Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering. This journal is © The Royal Society of Chemistry 2021

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

Electronic supplementary information (ESI)

Julien Dieu, François Jérôme,\* Catherine Batiot-Dupeyrat\*

## Description of the experimental set-up

The reactor used to carry out the reaction is a dielectric barrier discharge (DBD) plasma reactor made of an alumina cylinder (200 mm in length, 6 mm outside diameter and 4 mm inside diameter) comprising an outer and an inner electrodes, between which the plasma gas is created. The outer electrode is a 100 mm long copper tube and the central electrode is a 1 mm diameter stainless steel rod. The plasma volume between the two electrodes is 1.2 mL.



Figure S1: Experimental setup of the DBD plasma reactor

A sinusoidal AC signal was generated across the electrode using a wave generator (TG1010A Aim-TTi, Thurlby Thandar Instruments Brand), the signal was amplified by a high voltage

amplifier (Trek 20/20C). The discharge power injected was calculated with the Lissajous method (Figure S2). The voltage was varied from 12 to 15 kV while the frequency was kept constant at 800 Hz. The applied voltage was measured with high voltage probes (PMK, model PHV4-2757) using an oscilloscope (waveRunner 62 Xi, Lecroy).



**Figure S2**: Lissajous for a plasma with a power of 6 W a total flow rate of 50mL min<sup>-1</sup> and an ethylene ammonia ratio 0,6

A gas supply system (helium (He), ethylene ( $C_2H_4$ ) and ammonia (NH<sub>3</sub>)) is connected to the inlet of the DBD reactor. At the outlet of the DBD reactor, the gas phase is analyzed on-line by a gas chromatography (Shimatzu 2014, TCD detector) equipped with a poraplot Q column (30 m length, 0.53 mmm inner diameter). The use of three-way valves enables flow measurement (Figure S1). These GC analyses allowed the conversion of ethylene and the yield in ethylamine to be determined. Note that experiments were performed twice with a good accuracy, resulting in a margin error of  $\pm$  5 %.

For analysis, the GC program was fixed as follow: Initial temperature: 40°C, plateau 7 min, heating ramp of 20°C/min until 120°C, plateau : 1 min, heating ramp of 5°C/min until 180°C plateau : 10 minutes.



Figure S3. Typical gas chromatogram obtained by reacting NH<sub>3</sub> and ethylene in the presence of NTAP

## Hydroamination of *n*-octene with NH<sub>3</sub>

1-octene was introduced in the DBD reactor by bubbling part of helium stream through a saturator containing 1-octene, before being mixed with NH<sub>3</sub> and He. The flow was adjusted as follow: He (35 mL.min<sup>-1</sup>), NH<sub>3</sub> (5 mL.min<sup>-1</sup>) and 1-octene (2.5 mL.min<sup>-1</sup>). The applied voltage was 10 kV and the frequency 800 Hz, so that the calculated deposited power was 4W For the identification of 1-octylamine, an aliquot of the gas phase was picked up with a GC syringe at the exit of the DBD reactor and then analysed by GC using a HP5MS column. On this column, 1- and 2-octylamine have two different retention times. Standards of 1- and 2- octylamine have been used to validate the exclusive formation of 1-octylamine.



**Figure S4**. Typical gas chromatogram obtained by reacting NH<sub>3</sub> and 1-octene in the presence of NTAP (the gas phase was analyzed on a SCION 456-GC equipped with a HT-5MS column and a CP8400 autosampler.)