

19 November 1999

Chemical Physics Letters 313 (1999) 733-740

CHEMICAL PHYSICS LETTERS

www.elsevier.nl/locate/cplett

Analysis of products from a C_2H_2/N_2 microwave discharge: new nitrile species

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Received 12 July 1999; in final form 31 August 1999

Abstract

The production of gaseous hydrocarbons, nitriles, amines, and hydrazines in a continuous-flow microwave plasma discharge excited in a 20% $C_2H_2 + 80\% N_2$ mixture at a pressure of 20 Torr is reported. The product analysis was made by Li⁺ ion attachment mass spectrometry. A variety of N-containing organics (identified as HC_nN (n = 1-7), NC(C=C)_nCN (n = 0-2), NC(CH₂)_nCN (n = 0-6), $C_nH_{2n-1}NH_2$ (n = 0-6), $C_nH_{2n+1}N(H)NH_2$ (n = 0-5), etc.) were formed and these were tentatively assigned to nitriles, amines, and hydrazines. The mass-spectral analysis exhibited progressions differing by 14 mass units. Reaction schemes were proposed to explain the formation of some molecules. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

A microwave (MW) discharge plasma is a prime method for the production of various kinds of novel compounds, since many products may be generated in complex ways [1,2]. In the search for materials with new physical properties, nitrogen compounds are a reasonable target since the nitrogen atom forms 3, 4, or 5 covalent bonds leading to unique structural characteristics.

Several workers [3–8], including some astrophysicists [6,7], have reported the presence of various chemical groups produced by electrical discharges in C_2H_2 . For instance, Fujii [8] reported the unexpected formation of many unfamiliar neutral hydrocarbon (HC) products, among which were various free radicals such as C_nH_3 (n = 2 and 4), C_nH_5 (n = 2, 4, and 6), and C_nH_7 (n = 3 and 4). In recent studies related to C_2H_2 MW plasma, Bondybey and co-workers [9–11] identified a variety of conjugated molecular products: cyanocarbon series C_nN_2 (n = 4, 5) [9] and cyanopolyacetylene radical cations NC($C \equiv C$)_nCN⁺ [10,11]. These results suggested there would be considerable interest in seeking new products in a C_2H_2/N_2 MW discharge system.

The recently developed Li⁺ ion attachment mass spectrometry (Li⁺ MS) provides mass spectra of quasi-molecular ions formed by lithium ion attachment to chemical species under high pressure [12– 14]. Results are obtained in the form of mass-spectrometric traces of Li⁺ adducts. As an example [15,16], the method was successfully applied to the study of neutral species that emerge from CH_4/O_2 microwave discharge plasmas. It was demonstrated that Li⁺MS provides only molecular ions and direct

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determination of unstable, intermediary and reactive species is allowed.

In the present Letter, I report our mass-spectral observations of products from a C_2H_2/N_2 plasma and present analysis suggesting that they are nitriles, amines, and hydrazines – compounds of potential significance as new substances. I also report some new series of nitrile neutrals, such as NC(C=C)_nCN and NC(CH₂)_nCN, which are of considerable interest as potential interstellar or planetary species, as well as being of both theoretical and synthetic importance. Finally, plausible reaction schemes to explain their formation are considered.

2. Experimental

I utilized a MW discharge source/Li⁺ reactor/quadrupole mass spectrometer, as described previously [12–14]. This arrangement makes it pos-

sible to directly detect products, and is essentially identical to that used in an earlier identification study of unfamiliar products in a C_2H_2 plasma [8].

The MW source was constructed from a straight quartz tube (3 mm inner diameter, 6 mm outer diameter, 20 cm in length). The C_2H_2 gas, premixed with N_2 , flows down this tube. The MW plasma was created by connecting the cavity to a 2.465 MHz MW generator through a matching network. All the experiments were performed under the following conditions: total pressure upstream at the flow tube, 20 Torr; total pressure at the Li⁺ reactor, 0.2 Torr; MW power, 30 W; total gas flow rate, 10 cm³/min.

The species produced by the MW discharge effused via a flow tube into the Li^+ reactor. The products were monitored by measuring the Li^+ -adduct ion mass spectrum. Measurements were taken 135 mm away from the Li^+ emitter. Here the mass signal intensities of the ionic species coming from the plasma were confirmed to be negligible by con-



Fig. 1. Typical mass spectra of Li⁺ adducts showing the neutral products formed in the 20% $C_2H_2 + 80\%$ N₂ (A) and 20% $C_2H_2 + 80\%$ Ar (B) MW discharge plasmas. The experimental conditions were the same in both plasmas. Only those peaks with intensity > 3% of that of the base peak, m/z 48, in the (A) spectrum are drawn. Note: the signal intensity scale of (A) is different from that of (B).

trol experiments using continuous flow C_2H_2/N_2 mixtures of varied proportions but without Li⁺ emission. This arrangement was found optimal for accurate identification of the various neutral products. A second control experiment was performed using a continuous flow plasma discharge with Ar in place of the N₂. On the simple basis of the inertness of Ar, different products might be expected.

3. Results and discussion

3.1. Mass spectra

Typical Li⁺-adduct ion mass spectra of neutral chemical species produced in N₂ (80%)– C_2H_2 (20%)

Table 1

Neutral products^a formed by a MW discharge in a mixture of 20% $C_2H_2 + 80\%$ N₂ compared with those formed in a mixture of 20% $C_2H_2 + 80\%$ Ar. Relative intensities (in parentheses) are given as a percentage relative to the m/z = 48 peak from the N₂/C₂H₂ system. All products of both N₂/C₂H₂ and Ar/C₂H₂ plasmas with a relative peak intensity of > 3% are listed

$\overline{m/z^{a}}$	N_2/C_2H_2	Ar/C_2H_2	m/z^{a}	N_2/C_2H_2	Ar/C_2H_2
23	NH ₂ (29)		24	NH ₃ (65)	
25	2	H ₂ O (32)	33	$C_{2}H_{2}$ (6)	$C_{2}H_{2}(4)$
34	HCN (43)	$\tilde{C_{2}H_{3}}(12)$	35	2 2	$C_{2}H_{4}(3)$
36	$H_2C = NH(11)$	$C_{2}H_{5}(5)$	38	$CH_{3}NH_{2}$ (4.4)	2 4
39	$N_2 H_4$ (4.8)		46	CN (H)C (7.4)	
47	$C_{3}H_{4}(6)$	$C_{3}H_{4}(3)$	48	CH ₃ CN (100)	$C_{3}H_{5}(5)$
50	$C_{2}H_{3}NH_{2}$ (15)	$C_{3}H_{7}(6)$	51	$CH_{3}N = NH(21)$	5 5
52	$C_{2}H_{5}NH_{2}$ (14)		53	$CH_{3}N_{2}H_{3}(5.0)$	
56	C4H? (4.6)		57	$C_4 H_2 (4)$	$C_4 H_2$ (4)
58	HCCCN (51)	$C_4 H_3 (12)$	59	NCCN (10)	
60	$C_2H_3CN(18)$		61	C_2 HN=NH (6)	
62	$C_{2}H_{5}CN(24)$		63	$C_{2}H_{3}N=NH(8.9)$	
64	$C_{3}H_{5}NH_{2}(7.7)$		65	$C_2H_5N=NH(8.1)$	
66	$C_{3}H_{7}NH_{2}$ (9.1)		67	$C_2H_5N_2H_3$ (5.7)	
70	HCCCCN (8.2)		72	CH ₃ CCCN (35)	
73	NC-CH ₂ -CN (7.5)		74	$C_{3}H_{5}CN(21)$	
75	$C_{3}H_{3}N = NH(13)$		76	$C_{3}H_{7}CN(16)$	
77	$C_{3}H_{5}N=NH(8.5)$		78	$C_4 H_7 NH_2$ (6.5)	
79	$C_{3}H_{7}N = NH(6.6)$	$C_{6}(4)$	80	$C_4 H_9 N H_2$ (6.7)	
81	$C_{3}H_{7}N_{2}H_{3}$ (12)	$C_{6}H_{2}(3)$	82	HCCCCCN (46)	
83	NCCCCN (8.1)	$C_{6}H_{4}(6)$	84	CH ₃ CCCCN (11)	
85	$C_{6}H_{6}(6)$	$C_{6}H_{6}(6)$	86	$C_2H_5CCCN(13)^b$	
87	$NC-(CH_2)_2-CN$ (7.5)		88	$C_4 H_7 CN (5.6)$	
89	$C_4H_5N=NH(6.4)$		90	$C_4 H_9 CN (7.4)$	
91	$C_4H_7N=NH(8.0)$		92	$C_5 H_9 N H_2$ (3.6)	
93	$C_4 H_9 N = NH(6.1)$		94	HCCCCCCN (5.2)	
95	$C_4H_9N_2H_3(5.1)^c$		96	$CH_3CCCCCN(7.2)$	
98	CH ₃ CH ₂ CCCCN (5.6)		99	$C_{7}H_{8}(4)$	$C_7 H_8 (4)$
100	$CH_3 - (CH_2)_2 - CCCN$ ((9.5)	101	$NC-(CH_2)_3-CN$ (6.4)	
102	$C_5 H_9 CN (5.2)$		103	$C_5H_7N = NH(4.8)$	
104	$C_5 H_{11} CN (6.1)$		105	$C_5 H_9 N = NH (13)$	
106	HCCCCCCCN (19)		107	NCCCCCCN (5.2) ^d	$C_8 H_4 (3)$
108	$CH_3CCCCCCN (5.0)$		109	$C_5 H_{11} N_2 H_3 (3.5)$	$C_8 H_6 (3)$
110	CH ₃ CH ₂ CCCCCN (5.9	9)	114	$CH_{3}-(CH_{2})_{3}-CCCN(8.4)$	
115	$NC-(CH_2)_4-CN$ (5.8)		120	$CH_3CCCCCCCN$ (16)	
123	$C_6H_{13}N_2H_3$ (5.0)		124	$CH_{3}-(CH_{2})_{2}-CCCCCN (5.2)$	
128	$CH_{3}-(CH_{2})_{4}-CCCN(7.1)$			$C_8H_{15}NH_2$ (8.5)	
138	CH ₃ -(CH ₂) ₃ -CCCCC	CN (4.9)			

^aThe observed m/z due to the Li⁺-adduct.

^b, ^c, and ^d are possibly C₅H₅N, NCCCCCN, and C₅H₁₁N=NH, respectively.

and Ar (80%)– $C_2H_2(20\%)$ (vol–vol) MW plasmas under the same discharge conditions are shown in Fig. 1. Series of masses differing by 14 mass units (e.g., 34, 48, 62 and 76; 58, 72 and 86; 106, 120 and 134) are obvious.

The C_2H_2/N_2 plasma led to the formation of many neutral species, while the products formed in

the C₂H₂/Ar plasma were almost the same as those in previous experiments using pure C₂H₂ [8]. These products were mainly hydrocarbons (HCs), including radicals such as C_nH_{2n+1} and C_nH_{2n-1}, and some molecules such as C₄H₆ and C₆H₆. Most of the peaks that appeared in the C₂H₂/N₂ plasma had the same m/z values as those that appeared in the pure

Table 2

Classification analysis of products formed by the MW discharge in a mixture of 20% C_2H_2 and 80% N_2 . The representation is the same as that described in Table 1

Туре	Chemical species		
Nitriles:			
$C_n H_{2n+1} CN^a$	HCN (43), CH ₃ CN (100), C ₂ H ₅ CN (24), C ₃ H ₇ CN (16), C ₄ H ₉ CN (7.4), C ₅ H ₁₁ CN (6.1)		
$C_n H_{2n-1} CN$	CHCN ^c (7.4), C_2H_3CN (18), C_3H_5CN (21), C_4H_7CN (5.6), C_5H_9CN (5.2)		
$C_n H_{2n-3} CN$	HCCCN (51), CH ₃ CCCN (35), CH ₃ CH ₂ CCCN (13), CH ₃ -(CH ₂) ₂ -CCCN (9.5), CH ₃ -(CH ₂) ₃ -CCCN (8.4) CH ₃ -(CH ₂) ₄ -CCCN (7.1)		
C _u H _{2u} ₅ CN	HCCCCN (8.2), CH_2 -CCCCN (11), CH_2CH_2CCCCN (5.6)		
$C_{n}H_{2n} - 7CN$	HCCCCCN (46), CH ₂ CCCCCCN (7.2), CH ₂ CH ₂ CCCCCCN (5.9), CH ₂		
n 2n - 1	$-(CH_{3})_{3}$ -CCCCCN (5.2), $CH_{3}-(CH_{3})_{3}$ -CCCCCN (4.9)		
C _u H _{2u} oCN ^b	HCCCCCCN (5.2), CH ₂ CCCCCCCN (5.0)		
$C_nH_{2n-1}CN^b$	HCCCCCCCN (19). CH ₂ CCCCCCCN (16). CH ₂ CH ₂ CCCCCCN (8.5)		
$NC-(CH_2)$ -CN	NC-CN (10), NC-CH ₂ -CN (7.5), NC-(CH ₂) ₂ -CN (7.5), NC-(CH ₂) ₂ -CN (6.4), NC-(CH ₃) ₄ -CN (5.8),		
NC $(C \equiv C)_n^n CN$	NCCCCN (8.1), NCCCCCCN (5.2)		
Amines:			
$C_n H_{2n+1} N H_2^b$	NH_3 (65), CH_3NH_2 (4.4), $C_2H_5NH_2$ (14), $C_3H_7NH_2$ (9.1), $C_4H_9NH_2$ (6.7), $C_2H_4NH_3$ (5.2), $C_4H_4NH_4$ (5.0)		
$C_n H_{2n-1} N H_2^b$	$C_{5}H_{11}M_{2}(0.2), C_{6}H_{13}M_{12}(0.5)$ $CHNH_{2}(11), C_{2}H_{3}NH_{2}(15), C_{3}H_{5}NH_{2}(7.7), C_{4}H_{7}NH_{2}(6.5),$ $C_{5}H_{9}NH_{2}(3.6), C_{6}H_{11}NH_{2}(19),$ $C_{5}H_{9}NH_{2}(3.6), C_{6}H_{11}NH_{2}(19),$		
$C_nH_{2n-3}NH_2^a$	$C_7 H_{13} N H_2$ (16), $C_8 H_{15} N H_2$ (8.5)		
Hydrazines:			
$C_nH_{2n+1}N_2H_3$	$N_{2}H_{4}$ (4.8), $CH_{3}N_{2}H_{3}$ (5.0), $C_{2}H_{5}N_{2}H_{3}$ (5.7), $C_{3}H_{7}N_{2}H_{3}$ (12), $C_{4}H_{9}N_{2}H_{3}$ (5.1), $C_{5}H_{11}N_{2}H_{3}$ (3.5)		
$C_{n}H_{2n+1}N=NH$	$CH_2N=NH(21), C_2H_5N=NH(8.1), C_2H_7N=NH(6.6), C_4H_0N=NH(6.1), C_5H_1N=NH(5.2)$		
$C_{n}H_{2n-1}N=NH$	CHN=NH ⁴ (86), C ₂ H ₂ N=NH (8.9), C ₂ H ₅ N=NH (8.5), C ₄ H ₇ N=NH (8.0), C ₄ H ₈ N=NH (13)		
$C_n H_{2n-3} N = NH$	C_2 HN=NH (6), C_3H_3 N=NH (13), C_4H_5 N=NH (6.4), C_5H_7 N=NH (4.8)		
Others	$H_2C=NH(11), H_2NCN(86), NH_2(43),$		

^a The $C_n H_{2n-3} N H_2$ peaks are isobaric with the $C_n H_{2n+1} CN$ peaks of one lower *n* number. They were not distinguished in this study. We assume from the presence of homologues that the latter were dominant.

^bThe $C_nH_{2n-9}CN$ and $C_nH_{2n-11}CN$ peaks are isobaric with the $C_nH_{2n+1}NH_2$ and $C_nH_{2n-1}NH_2$ peaks of the same *n* number, respectively. We assume that both were present.

^cPossibly cyclic structure (see context).

^dPossibly cyclic structure, this molecule has the same mass number as H₂NCN.

 C_2H_2 plasma. However, their intensities were much larger, indicating the production of many new types of N-containing species in the C_2H_2/N_2 system.

The main peaks detected, their relative peak intensities, and their assignments are given in Table 1. Nitriles, amines, and hydrazines were identified. Many less volatile species remained as a film of solid on the flow tube wall. A black-brown solid was also obtained, but this material has not been characterized. Since the identification is based only on the mass number, the assignment is not free of ambiguity. For example, CH₃CNLi⁺ ions have the same m/z value as C₂HNH₂Li⁺ ions. Furthermore, the relative abundance of isomeric pairs, such as HCN · HNC and HCCCN · HCCNC, is inaccessible to mass spectrometry.

The relative intensities of the peaks in both systems represent the monoisotopic intensities (including contributions from all the isotopes for a given ion) with the relative intensities normalized to 100 units for the base peak of the CH₃CNLi⁺ species in the C₂H₂/N₂ plasma. With some exceptions, peaks with a height of < 3% of the highest peak (m/z = 48 in the C₂H₂/N₂ plasma) are not reported. When detecting neutral products by Li⁺ ion attachment, the sensitivity depends on the Li⁺ affinity. Fortunately, N-containing HC species have sufficiently high Li⁺ affinities to be attached at close to collision rates, so little discrimination is expected.

3.2. Classification analysis

The observed peaks are classified in Table 2. The MW discharge in C_2H_2/N_2 gave three types of N-containing species: nitriles, amines, and hydrazines, and also possibly some HCs.

3.2.1. Nitriles

Many products were formulated as $C_nH_{2n+1}CN$ (n = 1-5), $C_nH_{2n-1}CN$ (n = 5), $C_nH_{2n-3}CN$ (n = 7), $C_nH_{2n-5}CN$ (n = 3), $C_nH_{2n-7}CN$ (n = 5), $C_nH_{2n-9}CN$ (n = 3), and $C_nH_{2n-11}CN$ (n = 3). As can be assumed from previous experimental results [17], which showed that the dominant products from MW discharge in a CH_4/N_2 mixture were nitriles, these homologues (corresponding to additions of CH_2 units) may be saturated or unsaturated nitriles. Their abundance seems to vary smoothly with chain length, with CH_3CN being most abundant. Among many the nitriles produced, the cyanopolyynes, HC_nN , are particularly interesting due to their linear conjugated structures, their biological importance, and their abundance in the interstellar medium. The well-known interstellar cyanopolyynes HC_nN (n = 1, 3, 5, 7) [18] can be formed abundantly in the present system: HCN (relative intensity 43), HCCCN (51), HCCCCCN (46), and HCCCCCCCN (19). In this study, the even numbers of the HC_nN series (with n at 2, 4, and 6) were also detected; however, their relative intensities were much less than those of the cyanopolyynes with odd carbon numbers.

I observed other significant peaks at m/z = 59, 83, and 107, which can be assigned to dicyanopolyacetylenes NC(C=C), CN with n at 0, 1, and 2. Cvanogen, NCCN, is well known for its production in high-temperature environments [19] and its postulated presence in the interstellar medium. Since dicyanoacetylene, NCCCCN, was first reported in 1909, there have been surprisingly few studies of this species [20,21], despite being of interest as an unusual linear molecule which results in an extended π orbital (delocalization of the electrons along the whole molecule). The interest in these species can be expected to increase in view of the recent observations of Grosser and Hirsch [1]: They were able to produce large amounts of NC(C=C), CN molecules by vaporizing graphite under helium in a reactor designed for fullerene production in the presence of cyanogen, $C_2 n_2$.

Dicyanoalkanes, NC(CH₂)_{*n*}CN (n = 1-4), are interesting products found in this study that have not been reported before. The fraction was fairly constant, the observed intensity ratio of the mass lines corresponding to the compounds NC(CH₂)_{*n*}CN (n = 1-4) produced was 100:100:85:77, and the intensity was relatively constant over the *n* values. I speculate that these compounds will be synthesized in the future.

3.2.2. Amines

The products included alkyl amines with single, double, and triple bonds, with many homologous members often present in roughly equal yields (within a factor of 4). The higher homologues of $C_nH_{2n-1}NH_2$ (n = 6, 7, 8) were found in higher fractions, mainly because the corresponding mass lines were possibly enhanced with the same mass signal as HCCCCCCCN, $CH_3CCCCCCN$, and $C_2H_5CCCCCCCN$ species.

3.2.3. Hydrazines

Some products were formulated as C_nH_{2n+1} N(H)NH₂, C_nH_{2n+1} N=NH, C_nH_{2n-1} N=NH, and C_nH_{2n-3} N=NH. These homologues (corresponding to additions of CH₂ units) may be hydrazines. Again, other assignments are possible.

I also obtained other significant peaks at m/z = 36, which can be assigned to $H_2C=NHLi^+$. It is suggested that hot NH_2 or CN radicals generated by dissociation of initial amine or nitrile products can react with each other and with HC species to produce these unfamiliar organic compounds by way of their recombination.

The peak assignment of these nitrogenated products is not free of ambiguity. The $C_n H_{2n+1} CN$ compound peaks are isobaric with the $C_n H_{2n-1}$ peaks of one higher carbon number. Because HC radicals of the $C_n H_{2n-1}$ type were observed clearly in the C_2H_2/Ar plasma (see Fig. 1B), I tentatively speculate that both nitriles and HC radicals are formed. Also, the $CN(CH_2)_n CN$, $C_n H_{2n-9} CN$, $C_n H_{2n-1} CN$, $C_nH_{2n+1}N(H)-NH_2$, $C_nH_{2n-1}N(H)-NH_2$, and $C_nH_{2n-3}N(H)-NH_2$ peaks are isobaric with the $CN-N_n-CNLi^+$, $C_nH_{2n+1}NH_2$, $C_nH_{2n-1}NH_2$, $C_n H_{2n+1} N = NH$, $C_n H_{2n-1} N = NH$, and $C_n H_{2n-3} N = NH$ peaks of the same *n* number, respectively. The $C_n H_{2n-3} N H_2$ peaks are isobaric with the $C_n H_{2n+1} CN$ peaks of one lower carbon number. In this study they were not distinguished.

3.3. Products vs. gas component

It was instructive to study this system as a function of the feed gas component. A number of runs were made to increase the total intensities of adduct ions, ΣI_{adduct} , issuing through the Li⁺ ion attachment reactions. Because the gas component affected the Li⁺ emission for each successive run, I considered the normalized concentrations (% ΣI_{adduct}) of the neutral species in the plasma for comparison purposes.

The evolution of CH₃CNLi⁺ (m/z = 48), HCC-CNLi⁺ (m/z = 58), NCCNLi + (m/z = 59), $C_2H_3NH_2Li + (m/z = 50)$, and $CH_3N=NHLi^+$ (m/z = 51) against the gas composition is shown in Fig. 2. The first 2 were chosen as the 2 most intense species. The last 3 compounds represent the major products classified as $NC(C=C)_nCN$, $C_nH_{2n-1}NH_2$, and $C_nH_{2n+1}N=NH$ molecules, respectively. The homologous species generally followed similar variation patterns.

The component ratio of 20% C_2H_2 to 80% N_2 was most favorable in terms of the total intensity of adduct ions of the products and hence the classification analysis in the previous section concerned only this composition. However, it should be noted that the major constituents each followed an entirely different pattern. Although the present data are insufficient to arrive at a detailed explanation, a few facts are worth noting. Plotting the intensities of the examined peaks against the C_2H_2 ratio in the mixture gas confirmed that the variations came from the addition



Fig. 2. Li⁺-adduct intensity of the neutral products CH₃CNLi⁺ (m/z 48), C₂H₃NH₂Li⁺ (m/z 50), CH₃N = NHLi⁺ (m/z 51), HCCCNLi⁺ (m/z 58), and NCCNLi⁺ (m/z 59), produced in C₂H₂/N₂ plasmas, plotted against gas composition.

of acetylene to the system over the limited range, but not in the same ratio.

As the percentage of C_2H_2 increased, the peak intensity of NCCNLi⁺ increased to a maximum at ~ 10% C_2H_2 and finally disappeared at around 30% C_2H_2 . The CH₃CN (m/z = 48) and HCCCN (m/z = 58) peak heights increased monotonically with increasing C_2H_2 , reached their maximums at around 20% and 15% C_2H_2 , respectively, and then decreased. In contrast to the behaviors of CH₃CN (m/z = 48) and HCCCN (m/z = 58), as the C_2H_2 component increased from 5% to 30% the % Σ of $C_2H_3NH_2Li^+$ and CH₃N=NHLi⁺ increased almost linearly. These variations in behavior remain unexplained at this moment.

3.4. Mechanism considerations

A few types of reaction are briefly discussed to model the present results. In many studies simulating Titan's atmosphere, it is reported that electric discharge plasmas in a CH_4/N_2 gas mixture produce many products including HCs, nitriles, amines, hydrazines, etc. Most of these were also observed in the present C_2H_2/N_2 system and, in fact, these studies have proved helpful in explaining the observed results.

From the present results, one would expect radical chemistry to occur in the C_2H_2/N_2 discharge. Active nitrogen atoms, N^{*}, are a primary radical product; it is well known [22] that electrons present in the plasma should serve to produce active nitrogen atoms. The following polymerization reaction starts with this species.

If N * is supplied, then the interaction between N * and C_2H_2 or other HCs is highly probable – the free radical interaction with N * and other HCs is highly exothermic, suggesting the production of the larger N-bearing HC species. Reactions of radical-involved condensations leading to polymeric products may well dominate the chemistry of the C_2H_2/N_2 discharge.

For instance, following are the thermodynamically accessible channels and the corresponding enthalpies of reaction at T = 298 K for the reaction between N^{*} and C₂H₃, which have been directly observed [8] as a major product of a C_2H_2 discharge plasma.

N^{*} + C₂H₃
→ CH₂CN + H (
$$\Delta H^{\circ}$$
 = -74 kcal/mol), (1a)
→ CH₂CN (ΔH° = -167 kcal/mol), (1b)

$$\rightarrow$$
 CN + C₃ ($\Delta H^{\circ} = -46 \text{ kcal/mol}$), (1c)

$$\rightarrow \text{HCN} + \text{CH}_2 \quad (\Delta H^\circ = -60 \text{ kcal/mol}),$$
(1d)

$$\rightarrow \text{CHCN} + \text{H}_2 \quad (\Delta H^\circ = -75 \text{ kcal/mol}).$$
(1e)

This speculation is proved partially by the presence of the major component, CH_3CN . The cyano radical is considered capable of a whole range of additional reactions [23]. The assorted products of these reactions would result in the widespread peaks.

The most probable important reaction for the production of amine and hydrazine species is thought to be a reaction yielding an NH radical. It is well known [24] that NH can be produced exothermically in hydrogen-active nitrogen systems. It is assumed from the present observation of amines and hydrazines that NH radicals are rapidly converted into these species in combination with many HC species.

3.5. Concluding remarks

The C_2H_2/N_2 MW discharge led to the production of various kinds of chemical species, and effectively demonstrated that the MW discharge is a method for generating over 70 N-bearing products. They had the formulas C_mH_nCN , $NC(CH_2)_nCN$, $NC(C)_nCN$, $C_mH_nNH_2$, and $C_mH_nN_2H_3$ with *m* and *n* continuing on to 8 and 15. Direct observation of these species was allowed by the measurement of the Li⁺-adduct mass spectra. Further studies would benefit from investigation of total pressure dependencies, MW power variation and change of flow rate. I will report them in the near future.

Some interesting products found in this study were $H_2C=NH$ and $NC(CH_2)_nCN$. These components are predicted to be possible future products. The results may also have implications for our understanding of chemical evolution in the solar system. Our results suggest that nitriles, amines and hydrazines of higher molecular weight, and their derivatives, such as cyano-acetylenes and dinitriles, may have been synthesized as precursors of biologically important compounds in planetary lightning and plasmas associated with meteor impacts which may be acceptable analogs to MW plasmas.

Acknowledgements

This work was supported in part by the Japanese Ministry of Education, Science and Culture under a Grant-in-Aid for General Scientific Research (04804033). Thanks are due to N. Arai and T. Yamada for their technical contributions.

References

- T. Grosser, A. Hirsch, Angew. Chem., Int. Ed. Engl. 32 (1993) 1340.
- [2] C. Niu, Y.Z. Lu, C.M. Lieber, Science 261 (1993) 335.
- [3] H. Ehrhardt, R. Kleber, B. Scheppat, A. Fucha, W. Dworschak, J. Scherer, K. Jung, Plasma Surf. Eng. 2 (1988) 1113.
- [4] T. Mieno, T. Shoji, K. Kadota, Jpn. J. Appl. Phys. 31 (1992) 1879.
- [5] S.F. Durrant, R.P. Mota, M.A. Bica de Moraes, J. Appl. Phys. 71 (1992) 448.

- [6] J.O.P. Pedersen, B.J. Opansky, S.R. Leone, J. Phys. Chem. 97 (1993) 6822.
- [7] T.C. Killian, J.M. Vrtilek, C.A. Goottlieb, E.W. Gottlieb, P. Thaddeus, Astrophys. J. 365 (1990) L89.
- [8] T. Fujii, J. Appl. Phys. 82 (1997) 2056.
- [9] A.M. Smith, C. Engel, A. Thoma, G. Schallmoser, B.E. Wurfel, V.E. Bondybey, Chem. Phys. 184 (1994) 233.
- [10] J. Agreiter, A.M. Smith, M. Hartle, V.E. Bondybey, Chem. Phys. Lett. 225 (1994) 87.
- [11] J. Agreiter, A.M. Smith, V.E. Bondybey, Chem. Phys. Lett. 241 (1995) 317.
- [12] T. Fujii, Anal. Chem. 64 (1992) 775.
- [13] T. Fujii, Chem. Phys. Lett. 191 (1992) 162.
- [14] T. Fujii, K. Syouji, J. Appl. Phys. 74 (1993) 3009.
- [15] T. Fujii, K. Syouji, J. Phys. Chem. 97 (1993) 11380.
- [16] T. Fujii, K. Syouji, Phys. Rev. E 49 (1994) 657.
- [17] T. Fujii, N. Arai, Proceedings of the 14th International Mass Spectrometry Conference, Aug. 1997, Tampere (in disk form).
- [18] D. Smith, Chem. Rev. 92 (1992) 1473.
- [19] J. Goede, F.J.J. de Kanter, F. Bickelhaupt, J. Am. Chem. Soc. 113 (1991) 6104.
- [20] A.M. Smith, G. Schallmoser, A. Thoma, V.E. Bondyney, J. Chem. Phys. 98 (1993) 1776.
- [21] D. Fomey, P. Freivogel, J. Fulara, J.P. Maier, J. Chem. Phys. 102 (1995) 1510.
- [22] G. Marston, F.L. Neobitt, D.F. Nava, W.A. Payne, L.J. Stief, J. Chem. Phys. 93 (1989) 5769.
- [23] B. Atakan, J. Wolfrum, Chem. Phys. Lett. 186 (1991) 547.
- [24] D.R. Safrany, Prog. React. Kinet. 6 (1971) 1.