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## COMMUNICATION

## Hydroamination of ethylene with NH<sub>3</sub> induced by non-thermal atmospheric plasma

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**We show here that non-thermal atmospheric plasma induces the cleavage of the N-H bond of NH<sub>3</sub> to form aminium radicals, which then add onto ethylene to form ethylamine in 17% yield. This technology can be also extended to *n*-octene, leading to the formation of 1-octylamine, *i.e.* with anti-Markovnikov addition of NH<sub>3</sub>.**

Amines are ubiquitous molecules in our daily life, with a wide range of applications in the fields of agriculture, food, medicine, personal care, polymers, etc.<sup>1</sup> In this context, the hydroamination of alkenes is a reaction of considerable interest, as it provides a hydrogen-free access to amines in a 100 % atom economical fashion. So far, this reaction has been extensively explored in the presence of catalysts such as transition metals, bases and acids.<sup>2</sup> However, to overcome thermodynamic limitations ( $\Delta G \sim 0$  kJ/mol)<sup>3</sup> activated alkenes (*i.e.* featuring ring strain, conjugation, or substitution with electron-withdrawing groups) and/or intramolecular hydroamination reactions were mainly investigated.<sup>2</sup> The utilization of NH<sub>3</sub>, the simplest and the most abundant amine (160 million tons/year),<sup>4</sup> in the hydroamination of alkenes is much more challenging but, so far, there is a lack of technology to successfully perform this reaction.<sup>5</sup> Although it would open an access to primary alkyl amines from two cheap and abundant chemicals, utilization of NH<sub>3</sub> in the hydroamination of non-activated alkenes remains a longstanding goal of catalysis.<sup>6</sup> This reaction is indeed facing important scientific hurdles such as (i) the high N-H bond dissociation energy of NH<sub>3</sub> (415 kJ/mol),<sup>7</sup> (ii) the highest basicity of primary amines leading to a poisoning of the catalytic sites<sup>2a-e</sup> and (iii) high activation energy barriers due to strong electrostatic repulsions of the nitrogen electron lone pair of NH<sub>3</sub> with the electron-rich  $\pi$  cloud of the alkene.<sup>8</sup> Hence, high temperatures are often required to initiate this

catalytic reaction, which is unfortunately thermodynamically unfavorable.

In a pioneer study, Whitman reported that alkali metals, such as Li or Na, catalyzed the hydroamination of ethylene with NH<sub>3</sub> at 175-200°C, but at a very high pressure (> 800 bar) to thermodynamically favor the reaction.<sup>9</sup> Later, Deepa revisited this reaction in the presence of zeolites and reported a yield in ethylamine of 13%.<sup>10</sup> As demonstrated later by Bell, this low yield at the thermodynamic equilibrium was due to the high reaction temperature (360°C) required to desorb ethylamine from the acid sites, thus inducing the uncontrolled Hoffman degradation of ethylamine back to NH<sub>3</sub> and ethylene.<sup>11</sup> Interestingly, Knowles showed that the formation of aminium radical cation, using Ir-based photocatalysts, was a promising strategy not only to favor the addition of alkyl amines on alkenes in an anti-Markovnikov fashion, but also to lower the activation energy barrier of the hydroamination reaction, resulting in a decrease of the temperature to 45°C.<sup>12</sup> In 2020, Yoshida applied this concept to NH<sub>3</sub> and irradiated an aqueous NH<sub>3</sub> solution in the presence of TiO<sub>2</sub> photocatalysts and alkenes, affording primary amines in fair to good yields.<sup>13</sup> Although water limits the applicability of this work (low solubility of alkenes, side oxidation of NH<sub>3</sub> to NO<sub>x</sub> in water), it suggests that the radical pathway is a promising approach.

In this communication, we report preliminary results on a catalyst-free hydroamination of ethylene with NH<sub>3</sub> induced by non-thermal atmospheric plasma. Our strategy was inspired by a previous study of Swiderek who pointed out the formation of ammonium radical cation at low temperature by exposing NH<sub>3</sub> to a low-energy electron beam in an ultra-high vacuum chamber (10<sup>-10</sup> Torr).<sup>14</sup>

In this study, a non-thermal atmospheric plasma (NTAP) was created in a dielectric barrier discharge (DBD) reactor consisting of an alumina cylinder and a central electrode. The NTAP volume was 1.2 mL. More information on the DBD reactor can be found in the electronic supporting information (Fig. S1, S2). In such configuration, the electrons generated in the NTAP gas have mean energies in the range of 1 to 10 eV<sup>15</sup>, and thus can induce the cleavage of gaseous molecules such as CH<sub>4</sub>, O<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, etc.... In a typical procedure, a mixture of

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ethylene and  $\text{NH}_3$  ( $\text{C}_2\text{H}_4/\text{NH}_3$  ratio of 0.5) was first diluted in helium (70 vol%) and then continuously introduced (50 mL/min) into the DBD reactor at room temperature and atmospheric pressure. Dilution of  $\text{C}_2\text{H}_4/\text{NH}_3$  in He was preferred in this work to facilitate the formation of the plasma gas but also to facilitate analysis of the reaction products by gas chromatography. The applied voltage and the frequency were first fixed at 12 kV and 800 Hz, respectively, so that the deposited power was 4 W. At this low power, the average temperature of the DBD reactor does not exceed  $50^\circ\text{C}$  and, on the basis of previous reports,<sup>16</sup> the decomposition of  $\text{NH}_3$  to  $\text{N}_2$  and  $\text{H}_2$  is expected to be limited at this power. The gas outlet of the DBD reactor was connected to a gas chromatography (GC) to determine online the conversion of ethylene and the yield of ethylamine. To our delight, under the above conditions, 30% ethylene was converted and the formation of ethylamine was detected by GC, with a yield of 10% (Fig. S3). Formation of ethylamine was further confirmed by mass spectrometry. The selectivity to ethylamine was 33% indicating the formation of other products, presumably stemming from the side polymerization of ethylene, as suggested by a slight deposit of black carbon on the electrode surface. To the best of our knowledge, this result constitutes one of the first examples of catalyst-free addition of  $\text{NH}_3$  to ethylene.

Next, the total flow rate ( $\text{C}_2\text{H}_4/\text{NH}_3 = 0.5$  in helium) was varied from 50 to  $100 \text{ mL}\cdot\text{min}^{-1}$  in order to determine the optimized residence time ( $\tau$ ) in the DBD reactor.  $\tau$  is defined as the ratio between the volume of the reactor and the total flow rate. Results are presented in Fig. 1. The NTAP-induced hydroamination of ethylene with  $\text{NH}_3$  was a very fast reaction and occurred within 1 s. Extending the residence time over 1 s did not result in a significant increase of both the ethylamine yield and the ethylene conversion, suggesting that the reaction was thermodynamically limited, as commonly observed with catalytic reactions (hydroamination vs Hoffman elimination). As a further evidence, the selectivity to ethylamine was found to be constant (30-33%), whatever the conversion rate.

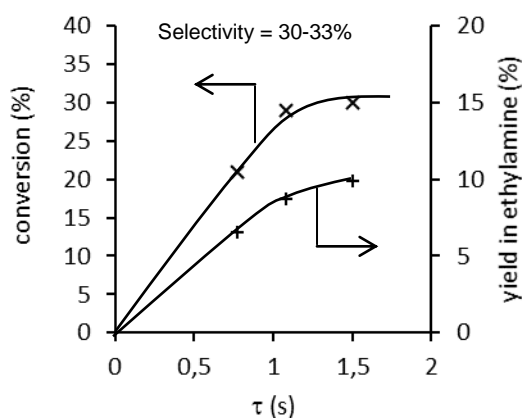


Figure 1 Influence of the residence time ( $\tau$ ) on the ethylene conversion and yield in ethylamine (total flow rate: 50, 70,  $100 \text{ mL}\cdot\text{min}^{-1}$ , ratio  $\text{C}_2\text{H}_4/\text{NH}_3 = 0.5$ , He: 70%,  $P = 4 \text{ W}$  (12 kV, 800Hz))

The  $\text{C}_2\text{H}_4/\text{NH}_3$  ratio was then varied from 0.25 to 1, while keeping unchanged the total flow rate of  $\text{C}_2\text{H}_4/\text{NH}_3/\text{He}$

( $50 \text{ mL}\cdot\text{min}^{-1}$ ) and the deposited power (4 W). Results are summarized in Figure 2. A steadily increase of the conversion of ethylene from 22% to 48% was observed when the  $\text{C}_2\text{H}_4/\text{NH}_3$  ratio was decreased from 1 to 0.25. However, it did not result in a further increase of the ethylamine yield (10%), suggesting the formation of a higher amount of side products at a  $\text{C}_2\text{H}_4/\text{NH}_3$  ratio of 0.25. At this stage of our investigations, and with the analytical apparatus coupled online to our DBD reactor, it was difficult to determine with accuracy the nature of side products. From the literature, one may suspect the formation of di-/triethylamine and oligomers of ethylene.<sup>5</sup> Hence, in the following experiments, the  $\text{C}_2\text{H}_4/\text{NH}_3$  ratio and the total  $\text{C}_2\text{H}_4/\text{NH}_3/\text{He}$  flow rate were kept to 0.5 and  $50 \text{ mL}\cdot\text{min}^{-1}$ , respectively.

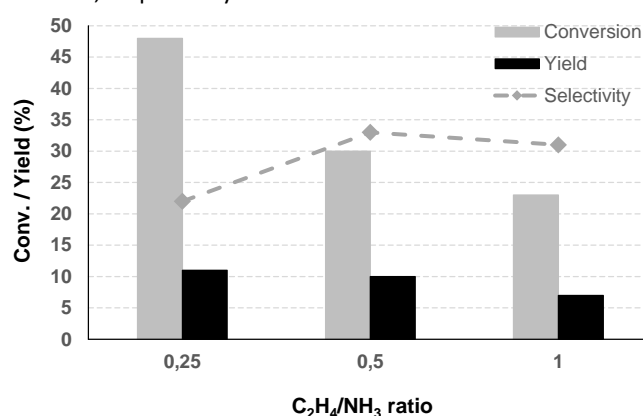


Figure 2 Influence of the ratio  $\text{C}_2\text{H}_4/\text{NH}_3$  (0.25, 0.5, 1), Total flow rate:  $50 \text{ mL}\cdot\text{min}^{-1}$ , He: 70%,  $P = 4 \text{ W}$  (12 kV, 800Hz)

The impact of the deposited power on the conversion of ethylene and yield in ethylamine was then assessed. It was observed that the conversion of ethylene was raised from 23 to 55% when the deposited power was concomitantly increased from 2 to 6 W (Fig. 3). This result might be explained by the formation of a higher concentration of energetic electrons at a higher power input.<sup>17</sup> Interestingly, independently of the deposited power, the selectivity to ethylamine remained constant (30%). As a result, the yield in ethylamine was improved from 9% at 2 W to 17% at 6 W. A higher deposited power was not explored due to the difficulty in this case to prevent C-C and C-N bond cleavage, as mentioned elsewhere.<sup>18</sup>

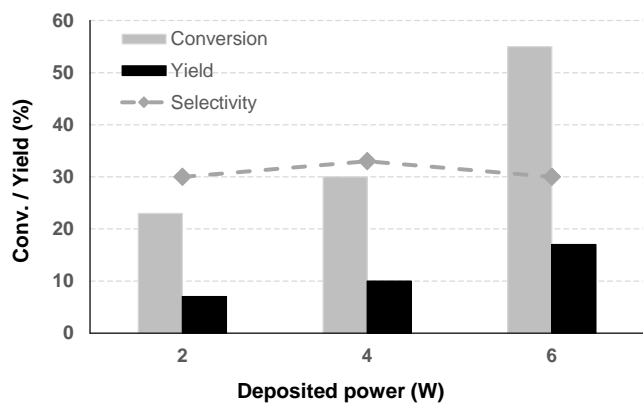


Figure 3 Influence of the deposited power on the conversion of ethylene and yield in ethylamine (Total flow rate: 50 mL.min<sup>-1</sup>, Ratio C<sub>2</sub>H<sub>4</sub>/NH<sub>3</sub> = 0.5, He: 70%).

The plot of the ethylamine selectivity *versus* the ethylene conversion (measured at a deposited power of 2-6 W, Fig. 4) shows that the selectivity remained almost constant and close to 30%, suggesting that (1) ethylamine is stable under our working conditions and thus (2) the formation of ethylamine and ethylene cracking/polymerization are two parallel reactions.

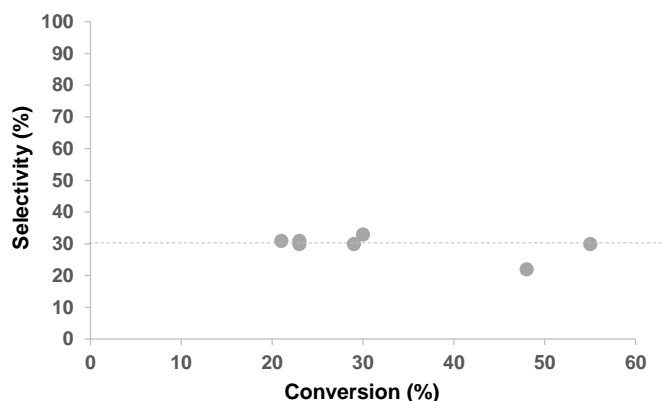


Figure 4 Selectivity to ethylamine versus conversion, P: 2 to 4W, ratio C<sub>2</sub>H<sub>4</sub>/NH<sub>3</sub>: 0.5-2, Total flow rate: 50-100 mL.min<sup>-1</sup>

The ionization of ammonia (NH<sub>3</sub> + e<sup>-</sup> → NH<sub>3</sub><sup>++</sup> + 2 e<sup>-</sup>) and ethylene (C<sub>2</sub>H<sub>4</sub> + e<sup>-</sup> → C<sub>2</sub>H<sub>4</sub><sup>++</sup> + 2 e<sup>-</sup>) is 10.1 and 10.5 eV<sup>19</sup>, respectively. Considering that the electrons energy generated within the NTAP gas is between 1-10 eV<sup>15</sup>, it means that ionization of NH<sub>3</sub> and ethylene is less likely occurs in our case. Hence, it suggests that the reaction proceeds through the formation of radicals through electron impact dissociation, as illustrated in a work of Lepoetre<sup>20</sup> who evidenced the dissociation of NH<sub>3</sub> into NH<sub>2</sub><sup>•</sup> and H<sup>•</sup> under plasma discharge. To support this claim, ethylene was replaced by 1-octene (Fig. 5). Indeed, as previously evidenced by Knowles,<sup>12</sup> addition of aminium radicals on alkenes occurs in an anti-Markovnikov fashion. In perfect agreement, when ethylene was replaced by 1-octene, formation of 1-octylamine was exclusively observed, supporting the occurrence of a radical mechanism (Fig. S4). It is noteworthy that this last result is of high interest, as acid, base and transition metal catalysts lead to a Markovnikov addition of the amine to the alkenes. The anti-Markovnikov addition of NH<sub>3</sub> is not only scientifically more challenging, but also much more desirable due to the broader spectrum of applications of linear amines.<sup>5</sup> At 4 W, with a 1-octene/NH<sub>3</sub> ratio of 0.5, the conversion of 1-octene reached 78% with a yield in 1-octylamine of 14%, showing in the meantime that this NTAP technology could be extended to other non-activated alkenes.

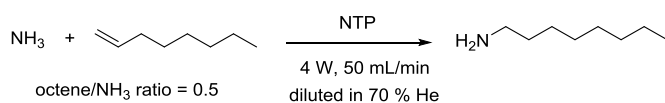


Figure 5. Anti-Markovnikov addition of NH<sub>3</sub> to *n*-octene induced by NTAP

In conclusion, these preliminary results show that non-thermal atmospheric plasma could induce the hydroamination of non-activated alkenes such as ethylene or *n*-octene with NH<sub>3</sub>. **The originality of this study stems from the absence of catalysts, ammonia being activated by electron collision.** Hence, the desorption (or decoordination) of primary amines from the catalytic sites is no more an issue. As a result, the pressure of NH<sub>3</sub> was reduced to atmospheric pressure, while the average temperature of the reactor remained close to 50°C.

Optimization of this reaction, in particular the use of more concentrated feeds of NH<sub>3</sub> and C<sub>2</sub>H<sub>4</sub>, the structural determination of side products and the coupling of non-thermal atmospheric plasma with catalysis is now the topic of current investigations in order to better control the selectivity of involved radical reactions and also to improve the space time yield of this reaction. Optimization of the reactor geometry is also under investigations to **improve the performances of this methodology in terms of energy consumption.**

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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