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The Production of H_2O_2 in the Microwave Discharge Plasma of CH_4/O_2

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Unexpectedly, the product analysis in microwave CH_4/O_2 discharge by Li^+ ion attachment mass spectrometry has brought forth a detection in the formation of the hydrogen peroxide H_2O_2. Furthermore, the observation of the minor $H_2O_2H^+$ peak gives indirect evidence of H_2O_2 formation. The studies have been done in terms of discharge conditions with a view of increasing the product rate and to confirm the possible production of this compound in the gas phase.

1. Introduction

The electric discharge of water vapor has been studies extensively in connection with the synthesis of H_2O_2.[1−3] When water vapor, dissociated by an electric discharge, passed into a cold trap, it yielded products that at room temperature consisted of H_2O_2 and H_2O after the O_2 evolution. H_2O_2 is formed only on a sufficiently cold surface (below −150 °C), suggesting the involvement of surface properties.

The reaction mechanism in electrically discharged water vapor is not very well understood: the necessary fundamental information is mostly lacking. For instance, the possible presence of H_2O_2 in the H_2O MW discharge plasma has been a matter of question from the viewpoint of the gas phase. During the present study some attempts have been made to determine whether H_2O_2 is really present in the gas phase of H_2O discharge plasma, using mass spectrometry with Li^+ ion attachment technique. The mass spectra show that no appreciable number of H_2O_2, $H_2O_2^+$, or $H_2O_2H^+$ has been observed, suggesting these species could neither form nor survive outside the plasma discharge.

In the course of investigations on the product analysis of the CH_4/O_2 microwave discharge plasma,[4,5] we have found that H_2O_2 may be produced. The Li^+ adduct mass spectra of the complex product mixture, obtained by mass spectrometry with Li^+ ion attachment technique, clearly show the peak *m/z* 41 ($H_2O_2Li^+$) among many peaks, suggesting that H_2O_2 is formed in the gas phase of the CH_4/O_2 plasma.

The unique interest of the H_2O_2 compound comes from the important role as intermediates of the chemical reactions.[6,7] According to the literature, English chemists Fabian and Bryce suggested[8] the formation of H_2O_2 during the discharge of CH_4/O_2 in 1956. They used electron impact mass spectrometry. Since this species is very labile and require special conditions for its formation, its detection was always difficult for a long time. The evidence was either indirect or doubtful. Therefore, it was still felt desirable to secure further direct evidence from another method.

The recently developed Li^+ ion attachment mass spectrometry (Li^+MS) provides mass spectra of quasi-molecular ions formed by lithium ion attachment to the chemical species under high pressure.[9−11] Results are obtained in the form of mass spectrometric traces of Li^+ adducts. For example,[4,5] the method was successfully applied to the study of neutral species that emerge from CH_4/O_2 microwave discharge plasmas. It was thus demonstrated that Li^+MS produce only molecular ions, permitting the direct determination of unfamiliar and reactive species.

This investigation was undertaken to supplement the previous studies, in which the techniques used are a Li^+ ion attachment−mass spectrometry and thereby arrive at a concrete evidence of the presence of the hydrogen peroxides. The most important advantage of the present study comes again from the fact that *m/z* 41, where the mass number of the Li^+ adduct complex is detected, is virtually free from the interference, in contrast with the most *m/z* fragments. The H_2O_2 densities were evaluated as a function of CH_4/O_2 gas pressure and composition, MW power input, and distance from the microcavity.

2. Experimental Section

The apparatus was essentially the same as used previously in this laboratory for studying the detection of free radicals formed in the microwave (MW) discharge plasma.[9−11] Briefly, the combined plasma flow tube−Li^+ ion attachment/mass spectrometer was constructed to detect the products (M) by mass analyzing an adduct formation ($M^+Li)^+$ and to assign their possible source.

The discharge system includes a MW cavity (Beenakker-type), MW generator (a Ewig model MR-301, 2.45 GHz), quartz discharge tube (15 cm long, 4 mm i.d.), and flow systems. A feed gas is formed by mixing CH_4 and O_2 in a mixing chamber and metered into the discharge flow tube. A typical run was discharged under the conditions that the pressure in the flow tube was monitored at the mixing chamber by means of a Convectron manometer (275, Granville-Phillip).

Mass spectra were obtained with plasma activation in two modes; (i) in the presence of Li^+, denoted as mode I, and (ii) in the absence of Li^+, as mode II. Thus, the intensity of any mass peak in mode II is subtracted from the corresponding mass peak in mode I and the results (modes I and II) shows the Li^+ adducts of particular neutral products, while mode II is a mode of ionic species detection. The mass spectrometric measurements have been performed at the downstream position with respect to the microwave cavity and the direction of the gas flow.

The sampling is performed by changing (1) gas composition, (2) the relative position of the MW cavity with respect to the Li^+ ion emission point, and (3) MW power input. This method enables one to obtain the most favorable conditions for the

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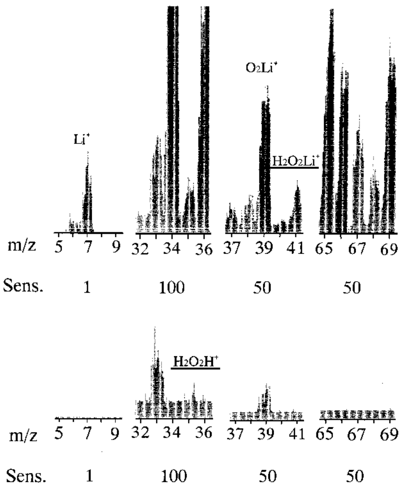

Figure 1. Oscilloscopic display of partial mass spectra of Li^+ ion adducts under two different conditions. The upper stage shows the Li^+ emitter-on conditions and the lower stage the Li^+ emitter-off conditions. The underlined peak indicates the $H_2O_2Li^+$ and the $H_2O_2H^+$ species.

formation of H_2O_2 with low ion concentrations. Mass spectrometry measurements have been performed at four positions of the cavity center with respect to the Li^+ ion emitter and the direction of the gas flow, namely, at position A (35 mm away from the Li^+ emitter), at position B (70 mm), at position C (100 mm), and at position D (150 mm).

3. Results and Discussion

1. Mass Spectrum. The appearance of many new species, as a product of reactions in the plasma, is initiated by the discharge activation. Figure 1 shows the partial mass spectral over region *m/z* 5−9, 32−36, 37−41, and 65−69. These Li^+ ion adduct data taken with the Li^+ emitter on (upper trace) have additional peaks in the spectrum, compared with the data taken with the Li^+ emitter-off (lower trace). Thus, the additional peaks in the upper stage are attributed to ion attachment to neutral chemical species effusing from the plasma. All measurements were made under conditions: total pressure in flow tube, 2.2 Torr; total pressure in Li^+ reactor, 0.16 Torr; MW power, 40 W; feed gas flow rate, CH_4(4.95 cm^3/min)/O_2(0.05 cm^3/min)

In view of the mass spectral observations, there are many peaks that are essentially the same as obtained in previous studies with different gas composition and have been reported in details.[4,5] Briefly, various O-containing stable polymer molecules, $C_nH_{2n+2}O$, $C_nH_{2n+2}O_2$, $C_nH_{2n+2}O_3$, $C_nH_{2n}O$, $C_nH_{2n}O_2$, and $C_nH_{2n}O_3$ (n goes up to 9), and hydrocarbon radicals have been detected. However, their intensity profiles are much different from those of the previous studies. It should be noted that these peaks have an uncertain identity since their validity is only based on the mass number. Assumption was presented that alcohols, aldehydes, and possibly, organic peroxides form in the CH_4/O_2 plasma. Besides that, the most conspicuous among the new features of the present spectra is the peak at *m/z* 41, with many intense peaks. This weak, but clear peak observed incidentally must be assigned to the H_2O_2, to which we have focused as a subject of the present study. Also the O_2Li^+ peak at *m/z* 39 may be anticipated as a result of the attachment of O_2 remained in the feed gas.

Repeated measurements to identify the active species present in the plasma as a function of O_2 composition in the feed gas have yielded species that gives the mass spectral peak at 41 amu. According to the NIST-ONLINE search,[12] there are, surprisingly, only eight chemical species which have 34 amu as the molecular weight: H_2S, H_3P, H_2O_2, HFN, CB_2, Be_2O, BLiO, CH_3F. Under the present experimental conditions, the possible compound is only H_2O_2.

Another explanation for the peak at *m/z* 41 would be an adduct of Li^+ with H_2O and CH_4. We can expect that a primary product of CH_4Li^+ (or H_2OLi^+) would then bind to water (or methane).

$$CH_4Li^+ + H_2O \rightarrow CH_4Li^+(H_2O) \tag{3.1}$$

$$H_2OLi^+ + CH_4 \rightarrow H_2OLi^+(CH_4) \tag{3.2}$$

The production rate of the Li^+ adduct depends on the size of the Li^+ affinity, which is strongly depending on the polarity or the polarizability of the target species. In other words, the chemical species captures the Li^+ ions and yields the Li^+ adduct if the Li^+ affinities are sufficiently high. Under our experimental conditions of Li^+ ion attachment mass spectrometry,[4,9,13] the compounds whose Li^+ affinities weaker than around 10 kcal/mol are hardly detectable even if they are present abundantly.

Almost nothing was known about the cation adducts of $H_2OLi^+CH_4$. The mixed cluster ions may be generated, but they are unable to be accessed. In this sense, a theoretical approach may help to provide some important insight into the factors such as binding energies and the intrinsic interaction between mixed cluster compounds and the Li^+ ion.[14−17]

Considering the difficulties in the experimentally derived $H_2OLi^+CH_4$ binding energies, we have examined the binding energies of Li^+ to H_2O/CH_4 complexes using density functional theory (DFT). A number of studies have shown that various ion affinities, obtained using DFT methods, are highly comparable in quality with the experimental values.[18−22] The molecules (H_2O and CH_4) and its adducts (H_2OLi^+ and CH_4Li^+) were optimized at the B3LYP/6-311+(2d,2p) level followed by the frequency calculation, and it was found that none of the ligands and adduct structures have any imaginary frequencies and all were identified as minima. All the calculations were performed within the framework of the Gaussian systems.[23] In analyzing the site-specificity of Li^+ addition to H_2O/CH_4, the lowest total energies of all the isomeric ions formed in these reactions have been sought.

Before the study on complexation energy of H_2OLi^+ with CH_4 and CH_4Li^+ with H_2O was started, we performed the calculation of Li^+ affinity of H_2O and CH_4 ligands. Binding enthalpies (Li^+ affinities of ligands) were calculated using the energies calculated at B3LYP/6-311+G(2d,2p) level with zero-point energy and other thermal energy corrections and compared with the previous experimental values. As expected, the present Li^+ affinity of H_2O, 34.38 kcal/mol, is in good agreement with the experimental value, 34.0 kcal/mol.[24] The calculated Li^+ affinity of CH_4 (12.98 kcal/mol) coincides well with our previously calculated value (12.59 kcal/mol).[21]

We optimized the structure of $H_2OLi^+CH_4$ using the same B3LYP/6-311+G(2d,2p) level followed by the frequency calculation. The stabilization energy (binding enthalpy) of H_2OLi^+ with CH_4 is calculated as 9.14 kcal/mol, which is weaker than that to be required for the $H_2OLi^+CH_4$ formation under our experimental conditions. On the other hand, the present calculations predict a large $CH_4Li^+H_2O$ bond dissociation energy (binding enthalpy between CH_4Li^+ and H_2O fragments), 30.53 kcal/mol, and hence we can reasonably predict that the complexes should be produced only with the very abundant CH_4Li^+ adducts presence like Li^+ primary ions in the Li^+ ion attachment mass spectrometry. But that is not the case

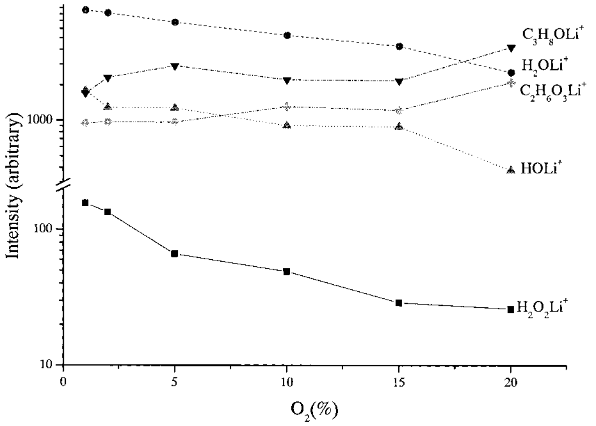

Figure 2. Li^+ adduct peaks of molecule species produced in CH_4/O_2 plasma as a function of CH_4/O_2 mixture component. Input power is 40 W, while the cavity position is C.

in our present experiments, and hence, the $H_2OLi^+CH_4$ may not be detectable.

2. Discharge Parameters. It would be instructive to study this system, especially the intensity of the *m*/*z* 41 peak, as a function of plasma discharge conditions, such as the feed gas component, the gaseous pressure in the flow tube, the distance between the discharge zone and the Li^+ ion emission, and the MW power input. A number of runs were made to broadly establish the operating characteristics of the apparatus designed and to increase the intensities of ions at *m*/*z* 41, issuing through the Li^+ ion attachment reactions.

Gas Component. Figure 2 displays the evolution of H_2OLi^+ (*m*/*z* 25), $HOLi^+$ (*m*/*z* 24), $H_2O_2Li^+$ (*m*/*z* 41), $C_3H_8OLi^+$ (*m*/*z* 65), and $C_2H_6O_3Li^+$ (*m*/*z* 85) against the gas composition. The first three have been chosen as the species possibly related to the production of H_2O_2. The last two oxygenated hydrocarbon compounds represent the major products, which are classified as $C_nH_{2n+2}O$ and $C_nH_{2n+2}O_3$ molecules, respectively. The homologous species generally followed similar variation patterns.

The increased oxygen is not responsible for the increased yields of $H_2O_2Li^+$ evolved under the present conditions. $H_2O_2Li^+$ decreases, as the relative amount of oxygen amount of oxygen in the mixture gas increases, and then the decrease may occur for a further decrease in oxygen after the maximum is reached at less than 1% O_2 composition, which cannot be realized experimentally, because of instrumental limitation. When comparing the component variation of the other species, the tendency for $H_2O_2Li^+$ is more similar to that of the $HOLi^+$ and H_2OLi^+ than that of the $C_3H_8OLi^+$ and $C_2H_6O_3Li^+$, indicating that there must be a process contributing to $H_2O_2Li^+$ formation that is dependent on the presence of these former species.

The component ratio CH_4(99%)/O_2(1%) is most favorable for the formation of H_2O_2 and possible related compounds and hence, further discussion will concern only this composition. It should be noted, however, that the major constituents of oxygenated hydrocarbons followed entirely different patterns. Regarding these compounds, the details were reported in the previous paper.[4,5]

*Gaseous Pressure***.** The normalized intensity of the *m*/*z* 41 peak with increasing the feed gas pressure in the plasma was examined over the limited pressure range of the flow tube 0.5−4 Torr for a fixed input power (40 W) and for a fixed composition of O_2(1%)/CH_4(99%). A plot of other neutral products as a function of pressure indicates the distribution among the products changes with pressure but less slightly than that with feed gas composition. The variation of H_2O is about the same as that for H_2O_2.

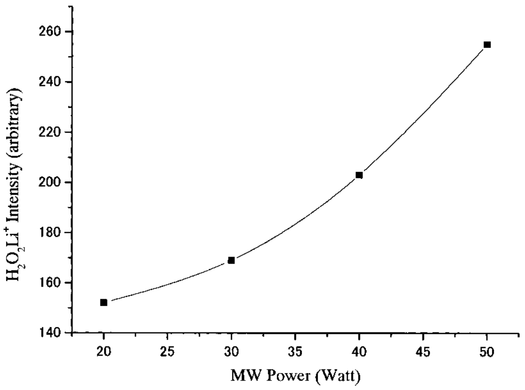

Figure 3. Intensities of the lithiated H_2O_2 as a function of discharge power at cavity position C.

MW Cavity Position along the Flow Tube. The intensities of some Li^+ adducts at the MW cavity positions were examined. In fact, shifting the cavity away from the reaction chamber slightly changed the distribution and concentration of the various products. It has been found that the $H_2O_2Li^+$ peak decreases slightly from upstream toward downstream position, while its protonated yield increases significantly with downstream position. The small peak of $H_2O_2H^+$ (refer to the lower trace of Figure 1), which does not allow accurate quantitative analysis, but only on a relative basis, adds indirect evidence to the existence of H_2O_2. Since the effect is small enough to assume that the main features of the H_2O_2 distribution are preserved, the behavior of the product H_2O_2 with other plasma parameters is presented for the upstream position C only.

Plasma Power. Finally, the considerable power effect in the formation of H_2O_2 is no doubt large. We have investigated the dependence of the $H_2O_2Li^+$ intensity on the MW power. Figure 3 compares the products observed at different MW discharge powers with the CH_4(99%)/O_2(1%) feed gas at the fixed flow rate of 5 cm^3. With increasing power from 20 to 50 W, the signal current of $H_2O_2Li^+$ increased from 150 to 240 (arbitrary units).

4. Concluding Remarks

The Li^+ mass spectra of the product species provide the first positive identification of stabilized H_2O_2 in the MW discharge CH_4/O_2 plasma. These are significant mainly from two viewpoints; mass spectrometric assignment of the peak at *m*/*z* 41 and isotopic consideration of the concerned peaks at *m*/*z* 40−41. We can luckily suppose that, under the present experimental conditions, the peak at *m*/*z* 41 is $H_2O_2Li^+$ as the source of the possible compounds whose molecular weights are 34 amu. As far as we know, no other mass spectrometric study of $H_2O_2Li^+$ has been published so far.

Regarding the mixed cluster ions of $H_2OLi^+CH_4$, binding enthalpies of (CH_4Li^+), ($H_2OLi^+-CH_4$), and ($CH_4Li^+-H_2O$) are calculated as 12.98, 9.14, and 30.53 kcal/mol, respectively. It can be seen from these data that CH_4 has weak Li^+ and H_2OLi^+ affinities and is not easily attached by both Li^+ and H_2OLi^+ ions. Therefore, $H_2OLi^+CH_4$ may not be observed with our Li^+ ion attachment mass spectrometric system.

It was observed in this study that the discharge parameters have some roles in the formation of the H_2O_2 species. The results, which do not allow accurate quantitative analysis, but only on a relative basis, add indirect evidence to the existence of H_2O_2. The variation of m/z 41 intensities with gas composition confirms the involvement of oxygen.

Furthermore, the preliminary experiment of the water discharge revealed that there is no evidence to the presence of H_2O_2, suggesting that the likely process for the H_2O_2 is not via free radical recombination,

$$H_2O \rightarrow H + OH \tag{4.1}$$

$$HO + OH \rightarrow H_2O_2 \tag{4.2}$$

This finding, together with the data from CH_4/O_2 discharge, shows that more than one species are involved in the production of H_2O_2.

The experimental technique used in this investigation may be regarded as an application of the Li^+ attachment technique. Its usefulness is exemplified in the detection of fragile species from the gas phase.

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