Analysis of Hydronitrogen Species Generated by a Microwave Discharge in (N_2H_4)/He

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We report the production of gaseous hydronitrogen chemical species in a continuous-flow microwave plasma discharge excited in hydrazine (N_2H_4) gas in helium. Products were analyzed by Li^+ ion attachment mass spectrometry. Plasma composition was investigated as a function of N_2H_4/He composition and microwave-induced power input. A variety of neutral and ionic products were formed and identified mass spectrometrically. The mass spectral analysis revealed the presence of various cluster compounds of N_2H_4, H_2O, and/or NH_3 as well as their ionized species. These cluster compounds were formed by condensation reaction processes. In addition, the interesting neutral hydronitrogen species N_3H_5 and N_4H_6 were tentatively assigned. No species with these chemical formulas are listed in the NIST database. Formation of N_3H_5 and N_4H_6 may involve rearrangement reactions.

Introduction

Hydrazine has been a subject of photochemical investigation since the 1960s.[1,2] Hydrazine vapor is photolyzed at a variety of wavelengths. In a review published in 1964, McNesby and Okabe[3] discussed three possible photoprocesses for this system.

$$N_2H_4 + h\nu \rightarrow N_2H_3 + H \qquad \Delta H = 76 \pm 5 \text{ kcal/mol} \quad (1)$$

$$N_2H_4 + h\nu \rightarrow 2NH \qquad \Delta H = 61 \pm 3 \text{ kcal/mol} \quad (2)$$

$$N_2H_4 + h\nu \rightarrow N_2H_2 + H_2 \qquad \Delta H = 26 \pm 5 \text{ kcal/mol} \quad (3)$$

Dissociation into two amino radicals (eq 2) was postulated by researchers[4] who used the flash photolysis technique (the amino radical is readily detected by absorption spectroscopy).

Several researchers[5−7] have reported the formation of unexpected species when N_2H_4 is subjected to a microwave (MW) discharge. For instance, Foner and Hudson reported[5,6] the formation of many previously undetected hydronitrogen species, including the free radicals NH_2, N_2H_3, and so on. In general, when the discharge products are condensed in a liquid nitrogen trap and then allowed to evaporate, diimide and ammonia evaporate simultaneously, followed by triazene and tetrazene at about the same time (tetrazene reaches its maximum rate of evaporation before triazene does) and then hydrazine. Foner and Hudson, however, reported that tetrazene was not present in the gaseous products of the hydrazine discharge. In a study related to the N_2H_4 MW plasma, Willis and Back[7] identified diimide (N_2H_2).

A MW discharge plasma is a prime candidate for producing various kinds of novel compounds, since many products may be generated in complex ways.[8,9] Nitrogen compounds are reasonable targets in the search for materials with new physical properties since the nitrogen atom forms three, four, or five covalent bonds, leading to unique structural characteristics.

Li^+ ion attachment mass spectrometry (Li^+MS), a recently developed technique, provides mass spectra of quasi-molecular ions formed by lithium ion attachment to chemical species under high pressure.[10−12] Results are obtained in the form of mass spectrometric traces of Li^+ adducts. Fujii successfully applied Li^+MS to the study of product species that emerge from CH_4/O_2 MW discharge plasmas and demonstrated that Li^+MS has the combination of sensitivity and quantification needed to detect even free radical species.[13,14]

Here we report our mass spectral analysis of the products from the N_2H_4 MW plasma. We suggest assignments for a variety of ionic hydronitrogen products ($N_xH_y^+$), compounds of potential significance as new substances. In addition, we report N_3H_5 and N_4H_6 as well as a series of N_2H_4 clustering neutrals. Finally, we consider plausible reaction schemes to explain the formation of the species observed in our experiments. In our experimental setup, we could not detect the radical intermediates diazene (N_2H_2) and NH or the postulated intermediates N_3H_3 and N_4H_4. At this moment we cannot conclude whether our experimental setup would not have allowed us to detect these species had they been produced or these species were not produced and therefore not detected in our experiment.

Experimental Section

We utilized a MW discharge source/Li^+ reactor/quadrupole mass spectrometer, as described previously.[15,16] This arrangement allows direct detection of products and is essentially identical to the setup used in an earlier identification study of unfamiliar products in a c−C_4F_8/Ar plasma.[16]

The MW discharge flow system employed a 2.465-GHz MW generator and a straight quartz flow tube (inner diameter, 3 mm; outer diameter, 6 mm; length, 20 cm). The N_2H_4/He gas mixture flowed down the tube at a flow rate of 10 cm^3/min. The resulting total pressure upstream of the flow tube was around 2,600 Pa, and the total pressure at the Li^+ reactor was 100 Pa. The temperature of the gas in the Li^+ reactor may be nearly close to the room temperature. The MW plasma was created by connecting a cavity to the 2.465-GHz MW generator through a matching network. The MW power was varied from 30 to 80 W.

MW discharge was made at the cavity, 100 mm away from the Li^+ emitter. We performed a control experiment (continuous flow, no Li^+ emission, varying N_2H_4 pressure) to confirm that

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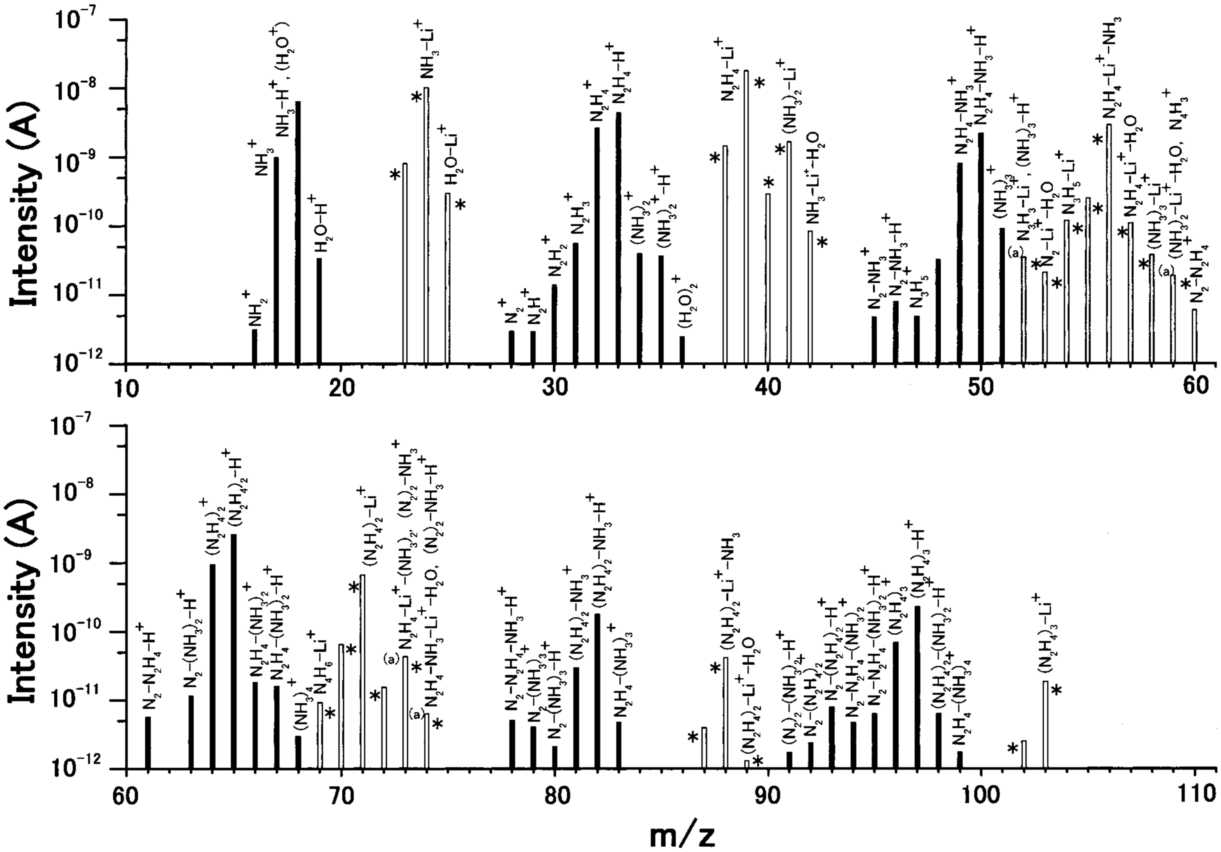

Figure 1. Mass spectra over the *m*/*z* range 10−110 for a N_2H_4/He gas mixture (N_2H_4 partial pressure, 30 Pa) under conditions: Li^+-on condition, MW discharge activation. The open-bar peaks with asterisks are due to the neutral species formed during the reaction of N_2H_4 in the MW discharge. The significantly larger peaks at *m*/*z* 52, 59, 73, and 74 may consist of ionic species and Li^+ ion adducts. These are marked "a".

the mass signal intensities of the ionic species from the plasma were appreciable at this location. This arrangement also allowed accurate identification of the various neutral products.

The mass spectral measurements were made under three different conditions:

(A) The N_2H_4 feed gas was introduced into the MW discharge tube, but without MW discharge activation. The gas entered the Li^+ reactor, where adducts were formed with Li^+ primary ions. The adduct ions were mass-analyzed.

(B) The N_2H_4 feed gas was introduced into the MW discharge tube and subjected to a MW discharge. The resulting products entered the Li^+ reactor, and the adduct ions of the neutral species formed during the MW discharge were mass-analyzed.

(C) The N_2H_4 feed gas was introduced into the MW discharge tube and subjected to a MW discharge as in (B). However, in this case no Li^+ ions were available to form Li^+ adducts (the Li^+ emitter was off). Therefore, only the ionic species formed during the MW discharge were mass-analyzed.

Hereafter, these conditions are denoted A(Li^+-on, no MW), B(Li^+-on, MW), and C(Li^+-off, MW), respectively.

Results and Discussion

1. Mass Spectra. The discharge was done about 100 mm away from the mass spectrometer sampling orifice to analyze the gaseous products associated with the blue color of the plasma. Mass spectrometric measurements (*m*/*z* range 10−110) for the three experimental conditions (Li^+-on, no MW; Li^+-on, MW; and Li^+-off, MW) are made. Many large peaks appear in the spectrum (not shown) for the Li^+-on, no MW condition (N_2H_4 pressure, 30 Pa; no plasma discharge). The peaks at *m*/*z* 25 and *m*/*z* 24 can be assigned to H_2OLi^+ and NH_3Li^+, respectively; other peaks can be assigned to cluster species (probably solvated ions since the concentrations of NH_3, N_2, N_2H_4, and H_2O are reasonably high). The presence of ~13% NH_3 as an impurity in the N_2H_4 sample (guaranteed purity of 95%) was estimated by conventional EI mass spectrometry.

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.[11] Results are obtained in the form of mass spectrometric traces of Li^+ adducts. As an example,[12,13,14] 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.

Typical mass spectra for the B(Li^+-on, MW) condition are depicted in Figure 1. Since fragmentation can be assumed to be negligible, the peaks can be attributed to ion attachment to genuine neutral species and ionic species effusing from the plasma. The presence of various neutral discharge products is indicated by the increase in the current of the Li^+ adduct ions. NH_3 is a significant product. The series of masses differing by 32 and/or 17 mass units (for example, 39, 71, 103 and 24, 41, 58, 75) are obvious.

The main peak assignments are also given in Figure 1. No nonvolatile species remained as a solid film on the flow tube wall. Since identification is based only on mass number, assignments are not free of ambiguity. For example, the NH_3-H^+ ion has the same *m*/*z* value as the H_2O^+ ion. The relative intensities of the peaks in both systems represent monoisotopic intensities (including contributions from all the isotopes for a

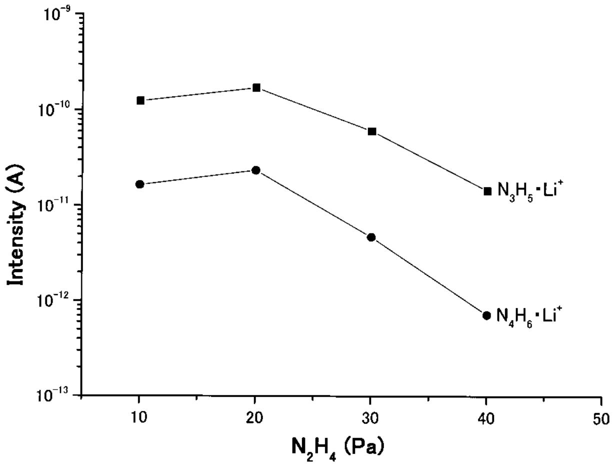

Figure 2. Evolution of $N_3H_5Li^+$ (*m*/*z* 54) and $N_4H_6Li^+$ (*m*/*z* 69) as a function of N_2H_4 pressure in the range 10−40 Pa (N_2H_4 partial pressure at the Li^+ reactor). MW power, 30 W.

given ion) normalized to 10×10^{-12} A. The sensitivity of detecting neutral products by Li^+ ion attachment depends on the Li^+ affinity. Fortunately, N-containing species have sufficiently high Li^+ affinities to attach at nearly collision rates, so little discrimination is expected.

The N_3H_5 and N_4H_6 hydronitrogen products found in this study are interesting and have not been reported before. We assume that it is always possible for these compounds to form in the N_2H_4 plasma. The N_2H_4 plasma also produces many neutral species associated with NH_3, N_2, and/or H_2O. The reactions occurring in the hydrazine plasma are very complex, as evidenced by the presence of higher order hydronitrogen compounds and associated species.

Some peaks common to spectra taken at B and C conditions, had different intensities in the two spectra. For example, the peak at *m*/*z* 52 is higher in the condition B, indicating conversion to new types of species (possibly triazene, N_3H_3) in the N_2H_4 plasma system. However, this is not the case for the peaks at *m*/*z* 37 and 67, which may be assigned to diimide (N_2H_2) and tetrazene (N_4H_4). These compounds were identified in the decomposition products condensed on a liquid nitrogen cooled surface[17,18] and are postulated to play an important role in organic synthesis. However, the present data are not sufficiently good to allow us to conclude that N_3H_3 is actually generated in the plasma and that N_2H_2 and N_4H_4 are not; interference with ionic species cannot be completely ignored.

In the ionic mode, our spectrum shows characteristic features. Peaks attributable to ions associating with NH_3, H_2O, and N_2 are prominent in the spectrum, indicating that the discharge produces efficiently clustering radical cations. The exceptional species are the rearranged ions $N_3H_5^+$, $N_4H_6^+$, and $N_4H_3^+$, which have not been reported before. Comparison makes it clear that all these ionic products, except $N_4H_3^+$, are species whose corresponding neutrals were observed in the plasma. The ionic species produced in the discharge are, somehow, representative of the neutral species being produced.

2. Product Formation as a Function of Gas Pressure and MW Power. *Gas Pressure.* Figure 2 displays the evolution of $N_3H_5Li^+$ (*m*/*z* 54) and $N_4H_6Li^+$ (*m*/*z* 69) as a function of feed gas pressure at the reaction chamber. $N_3H_5Li^+$ and $N_4H_6Li^+$ were selected as representative rearranged species through conversion reactions. The peak heights slightly increased with increasing pressure until ∼20 Pa and then gradually decreased. The quantum yields of ionic formation were also highest at an N_2H_4 pressure of 20 Pa.

MW Power. Peak intensities increased, passed through a wide maximum around 50 W, and then decreased with increasing MW power for all ionic species examined except $N_3H_5Li^+$ and $N_4H_6Li^+$, but with different patterns from species to species (data not shown; feed gas, 20 Pa N_2H_4/80 Pa He). The N_3H_5-Li^+ (*m*/*z* 54) and $N_4H_6Li^+$ (*m*/*z* 69) quantum yields were unaffected over the examined range. We are not able to explain this result.

3. Mechanistic Considerations. It is conceivable that hydrazine molecules are ionized by electrons in the plasma. We consider the following reactions:

$$N_2H_4^+ \rightarrow N_2H^+ + 3H \quad (4)$$

$$\rightarrow NH_2^+ + NH_2 \quad (5)$$

$$\rightarrow N_2H_2^+ + H_2 \quad (6)$$

$$\rightarrow N_2H_3^+ + H \quad (7)$$

These ions may participate in a whole range of additional reactions. The products of these reactions would result in some peaks.

$$N_2H_2^+ + N_2H_4 \rightarrow N_4H_6^+ \quad (8)$$

$$N_2H_3^+ + N_2H_4 \rightarrow N_4H_3^+ + 2H_2 \quad (9)$$

$$N_2H_4^+ + N_2H_4 \rightarrow N_3H_5^+ + NH_3 \quad (10)$$

These mechanisms are totally speculative and assume the presence of products such as $N_3H_5^+$, $N_4H_6^+$, and $N_4H_3^+$. Reactions of ion-involved condensations leading to products of higher mass number may well dominate the chemistry of the hydrazine discharge.

The important reaction for the production of neutral species is thought to be a reaction that yields an N_2H_3 or NH_2 radical, since N_2H_3 or NH_2 can be produced efficiently in hydrazine discharge plasma systems[3]. We also speculate from the present observation of N_3H_5 and N_4H_6 that these radicals are rapidly converted into these species in combination with many other species.

Concluding Remarks

Hydrazine in a fast-flow system was subjected to a MW discharge near the sampling orifice of an ion attachment mass spectrometer. We observed the ionic species NH_2^+, $N_2H_2^+$, $N_2H_3^+$, $N_3H_5^+$, $N_4H_3^+$, and $N_4H_6^+$; various cluster compounds of $N_2H_4^+$ with N_2H_4, NH_3, N_2, and H_2O; and the neutral products N_3H_5 and N_4H_6 and various associated species. Unlike other mass spectrometric methods, Li^+MS allowed us to directly observe these species.

In this paper, we have presented mass spectrometric evidence for the neutral hydronitrogen compounds N_3H_5, N_4H_6 (possibly recombination product of N_2H_3) and possibly N_3H_3 and data on many ionic hydronitrogen species, effectively demonstrating that a MW discharge can be used to generate new products.

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