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Production of large O-containing neutral hydrocarbon species by a CH_4-O_2 microwave discharge

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The product of O-containing species in CH_4-O_2 plasmas has been studied as a function of the oxygen partial pressure in a microwave flow tube with 2.465 GHz, 6 W, and 2.2 torr total pressure. Mass spectrometry, coupled with Li^+-ion attachment techniques, was used for the identification of the products. Studies have clearly shown the presence of various O-containing stable polymer molecules, $C_nH_{2n+2}O$, $C_nH_{2n}O$, and $C_nH_{2n}O_2$ (n goes up to 9). The relative concentration profiles of these products have been determined as a function of O_2 composition in the feed gas. An assumption was presented that alcohols, aldehydes, and possibly O-containing radical species form in the CH_4-O_2 plasma. A reaction scheme is speculated which may account for these observed profiles.

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INTRODUCTION

We have recently described (a) the complete Li^+-adduct mass spectrum of the CH_4 microwave (MW) discharge plasma [1], obtained by ion-attachment techniques [2], (b) evidence that many chemical species are produced in the plasma, and (c) a mass spectral identification analysis. The identified species includes various polymer hydrocarbon radicals such as C_nH_{2n-1} ($n=2$ to 11) and C_nH_{2n+1} ($n=2$ to 11).

A novel device has been developed [3] which permits sampling at high pressure followed by soft ionization mass spectrometry. Sample gases are introduced through a small aperture into an ionization reaction chamber containing a lithium-ion emitter. In this ionization reaction chamber, lithium-ion attachment to the chemical species [4] takes place selectively. The ionized adduct is detected by a quadrupole mass spectrometer. With this instrument incorporating soft ionization, it should be possible to detect chemical species, including radical intermediates, on a real time basis. Thus, the product analysis of the MW plasma may be feasible.

On the other hand, the use of CH_4 plasma formed in the electric discharge has received considerable attention [5], especially in the field of plasma polymerization and deposition of hard carbon films. Several experiments have now been performed which indicate that microwave discharge methods [6,7] may be used to form various kinds of chemical substances. Since many products may be generated in complex ways [7,8], depending strongly on the discharge conditions, their measurements are always a major experimental problem in order to explain chemical reactions in the MW plasma. Much work has also been done with respect to the significant production parameters [9]. Among them, the effect of the additive gases may be great, and hence a variety of gases should be studied for the development of plasma processing. Although the primary aim of this work was the investigation of the role of various kinds of gas as additives, the CH_4-O_2 system has yielded some interesting results.

The present paper reports the production of O-containing polymer species, possibly O-containing radicals, under the plasma conditions during the CH_4-O_2 MW discharge. Mass spectrometry, coupled with a Li^+-ion attachment technique, has been used to identify all the products and monitor their Li^+-adduct intensities, as a function of feed gas composition. The aim of this paper is first to show that stable oxygenated organic molecules exist in the gas phase of CH_4-O_2 MW plasma, and second to gain a better understanding of the chemistry involved in the system. Consideration is given to the plausible reaction.

EXPERIMENT

The experiments were performed with a MW source, Li^+ reactor, and quadrupole mass spectrometer setup that has been described previously [1,2]. It is essentially identical to that used in early identification study of neutral radicals in CH_4 plasma. However, in this study the neutral chemical species sampled from the MW plasma were studied with the mixing gas system of CH_4 and O_2 A mixture of dry O_2 and methane is formed in a dynamic dilution system and metered into the flow tube reactor.

All the experiments were performed under the following conditions: total pressure (in flow tube): 2.2 torr; total pressure (in Li^+ reactor): 0.16 torr; MW power: 6 W; total gas flow rate: 12 cm^3/min.

The species produced by MW discharge in CH_4-O_2 feed gas effuse via a flowtube into the Li^+ reactor. The products were monitored by measuring the Li^+-adduct ion mass spectrum. Blank runs with a variation in the oxygen content of the discharge feed gases confirmed the absence of other possible reactant ions, such as LiO^+, $LiOH^+$, and Li_2O^+. They also showed only a minor change (within ±3%) in the production of Li^+ reactants.

Reactions occurring in the space between the discharge and sampling cone must have some effects on the distri-

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bution of product species observed. Radical-radical, radical-molecule, or ion-molecule reactions may take place beyond the edge in the downstream region. In fact, shifting the cavity away from the reaction chamber slightly changed the distribution and concentration, but the effect is small enough to assume that the main features of the distribution are preserved.

RESULTS AND DISCUSSION

Mass spectra

When large amounts of oxygen are added to a methane discharge a drastic change is expected. The effect is readily visible as oxygen changes the color from light pink to yellowish blue, and as the O_2 concentration increases, the discharge expands.

Portions of the Li^+-ion adduct mass spectra of chemical species produced in pure CH_4 and $CH_4(80)$-$O_2(20)$ (vol-vol) MW plasma under the same discharge conditions are shown in Fig. 1. The mass spectra obtained in the mass range 30–160 amu are shown in Fig. 2, when 20% O_2 was added to the 80% CH_4 stream, in terms of the flow rate. The oxygen components in the CH_4 plasma will lead to the formation of a new type of many O-containing species. The main peaks detected, their relative peak intensities, and their assignments, if possible, are shown in Table I. Peaks with a height of less than 5% versus the highest peak ($m/z = 34$ and 67 in pure CH_4 and CH_4-O_2 plasma, respectively) are not reported.

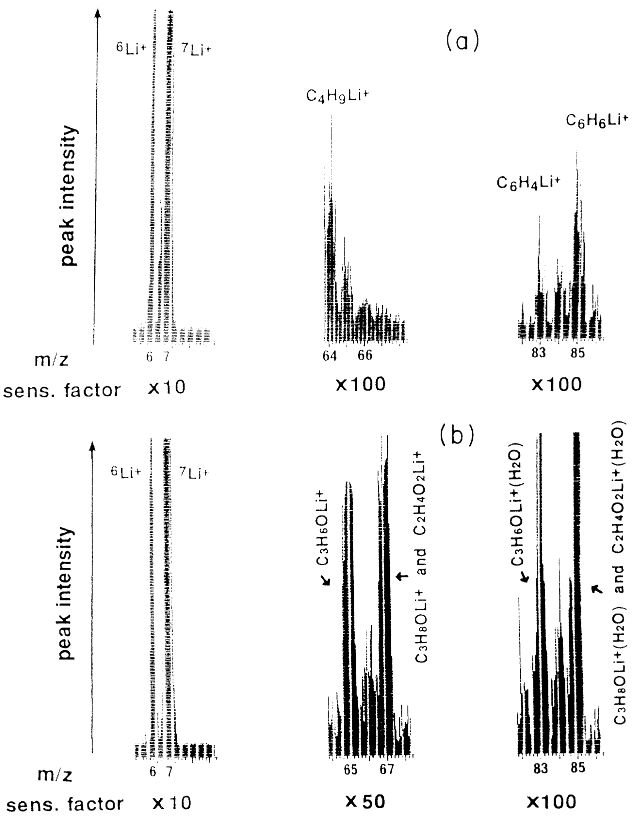

FIG. 1. A typical oscilloscope trace showing Li^+-adduct mass spectrum from the pure CH_4 plasma (a) and the $CH_4(80)$-$O_2(20)$ mixture plasma (b).

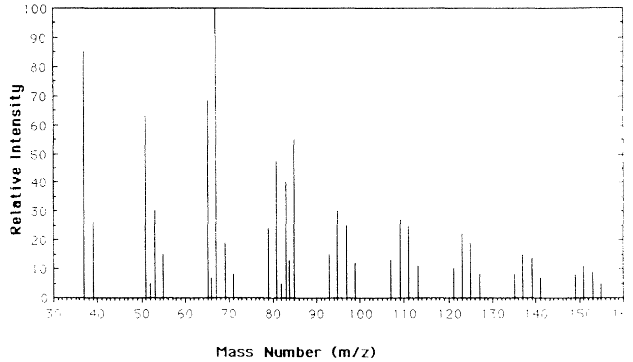

FIG. 2. Mass spectra of neutral products in $CH_4(80)$-$O_2(20)$ mixture plasma which was generated with a MW discharge. The main peaks detected and their possible assignments are shown in Table I.

Since the temperature of the Li^+-ion reaction chamber is relatively low (at approximately ambient temperature), some of these peaks can be due to hydrated ions. For example, the species at $m/z = 55$, 69, 83, 97, 111, 125, 139, and 153 in the Li^+-adduct mass spectra (Table I) are very likely due to $C_nH_{2n+2}OLi^+(H_2O)$, a monohydrate of lithiated $C_nH_{2n+2}O$ ($n = 1-8$), respectively. Similarly the peaks at $m/z = 71$, 85, 99, 113, 127, 141, and 155 may be from $C_nH_{2n+2}OLi^+(H_2O)$ and $C_nH_{2n}O_2Li^+(H_2O)$. These solvated ions are quite possible products in the reaction chamber (RC) having longer path length at these pressures if the RC temperature is low and the concentrations of the water and target species are reasonably high.

These peaks are classified in Table II as follows: $C_nH_{2n+2}O$, $C_nH_{2n}O$, and $C_nH_{2n}O_2$. Since identification is based only on the mass number, the peak assignment of these oxygenated products is not free of ambiguity. Therefore, all the possible compounds are listed for each group in Table II. For example, the $C_nH_{2n+2}O$ compound could be assigned as either alcohols R—OH or ethers R—O—R where R is an alkyl radical or hydrogen atom. The $C_nH_{2n}O$ group assigned as R—CHO could be carbonyls (R—CO—R), olefins with one hydroxyl attached or cyclic ether, and so on. Furthermore, the $C_nH_{2n+2}O$ peaks are isobaric with the $C_nH_{2n}O_2$ peaks of one lower carbon number. Unfortunately, very few of the high molecular weight products can be uniquely identified.

However, we speculate tentatively that both R—OH and R—CHO groups are formed, because (a) CH_3OH and HCHO molecules were observed clearly and hence, higher alcohol and aldehyde species may be produced, and (b) Flamm and Wydeven [10] reported the formation of both compounds in the experiment of an 11.8-MHz glow discharge of CH_4-O_2.

Table II also shows the relative peak intensities of the principal products, indicating that the compounds of the

TABLE I. Assignments of Li^+ adduct peaks of neutral products and their relative peak intensities (percent values) in pure CH_4 plasma and in $CH_4(80)$-$O_2(20)$ plasma. The relative intensities of monoisotopic species are reported.

	Pure CH_4 plasma		$CH_4(80)$-$O_2(20)$ plasma	
m/z	Li^+ adduct	Rel. Int.	Li^+ adduct	Rel. Int.
33	$C_2H_2Li^+$	10		
34	$C_2H_3Li^+$	100		
35	$C_2H_4Li^+$	8		
36	$C_2H_5Li^+$	65		
37	$C_2H_6Li^+$(?)	8	CH_2OLi^+	85
39			CH_4OLi^+	26
48	$C_3H_5Li^+$	70		
50	$C_3H_7Li^+$	47		
51	$C_3H_8Li^+$(?)	10	$C_2H_4OLi^+$	68
52			$C_2H_5OLi^+$	5
53			$C_2H_6OLi^+$ $CH_2O_2Li^+$	30
55			$CH_2OLi^+(H_2O)$[a]	15
57	$C_4H_2Li^+$	9		
58	$C_4H_3Li^+$	52		
59	$C_4H_4Li^+$	7		
60	$C_4H_5Li^+$	14		
61	$C_4H_6Li^+$	5		
62	$C_4H_7Li^+$	72		
64	$C_4H_9Li^+$	32		
65	$C_4H_{10}Li^+$	12	$C_3H_6OLi^+$	63
66			$C_3H_7OLi^+$	7
67			$C_3H_8OLi^+$ $C_2H_4O_2Li^+$	100
69			$C_2H_4OLi^+(H_2O)$	19
71			$C_2H_6OLi^+(H_2O)$ $CH_2O_2Li^+(H_2O)$	8
72	$C_5H_5Li^+$	21		
73	$C_5H_6Li^+$	11		
74	$C_5H_7Li^+$	11		
76	$C_5H_9Li^+$	22		
78	$C_5H_{11}Li^+$	29		
79	$C_5H_{12}Li^+$	6	$C_4H_8Li^+$	24
81			$C_4H_{10}OLi^+$ $C_3H_6O_2Li^+$	47
83	$C_6H_4Li^+$	16	$C_3H_6OLi^+(H_2O)$	40
84	$C_6H_5Li^+$	14		
85	$C_6H_6Li^+$	25	$C_3H_8OLi^+(H_2O)$ $C_2H_4O_2Li^+(H_2O)$	55
86	$C_6H_7Li^+$	6		
90	$C_6H_{11}Li^+$	18		
92	$C_6H_{13}Li^+$	23		
93			$C_5H_{10}OLi^+$	15
95			$C_5H_{12}OLi^+$ $C_4H_8O_2Li^+$	30
97			$C_4H_8OLi^+(H_2O)$	25
99			$C_4H_{10}OLi^+(H_2O)$ $C_3H_6O_2Li^+(H_2O)$	12
104	$C_7H_{13}Li^+$	6		
106	$C_7H_{15}Li^+$	14		
107			$C_6H_{12}OLi^+$	13
109			$C_6H_{14}OLi^+$ $C_5H_{10}OLi^+$	27
111			$C_5H_{10}OLi^+(H_2O)$	25
113			$C_5H_{12}OLi^+(H_2O)$ $C_4H_8O_2Li^+(H_2O)$	11
120	$C_8H_{17}Li^+$	10		
121			$C_7H_{14}OLi^+$	10
123			$C_7H_{16}OLi^+$ $C_6H_{12}O_2Li^+$	22
125			$C_6H_{12}OLi^+(H_2O)$	19
127			$C_6H_{14}OLi^+(H_2O)$ $C_5H_{10}O_2Li^+(H_2O)$	8
135			$C_8H_{16}OLi^+$	8
136	$C_9H_{19}Li^+$	5		
137			$C_8H_{18}OLi^+$ $C_7H_{14}O_2Li^+$	15
139			$C_7H_{14}OLi^+(H_2O)$	14
141			$C_7H_{16}OLi^+(H_2O)$ $C_6H_{12}O_2Li^+(H_2O)$	7

TABLE I. (*Continued*).

	Pure CH_4 plasma		$CH_4(80)$-$O_2(20)$ plasma	
m/z	Li^+ adduct	Rel. Int.	Li^+ adduct	Rel. Int.
149			$C_9H_{18}OLi^+$	8
151			$C_9H_{20}OLi^+$ $C_8H_{16}O_2Li^+$	11
153			$C_8H_{16}OLi^+(H_2O)$	9
155			$C_8H_{18}OLi^+(H_2O)$ $C_7H_{14}O_2Li^+(H_2O)$	5

[a]This species could possibly be assigned as O_3Li^+.

$C_nH_{2n+2}O$ homologous series are abundant products. As mentioned previously, these species interfere with the same signal as the $C_nH_{2n}O_2$. Since these are not distinguished, the relative peak intensities of both series, to which the same values are given in Table II, are the summation of both compounds with the exception of CH_4O. The $C_nH_{2n}O$ compounds (*n* up to 9) have also proved to be the main products detected. Their peak intensity distributions are different from those of the $C_nH_{2n+2}O$ homologs. Their intensity trend is clear: species with higher carbon numbers decrease in intensity.

O-containing radical species may be generated in the CH_4-O_2 MW plasma. This is based upon the following considerations: (a) the peaks at $m/z=52$ and 66 were observed which are formulated as $C_2H_5OLi^+$ and $C_3H_7OLi^+$, respectively, and (b) the observation of these species is presumably due to the Li^+-ion attachment to the dissociative products (M—H) of the main primary molecular products (M) of C_2H_6O and C_3H_8O.

It is noted that the present observation is in contrast to the findings of Wong and Potter [11] in which the major products in a stirred reactor for the $O+CH_4$ were CO, H_2O, CO_2, and H_2; and in which no formic acid, formaldehyde, methanol, and any other intermediate oxidation product was observed.

Products as a function of gas composition

Figure 3 gives the evolution of the peak intensities of various gaseous products in CH_4-O_2 plasma, as a function of the gas composition. In Fig. 3, we have plotted the peak heights of $C_3H_6OLi^+$ ($m/z=65$), $C_3H_8OLi^+$ and $C_2H_4O_2Li^+$ ($m/z=67$), $C_2H_4OLi^+(H_2O)$ ($m/z=69$), and $C_2H_6OLi^+(H_2O)$ and $CH_2O_2Li^+(H_2O)$ ($m/z=71$). The logarithmic scale was used to display, in the same figure, the peak intensities with four orders of magnitude. These curves clearly demonstrate that when O_2 was added to the CH_4 stream the intensities of oxygen-containing species increased. Their enhancement was found to be somehow proportional to the increase of O_2 on the gas mixture. In contrast to this, the amount of all the hydrocarbon (HC) radicals decreases monotonically with the decrease of CH_4 volume in the mixture. The variation in the peak heights of $C_2H_3Li^+$ ($m/z=34$), as the representative of HC radicals, is also shown in Fig. 3. The increase of O_2 concentration above the O_2-CH_4 flow rate ratio of $\frac{1}{9}$ completely depressed all the HC radicals. This indicates the conversion of the HC species along with the movement of the O_2 molecules.

The tendency in terms of the component variations for the species classified into the same group is quite similar.

TABLE II. Classification analysis of neutral products formed from the MW discharge of the mixture gas of $CH_4(80)$-$O_2(20)$. The representation is the same as that described in the text.

Type	Possible[a] compounds	Product distribution		
$C_nH_{2n+2}O$[b]	R—OH	$CH_4O(26)$[c]	$C_2H_6O(30)$	$C_3H_8O(100)$
	R—O—R	$C_4H_{10}O(47)$	$C_5H_{12}O(30)$	$C_6H_{14}O(27)$
		$C_7H_{16}O(22)$	$C_8H_{18}O(15)$	$C_9H_{20}O(11)$
$C_nH_{2n}O$	R—CHO	$CH_2O(85)$	$C_2H_4O(68)$	$C_3H_6O(63)$
	R—CO—R	$C_4H_8O(24)$	$C_5H_{10}O(15)$	$C_6H_{12}O(13)$
	Olefin—OH	$C_7H_{14}O(10)$	$C_8H_{16}O(8)$	$C_9H_{18}O(8)$
	Cyclic ether			
$C_nH_{2n}O_2$[b]	R—COOH	$CH_2O_2(30)$	$C_2H_4O_2(100)$	$C_3H_6O_2(47)$
	R—COO—R	$C_4H_8O_2(30)$	$C_5H_{10}O_2(27)$	$C_6H_{12}O_2(22)$
	Olefin—$(OH)_2$	$C_7H_{14}O_2(15)$	$C_8H_{16}O_2(11)$	
$C_nH_{2n+1}O$	Radical	$C_2H_5O(5)$	$C_3H_7O(7)$	

[a]The oxygen-containing multifunctional compounds, which would be expected, are not considered for simplicity.

[b]The $C_nH_{2n+2}O$ peaks are isobaric with the $C_nH_{2n}O_2$ peaks of one lower carbon number. Since in this study they are not distinguished, we assume both are present in the plasma. Thus, summation of their relative intensities is shown for both species.

[c]The relative intensities representing percent values are given.

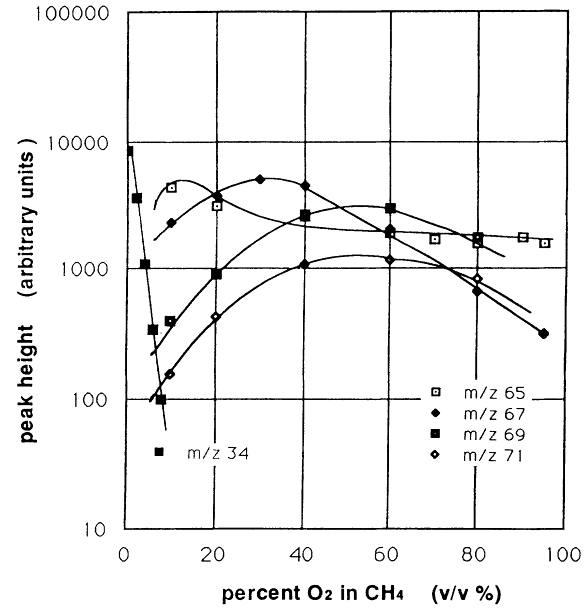

FIG. 3. Li^+-adduct peaks of stable molecule species produced in CH_4-O_2 plasma as a function of CH_4-O_2 (vol-vol) mixture component. (1) $C_3H_6OLi^+$ ($m/z=65$), (2) $C_3H_8OLi^+$ ($m/z=67$), (3) $C_2H_4OLi^+(H_2O)$ ($m/z=69$), and (4) $C_2H_6OLi^+(H_2O)$ and $CH_2O_2Li^+(H_2O)$ ($m/z=71$).

As the size of the molecule increases, the slope of the curve shows only a slight increase. The differences between the product intensities emphasize the effect of O and O_2 consumption on the various secondary reactions which produced O-containing organic compounds. The $C_3H_5OLi^+$ ($m/z=65$) or $C_3H_8OLi^+$ ($m/z=67$) peak sharply increases and decreases monotonically after reaching a maximum at around $CH_4(95)$-$O_2(5)$ and $CH_4(70)$-$O_2(30)$ (vol-vol) ratio, respectively, as the O_2 volume in the mixture increases. In other words, the tendency for the minor O_2 component of the feed to attain a high degree of conversion is more pronounced in the case of the $C_nH_{2n}O$ homologs than in the case of the $C_nH_{2n+2}O$ and $C_nH_{2n}O_2$ homologs. Besides, these are in contrast to hydrated ions (peaks at $m/z=69$ and 71) in the curves which are generated from the subsequent solvation reactions. These solvated ions increase and decrease more gradually with the maximum around 50% oxygen in methane. As expected, the discharge in the pure O_2 gases resulted in the disappearance of an O_2-derived HC species.

Concluding remarks

The use of O_2 additive gases with the mononer CH_4 MW discharge leads to the production of various kinds of chemical species, effectively demonstrating that the MW discharge is a method for generating an interesting oxygenated polymer species. Direct observation of these species is allowed by the measurement of the Li^+-adduct mass spectrum. Interestingly, the product species have the formulas $C_nH_{2n}O$ (presumably R—OH), $C_nH_{2n}O_2$, and $C_nH_{2n+2}O$ (presumably R—CHO) with n continuing on to 8 and beyond.

It is found that part of the O_2 or O (obtained from the discharge) reacts with almost all the HC radicals to form the O-containing HC molecules since the increase in their concentrations is associated with the decrease in the HC radicals. But it is felt that the experimental data are not of sufficient precision and completeness to allow formulation of a mechanism to clearly explain the reactions. However, it seems likely that the reaction is a chain reaction, as proved by the polymer production of the complex form, and that the following reaction schemes describe the CH_4 oxidation process in the MW plasma. This scheme is based on previously reported kinetics and is parallel with the proposed reaction sequence to describe the CH_4 oxidation process in a rf discharge by Flamm and Wydeven [10].

The most probable primary reaction is thought to be a reaction to yield a peroxy radical. It is well known that alkyl radicals R are rapidly converted into peroxy radicals in combination with molecular oxygen [12]:

$$R+O_2 \rightarrow R\text{—}OO\ . \tag{1}$$

The peroxy radical is considered to be capable of a whole range of additional reactions, such as an abstraction reaction of oxygen [13]:

$$R\text{—}OO+R\text{—}OO \rightarrow R\text{—}CHO+R\text{—}OH+O_2\ . \tag{2}$$

The assorted products of these reactions would result in widespread peaks. This speculation is proved partially by the presence of the R—CHO and R—OH species.

To summarize the main features of the distributions of neutral product species, we note that the conversion of CH_4 increases with increasing O_2 concentration, favoring production of highly polymerized O-containing molecules. Thus, it has been possible to control the relative concentration profiles of products as a function of the feed composition during the MW discharge plasma.

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