Plasma-Triggered CH₄/NH₃ Coupling Reaction for Direct Synthesis of Liquid Nitrogen-Containing Organic Chemicals

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Supporting Information

ABSTRACT: Nitrogen-containing organic chemicals such as amines, amides, nitriles, and hydrazones are crucial in chemical and medical industries. This paper reports a direct synthesis of N,N-dimethyl cyanamide [(CH₃)₂NCN] and amino acetonitrile (NH₂CH₂CN) through a methane/ammonia (CH₄/NH₃) coupling reaction triggered by dielectric barrier discharge plasma, with by-products of hydrazine, amines, and hydrazones. The influence of CH₄/NH₃ molar ratio, feedstock residence time, and specific energy input on the CH₄/NH₃ plasma coupling reaction has been investigated and discussed. Under the optimized conditions, the productivities of (CH₃)₂NCN and NH₂CH₂CN reached 0.46 and 0.82 g·L⁻¹·h⁻¹, respectively, with 8.83% CH₄ conversion. In addition, through combining the optical emission spectra diagnosis and the reaction results, a possible CH₄/NH₃ plasma coupling reaction mechanism has been proposed. This paper provides a potential fine application of CH₄ and NH₃ in green synthesis of liquid nitrogen-containing organic chemicals, such as nitriles, amines, amides, and hydrazones.

1. INTRODUCTION

Nitrogen-containing organic chemicals, such as amines, amides, nitriles, and hydrazones are crucial in chemical and medical industries. The productive processes of these nitrogen-containing chemicals, however, are usually multistep and complicated, in which massive waste gas, waste liquid, and solid waste were brought inevitably. In addition, some rare and expensive nitrogen reagents such as azides and metallonitrene were usually used.1−5 Therefore, there have been increasing interests on developing some novel and green methodologies to synthesize these nitrogen-containing chemicals using simpler and cheaper feedstocks.6−9

Cyanamides and amino nitriles, two building blocks containing C≡N bond, are the basic structure in organic synthesis, especially in the synthesis of heterocyclic compounds10−14 and amino acids.15 Currently, N,N-dimethyl cyanamide [(CH₃)₂NCN] and amino acetonitrile (NH₂CH₂CN) are two important chemical intermediates in medicine synthesis. However, the industrial synthesis of (CH₃)₂NCN and NH₂CH₂CN requires several steps and emits acidic wastes, as shown in Scheme 1.16 The direct coupling reaction of methane (CH₄) and ammonia (NH₃) to form C≡N bond is very significant and highly desired because the feedstocks (CH₄ and NH₃) are relatively abundant and cheap. Industrially, the CH₄/NH₃ coupling reaction has been conducted over Pt gauze catalysts for the synthesis of hydrogen cyanide (HCN), where high reaction temperature (>1100 °C) is required due to the high thermodynamic stability of CH₄ and NH₃ molecules, as shown in Scheme 2.17 This coupling reaction has been attempted using a microwave plasma,18 and 78% CH₄ conversion was achieved at 500 W input power. However, no product other than HCN was obtained. In fact, the synthesis of chemicals by using plasma technologies has a long history. Ozone was synthesized from air silent discharge in 1857,19 and dielectric barrier discharge (DBD) plasma is still the most effective method for industrial production of ozone. In 1967, Spedding reported the direct synthesis of hydrazine from NH₃ employing a gas discharge reactor,20 and he also demonstrated that hydrocarbons can take place isomerization reaction, elimination reaction, bimolecular addition reaction, and selective oxidation reaction.21 Recently, Liu reported that long-chain hydrocarbons were produced from CH₄ plasma and CH₄/CO₂ plasma;22,23 Cooks published a paper reporting the selective reduction of benzene in a helium plasma;24 Benoit reported that nonthermal atmospheric plasma can be considered as a promising technology for enhancing the depolymerization of recalcitrant cellulose toward hydrolysis.25

Received: July 25, 2017
Accepted: October 5, 2017
Published: December 27, 2017
Our group demonstrated that DBD plasma is a potential method for direct synthesis of high purity H$_2$O$_2$ from H$_2$ and O$_2$ without using any catalysts.$^{27-30}$ We also reported that high-value liquid chemicals and fuels were produced through a CH$_4$−CO$_2$ reforming reaction in a designed DBD plasma reactor.$^{31}$ For the best of our knowledge, the direct synthesis of the C≡N group containing compounds except HCN by CH$_4$/NH$_3$ plasma coupling reaction has not yet been reported.

This paper reports that, under ambient temperature and atmospheric pressure, NH$_2$CH$_2$CN and (CH$_3$)$_2$NCN can be produced as the major products from the CH$_4$/NH$_3$ DBD plasma, while, some other liquid chemicals, such as hydrazine, amines, and hydrazones, were produced as well. The direct synthesis of high-value NH$_2$CH$_2$CN, (CH$_3$)$_2$NCN, and HCN from CH$_4$/NH$_3$ plasma could not only promote the fine utilization of CH$_4$ and NH$_3$ but also open a new way for the green synthesis of compounds containing both the C≡N bond and the amino group.

2. EXPERIMENTAL SECTION

2.1. Experimental Setup. The schematic of the experimental setup is shown in Figure 1. The flow of CH$_4$ and NH$_3$ was controlled by mass flow controllers. Before discharge, CH$_4$ and NH$_3$ were mixed homogeneously to pass through the DBD plasma reactor for 10 min. Then, the voltage of a high-voltage electrode (HVE) was adjusted to initiate the DBD discharge (high-performance computerized plasma and corona discharge experiment generators CTP-2000K). The discharge voltage, discharge current, and input power were measured on site by a digital oscilloscope (Tektronix DPO 3012, HV probe Tektronix P6015A, current probe Pearson 6585). The discharge images were taken by a camera (Nikon D50). The optical emission spectra of CH$_4$/NH$_3$ plasma were monitored by optical emission spectroscopy (OES) (Princeton Instrument SP 275S, 300 g/mm grating, 40 μm slit width, and 1 s explosion time) to study the mechanism of reaction between CH$_4$ and NH$_3$. Gas chromatography (GC) was used to analyze the gas phase products. CO with a fixed flow rate (10 mL/min) was introduced at the outlet to mix with the exhaust gas as an external standard to measure the flow rate of the exhaust gas.

Scheme 1. Reaction Process for the Industrial Synthesis of (CH$_3$)$_2$NCN and NH$_2$CH$_2$CN

\[
C_2H_2 + 1000-1100^\circ C, N_2 \rightarrow C_2(CN)_2 \rightarrow H_2O, CO_2 \rightarrow NH_2C \equiv N \rightarrow (CH_3)_2NC \equiv N
\]

\[
N_2C \equiv N \rightarrow HCHO, NH_3, CH_2COOH \rightarrow CH_2 = NCH_2C \equiv N \rightarrow H_2SO_4 \rightarrow NH_2CH_2C \equiv N
\]

Scheme 2. Reaction Process for the Industrial Synthesis of HCN

\[
2CH_4 + 2NH_3 + 3O_2 \rightarrow 2H_2O(Andrussov\text{ Process}) \rightarrow 2HCN + 6H_2O
\]

\[
CH_4 + NH_3 \rightarrow 1200^\circ C, Pt\text{ Gauge} \rightarrow HCN + 3H_2(Degussa\text{ Process})
\]

Figure 1. Schematic of the DBD experimental setup for the CH$_4$/NH$_3$ plasma coupling reaction.
Then, the mixed exhaust gas was analyzed using an online GC equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The FID was used to analyze the concentration of hydrocarbons in the exhaust gas. The TCD was used to analyze the concentration of CH4 and CO2, whereas a little N2 was also detected, which may come from NH3 decomposition. After that, the total flow rate of the exhaust gas can be calculated according to the flow rate and concentration of CO (calculated using external standard curve); then, the flow rate of CH4 in the exhaust gas can be calculated according to the concentration of CH4 and the total flow rate. The liquid product was collected by the coolant of ice water first and then analyzed using gas chromatography–mass spectrometry (GC–MS) (Agilent 7890A GC, 5975C single-level four-poles mass spectrometry) and Fourier transform infrared (FTIR) (Japan company: Nicolet 6700, ZnSe window plates). Interestingly, in the gas phase, little hydrocarbons were detected by the FID, indicating that most of the products were collected in the liquid. It is worth noting that, to prevent poisoning and environmental pollution, the experiment operators should always wear a gas mask and gloves; the liquid product was sealed in a bottle and stored in a fridge; and the exhaust gas in the outlet of GC was burned in a high-temperature furnace.

2.2. Plasma Reactor. A single DBD (SDBD) reactor (Figure 2) was used for the CH4/NH3 DBD plasma coupling reaction for the direct synthesis of NH2CH2CN and (CH3)2NCN.

Figure 2. Schematic of the SDBD reactor for the CH4/NH3 plasma coupling reaction (1—HVE; 2—gas inlet; 3—circulating water inlet; 4—collector; 5—gas outlet; 6—ground electrode (GE); and 7—circulating water outlet).

reaction. The SDBD reactor had two coaxial glass cylinders and two electrodes. The inner cylinder was made of pyrex with an inner diameter of 8 mm and an outer diameter of 10 mm. The wall of the inner cylinder served as a dielectric barrier for the discharge. The outer cylinder, which had a liquid inlet at the bottom and a liquid outlet at the top, was also made of glass, and it was used to form an annular gap between the inner and outer cylinders.

The HVE of the SDBD reactor was a stainless-steel rod (2 mm o.d., surface composition: Fe 68.5 wt %, Cr 19.9 wt %, Ni 8.1 wt %, Mn 2.0 wt %, Si 0.5 wt %, Cu 0.7 wt %, Ag 0.1 wt %, Al 0.1 wt %, and C 0.1 wt %), which was installed along the axis of the inner glass cylinder and was connected to the alternating current (ac) power supply. The GE was composed of circulating water (30 °C), which filled in the annular gap of the glass cylinders, and was linked to the grounding wire through a tungsten connection welded across the wall of the outer cylinder. Thus, the reaction temperature in the SDBD reactor was maintained at nearly 30 °C, which was confirmed by the thermal infrared imager (Figure S1 in the Supporting Information). A cylindrical discharge space with a length of 50 mm and a volume of 2.36 mL was formed between HVE and GE.

2.3. Qualitative Analysis of Products. As mentioned in the experimental setup, the chemicals in the liquid product were qualitatively analyzed using GC–MS (Agilent 7890A GC, 5975C single-level four-poles mass spectrometry). Liquid product (1 μL) was injected into the sample inlet before starting the GC–MS program (20 °C/min). The liquid product was also qualitatively analyzed using FTIR (Japan company: Nicolet 6700, ZnSe window plates).

2.4. Quantitative Analysis of Reaction Results. The CH4 conversion F1, the productivities of NH2CH2CN and (CH3)2NCN F2, and the energy efficiency F3 have been used to evaluate the performance of the CH4/NH3 plasma coupling reaction for the direct synthesis of NH2CH2CN and (CH3)2NCN.

In F1, the moles of initial CH4 were controlled by a mass flow controller; the moles of CH4 converted were measured by GC, as described in section 2.1. In F2, the mass of the product was calculated using the concentration of products [NH2CH2CN and (CH3)2NCN], and the total mass of the liquid product was collected. Because the standard samples of some other chemicals were not available, the internal standard analysis method of GC could not be carried out; thus, the concentrations of products [NH2CH2CN and (CH3)2NCN] were measured by GC using the external standard method, and no internal standard was used. The mass of the product in F3 is the same as that in F2. The GC external calibration curves of (CH3)2NCN and NH2CH2CN are shown in Figures S2 and S3, respectively.

\[
C_{\text{CH}_4} = \frac{\text{moles of CH}_4 \text{ converted}}{\text{moles of initial CH}_4} \times 100\% \quad (F1)
\]

\[
P = \frac{\text{mass of the product}}{\text{reaction time } \times \text{ reactor volume}} \times 100\% \quad (F2)
\]

\[
E = \frac{\text{mass of the product}}{\text{reaction time } \times \text{ discharge power}} \times 100\% \quad (F3)
\]

3. RESULTS AND DISCUSSION

3.1. Typical Results of the CH4/NH3 Plasma Reaction. Under the conditions of 20 mL/min CH4, 20 mL/min NH3, 3.5 s feedstock residence time, 12 kHz discharge frequency, 60 W input power, and 8 h discharge time, some liquid products were obtained in the collector of the SDBD reactor. The GC–MS chromatograph profile of the liquid products is shown in Figure 3, which indicates that there were about 10 kinds of chemicals (marked with capital letter A–J) in the liquid. The belongings of the 10 chemicals identified by mass spectrometry (Figure S2, Supporting Information) are shown in Table 1. Figure 3 and Table 1 show that NH2CH2CN (marked by H) and (CH3)2NCN (marked by G) were produced. In addition,
hydrazine (marked by C), amines (marked by B and D), triazole (marked by I), and hydrazones (marked by E, F, and J) were also synthesized by the CH4/NH3 plasma reaction. The liquid products were also qualitatively analyzed using FTIR (Japan company: Nicolet 6700, ZnSe window plates). FTIR results (Figure S3, Supporting Information) indicate that the product molecules possess NH2, C≡N, and CH functional groups, which agree with the belongings of the products in Table 1.

As mentioned in the Introduction section, NH2CH2CN and (CH3)2NCN are the two important chemical intermediates in medicine synthesis. Therefore, although hydrazine, amines, and hydrazones were also produced by the CH4/NH3 plasma reaction, this paper focused on the synthesis of NH2CH2CN and (CH3)2NCN. However, the standard samples of some other chemicals, such as B, E, F, I, and J in Table 1, were not available; hence, the chemicals B, E, F, I, and J have not been analyzed quantitatively. As a result, it is difficult to calculate the carbon balance and nitrogen balance accurately, as well as the selectivity of NH2CH2CN and (CH3)2NCN. Therefore, the CH4 conversion (F1), the productivities of NH2CH2CN and (CH3)2NCN (F2), and the energy efficiency (F3) have been used to evaluate the performance of the CH4/NH3 plasma coupling reaction for the direct synthesis of NH2CH2CN and (CH3)2NCN.

3.2. Optimization of Experimental Conditions of CH4/NH3 Plasma Reaction. Figure 4 shows that the CH4 conversion increased when the CH4/NH3 molar ratio varied from 1:1 to 1:2, 1:3, and 1:4 gradually, at fixed total feed gas flow (60 mL/min), residence time 2.4 s, 60 W input power, and 90 J/mL specific energy input (SEI).

Table 1. Belongings of Peaks in the GC Profile in Figure 3

| Mark Number | Residence Time (min) | Belonging of the Peaks          |
|-------------|----------------------|----------------------------------|
| A           | 7.012                | HC≡N                             |
| B           | 8.533                | CH3-NH-CH2-CH2-NH2               |
| C           | 8.808                | NH2-NH2                          |
| D           | 9.370                | (CH3)2-C≡N                       |
| E           | 9.965                | CH3-NH-N≡-CH-CH                  |
| F           | 10.659               | (CH3)2-C≡N-NH-CH                 |
| G           | 11.529               | (CH3)2-N-C≡N                     |
| H           | 12.455               | NH2-CH2-C≡N                      |
| I           | 12.521               |                                   |
| J           | 12.752               | CH3-(NH2)-N-CH2-C≡CH             |

Figure 4. CH4 conversion under varying CH4/NH3 molar ratios [total flow rate 60 mL/min, residence time 2.4 s, 60 W input power, and 90 J/mL specific energy input (SEI)].
shown in Figure 5. Interestingly, the productivities of NH₂CH₂CN and (CH₃)₂NCN, shown in Figure 6, exhibited an inverse variation trend compared with CH₄ conversion, and they increased with an increasing CH₄ content (from 1:4 to 1:3, 1:2, and 1:1) in the mixture. At 1:1 CH₄/NH₃ molar ratio, the productivities of NH₂CH₂CN and (CH₃)₂NCN reached 0.40 and 0.23 g·L⁻¹·h⁻¹, respectively, which were higher than those obtained in the other three cases (Figure 6), whereas the quantity of converted CH₄ was nearly the minimum value (Figure 5), indicating that it is more selective to produce NH₂CH₂CN and (CH₃)₂NCN when the CH₄/NH₃ molar ratio was 1:1. It is worth mentioning that when the content of CH₄ was increased further, that is, the CH₄/NH₃ molar ratio was 2:1 or higher, some hydrocarbons, such as C₂H₆ and C₃H₈, were dominantly produced in the gas phase, and some black-colored carbon, such as coke, was deposited on the HVE, which prevented the discharge. In addition, less liquid products were collected. These results show that the optimal molar ratio of CH₄/NH₃ for the synthesis of NH₂CH₂CN and (CH₃)₂NCN could be 1:1, approximately, and a high CH₄/NH₃ molar ratio was unfavorable to the production of liquid nitrogen-containing organic chemicals.

The effect of feed gas residence time on the synthesis of NH₂CH₂CN and (CH₃)₂NCN was investigated by changing the total flow rate with a fixed CH₄/NH₃ molar ratio (1:1). Figure 7 shows that when the residence time of feedstock increased from 1.4 to 7.1 s, the CH₄ conversion increased gradually. Nevertheless, the quantity of converted CH₄ first increased sharply and then decreased slowly. As shown in Figure 8, the quantity of converted CH₄ reached the highest value at about 2.4 s, and it remained at a high level when the residence time of feedstock was in the range of 2−4 s. Figure 9 shows that the productivity of (CH₃)₂NCN increased gradually with residence time. However, the productivity of NH₂CH₂CN presented a parabolic-like curve versus the residence time, and the highest value appeared at about 3.5 s. Comprehensively, the optimum residence time seems to be 3.5 s, at which the productivities of (CH₃)₂NCN and NH₂CH₂CN reached 0.28 and 0.60 g·L⁻¹·h⁻¹, respectively, with a CH₄ conversion of 7.49%.

The influence of SEI, which was calculated using the input power divided by the feed gas flow rate, on the synthesis of (CH₃)₂NCN and NH₂CH₂CN was investigated at the optimized CH₄/NH₃ molar ratio (1:1) and the optimized feedstock residence time (3.5 s). The discharge power was
adjusted through changing the discharge voltage. Figure 10 shows that as the SEI increased from 45 to 135 J/mL, the CH₄ conversion increased significantly from 3.0 to 10.5%, whereas the productivities of (CH₃)₂NCN and NH₂CH₂CN first increased and then decreased, as shown in Figure 11. When the SEI was 105 J/mL, both the productivities of (CH₃)₂NCN and NH₂CH₂CN reached their maximum values, 0.46 and 0.82 g·L⁻¹·h⁻¹, respectively. In other words, the optimum SEI for the CH₄/NH₃ plasma coupling reaction to synthesize (CH₃)₂NCN and NH₂CH₂CN could be at about 105 J/mL. When the SEI reached 135 J/mL or higher, some carbonaceous soot was formed adhering to the HVE, which usually prevented the discharge and quenched the CH₄/NH₃ plasma reaction, and less liquid products were produced, demonstrating that high SEI inhibited the production of liquid nitrogen-containing organic chemicals.

Under the optimized reaction conditions (1:1 CH₄/NH₃ molar ratio, 3.5 s residence time, and 105 J/mL SEI), the CH₄/NH₃ plasma coupling reaction in the SDBD reactor was carried out for 24 h continuously, and the results are shown in Figure 12. It can be seen that CH₄ conversion remained nearly constant at about 8.8% during the reaction process. Meanwhile, the productivities of (CH₃)₂NCN and NH₂CH₂CN did not vary with the reaction time and were still kept at about 0.46 and 0.82 g·L⁻¹·h⁻¹, respectively. These results indicate that the CH₄/NH₃ plasma coupling reaction can be carried out relatively stable in a certain period of time to synthesize liquid nitrogen-containing organic chemicals, whereas high SEI (more than 135 J/mL) and high CH₄/NH₃ molar ratio (more than 2:1) are unfavorable for the synthesis of liquid nitrogen-containing organic chemicals.

### 3.3. Activation of CH₄ and NH₃ in CH₄/NH₃ DBD Plasma

The CH₄/NH₃ plasma in the SDBD reactor has been diagnosed by an optical emission spectrograph, and the OES profiles are shown in Figure 13. It can be seen that three major bands at 564−567, 610−670, and 720−780 nm were captured. The first band at 564−567 nm is attributed to the decay of NH₃* (Schuster’s bands), and the later two bands are attributed to the decay of NH₂* (NH₃ α bands). In addition, a line at 656.3 nm appeared in the profile, and it is attributed to the decay of hydrogen atoms (H₂⁺ 2p2P⁰⁻→ 3d²D⁰⁻). These results indicate that there were abundant NH₃* and NH₂* species in the CH₄/NH₃ plasma, as well as α-H species.

Several tiny lines and bands, however, were also observed in the OES profile (300−450 nm in Figure 13). The local amplification of the OES profile in the range of 300−450 nm
The generation of \( \cdot \text{NH}_2 \) species from \( \text{NH}_3 \) molecules in DBD plasma is mainly achieved by energetic electrons through inelastic collisions. Benarfa et al. studied the inelastic collision cross section between energetic electrons and \( \text{NH}_3 \) molecules, and the results show that the electrons in the energy range of 3–10 eV can excite the ground-state \( \text{NH}_3 \) into vibrational excited states.\(^{42}\) d’Agostino et al. found that when the vibrational energy of the vibrationally excited \( \text{NH}_3 \) molecule was higher than the \( \text{N}–\text{H} \) bond energy (4 eV), \( \text{NH}_3 \) molecules could break the \( \text{N}–\text{H} \) bond to produce \( \cdot \text{NH}_2 \) and \( \cdot \text{NH} \) radicals.\(^{31}\) In addition, ground-state \( \text{NH}_3 \) can also be directly dissociated to produce \( \cdot \text{NH}_2 \) and \( \cdot \text{NH} \) radicals through inelastic collision with energetic electrons, that is, reactions R1–R3 (\( e^\ast \) represent the electron with higher energy than \( e \)).\(^{35}\) Their threshold energy values were 4.0, 5.6, and 8.6 eV, respectively.\(^{44}\)

\[
\begin{align*}
\text{(R1)} & \quad e^\ast + \text{NH}_3 \rightarrow \cdot \text{NH} + \text{H}_2 + e \\
\text{(R2)} & \quad e^\ast + \text{NH}_3 \rightarrow \cdot \text{NH}_2 + \cdot \text{H} + e \\
\text{(R3)} & \quad e^\ast + \text{NH}_3 \rightarrow \cdot \text{NH} + 2 \cdot \text{H} + e \\
\end{align*}
\]

In DBD plasma, the production of \( \cdot \text{CH}_2 \) species from \( \text{CH}_4 \) molecules by energetic electrons could be realized through the following two pathways: the first pathway is that the ground-state \( \text{CH}_4 \) molecules were excited into its vibrational states, which were further excited into electronic states \( \text{S}_1 \) (9.6 eV) and \( \text{S}_2 \) (11.7 eV), followed by producing \( \cdot \text{CH}_3, \cdot \text{CH}_2 \) and \( \cdot \text{CH} \) radicals spontaneously;\(^{45,46}\) the second pathway is the direct dissociation of \( \text{CH}_4 \) molecules into \( \cdot \text{CH}_2, \cdot \text{CH}_3 \) and \( \cdot \text{CH} \) radicals, that is, reactions R4–R6, through inelastic collision with high energy electrons, and their threshold energy values were 7.5, 8.5, and 15.5 eV, respectively.\(^{47,48}\) De Bie et al. simulated the reaction of \( \text{CH}_4 \) in DBD plasma using the 1D fluid model, and the results showed that the probability of producing \( \cdot \text{CH}_2, \cdot \text{CH}_3 \) and \( \cdot \text{CH} \) radicals from \( \text{CH}_4 \) by electrons was 79, 15, and 5%, respectively.\(^{49}\)

\[
\begin{align*}
\text{(R4)} & \quad e^\ast + \text{CH}_4 \rightarrow \cdot \text{CH}_2 + \cdot \text{H} + e \\
\text{(R5)} & \quad e^\ast + \text{CH}_4 \rightarrow \cdot \text{CH}_3 + \text{H}_2 + e \\
\text{(R6)} & \quad e^\ast + \text{CH}_4 \rightarrow \cdot \text{CH} + \text{H}_2 + \cdot \text{H} + e \\
\end{align*}
\]

The electron energy range in the DBD plasma is usually 1–10 eV. On the basis of the above-mentioned activation pathways of \( \text{CH}_4 \) and \( \text{NH}_3 \) molecules, it, therefore, can be inferred that \( \text{CH}_4 \) and \( \text{NH}_3 \) molecules in the \( \text{CH}_4/\text{NH}_3 \) plasma have been dissociated into \( \cdot \text{CH}_2, \cdot \text{CH}_3 \) and \( \cdot \text{CH} \) radicals from \( \text{CH}_4 \) by electrons, which are very important in the dehydrogenation of \( \text{NH}_3 \) in DBD plasma.\(^{50}\) The possible dissociation of \( \text{CH}_4 \) and \( \text{NH}_3 \) molecules in the \( \text{CH}_4/\text{NH}_3 \) plasma, however, could be different, which may be related to the specific different characters of \( \text{CH}_4 \) and \( \text{NH}_3 \) molecules, such as bond energies, cross sections with energetic electrons, and so forth.

### 3.4. Role of \( \text{CH}_4/\text{NH}_3 \) Molar Ratio

To reveal the effects of the \( \text{CH}_4/\text{NH}_3 \) mole ratio on the synthesis of \( \text{NH}_2\text{CH}_2\text{CN} \) and \( \text{CH}_3\text{CN} \), the \( \text{CH}_4/\text{NH}_3 \) plasma with varying molar ratios has been diagnosed using OES, and the results are shown in Figures 15 and 16. It can be seen from Figure 15 that the intensities of \( \cdot \text{NH}_2 \) and \( \cdot \text{NH}_3 \) species decreased gradually when the content of \( \text{NH}_3 \) decreased from 80 to 50%, corresponding to 1:4 and 1:1 \( \text{CH}_4/\text{NH}_3 \) molar ratio, respectively. Furthermore, as shown in Figure 16, the intensity of \( \text{NH}_2 \) and \( \text{NH}_3 \) species decreased remarkably, whereas the intensity of \( \cdot \text{CH}_2 \) species increased dramatically. These results indicate that when the \( \text{CH}_4/\text{NH}_3 \) molar ratio varied from 1:4 to 1:3, 1:2, and...
nearly almost dominant by NH$_3$ mixture, the OES pro
worth noting that the intensity of species decreased gradually, especially the species increased, whereas the concentration of (alkane, olefin, alkynel, or aromatics) was produced, whereas hydrazine (NH$_2$) was produced with a considerable intensity of NH$_3$ species, that is, the concentration of NH$_3$ species, even at 1:1 CH$_4$/NH$_3$ molar ratio. Usually, CH$_4$ radical species react with each other to produce hydrocarbons; NH$_2$ radical species react with each other to generate hydrazine (NH$_2$−NH$_2$). In the Experimental Section, it has been claimed that a little hydrocarbon product (alkane, olefin, alkynel, or aromatics) was produced, whereas hydrazine (NH$_2$−NH$_2$) was produced with a considerable amount (Figure 3 and Table 1), inferring that, in the CH$_4$/NH$_3$ plasma, the concentration of NH$_4$ species might be much higher than that of CH$_4$ species and C≡N species, notwithstanding that they have not been measured precisely. In other words, in the CH$_4$/NH$_3$ plasma, the activation of NH$_3$ could be much easier than that of CH$_4$ which is consistent with the threshold energy values required for the dissociation of CH$_4$ and NH$_3$ molecules (R1−R6). Therefore, the rate of the CH$_4$/NH$_3$ plasma coupling reaction for the synthesis of NH$_2$CH$_2$CN and (CH$_3$)$_2$NCN could be determined by the activation of CH$_4$ because it might be slower than that of NH$_3$. That is, the concentration of CH$_4$ species could be the key factor for the synthesis of NH$_2$CH$_2$CN and (CH$_3$)$_2$NCN. The increased productivities of NH$_2$CH$_2$CN and (CH$_3$)$_2$NCN with an increasing CH$_4$ content (Figure 6), therefore, could be attributed to the increase of CH$_4$ species concentration. However, too high concentration of CH$_4$ species may not be helpful to produce liquid nitrogen-containing organic chemicals. As mentioned in section 3.2, a high CH$_4$/NH$_3$ molar ratio (2:1 or higher) produced some hydrocarbons, such as C$_2$H$_6$ and C$_3$H$_8$, in the gas phase and some black-colored carbon in the solid phase, which could be generated by abundant CH$_4$ species.

3.5. Role of Residence Time. In the process of a chemical reaction, the residence time of feedstock, usually, has a great influence on the product distribution because the product distribution is generally related with chemical kinetics. That is, short residence time favors the relatively fast chemical reactions, whereas long residence time benefits the relatively slow chemical reactions. As shown in Figure 9, the productivity of (CH$_3$)$_2$NCN increased gradually with the increasing residence time, whereas the productivity of NH$_2$CH$_2$CN presented a parabolic-like curve versus the residence time, and the highest value appeared at 3.5 s approximately. The GC profiles of the liquid products obtained with residence times at 1.4, 3.5, and 7.1 s are shown in Figure 17. Those GC profiles may provide some further information about the variation in the trend of liquid product distribution versus residence time, although some products have not been analyzed quantitatively. First, it can be seen from Figure 17 that the intensities of peaks A (HCN) and C (NH$_2$−NH$_2$) decreased with the increase of residence time, especially peak C disappeared when the
residence time reached 7.1 s. Second, the intensities of peaks D \([(\text{CH}_3)_2\text{C}−\text{N}\equiv\text{N}]\), E \((\text{CH}_3−\text{NH}−\text{N}≡\text{CH}−\text{CH}_3)\), F \([(\text{CH}_3)_2\text{C}≡\text{N}−\text{NH}−\text{CH}_3]\), and G \([(\text{CH}_3)_2\text{N}−\text{C}≡\text{N}]\) increased with the increase of residence time. Third, there were an increasing number of peaks when the residence time was extended (7.1 s). These results indicate that short residence time (1.4 s) favored the production of HCN and NH$_2$−NH$_2$; then, at an extended residence time (3.5 and 7.1 s), the produced HCN was further converted into NH$_2$CH$_2$CN and (CH$_3$)$_2$NHCN, whereas the produced NH$_2$−NH$_2$ was transformed into some hydrazones (E, F, and J). That is, with the increase of residence time, more and more big molecules, such as E \((\text{CH}_3−\text{NH}−\text{N}≡\text{CH}−\text{CH}_3)\) and F \([(\text{CH}_3)_2−\text{C}≡\text{N}−\text{NH}−\text{CH}_3]\), were produced. Furthermore, these experimental results seemingly provided us an insight into the kinetics of the CH$_4$/NH$_3$ plasma reaction, that is, the formation of C≡N and N−N bonds was relatively rapid, whereas the formation of C−C and C−N bonds was relatively torpid, although the rate coefficients of these reactions were not measured. In a word, shorter residence time (1.4 s) favored the generation of small molecules with less atomic number, such as HCN (A) and NH$_2$−NH$_2$ (C); moderate residence time (3.5 s) favored the synthesis of molecules with moderate atomic number such as NH$_2$CH$_2$CN (Figure 9); longer residence time (7.1 s) favored the production of relatively big molecules with more atoms, such as B, D, E, F, and G.

3.6. Role of SEI. Generally, in the plasma chemical reaction, the higher the SEI, the higher the conversion of feed gas, as well as the productivity of products. Experimental results, however, indicate that the conversion of CH$_4$ increased gradually with the increasing SEI (Figure 10), whereas the productivity productivities of (CH$_3$)$_2$NHCN and NH$_2$CH$_2$CN first increased and then decreased (Figure 11). To uncover the effects of SEI on the CH$_4$/NH$_3$ plasma reaction, the CH$_4$/NH$_3$ plasma with varying SEIs has been diagnosed using an oscilloscope (monitoring the discharge current and discharge voltage) and OES.

In an atmospheric plasma chemical process, two critical parameters, such as the electron density and average electron energy, usually determine the distribution of active species and subsequently influence the final reaction results. Generally, the variation of the electron density and average electron energy are synchronous with the discharge current and discharge voltage, respectively. During the experimental process, the SEI was modulated by varying the applied discharge voltage. As shown in Figure 18, it can be seen that a higher SEI corresponded to a higher discharge voltage. That is, the electric field intensity in the discharge region increased with the increasing SEI. A higher electric field intensity means that the electrons could gain a higher kinetic energy at a fixed accelerating distance. Thus, it can be speculated that the average electron energy in the CH$_4$/NH$_3$ plasma increased with the SEI. Meanwhile, the discharge current also increased gradually with the increase of the SEI (Figure 18), indicating that the electron density increased gradually with the SEI.

The OES profiles of the CH$_4$/NH$_3$ plasma with varying SEIs are shown in Figures 19 and 20. It can be observed that the OES intensities of the NH$_3^+$, ·NH$_2$, and ·NH species increased only a little with increasing SEIs, however, that of the ·CH species increased remarkably. These results indicate that, with the increase of the SEI, both concentrations of ·CH$_2$ and ·NH$_2$ species increased, but the concentration of ·CH$_3$ species increased much faster than that of ·NH$_2$ species. The higher concentration of ·CH$_2$ and ·NH$_2$ species means the faster reaction rate, which may have induced the higher CH$_4$ conversion, as well as the increasing productivities of (CH$_3$)$_2$NHCN and NH$_2$CH$_2$CN. However, why the productivities of (CH$_3$)$_2$NHCN and NH$_2$CH$_2$CN decreased when the SEI was higher than 105 J/mL? An experimental phenomenon
In the CH4/NH3 DBD plasma, the OES results show that there were abundant \( \cdot \text{NH}_2 \) and \( \cdot \text{NH} \) radical species. However, there were several kinds of hydrazone products containing an N–N functional group, which indicate that the hydrazine molecule (\( \text{NH}_2\text{–NH} \)) might take a role of the reaction intermediate. The reaction results with different residence times could also prove this point because the intensities of the hydrazone GC peaks increased versus the residence time; meanwhile, the intensity of the hydrazone GC peak decreased versus the residence time or even disappeared at 7.1 s. Generally, the recombination of \( \cdot \text{NH} \) species produces \( \text{N}_2 \) and \( \text{H}_2 \) (R10),\(^{51}\) which could be the origin of \( \text{N}_2 \) and \( \text{H}_2 \) detected by OES (Figures 14, 16, and 20). However, the recombination of \( \cdot \text{NH}_3 \) species usually generates hydrazine, that is, \( \text{NH}_2\text{–NH}_2 \) (R11).\(^{51}\) In addition, the recombination between \( \cdot \text{NH} \) radical and \( \cdot \text{NH}_3 \) molecules also produces \( \text{NH}_2\text{–NH}_2 \) (R12).\(^{52}\)

\[
\text{·NH} + \cdot \text{NH} \rightarrow \text{N}_2 + \text{H}_2 \quad (R10)
\]

\[
\text{·NH}_2 + \cdot \text{NH} \rightarrow \text{NH}_2\text{–NH}_2 \quad (R11)
\]

\[
\text{·NH} + \cdot \text{NH}_3 \rightarrow \text{NH}_2\text{–NH}_2 \quad (R12)
\]

On the basis of the above experimental results and discussions, a simplified \( \text{CH}_4/\text{NH}_3 \) plasma coupling reaction mechanism has been proposed, as shown in the Scheme 3. First, \( \cdot \text{CH}_4 \) and \( \cdot \text{NH}_3 \) molecules were dissociated into \( \cdot \text{CH}_4 \) and \( \cdot \text{NH}_3 \) radical species, respectively, through inelastic collision with energetic electrons of the plasma; then, at moderate residence time, some simple-structure reaction intermediates such as HCN and \( \text{N}_2\text{H}_4 \) species were formed; finally, with the increase of the residence time, more big molecules, such as amine, amide, nitrile, cyanamide, hydrazone, and azine, were produced through some complicated radical reactions between the primary radicals and reaction intermediates. However, the real \( \text{CH}_4/\text{NH}_3 \) plasma coupling process should be extremely complicated because it might involve tens or even hundreds of elementary radical reactions.

### 4. CONCLUSIONS AND PERSPECTIVES

In summary, the \( \text{CH}_4/\text{NH}_3 \) plasma coupling reaction operated at room temperature and atmospheric pressure synthesized several kinds of nitrogen-containing organic chemicals, such as amines, nitriles, cyanamides, and hydrazones, where \( \text{NH}_2\text{CH}_2\text{CN} \) and \( (\text{CH}_3)_2\text{NCN} \) were produced as the main products. The feed gas ratio, the feed gas residence time, and...
the SEI have significant effects on the CH4/NH3 plasma coupling reaction, where 1:1 CH4/NH3 molar ratio, moderate residence time, and moderate SEI favored the synthesis of NH2CH2CN and (CH3)2NCN. Under the optimized conditions (CH4/NH3 = 1:1, 3.5 s gas residence time, and 105 J/mL SEI), the productivities of (CH3)2NCN and NH2CH2CN reached 0.46 and 0.82 g L⁻¹ h⁻¹, respectively, with a CH4 conversion of 8.83%. The energy efficiencies for the synthesis of (CH3)2NCN and NH2CH2CN, however, were only 15.1 and 26.9 mg kJ-h⁻¹, respectively, which were still much lower than that of the industrial process.

The C≡N bond as an important functional group has irreplaceable applications in medicine (antitumor drug, care amine; antitumor medicine, stubborn azole; antidepressant drug, cilostatram; and antipsychotic medicine, pericazine). Chemicals containing C≡N bond also have great potential in the synthesis of organic compounds, such as pyrimidine, tetrazene, pyrrole, amine, imine, and natural product molecules. Therefore, this paper provides a potential carbon-nitrogen coupling path to form C≡N bond functional containing C≡N bond and functional chemical containing C≡N bond, which are very significant in medicine and organic synthesis. The present work is an encouraging beginning, and continuous attention will be paid to increase the conversion of CH4 and productivities of NH2CH2CN and (CH3)2NCN, as well as the energy efficiency, through combining the DBD plasma with some particular catalysts.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on free charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01060.

Thermal infrared image of the CH4/NH3 plasma, GC external calibration curves, MS results of liquid products, and FTIR results of liquid products (PDF)

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Notes

The authors declare the following competing financial interest(s): There is conflict of interest with the patent (ZL 2015101524352.2).

## ACKNOWLEDGMENTS

We acknowledge the financial support from the National Natural Science Foundation of China [grant numbers 21503032, 2015] and the China Postdoctoral Science Foundation [grant numbers 2015MS80220 and 2016T90217, 2016].

## NOTATION

DBD, dielectric barrier discharge; SDBD, single dielectric barrier discharge; HVE, high-voltage electrode; ac, alternating current; GE, grounding electrode; OES, optical emission spectroscopy; SEI, specific energy input

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