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# Mass spectrometric analysis of a $N_2/H_2$ microwave discharge plasma

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## Abstract

Using $Li^+$-ion attachment mass spectrometry, we studied the products of microwave discharges through $N_2/H_2$ in a flowing gas system at a pressure of 840 Pa (6.3 Torr) and a total flow rate of 6 mL/min. The discharges produced various neutral and ionic species in amounts that depended upon the experimental arrangement and the discharge parameters. Ionic products were $N^+$, $N_2{}^+$, $N_2H^+$, $N_2H_2{}^+$, $NH_3{}^+$, and $(NH_3)_nH^+$ ($n = 1$–3). In addition to $NH_3$ as a major neutral product, we observed a significant peak at *m*/*z* 65 and tentatively assigned it to the $Li^+$-ion adduct species $N_4H_2Li^+$. This interesting product species has not been reported before. (Int J Mass Spectrom 216 (2002) 169–175) © 2002 Published by Elsevier Science B.V.

*Keywords:* Ion attachment; Product analysis; Plasma; Microwave discharge; $N_4H_2$

## 1. Introduction

Microwave discharges through molecular $N_2/H_2$ gas mixtures are ubiquitously used for the synthesis of ammonia and other reagents as well as for plasma processing [1,2]. Most of the processing mixtures have aroused considerable attention as cleaning systems, while among the $H_xN_y$ products, the well characterized compounds diazene (HNNH) and isodiazene ($H_2NN$) [3] are widely used as synthetic reagents [4].

Dervan et al. reported [5] the generation and characterization of unsubstituted isodiazene in a low-temperature matrix isolation study. The isodiazenes have been predicted to play a key role as intermediates in the chemistry of azo compounds for a long time. The findings of Dervan et al. were supported by studies of the photolysis of amino isocyanates in an argon matrix at 12 K [6]. Ammonia synthesis in low-pressure $N_2/H_2$ plasma has also been studied [7–9]. The ammonia yield increases when catalysts are inserted in the plasma region, the after-glow region, and the cold trap. The NH radical has been identified as a short-lifetime intermediate in the formation of ammonia. Kogoma et al. have reported the syntheses of $NH_3$ and $N_2H_2$ in $H_2/N_2$ plasma [9].

Evidence for the existence of HNNH and $H_2NN$ as solitary molecules in the gas phase has been reported [10,11]. However, the understanding of molecular collisions in highly excited molecular gas mixtures is not advanced [12]. The corresponding cations of these intermediates have also been shown to be of considerable interest for the understanding of chemical processes taking place in the plasma environment [13], but, with a few exceptions, no experimental data for them are available.

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We have developed a novel apparatus [14] that 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 chamber, $Li^+$-ion attachment to the chemical species [15] takes place selectively. The ionized adducts are detected with a quadruple mass spectrometer. With this apparatus, the detection of chemical species, including radical intermediates, on a real-time basis should be possible. This $Li^+$-ion attachment mass spectrometer makes use of the well known principle for obtaining mass spectra consisting solely of quasi-molecular ions [16–18] formed by the addition of $Li^+$ ions to the sample molecules. Analysis of the products of the microwave discharge plasma may be feasible with this apparatus.

In the present study, we report the first gas-phase characterization of the neutral and cationic $H_xN_y$ species in a $N_2/H_2$ microwave discharge plasma. We used mass spectrometry coupled with a $Li^+$-ion attachment technique to identify all the products and to monitor their $Li^+$ adduct intensities as a function of feed gas composition. To support our conclusions, we studied the cations and their neutral analogues by the same experimental techniques. We present the first mass spectrometric evidence for the elusive chemical compound $N_4H_2$ (theoretically confirmed), but we did not detect the radical intermediates diazene ($N_2H_2$) and NH, which have been postulated as intermediates in the $H_2/N_2$ discharge plasma.

## 2. Experimental

The apparatus was essentially the same as that used previously in this laboratory for detecting free radicals formed in microwave discharge plasma [19–21]. We employed a plasma flow tube and a $Li^+$-ion attachment mass spectrometer (IAMS, ANELVA Corp., Tokyo) to detect the products (M) by mass-analyzing the adduct formed $(M + Li)^+$ and to assign their possible source.

The discharge system included a microwave cavity (Beenakker-type), a microwave generator (Ewig model MR-301, 2.45 GHz, Ewig, Tokyo), a quartz discharge tube (15 cm long, 4 mm i.d.), and flow systems. The feed gas, formed by mixing $H_2$ and $N_2$ in a mixing chamber, was metered into the discharge flow tube. In a typical run, 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: (1) in the presence of $Li^+$, denoted as mode I, and (2) in the absence of $Li^+$, mode II. Thus, the intensity of any mass peak in mode I is subtracted from the corresponding mass peak in mode II, and the result (mode II − mode I) shows the $Li^+$ adducts of particular neutral products; mode II is a mode for the detection of ionic species. The mass spectrometric measurements were performed at the downstream position with respect to the microwave cavity and the direction of the gas flow (the distance between the discharge zone and the emitter ion source was 10 cm). The $H_2$ composition in the $N_2/H_2$ feed gas was varied between 4 and 16%; the pressure (100 Pa) at the $Li^+$-ion attachment reaction chamber was maintained at a constant total flow rate of 6 mL/min; the temperature in the reaction zone is nearly at room temperature; and the microwave discharge power ranged from 30 to 70 W.

## 3. Results and discussion

### 3.1. General observations

The microwave discharge was done at a fixed position about 10 cm away from the $Li^+$-ion emitter so that we could analyze the gaseous products associated with the blue color. Fig. 1 shows a typical mass spectrum over the *m/z* range 10–70 obtained for the $N_2/H_2$ (90/10%) plasma when the $Li^+$ emitter was on (Fig. 1A) and off (Fig. 1B). Because fragmentation can be assumed to be negligible and because each peak represents a molecule present in the plasma plus the lithium-ion, we attributed the additional peaks in Fig. 1A to the attachment of $Li^+$ to genuine neutral species effusing from the plasma; the peaks in Fig. 1B were due to ionic species formed in the plasma.

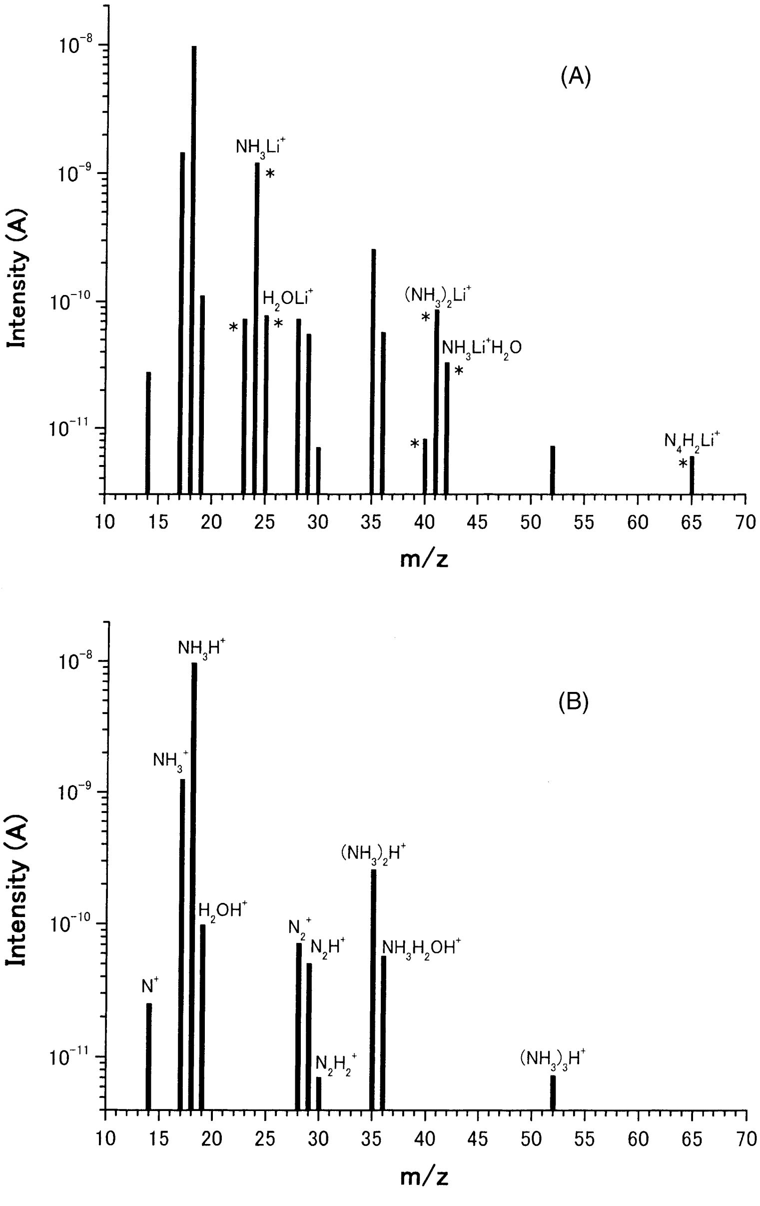

Fig. 1. Mass spectra of a 30 W, 840 Pa $N_2/H_2$ (90/10%) microwave discharge plasma (total flow rate 6 mL/min). (A) sampled in the $Li^+$-on condition; (B) sampled in the $Li^+$-off condition (ionic species detection). Additional peaks in A due to $Li^+$-ion adducts are marked with asterisks.

The presence of various neutral discharge products is denoted by an increase in the current of the $Li^+$ adduct ions.

A nitrogen–hydrogen plasma is composed of the following chemical species: $NH_3$, $N_4H_2$, $N^+$, $NH_3^+$, $NH_3H^+$, $N_2^+$, $N_2H^+$, $N_2H_2^+$, and their clustering ionic or neutral species. There has not been substantial previous work on $N_2/H_2$ discharge plasma to compare with the present results. It was found that $NH_3$ was the most abundant neutral species produced by microwave discharge through a $N_2/H_2$ gas mixture.

According to Bochway and Venugopalalan [8], $NH_3$ formation occurs mainly via NH and $NH_2$ radicals produced in the plasma region, but no one has experimentally verified the precursor of $NH_3$. The exact kinetics of the synthesis reaction is still not clear. Thus, the aim of our study was to determine the most important active species in the synthesis. Using various microwave discharge conditions, we searched carefully for NH and $NH_2$, with negative results. The failure to observe them may be not because NH and $NH_2$ radicals do not react with $Li^+$—nitrogen-containing species have sufficiently high $Li^+$ affinities that they are attached efficiently—but because the conversion reaction is extremely rapid.

### 3.1.1. $N_4H_2$

We observed a significant peak at *m/z* 65, which we have tentatively assigned to $N_4H_2Li^+$, the Li adduct of an interesting neutral product that has not been reported before. We speculate that this compound will be synthesized in the future. The elusive homologs triazene ($N_3H_3$) and tetrazene ($N_4H_4$) are known to be produced under discharge conditions [22]. If the discharge products are condensed in a liquid nitrogen trap and then allowed to evaporate, triazene and tetrazene start showing up at about the same time. We expected to observe these species rather than $N_4H_2$, but we did not detect even trace levels of them.

### 3.1.2. Ionic species

Various ionic species were clearly present. The mass spectrum (Fig. 1B) shows the ionic species: ammonium ions associated with some numbers of ammonium or $H_2O$ were present. The three most prevalent ions sampled were related to ammonium ions. The detection of ${N_2H_2}^+$—the ionic form of diimide, $N_2H_2$, the parent of the azo compounds—in our microwave discharge through $N_2/H_2$ is interesting. Although diimide has been suggested as an intermediate in the chemistry of azo compounds for a long time, no definitive mass spectrometric evidence of its existence has hitherto been presented.

### 3.1.3. The presence of water

It should be noted that there is considerable evidence of $H_2O$ contamination in the mass spectra (Fig. 1). The peak for the $H_2OLi^+$ adduct in the neutral mode is up to one-tenth as intense as the peak for the $NH_3Li^+$ adduct. Undoubtedly, the former ion comes from water contaminating the feedstock $N_2$ and $H_2$ gases and the background residual gas. Unfortunately, it is not clear how much of the signal assigned to ${NH_4}^+$ is due to $H_2O^+$, because we did not take measures to remove the effects of oxygen-containing ions from the mass spectra.

## 3.2. Plasma parameters

### 3.2.1. Microwave cavity position along the flow tube

Reactions occurring in the space between the discharge zone and the sampling cone may have some effect on the distribution of product species observed. We found that all the adduct peaks decreased slightly with distance, but the yields of the ionic species decreased significantly with distance. However, because the effect of distance on the ionic distribution was small enough to allow us to assume that the main features of the distribution were preserved, we present the dependence of the product on other plasma parameters for a fixed cavity position only (10 cm away from the $Li^+$-ion emitter).

### 3.2.2. Mixing ratio (composition)

Figs. 2 and 3 show the dependence of the intensities of ionic and neutral products in the plasma on the hydrogen composition in the plasma tube. Fig. 2 is a plot of the peak intensity for ${NH_3}^+$ (*m/z* 17), $NH_3H^+$ (*m/z* 18), $N_2H^+$ (*m/z* 29), and ${N_2H_2}^+$ (*m/z* 30) against the gas composition. These species were chosen to represent the major products. The peak intensities of ${NH_3}^+$, $NH_3H^+$, and $(NH_3)_2H^+$ (*m/z* 35, not shown in the figure) increased in a similar manner with increasing $H_2$ composition (pressure) in the flow tube, suggesting that these ions are in equilibrium one another. In contrast, $N_2H^+$ and ${N_2H_2}^+$ show fairly constant intensities.

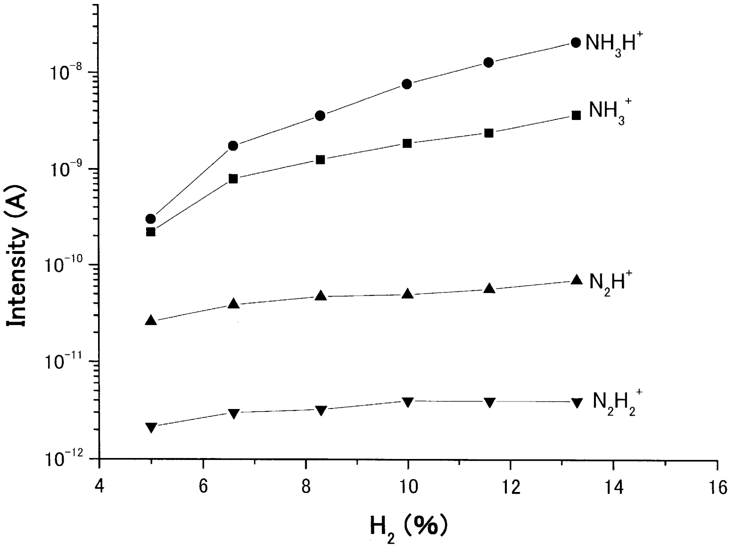

Fig. 2. Intensities of the four ionic products produced in the $N_2/H_2$ plasma as a function of the $H_2$ composition (microwave power 30 W).

Fig. 3 shows results for the $NH_3Li^+$, $(NH_3)_2Li^+$, and $N_4H_2Li^+$ species. The peak intensities for $NH_3Li^+$ and $(NH_3)_2Li^+$ increased significantly over the range from 5 to 7% $H_2$ composition and then leveled off. The intensity of $N_4H_2$ decreased by a factor of 8 over the range from 5 to 14% $H_2$. This decrease indicates that the conversion of $NH_3$ proceeds more efficiently as the $H_2$ composition (pressure) increases.

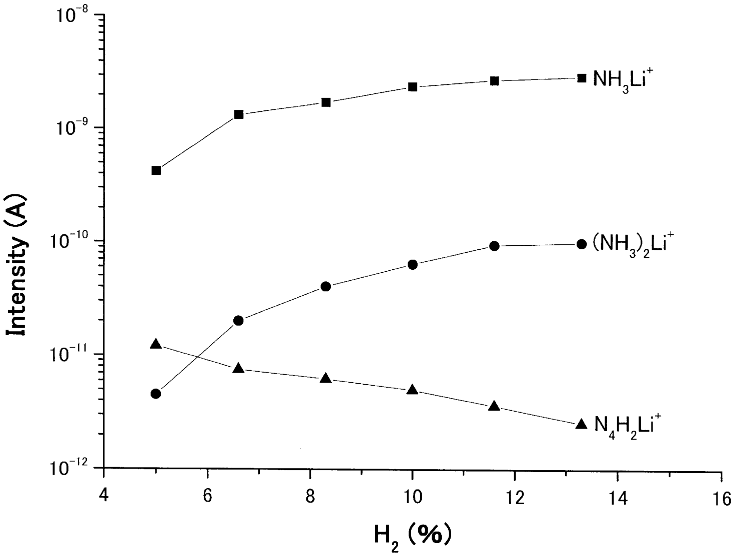

Fig. 3. Intensities of lithium adducts $NH_3Li^+$, $(NH_3)_2Li^+$, and $N_4H_2Li^+$ produced in the $N_2/H_2$ plasma as a function of the $H_2$ composition (microwave power 30 W).

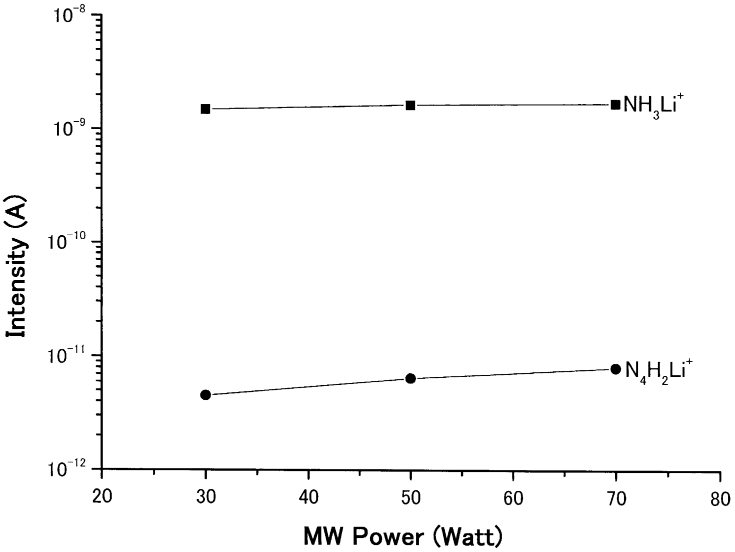

Fig. 4. Intensities of lithiated $N_4H_2$ and $NH_3$ as a function of discharge power (feed gas mixture $N_2/H_2$ (90/10%)).

### *3.2.3. Discharge power*

Finally, the effect of the discharge power on the formation of products may be large. We investigated the dependence of the $NH_3Li^+$ and $N_4H_2Li^+$ peak intensities on the microwave power. Fig. 4 compares peak intensities for the products $NH_3Li^+$ (*m*/*z* 24) and $N_4H_2Li^+$ (*m*/*z* 65) observed at different microwave discharge powers with the $N_2/H_2$ (90/10%) feed gas at a fixed flow tube pressure of 840 Pa (6.3 Torr). In the range from 30 to 70 W, however, the microwave power had little effect on the peak intensity of either species.

### *3.3. Concluding remarks*

Microwave discharge through a $N_2/H_2$ mixture produced various kinds of chemical species. We have presented mass spectrometric evidence for the elusive chemical compound $N_4H_2$. No species with chemical formula $N_4H_2$ is listed in the NIST database [23]. Recent ab initio studies of the structure, vibrational frequencies, and intensities of the open-chain species HN=N–N=NH [24] indicate that there are a considerable number of possible conformations for $HN_4H$. This species can be assumed as a possible molecule. We expected to observe triazene and tetrazene as intermediates in the $N_2/H_2$ microwave plasma, but neither species was directly observed in the $Li^+$ adduct mass spectrum.

The ionic components observed were $N^+$, $NH_3{}^+$, $NH_3H^+$, $(NH_3)_nH^+$ ($n = 1$–3), $N_2{}^+$, $N_2H^+$, $N_2H_2{}^+$, and some clustered ions. $N_2H$ and $N_2H_2$ were not observed in the neutral form. The yields of these species readily varied when the gas composition was changed, just as the yields of the neutral species did.

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