}(CH_2)_5{-}CNLi^+$/.....	
130	$C_7H_{13}CNLi^+$/.....	
131	$C_7H_{11}N{=}NHLi^+$/.....	
132	$C_7H_{15}CNLi^+$/.....	
133	$C_7H_{13}N{=}NHLi^+$/.....	
134	$C_8H_{15}NH_2Li^+$/.....	
143	$NC{-}(CH_2)_6{-}CNLi^+$/.....	
144	$C_8H_{15}CNLi^+$/....	

[a] The hydrocarbon species were assigned from the corresponding mass spectra of the CH_4/Ar MW discharge plasma. [b] The saturated hydrocarbons that have a low Li^+ affinity should have abundance higher than we detected.

subtracted from the corresponding mass peak in Mode I and the result (Mode I − Mode II) shows the Li^+ adducts of particular neutral products. Mode II is a mode of ionic species detection. The mass spectrometric measurements were performed at the downstream position with respect to the microwave cavity and the direction of the gas flow.

The analysis of the mass spectra was made in terms of mass assignment and classification. A control experiment was performed using a continuous flow plasma discharge with Ar in place of the N_2. On the simple basis of the inertness of Ar, different products might be expected. When detecting neutrals by Li^+ ion attachment, the sensitivity depends on their Li^+ affinity. Fortunately, N-containing hydrocarbon species have sufficiently high Li^+ affinities that they are attached at nearly collision rates, so that little discrimination is expected. However, until the rate coefficients for Li^+ attachment to a wide range of N-containing hydrocarbons have been measured, some caution must be applied.

Results and Discussion

1. Mass Spectrum. Typical mass spectra over the mass range *m*/*z* 20−150 obtained for 80%CH_4−20%N_2 and 80%CH_4−20%Ar plasmas are shown in Figure 1 parts A and B, respectively. These peaks were taken with MW power at 30 W, cavity position 60 mm away from the Li^+ emitter, and a mixture flow rate of 4 mL/min.

The CH_4/N_2 plasmas led to the formation of many neutral species, while the products formed in the CH_4/Ar plasmas were mainly hydrocarbons, including radicals such as C_nH_{2n+1} and C_nH_{2n-1}, and some molecules. Most of these peaks have the same *m*/*z* values as those that appeared in the CH_4/N_2 plasma. However, their intensities were much smaller, indicating the production of many new types of N-containing species in the CH_4/N_2 system.

The mass spectra of the 80%CH_4−20%N_2 plasma show a significant difference in the distribution of neutral products in comparison with those of the 10%CH_4−90%N_2 plasma in previous reports.[19] Larger polymer species were observed in greater abundance in the 80%−20% plasma spectra. In the case of Mode II (the ionic mode), two characteristic features should be pointed out. (a) The nitrogen components in the CH_4 plasma led to the formation of many N-containing ionic species, just like the neutral products. However, there was not such a significant difference between the 80%−20% and the 10%−

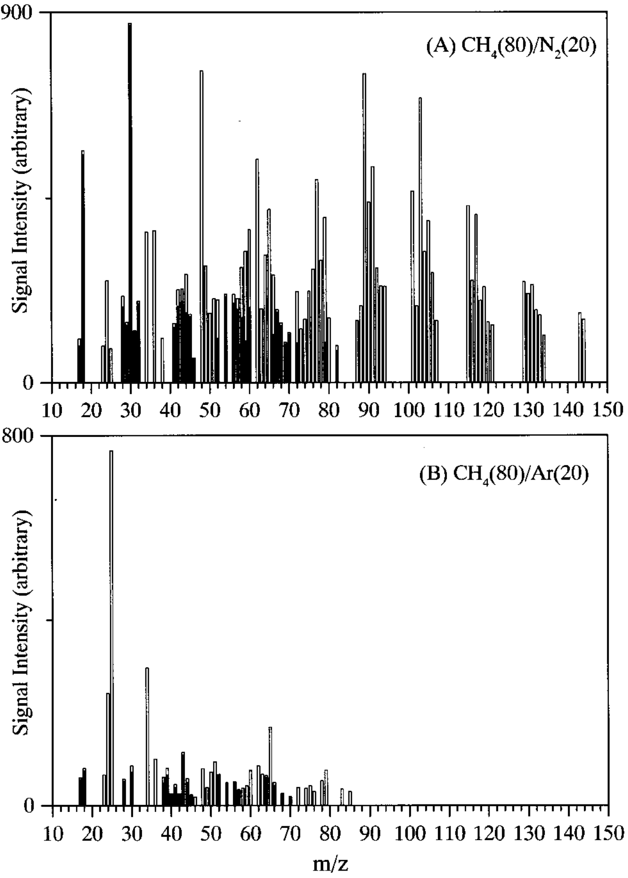

Figure 1. Mass spectra showing the neutral and ionic products formed in (A, upper chart) the 80%CH_4/20%N_2 and (B, lower chart) the 80%CH_4/20%Ar MW discharge plasmas. The experimental conditions (30 W, 0.6 Torr) were exactly the same in both plasmas. Peaks greater than 3% of the base peak in the spectrum are shown. Note: the signal intensity scale of (A) is different from that of (B). Solid-bar peaks were taken in the Li^+-off condition (Mode II, ionic species detection). The open-bar peaks in the mass spectra are attributed to ion attachment to neutral, genuine chemical species effusing from the plasma. These were sampled in the Li^+-on conditions (Mode I). The main peaks and these possible assignments and classifications are shown in Tables 1 and 2.

90% plasmas in the distribution of the ionic products. The main peaks detected for 80%CH_4−20%N_2 plasma and their possible assignments are shown in Table 1. It should be noted that as far as the assignment of the mass spectral peaks goes, the validity is based principally on the mass number. (b)As was expected from data regarding the neutral species in previous reports[19] where the experimental conditions were close to the present ones, the MW discharge in CH_4/N_2 gave 3 types of neutral N-containing species: nitriles, amines,and hydrazines, and hydrocarbons (HCs). It should be noted that the C_nH_{2n+1}-$CNLi^+$ peaks are isobaric with the $C_nH_{2n-3}NH_2HLi^+$ peaks of one lower carbon number. We assume from the classification analysis (see next section) that both were present in the plasma.

The ionic species are listed in the left column of Table 1. Almost all the species are protonated species, suggesting that the proton transfer reaction is a more likely (dominant) process than the electron ionization. The peak assignments of these ionic products are also not free of ambiguity. The $C_nH_{2n+1}CN$ compound peaks are isobaric with C_nH_{2n-1} peaks of one higher carbon number. Because HC ions of the C_nH_{2n-1} type were observed clearly in the CH_4/Ar plasma (see Figure 1), we tentatively speculate that both protonated nitriles and hydrocarbon ions are formed. The ion spectra for the CH_4(80)/Ar(20) mixture were essentially identical to those measured in an earlier study of ionic products in a CH_4 MW plasma.[20]

2. Classification. Both neutral and ionic species are classified (Table 2) into groups made up of species having the following formulas. The products included several saturated and unsaturated nitriles, $C_nH_{2n+1}CN$ (up to $n = 7$), $C_nH_{2n-1}CN$ ($n = 8$), $C_nH_{2n-3}CN$ ($n = 3$), and $CN-(CH_2)_n-CN$ ($n = 6$). Their abundance seems to decrease only slowly with chain length.

Alkylamines with single, double, and triple bonds, with homologous members were often present in roughly equal yields (within a factor of 4), while some products are formulated as $C_nH_{2n+1}N{=}NH$, $C_nH_{2n-1}N{=}NH$, and $C_nH_{2n-3}N{=}NH$. These homologues (corresponding to additions of CH_2 units) may be hydrazines, but other assignments are possible. Minor yields of $C_nH_{2n+1}N-NH_2$, $C_nH_{2n-1}N-NH_2$, and $C_nH_{2n-3}N-NH_2$ would have escaped detection.

Several hydrocarbons were identified in the CH_4/Ar plasma. Various free radicals as well as stable polymer molecules were clearly present. Radicals such as C_nH_3 ($n = 2$, 3, and 4), C_nH_5 ($n = 2$, 3, 4, and 5), C_nH_7 ($n = 4$ and 5), and C_nH_9 ($n = 4$ and 5) were detected. Some of them may be identified as species having an aromatic ring such as C_6H_4 and C_6H_6.

We also obtained other intense peaks at m/z 36 and 49, which can be assigned as $H_2C{=}NHLi^+$ [21] and H_2NCNLi^+.[22] We suggest that hot NH_2 or CN radicals generated by dissociation of initial amine or nitrile products can react with each other and with hydrocarbon species to produce these unfamiliar organic compounds[23] by way of their recombination.

Ionic Species. The ionic products include protonated alkylamines with single, double, and triple bonds, with homologous members, while some products are formulated as C_nH_{2n+1}-NH_2H^+, $C_nH_{2n-1}NH_2H^+$, $C_nH_{2n+1}N{=}NHH^+$, $C_nH_{2n-1}N{=}NHH^+$, and $C_nH_{2n-3}N{=}NHH^+$. The $C_nH_{2n+1}CNH^+$ homologues were the most common species with n up to 3. All the ionic products were species whose corresponding neutrals were observed in the plasma.

3. Products as a Function of Gas Component. When large amounts of nitrogen are added to a methane discharge a drastic change is expected. The effect is readily visible as nitrogen changes the color from yellowish blue to light pink and, as the N_2 concentration increases, the discharge expands. The nitrogen components in the CH_4 plasma will lead to variation of the product distribution.

We plotted the evolution of the peak intensities of various gaseous products in CH_4/N_2 plasma, as a function of the gas composition (Figure 2). The peak heights we plotted were those of CH_3CNLi^+ ($m/z = 48$), $C_2H_3NH_2Li^+$ ($m/z = 50$), $C_2H_3N{=}NHLi^+$ ($m/z = 63$), and $NC-CH_2-CNLi^+$ ($m/z = 73$), which we chose to represent the major products, classified as C_nH_{2n+1}-CN, $C_nH_{2n-1}NH_2$, $C_nH_{2n-1}N{=}NH$, and $NC-(CH_2)_n-CN$ compounds, respectively. The homologous species may follow similar variation patterns.

Figure 3 shows the evolution of CH_3CNH^+ ($m/z = 42$), C_2H_3-NH_2H^+ ($m/z = 44$), $C_2H_3N{=}NHH^+$ ($m/z = 57$), and $NC-CH_2-CNH^+$ ($m/z = 67$) intensities relative to the percentage of N_2 in the CH_4/N_2 mixture. We chose these compounds as representing protonated species for CH_3CN, $C_2H_3NH_2$, $C_2H_3N{=}NH$ and $NC-CH_2-CN$ molecules, respectively, which were investigated in terms of their productivity as a function of the gas component (Figure 2), to derive the relationship between neutral and ionic species.

From the overview of the variations in abundance of neutral or ionic species as a function of gas composition, we make several remarks. (a) We can reasonably assume that N-

TABLE 2: Classification Analysis of Neutral and Ionic Products Formed the MW Discharge of the Mixture of $CH_4(80\%)/N_2(20\%)$[a]

	neutral species	ionic species
nitriles		
$C_nH_{2n+1}CN$[b]	HCN, CH_3CN, C_2H_5CN, C_3H_7CN, C_4H_9CN, $C_5H_{11}CN$, $C_6H_{13}CN$, $C_7H_{15}CN$	$HCNH^+$, CH_3CNH^+, $C_2H_5CNH^+$, $C_3H_7CNH^+$
$C_nH_{2n-1}CN$	C_2H_3CN, C_3H_5CN, C_4H_7CN, C_5H_9CN, $C_6H_{11}CN$, $C_7H_{13}CN$, $C_8H_{15}CN$	$C_2H_3CNH^+$, $C_3H_5CNH^+$, $C_4H_7CNH^+$
$C_nH_{2n-3}CN$	HCCCN, CH_3CCCN	$HCCCNH^+$, CH_3CCCNH^+
$NC-(CH_2)_n-CN$	NC−CN, $NC-CH_2-CN$; $NC-(CH_2)_2-CN$, $NC-(CH_2)_3-CN$, $NC-(CH_2)_4-CN$, $NC-(CH_2)_5-CN$, $NC-(CH_2)_6-CN$	$NC-CH_2-CNH^+$, $NC-(CH_2)_2-CNH^+$
amines		
$C_nH_{2n+1}NH_2$	NH_3, CH_3NH_2, $C_2H_5NH_2$, $C_3H_7NH_2$, $C_4H_9NH_2$, $C_5H_{11}NH_2$	NH_3H^+, $CH_3NH_2H^+$, $C_2H_5NH_2H^+$, $C_3H_7NH_2H^+$
$C_nH_{2n-1}NH_2$	$C_2H_3NH_2$, $C_3H_5NH_2$, $C_4H_7NH_2$, $C_5H_9NH_2$, $C_6H_{11}NH_2$, $C_7H_{13}NH_2$, $C_8H_{15}NH_2$	$C_2H_3NH_2H^+$, $C_3H_5NH_2H^+$, $C_4H_7NH_2H^+$
hydrazines		
$C_nH_{2n+1}N{=}NH$	$CH_3N{=}NH$, $C_2H_5N{=}NH$, $C_3H_7N{=}NH$, $C_4H_9N{=}NH$, $C_5H_{11}N{=}NH$, $C_6H_{13}N{=}NH$	$CH_3N{=}NHH^+$, $C_2H_5N{=}NHH^+$
$C_nH_{2n-1}N{=}NH$	$C_2H_3N{=}NH$, $C_3H_5N{=}NH$, $C_4H_7N{=}NH$, $C_5H_9N{=}NH$, $C_6H_{11}N{=}NH$, $C_7H_{13}N{=}NH$	$C_2H_3N{=}NHH^+$
$C_nH_{2n-3}N{=}NH$	$C_3H_3N{=}NH$, $C_4H_5N{=}NH$, $C_5H_7N{=}NH$, $C_6H_9N{=}NH$, $C_7H_{11}N{=}NH$	$C_3H_3N{=}NHH^+$
others		
	H_2NCN, $H_2C{=}NH$	H_2NCNH^+, $H_2C{=}NHH^+$

[a] Only N-containing species are reported. [b] The $C_nH_{2n-3}NH_2$ peaks are isobaric with the $C_nH_{2n+1}CN$ peaks of one lower *n* number. In this study they are not distinguished. We assume that the latter is dominant.

containing ionic species will increase with N_2 addition in a manner similar to the observed intensities of the N-containing neutral species (Li^+ adduct). (b) Product enhancement was found to be somehow proportional to the increase of N_2 in the gas mixture, suggesting an effect of N and N_2 consumption on the various secondary reactions producing N-containing organic compounds. (c) As the N_2 volume in the mixture increases, all the ionic peaks sharply increase to a maximum at around $60\%CH_4-40\%N_2$ (vol−vol) ratio and then decrease. The tendency for the minor N_2 component of the feed to attain a high degree of conversion is more pronounced in the case of the ionic species in contrast to neutral species where the curves vary more gradually. As expected, the discharge in the pure N_2 gases resulted in the disappearance of any N_2-derived hydrocarbon species. (d) Because of the known fast reactions of N_2^+ with CH_4, the initial distribution of ions would change significantly as the composition of the gas changed from predominantly CH_4 to predominantly N_2. However, the distribution of ionic species is barely affected by varying the percentage of N_2 over the entire component. At this moment we cannot explain these conflicting results. (e) Comparing Figures 2 and 3, it is obvious that some remarkable similarities exist between the variations with N_2 concentration of some MLi^+ and MH^+ ions. Despite the wide variation of gas components, the gross similarities in product variation suggest a common chemical process. That is, the protonation of the neutral species, formed primarily in the plasma, produces MH^+ as terminal domination ions. The proton transfer reaction is a more likely process than dissociative electron ionization or charge exchange reaction in the CH_4/N_2 plasma. This conclusion is consistent with the behavior of the protonation reagents observed in the CH_4 plasma. (f) Note, however, that some neutral and ionic species have complex dependencies on the percentage of N_2, most of which cannot be rationalized and remain unanswered to date. In other words, the experimental results show much complexity since some of the reaction products, along with ambiguous identification, appear to interfere with the analytical determination.

4. Reaction Pathway. A few types of reaction are briefly discussed to model the present results. From the present results, one would expect radical chemistry to occur in the CH_4/N_2 discharge. Active nitrogen atoms, N* (presumably ^2P and ^2D),[24] are a primary radical product; it is well-known[25] that electrons present in the plasma should serve to produce active nitrogen atoms.

If N* is supplied, then interaction between N* and CH_4 or other hydrocarbons is highly probable (highly exothermic), suggesting the production of the larger N-bearing HC species. Reactions of radical-involved condensations leading to polymeric products may well dominate the chemistry of the CH_4/N_2 discharge.

For instance, the following are the thermodynamically accessible channels and the corresponding enthalpies of reactions at $T = 298$ K for the reaction between N* and C_2H_3, which has been directly observed[14] as a major product of a CH_4 discharge plasma.

$$N^* + C_2H_3 \rightarrow CH_2CN + H \; (\Delta H^\circ = -74 \text{ kcal/mol}) \tag{1a}$$

$$\rightarrow CH_3CN \; (\Delta H^\circ = -167 \text{ kcal/mol}) \tag{1b}$$

$$\rightarrow CN + CH_3 \; (\Delta H^\circ = -46 \text{ kcal/mol}) \tag{1c}$$

$$\rightarrow HCN + CH_2 \; (\Delta H^\circ = -60 \text{ kcal/mol}) \tag{1d}$$

$$\rightarrow CHCN + H_2 \; (\Delta H^\circ = -75 \text{ kcal/mol}) \tag{1e}$$

This speculation is partially proved by the presence of the major component, CH_3CN. The cyano radical is considered capable of a whole range of additional reactions.[26] The assorted products of these reactions would result in the widespread peaks.

The most probable important reaction for the production of amine and hydrazine species is thought to be a reaction yielding an NH radical. It is well-known[27] that NH can be produced exothermically in hydrogen-active nitrogen systems. We assume from the present observation of amines and hydrazines that NH

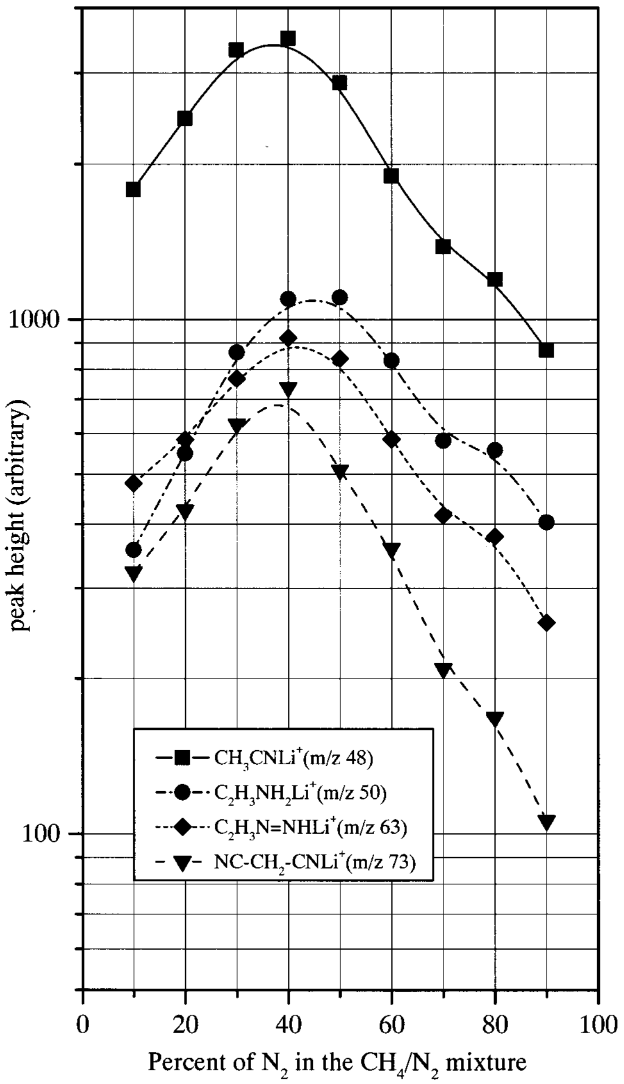

Figure 2. Li^+ adduct intensities of neutral products of CH_3CNLi^+ (*m*/*z* 48), $C_2H_3NH_2Li^+$ (*m*/*z* 50), $C_2H_3N{=}NHLi^+$ (*m*/*z* 63), $NC{-}CH_2\text{-}CNLi^+$ (*m*/*z* 73), produced in CH_4/N_2 plasmas, as a function of the proportion of N_2 in the mixture.

radicals are rapidly converted into these species in combination with many hydrocarbon species.

5. Concluding Remarks

The CH_4/N_2 MW discharge led to the production of various kinds of chemical species, and effectively demonstrated that a MW discharge is a method for generating over 50 N-bearing products. They had the formulas C_mH_nCN, $NC(CH_2)_nCN$, $C_mH_n\text{-}NH_2$, and $C_mH_nN_2H_3$, with *m* and *n* continuing on to 8 and 15, respectively.

Some interesting products found in this study were $H_2C{=}NH$ and $NC(CH_2)_nCN$. These components are predicted to be possible uses as industrial products. Direct observation of these species was allowed by the measurement of the Li^+ adduct mass spectra.

The features of the ion chemistry in CH_4/N_2 discharge can be summarized as follows: (a) the N_2 (or N atoms) interacts with various hydrocarbon species to produce nitrogenated polymer hydrocarbons, and (b) mass spectra show that these neutral species undergo protonation ion−molecule reactions with proton transfer reagents, presumably CH_5^+, $C_2H_5^+$, and so on, in addition to primary electron impact ionization of the corresponding neutral species. The distribution of ionic species from a discharge is, somehow, representative of the neutral species being protonated.

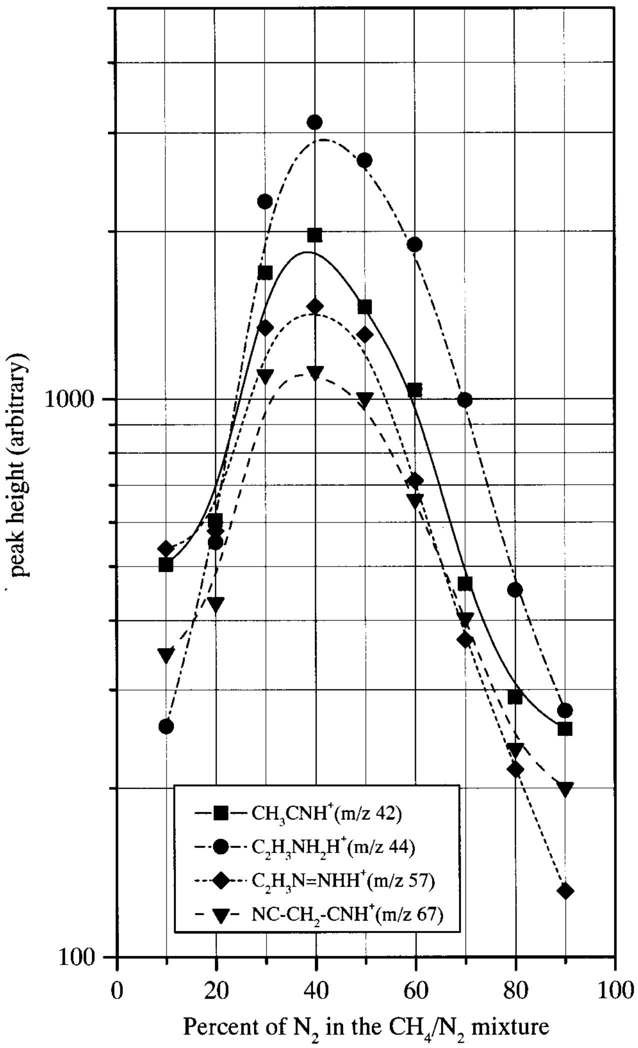

Figure 3. Mass spectral intensities of ionic species of CH_3CNH^+ (*m*/*z* 42), $C_2H_3NH_2Hi^+$ (*m*/*z* 44), $C_2H_3N{=}NHH^+$ (*m*/*z* 57) $NC{-}CH_2{-}CNH^+$ (*m*/*z* 67), produced in CH_4/N_2 plasmas, as a function of the proportion of N_2 in the mixture. Compared with Figure 2.

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