Diagnostic Studies of a CH_4/H_2 Microwave Plasma by Mass Spectrometry: Ionic and Neutral Species

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The major ionic and neutral product species in CH_4/H_2 plasmas were studied as a function of the hydrogen composition in a 2.465-GHz microwave flow tube at 30-W power and 2.2-Torr total pressure. Mass spectrometry, coupled with Li^+ ion attachment techniques, was used for identification of the products. Various neutral and ionic polymer molecules with carbon numbers of up to 12 were identified, and the relative concentration profiles of these species were determined as a function of H_2 composition in the feed gas. A possible reaction scheme to account for these observed profiles is suggested. From a comparison of the ionic species with the neutral species in this plasma, it is apparent that dissociative electron ionization is a likely process in the ion chemistry of the CH_4/H_2 plasma. In addition, a general interpretation of the results was attempted for polymeric neutral product formation, particularly with regard to the role of hydrogen atom abstraction processes and radical processes.

Introduction

The CH_4/H_2 MW (microwave) plasma[1−3] has been used in plasma chemical vapor deposition (CVD) of diamond films over the past decade. Despite the importance of understanding the properties of this system and the high level of interest, the chemistry involved with the CH_4/H_2 plasma is not yet well understood. Analysis of the CH_4/H_2 MW discharge plasma to investigate its chemical reactions is always a major experimental problem, and a useful tool to characterize it would be desirable.

In a series of laboratory experiments designed to model the chemistry of the Uranian Aurora,[4] the chemistry of H_2−He−CH_4 systems in a continuous-flow coronal discharge excited by a high-frequency voltage electrodeless source was investigated. Continuous flow ensures the processing of enough gas at low pressure and/or low CH_4 content to permit the detection of products. Much of the matter in the Aurora is ionized, and the corresponding ionized chain compounds are also expected to be abundant. Mass spectrometric studies of these ionized chain compounds in CH_4/H_2 systems are of considerable interest.

The understanding of reactions in plasmas is largely impeded due to the complex nature of plasmas.[5] The most difficult task is to determine the relative importance of ions and neutral species in these reactions. Over the past 40 years, several reports of mass spectrometric sampling of electric discharges have appeared,[6] but few attempts[7] have been made to obtain correlations between the ions and neutral species, and the extent of their participation in the reactions is still unclear.

We recently reported the detection of various neutral polymer hydrocarbon (HC) radicals.[8,9] This was followed by reports on CH_4/O_2 and CH_4/N_2 plasmas,[10−12] which presented (a) the complete Li^+ adduct mass spectrum for identification of the products, (b) evidence that many neutral chemical species are generated in the plasma, and (c) the identification of unfamiliar species such as H_2O_3,[13] $NC(CC)_nCN$,[14] and possibly C_3N_4. The present investigation continues this work and deals with the ionic as well as the neutral species in the plasma.

The aims of this paper are (a) to report both the ionic and neutral products in CH_4/H_2 MW discharge plasmas, as determined by mass spectrometry; (b) to present 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 CH_4/H_2 plasma system.

Experimental Section

Detailed descriptions of the experimental setup can be found elsewhere;[8,15,16] we will 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 (QMS) through a skimmer, and the spectrum was recorded. Use of this apparatus, which samples the ionic and neutral species that effuse through the discharge tube, facilitates separation of neutral species from ions and makes it possible to study the pertinent chemical reactions occurring in this process.

The MW source was constructed from a straight quartz tube (4-mm i.d., 6-mm o.d., 30-cm length). A mixture of dry H_2 and CH_4 was formed in a dynamic dilution system and was metered into the flow tube. The MW plasma was created by connecting a cavity to a 2.465-GHz MW generator through a matching network.

Mass spectra were obtained with plasma activation in two 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 subtracted from the intensity of the corresponding mass peak

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

Spectra were analyzed by assigning peaks according to mass-to-charge (*m*/*z*) ratios, determining peak heights as the normalized concentration of each *m*/*z* considered, and classifying species into homologous groups. Products were evaluated as a function of the gas composition, confirming the formation and involvement of free radicals in the CH_4/H_2 MW plasma.

In analysis of the products, the Li^+ adduct mass spectrum gives qualitative results, that is, the spectral data showed pronounced trends. Species are modified by the difference value of the Li^+ affinities of the respective chemical species. Fortunately, hydrocarbon species have somehow equal Li^+ affinities that they are attached at nearly equal rates, so that little discrimination is expected. However, until the Li^+ affinities to a wide range of hydrocarbons have been obtained experimentally or theoretically, some caution must be applied.

Results and Discussion

Mass Spectrum. Typical mass spectra over the mass range *m*/*z* 20−150 obtained for 10% CH_4/90% H_2 and 90% CH_4/10% H_2 plasmas are shown in Figure 1A and B, respectively (MW power, 30 W; cavity position, 60 mm away from the Li^+ emitter; gas mixture flow rate, 10 mL/min). Differences in the spectra of modes I and II result from newly formed neutrals in the plasma tube. The major peaks detected and their possible assignments are summarized in Table 1; differences between the 10% CH_4/90% H_2 and 90% CH_4/10% H_2 plasmas are also compared. The ionic species are listed in the left column of Table 1. The peak assignments of these products are not free of ambiguity; for instance, the C_nH_{12} peaks are isobaric with C_{n+1} peaks of one higher carbon number.

The mass spectra of many saturated and unsaturated hydrocarbons (HCs) of both neutrals and ions in the microwave plasma indicate that polymerization to higher hydrocarbons (up to C_{12}) occurred; various types of reactions, such as ion−molecule and radical−molecule reactions, can lead to polymer formation in this system. The mass spectra of the 90% CH_4/10% H_2 and 10% CH_4/90% H_2 plasmas show a significant difference in the distribution of neutral products. Larger polymer species were observed in greater abundance in the 90% CH_4/10% H_2 plasma spectra. In mode II (the ionic mode), two characteristic features are apparent: a lower number of peaks are present in the 90% CH_4/10% H_2 plasma, and the higher hydrogen composition in the CH_4/H_2 plasma led to the formation of many ionic species.

Classification. Both neutral and ionic species were classified (Table 2) into groups made up of species having the same carbon number; abundance of each group appears to vary with hydrogen number.

Several neutral HCs were identified in the CH_4/H_2 plasma. Various free radicals, such as C_nH_3 ($n = 2-4$), C_nH_5 ($n = 2-5$), C_nH_7 ($n = 4, 5$), and C_nH_9 ($n = 4, 5$), as well as stable polymer molecules were clearly present, and some species were identified as aromatic. Intense peaks at *m*/*z* 43, 55, and 67 were assigned as carbon clusters, C_3Li^+, C_4Li^+, and C_6Li^+, with the even-numbered carbon clusters predominant. It is suggested that hot H radicals generated by the dissociation of hydrogen can react with HC species to produce these compounds through an abstraction reaction.

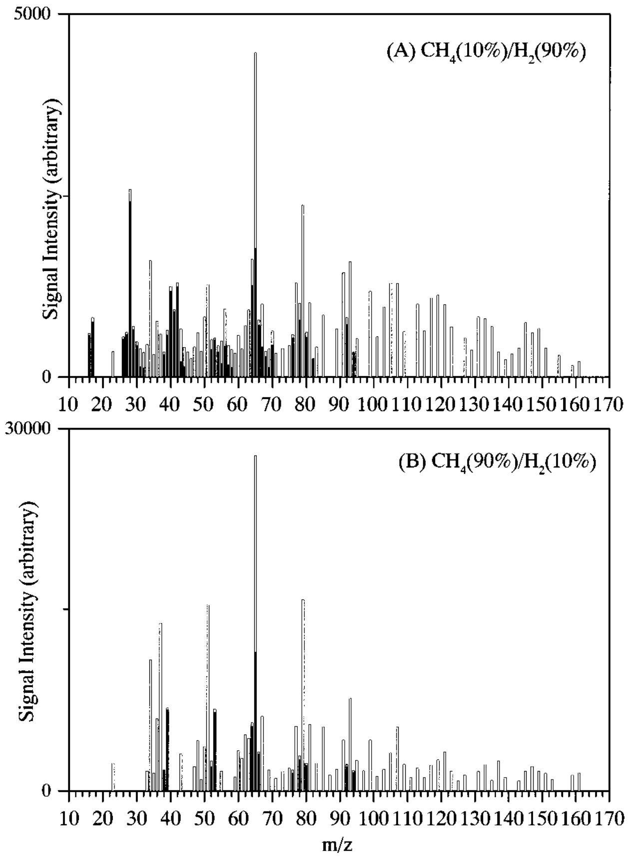

Figure 1. Mass spectra showing the neutral and ionic products formed in 10% CH_4/90% H_2 (A, upper chart) and 90% CH_4/10% H_2 (B, lower chart) MW discharge plasmas. Experimental conditions (30 W, 2.2 Torr) were exactly the same in both plasmas. Peaks greater than 3% of the base peak in the spectrum 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 condition (mode I). The main peaks and the possible assignments and classifications are shown in Tables 1 and 2.

The ionic products included homologous HC species with single, double, and triple bonds and some species, such as $C_6H_6^+$ and $C_6H_8^+$, with aromatic rings; even-numbered mass ions were predominant. The $C_nH_{2n+2}^+$ 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.

C−C bond production is clearly indicated from the presence of $C_2H_n^+$ ($n = 2-7$), $C_3H_n^+$ ($n = 2, 4, 5$), $C_4H_n^+$ ($n = 2-7$), $C_5H_n^+$ ($n = 2-4$), and $C_6H_n^+$ ($n = 2-5$). Ion−molecule reactions certainly play a great role in the chemistry of CH_4/H_2 plasmas, and a rationalization of the ionic products in the discharge must include reactions of ions with neutral methane.

Products as Functions of Gas Component Composition. The effects of feed gas composition in the discharge tube were investigated at 30-W power and 2.2-Torr pressure to determine the variation of the product distribution with changes in the amount of hydrogen. Figure 2 shows the evolution of the (normalized) peak intensities of various gaseous products [$C_2H_3Li^+$ (*m*/*z* 34), $C_2H_5Li^+$ (*m*/*z* 36), $C_4H_{10}Li^+$ (*m*/*z* 65), C_6Li^+ (*m*/*z* 79), $C_6H_2Li^+$ (*m*/*z* 81), and $C_6H_4Li^+$ (*m*/*z* 83)] in CH_4/H_2 plasma as a function of gas composition. We chose these peak heights to represent the major products, classified as C_nH_{2n+1}, C_nH_{2n-1}, C_nH_{2n+2}, C_n and aromatic compounds. The homologous species may follow similar variation patterns.

Figure 3 shows the evolution of $C_2H_4^+$ (*m*/*z* 28), $C_2H_5^+$ (*m*/*z*

TABLE 1: Assignment of Mass Spectral Peaks and Their Relative Peak Intensities for 10% CH_4/90% H_2 and 90% CH_4/10% H_2 Plasmas with a MW Power of 30 W and a CH_4/H_2 Flow Rate of 10 cm^3/min[a]

	neutral species			ionic species		
		intensity			intensity	
m/z	formula	10%CH_4/ 90%H_2	90%CH_4/ 10%H_2	formula	10%CH_4/ 90%H_2	90%CH_4/ 10%H_2
16				CH_4^+	22	
17				CH_5^+	31	
23	CH_4Li^+	13	14			
26				$C_2H_2^+$	21	
27				$C_2H_3^+$	22	
28				$C_2H_4^+$	99	
29				$C_2H_5^+$	26	
30				$C_2H_6^+$	18	
33	$C_2H_2Li^+$	17	10			
34	$C_2H_3Li^+$	60	66			
35	$C_2H_4Li^+$	12	9			
36	$C_2H_5Li^+$	29	37			
37	$C_2H_6Li^+$	22	85			
38				$C_3H_2^+$	13	11
39				$C_3H_3^+$	24	42
40				$C_3H_4^+$	47	
41				$C_3H_5^+$	35	
42				$C_3H_6^+$	49	
43	C_3Li^+	17	19	$C_3H_7^+$	8	
44	C_3HLi^+	10		$C_3H_8^+$	5	
45	$C_3H_2Li^+$	9				
46	$C_3H_3Li^+$	10				
47	$C_3H_4Li^+$	16	12			
48	$C_3H_5Li^+$	23	25			
49	$C_3H_6Li^+$	13	6			
50	$C_3H_7Li^+$	31	22			
51	$C_3H_8Li^+$	48	94			
52				$C_4H_4^+$	19	14
53				$C_4H_5^+$	20	40
54				$C_4H_6^+$	16	
55	C_4Li^+	12	10	$C_4H_7^+$	7	
56	C_4HLi^+	19		$C_4H_8^+$	16	
57	$C_4H_2Li^+$	10		$C_4H_9^+$	6	
58	$C_4H_3Li^+$	9		$C_4H_{10}^+$	5	
59	$C_4H_4Li^+$	12	7			
60	$C_4H_5Li^+$	22	20			
61	$C_4H_6Li^+$	14	16			
62	$C_4H_7Li^+$	27	29			
63	$C_4H_8Li^+$	35	27			
64				$C_5H_4^+$	61	34
65	$C_4H_{10}Li^+$	100	100	$C_5H_5^+$	40	41
66				$C_5H_6^+$	29	19
67	C_5Li^+	22	38	$C_5H_7^+$	16	
68				$C_5H_8^+$	13	
69	$C_5H_2Li^+$	9	11	$C_5H_9^+$	5	
70				$C_5H_{10}^+$	24	
71	$C_5H_4Li^+$	12	6			
73	$C_5H_6Li^+$	15	10			
75	$C_5H_8Li^+$	16	11			

	neutral species			ionic species		
		intensity			intensity	
m/z	formula	10%CH_4/ 90%H_2	90%CH_4/ 10%H_2	formula	10%CH_4/ 90%H_2	90%CH_4/ 10%H_2
76				$C_6H_4^+$	22	11
77	$C_5H_{10}Li^+$	49	33			
78				$C_6H_6^+$	38	18
79	C_6Li^+	89	97			
80				$C_6H_8^+$	23	14
81	$C_6H_2Li^+$	38	34			
82				$C_6H_{10}^+$	10	
83	$C_6H_4Li^+$	15	14			
85	$C_6H_6Li^+$	32	32			
87	$C_6H_8Li^+$		8			
89	$C_6H_{10}Li^+$	25	11			
91	C_7Li^+	54	26			
92				$C_7H_8^+$	31	13
93	$C_7H_2Li^+$	59	47			
94				$C_7H_{10}^+$	13	10
95	$C_7H_4Li^+$	20	16			
97	$C_7H_6Li^+$		10			
99	$C_7H_8Li^+$	44	26			
101	$C_7H_{10}Li^+$	21	7			
103	C_8Li^+	36	11			
105	$C_8H_2Li^+$	48	19			
107	$C_8H_4Li^+$	48	32			
109	$C_8H_6Li^+$	23	13			
111	$C_8H_8Li^+$		7			
113	$C_8H_{10}Li^+$	38	12			
115	C_9Li^+	24	7			
117	$C_9H_2Li^+$	41	13			
119	$C_9H_4Li^+$	42	16			
121	$C_9H_6Li^+$	37	20			
123	$C_9H_8Li^+$	26	10			
125	$C_9H_{10}Li^+$		5			
127	$C_{10}Li^+$	20	8			
129	$C_{10}H_2Li^+$	14				
131	$C_{10}H_4Li^+$	31	10			
133	$C_{10}H_6Li^+$	30	13			
135	$C_{10}H_8Li^+$	26	5			
137	$C_{10}H_{10}Li^+$	13	15			
139	$C_{11}Li^+$	9	7			
141	$C_{11}H_2Li^+$	12				
143	$C_{11}H_4Li^+$	15	5			
145	$C_{11}H_6Li^+$	28	10			
147	$C_{11}H_8Li^+$	23	12			
149	$C_{11}H_{10}Li^+$	25	10			
151	$C_{12}Li^+$	15	9			
153	$C_{12}H_2Li^+$		6			
155	$C_{12}H_4Li^+$	11				
159	$C_{12}H_8Li^+$	6	8			
161	$C_{12}H_8Li^+$	8	9			

[a] Pressure 2.2 torr. [b] Peak intensity is normalized to the $C_4H_{10}Li^+$ peak. Peaks greater than 5% of reference peak in the spectrum are listed.

29), $C_3H_4^+$ (*m/z* 40), $C_4H_4^+$ (*m/z* 52), $C_5H_5^+$ (*m/z* 65), and $C_6H_6^+$ (*m/z* 78) intensities relative to the percentage of H_2 in the CH_4/H_2 mixture. These compounds also represent major products in the plasma reactions. We tried to derive a relationship between the production of neutral and ionic species, but a similarity between the two species in either product abundance or variation could not be clearly observed.

From the overview of the variations in abundance of neutral or ionic species as a function of gas composition, we can make several remarks:

(a) The total intensity of the neutral species ($\Sigma I_{neutral}$) decreases almost linearly with the increasing CH_4 component (Figure 2). However, the normalized concentrations of all species, including the product radicals, hardly change (within a factor of 2) over the entire range of gas compositions. Among the listed species, the normalized peak intensity of $C_5H_5Li^+$ was highest and that of $C_2H_5Li^+$ was lowest for all gas compositions studied.

(b) In other words, more CH_4 produces more neutral species, including radical species, in the MW discharge. Almost twice as many C_2H_3 radicals were produced by increasing the CH_4 composition from 10 to 90%. The increase of the neutral species was found to be somehow proportional to the increase of CH_4 in the gas mixture, suggesting an effect of CH_4 consumption on the various secondary reactions producing neutral organic compounds.

(c) In contrast, the total intensity of the ionic species (ΣI_{ionic}) increases almost linearly with increasing H_2 (Figure 3). However, the normalized concentrations of almost all species change

TABLE 2: Analysis of Neutral and Ionic Species Fomed from a CH_4/H_2 MW Discharge Plasma Identification and Classification by Formula

type	formula										
					Neutral Species						
CH_n					CH_4						
C_2H_n			C_2H_2	C_2H_3	C_2H_4	C_2H_5	C_2H_6				
C_3H_n	C_3	C_3H	C_3H_2	C_3H_3	C_3H_4	C_3H_5	C_3H_6	C_3H_7	C_3H_8		
C_4H_n	C_4	C_4H	C_4H_2	C_4H_3	C_4H_4	C_4H_5	C_4H_6	C_4H_7	C_4H_8		C_4H_{10}
C_5H_n	C_5		C_5H_2		C_5H_4		C_5H_6		C_5H_8		C_5H_{10}
C_6H_n	C_6		C_6H_2		C_6H_4		C_6H_6		C_6H_8		C_6H_{10}
$^{C}{}_7H_n$	C_7		C_7H_2		C_7H_4		C_7H_6		C_7H_8		C_7H_{10}
C_8H_n	C_8		C_8H_2		C_8H_4		C_8H_6		C_8H_8		C_8H_{10}
C_9H_n	C_9		C_9H_2		C_9H_4		C_9H_6		C_9H_8		C_9H_{10}
$C_{10}H_n$	C_{10}		$C_{10}H_2$		$C_{10}H_4$		$C_{10}H_6$		$C_{10}H_8$		$C_{10}H_{10}$
$C_{11}H_n$	C_{11}		$C_{11}H_2$		$C_{11}H_4$		$C_{11}H_6$		$C_{11}H_8$		$C_{11}H_{10}$
$C_{12}H_n$	C_{12}		$C_{12}H_2$		$C_{12}H_4$				$C_{12}H_8$		$C_{12}H_{10}$
					Ionic Species						
CH_n^+					CH_4^+	CH_5^+					
$C_2H_n^+$			$C_2H_2^+$	$C_2H_3^+$	$C_2H_4^+$	$C_2H_5^+$	$C_2H_6^+$				
$C_3H_n^+$			$C_3H_2^+$	$C_3H_3^+$	$C_3H_4^+$	$C_3H_5^+$	$C_3H_6^+$	$C_3H_7^+$	$C_3H_8^+$		
$C_4H_n^+$					$C_4H_4^+$	$C_4H_5^+$	$C_4H_6^+$	$C_4H_7^+$	$C_4H_8^+$	$C_4H_9^+$	$C_4H_{10}^+$
$C_5H_n^+$					$C_5H_4^+$	$C_5H_5^+$	$C_5H_6^+$	$C_5H_7^+$	$C_5H_8^+$	$C_5H_9^+$	$C_5H_{10}^+$
$C_6H_n^+$					$C_6H_4^+$		$C_6H_6^+$		$C_6H_8^+$		$C_6H_{10}^+$
$^{C}{}_7H_n^+$									$C_7H_8^+$		$C_7H_{10}^+$

(within a factor of 20) over the entire compositional range. The distribution of ionic species is affected much more than that of the neutral species by varying the percentage of H_2. As expected, discharge in pure H_2 gases resulted in the disappearance of any HC species.

(d) As the H_2 volume in the mixture increases, ionic species having a smaller carbon number appear and sharply increase to a maximum at 90% H_2. The tendency for the higher H_2 component feed gas to produce species with lower carbon numbers is more pronounced in the case of the ionic species, in contrast to neutral species, where no significant changes in the distribution of products is observed with changes in H_2 composition.

(e) The CH_4/H_2 plasma produces mostly even-numbered mass ions as terminal domination ions. The MH^+ type of ion is missing when M is the C_nH_{2n+2} molecule, which is formed abundantly in the plasma. This suggests that protonation is a

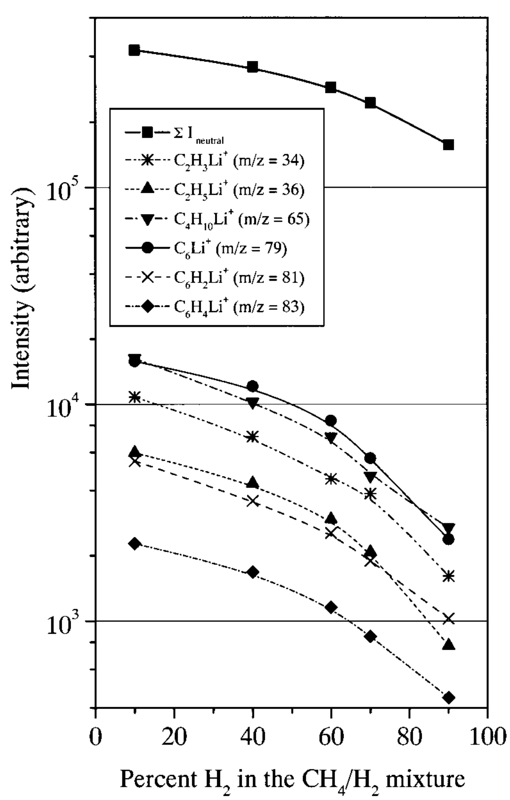

Figure 2. Li^+ adduct intensities of neutral products of $C_2H_3Li^+$ (*m/z* 34), $C_2H_5Li^+$ (*m/z* 36), $C_4H_{10}Li^+$ (*m/z* 65), C_6Li^+ (*m/z* 79), $C_6H_2Li^+$ (*m/z* 81), and $C_6H_4Li^+$ (*m/z* 83) produced in CH_4/H_2 plasmas as a function of the proportion of H_2 in the mixture. The total intensities of neutral species are also given.

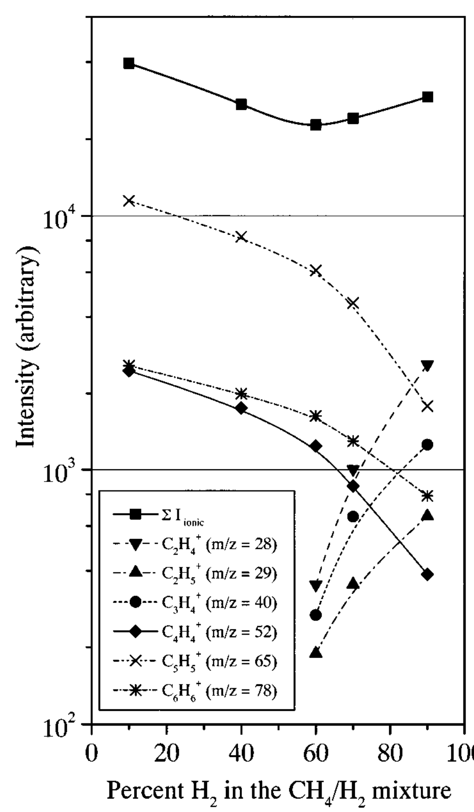

Figure 3. Total intensity of ionic species (ÓI_{ionic}) and relative intensities of ionic species of $C_2H_4^+$ (*m/z* 28), $C_2H_5^+$ (*m/z* 29), $C_3H_4^+$ (*m/z* 40), $C_4H_4^+$ (*m/z* 52), $C_5H_5^+$ (*m/z* 65), and $C_6H_6^+$ (*m/z* 78) produced in CH_4/H_2 plasmas as a function of the proportion of H_2 in the mixture. Compare with Figure 2.

less likely process than dissociative electron ionization in the CH_4/H_2 plasma.

(f) Note that the variation in production of most neutral and ionic species depends rather simply on the percentage of H_2. Most of these results, however, cannot yet be explained; to interpret them fully, it will be necessary to include rate constants for the formation of neutral molecules and ions. Few attempts have been made to obtain the data on ion−molecule reactions in which H_2 takes part. The rate constants of reactions of a few positive ions with H_2 have been shown to be slow, which leads to difficulty in providing a detailed mechanism of CH_4/H_2 discharge plasma reactions. Furthermore, in addition to problems with ambiguous identifications, some of the reaction products appear to interfere with the analytical determination.

Conclusion

The mass spectrometer-Li^+ reactor setup was successfully used for qualitative and quantitative analysis of the neutral and ionic species in the CH_4/H_2 system. The principal feature of this technique is its ability to monitor many kinds of species simultaneously. Reactive neutral species can be detected with a considerable sensitivity, and the technique can be equally applied to other plasma systems. At this moment, we cannot make estimates even on the orders of magnitudes of the densities of the neutrals as compared to those of the ionic species in the plasma. However, the ability of the present technique to measure both neutral and ionic species at the same time (or at least under the same conditions) proved valuable in diagnosis of any plasma system.

Features of the chemistry of CH_4/H_2 discharge can be summarized as follows:

(a) The reaction of CH_4/H_2 in MW plasma leads to a polymerization process. The presence of neutral radicals suggests a radical-involved reaction that may be one of the mechanisms in the polymerization.

(b) An increase in the CH_4 component of the feed gas leads to greater formation of many neutral species, whose distribution hardly changes over the entire range of feed gas composition.

(c) Mass spectra of ionic products show that all these species, with even-numbered mass ions predominant, were species with corresponding neutrals observed in the plasma. However, no remarkable similarities in abundances exist between ionic and neutral product species. The distribution of ionic species from a discharge is not representative of the neutral being protonated.

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