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Conversion of ammonia to hydrazine induced by high frequency ultrasound

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Abstract: Hydrazine is a chemical of outmost importance in our society, either for organic synthesis or energy purpose. The direct conversion of NH_3 to hydrazine is highly appealing but it remains a very difficult task because the degradation of hydrazine is thermodynamically more feasible than the cleavage of the N-H bond of NH_3 . As a result, any catalyst capable of activating NH_3 will thus unavoidably decompose N_2H_4 . Here we show that cavitation bubbles, created by ultrasonic irradiation of aqueous NH_3 at a high frequency, act as micro-reactors to activate and convert NH_3 to NH species, without assistance of any catalyst, yielding hydrazine at the bubble-liquid interface. The compartmentation of *in situ* produced hydrazine in the bulk solution, which is maintained close to 30°C , advantageously prevents its thermal degradation, a recurrent problem faced by previous technologies. This work also points towards a path to scavenge $\bullet\text{OH}$ radicals by adjusting the NH_3 concentration.

Hydrazine (N_2H_4) is a chemical of outmost importance in the chemical industry. The hydrazine hydrate market size was 356 million USD in 2015 and is expected to reach 530 million USD in 2024, mostly boosted by the growing need of our society for the manufacture of polymer foams and agrochemicals, the actual two biggest market shares of hydrazine.^[1] Besides, the rapid development of hydrazine hydrate fuel cells,^[2] nowadays demonstrated with electric vehicles, should also open up new perspectives for hydrazine in the future. Projections showed that hydrazine is one of the chemicals expected to record immense growth prospects across the forecast period of 2020-2030.^[3]

Hydrazine is industrially produced by partial oxidation of NH_3 , either with hypochlorite or with peroxide.^[4] In the widest spread industrial processes (Bayer-ketazine and peroxide process), hydrazine is trapped *in situ* under the form of a ketazine, by reaction with a ketone, to prevent its decomposition (Fig. S1). Ketazine is then hydrolyzed to release hydrazine and regenerate the ketone. The direct production of hydrazine from NH_3 or $\text{N}_2/\text{H}_2\text{O}$ is economically and environmentally highly attractive, but it remains a very difficult task. One of the reason stems from the high N-H and N-N bond dissociation of NH_3 (435 kJ/mol) and N_2 (946 kJ/mol), respectively, requiring harsh conditions of temperature and pressure, which are not compatible with the stability of hydrazine. Indeed, the decomposition of hydrazine is thermodynamically more favorable ($\Delta G = -150$ kJ/mol) than the

conversion of NH_3 ($\Delta G = 16.5$ kJ/mol) or $\text{N}_2/\text{H}_2\text{O}$ ($\Delta G = 184$ kJ/mol) to hydrazine, making the accumulation of hydrazine scientifically challenging.^[5]

Physical activation of the N-H and N-N bond of NH_3 and N_2 , respectively, at low temperature with electron beam,^[6] plasma,^[7] light,^[8] or by the coupling of these technologies with catalysis such as electrocatalysis for instance have been explored for the synthesis of hydrazine.^[5a, 9] Although fascinating results were reported, the *in situ* decomposition of hydrazine cannot be avoided, leading to the formation of very diluted feeds of hydrazine (*i.e.* micromolar).

High frequency ultrasound (HFUS), a technology based on cavitation phenomenon, is gaining more and more interest in the field of chemistry.^[10] Due to the extreme conditions of pressures and temperatures existing inside the cavitation bubbles, it was shown by sonoluminescence spectroscopy that gaseous molecules, with high bond dissociation energies such as N_2 , O_2 , CO_2 , CH_4 , can be cleaved inside the cavitation bubbles, leading to the formation of radicals and the occurrence of sonochemical reactions.^[11] So far, the activation of NH_3 by HFUS has been investigated sporadically, and the rare previous studies were mainly focused on the elimination of NH_3 from waste water (by degassing, pyrolysis).^[12] In 2017, a pioneer work of Pflieger demonstrated, by sonoluminescence spectroscopy, that NH species can be formed inside the cavitation bubbles, by subjecting an aqueous solution of NH_3 (0.17 wt%) to an ultrasonic irradiation at 359 kHz.^[13] Inspired by these results, we investigate here the sonochemical conversion of NH_3 to N_2H_4 . Unlike previous works, we show here that by adjusting the temperature of the solution and the concentration of NH_3 , it was possible to limit the decomposition of hydrazine, a scientific and technological problem faced by previous routes.

In a first set of experiments, NH_3 was continuously bubbled (30 mL/min) in 100 mL of water subjected to an ultrasonic irradiation at 525 kHz, with an acoustic power of 0.17 W/mL. The aqueous solution of NH_3 was maintained at 30°C using a cooling system coupled to the ultrasonic reactor (Fig. S2). Hydrazine was titrated by spectrophotometry and results were doubly confirmed by HPLC titration (Fig. S3-S7). Hereafter, the formation rate of hydrazine is given with an uncertainty of 5%.

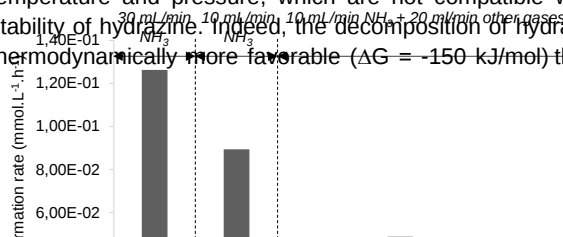


Figure 1. Influence of gases on the initial formation rate of N_2H_4 (10 ml/min NH_3 + 20 ml/min gas, 525 kHz, 0.17 W/mL, 30°C). All reactions were conducted at atmospheric pressure.

Pleasingly, under these conditions, hydrazine was continuously produced at a rate of $0.12 \text{ mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ (Fig. S8). The dilution of NH_3 in gases such as O_2 , N_2 , Ar, or He resulted in a decrease of the formation rate of hydrazine (Fig. 1). No correlation was established between the physicochemical properties of the gas (thermal conductivity, heat capacity, etc...) and the formation rate of N_2H_4 . As a result, we suspect that the formation rate of N_2H_4 is more related to the solubility of NH_3 in water. To support this claim, aqueous NH_3 solutions with different concentrations (from 0.1 to 20 wt%) were subjected to an ultrasonic irradiation (525 kHz) under air (*i.e.* no bubbling of NH_3). The plot of the formation rate of hydrazine as a function of the NH_3 concentration is reported in Fig. 2.

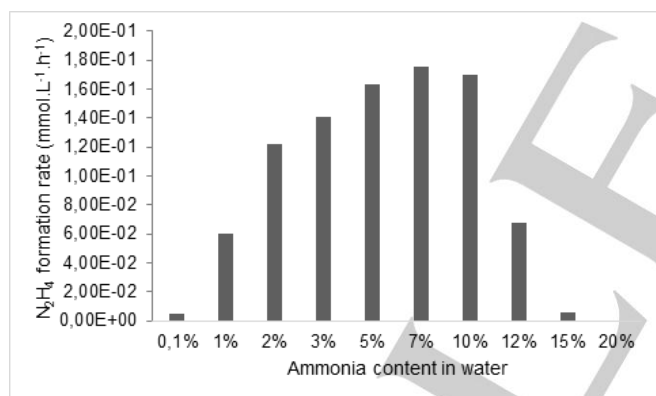


Figure 2. Effect of the NH_3 concentration on the formation rate of hydrazine (525 kHz, 0.17 W/mL, 30°C).

A volcano-type curve was obtained. The formation rate of hydrazine gradually increased with a concomitant increase of the NH_3 concentration from 0.1 to 7 wt%, to reach a maximum of $0.17 \text{ mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ at 7 wt% NH_3 . At higher concentration of NH_3 , the formation rate of hydrazine declined, and was even inhibited at a NH_3 concentration over 15 wt%. This result can be understood in terms of thermodynamics. The sonochemical decomposition of NH_3 is endothermic. Hence, when the concentration of NH_3 inside the cavitation bubbles is increasing, it decreases the maximum temperature and pressure that can be reached inside the cavitation bubbles, thus finally quenching sonochemical reactions.^[14]

In order to get more insight on the reaction mechanism, we first checked any possible role of the metallic reactor wall (316 L stainless steel) on the hydrazine production. To this end, a similar experiment was conducted by confining the aqueous solution of NH_3 (5 wt%) in a polyethylene flask (material transparent to the ultrasonic waves) immersed into the ultrasonic reactor filled with water. No significant change in hydrazine production rate was observed, ruling out a possible contribution of the metallic reactor wall in the reaction mechanism (Fig. S9-S10). Next, the concentration of hydrazine was plotted as a function of the reaction time (30°C, NH_3 at 30 mL/min, 0.21 W/mL). Very interestingly, over a period of 20 h, the reaction never plateaued and hydrazine was continuously produced (Fig. 3). At 20 h of ultrasonic irradiation at 525 kHz, the concentration of hydrazine reached 3.3 mmol/L, which is about 1000 times higher than in previously reported works. These results also suggest that the formation rate of hydrazine is faster than its decomposition, which constitute one of the unique examples in the state of the art.

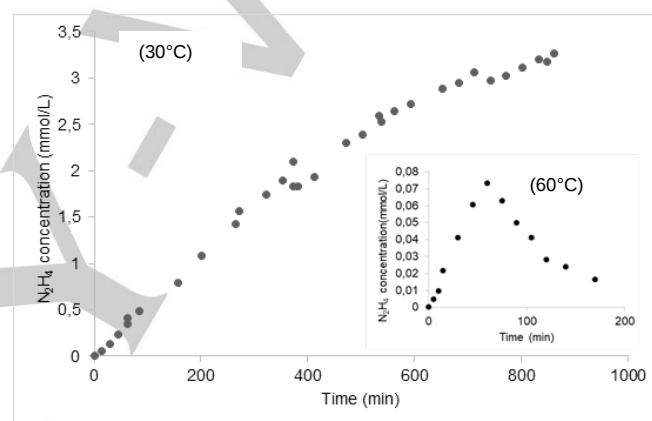


Figure 3. Concentration of hydrazine as a function of the reaction time (bubbling of NH_3 at 30 mL/min, 525 kHz, 0.21 W/mL) at 30°C and 60°C.

One of the explanations for this result stems from the low temperature of the aqueous NH_3 solution (30°C), preventing the thermal decomposition of hydrazine. Indeed, under silent conditions, hydrazine was found stable in aqueous NH_3 (5 wt%) at 30°C, while at 60°C a degradation was observed (Fig. S11). To support this claim, the temperature of the ultrasonic reactor was increased from 30 to 60°C. At 60°C, the formation of hydrazine remained very low and reached only 0.073 mmol/L after 60 min, (Fig. 3), confirming the negative impact of the temperature on the hydrazine production. Although high temperatures are reached in the cavitation bubbles, the bulk aqueous solution of NH_3 can be maintained at 30°C, which represents a noticeable advantage of this technology to prevent the thermal degradation of hydrazine.

The second explanation can be understood in terms of $\bullet\text{OH}$ radical scavenging by NH_3 . It has been previously demonstrated, by sonoluminescence spectroscopy, that ultrasonic irradiation of an aqueous solution of NH_3 concomitantly generate NH and $\bullet\text{OH}$ radicals.^[13] $\bullet\text{OH}$ radicals are known to decompose hydrazine.^[15] To assess the reactivity of *in situ* produced $\bullet\text{OH}$ radicals, we first measured the amount of H_2O_2 formed, resulting from the recombination of $\bullet\text{OH}$ radicals (Fig. S12, 13). Interestingly, when the concentration of NH_3 is over 1 wt%, no H_2O_2 was detected, confirming that $\bullet\text{OH}$ radicals are quickly scavenged *in situ* (Fig.

S14). Two scenarios are thus possible: (1) the scavenging of $\bullet\text{OH}$ radicals by NH_3 , to form $\bullet\text{NH}_2$ radical and water, or (2) the scavenging of $\bullet\text{OH}$ radicals by hydrazine, inducing its partial decomposition to N_2 and H_2O . To discriminate between these two scenarios, a solution of hydrazine (0.1 mmol/L) was subjected to an ultrasonic irradiation either with or without NH_3 . In line with previous reports, without NH_3 , hydrazine was nearly completely decomposed after only 2 h of irradiation by *in situ* produced $\bullet\text{OH}$ radicals (Fig. 4). In contrast, in an aqueous solution of NH_3 (5 wt%), the concentration of hydrazine kept increasing, indicating that $\bullet\text{OH}$ radicals are scavenged by NH_3 (Fig. 4). A similar behavior was observed with 1 mmol/L of hydrazine (Fig. S15). These results can be explained in terms of probability. Indeed, the concentration of NH_3 (1–5 wt% = 0.6–3 mol/L) is much higher than that of hydrazine. As a result, the probability for the $\bullet\text{OH}$ radical to react with NH_3 is much higher than with hydrazine.

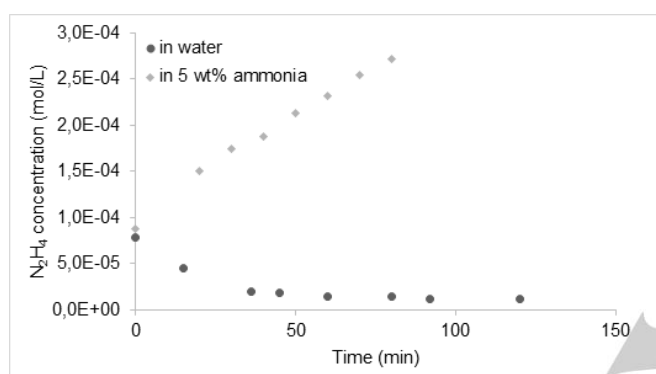


Figure 4. Stability of hydrazine under ultrasonic irradiation with and without NH_3 (initial hydrazine concentration = 0.1 mmol/L in water or in 5 wt% ammonia, 525 kHz, 30°C, 0.17 W/mL).

From these data, a plausible reaction mechanism can be proposed. During the ultrasonic irradiation, NH_3 and vapors of water diffuse within the cavitation bubbles to produce NH and $\bullet\text{OH}$ radicals as observed elsewhere.^[13] NH species can react either with NH_3 to form two $\bullet\text{NH}_2$ radicals or with H_2O to form $\bullet\text{NH}_2$ and $\bullet\text{OH}$ radicals. These recombination reactions can occur either inside the cavitation bubbles or at the cavitation bubble-liquid interface. As the amount of H_2O is 18 times higher than that of NH_3 in our reactor (at 5 wt% NH_3), we assume that the main reaction taking place for NH is the reaction with H_2O . On the other hand, and as discussed above, $\bullet\text{OH}$ radicals are rapidly trapped by NH_3 , the second largest abundant chemical in the HFUS reactor, presumably to form $\bullet\text{NH}_2$ radicals and water, a reaction which is thermodynamically favored ($\Delta G = -46$ kJ/mol).^[16] In terms of probability, the recombination of $\bullet\text{NH}_2$ radicals with $\bullet\text{OH}$ radicals is less likely to occur, as $\bullet\text{OH}$ radicals are rapidly scavenged by NH_3 . To check this hypothesis, the as-obtained aqueous solution was fully analyzed by HPLC, in particular to detect the formation of nitrate. Indeed, it is known that $\bullet\text{OH}$ radical can react with $\bullet\text{NH}_2$ radical to form NH_2OH which is instable and further rapidly convert to nitrate.^[17] As expected, with a bubbling of NH_3 (30 mL/min), the amount of nitrate remained below the detection limit of our apparatus, supporting that the recombination of $\bullet\text{NH}_2$ with $\bullet\text{OH}$ is not a dominant reaction. Hence, $\bullet\text{NH}_2$ radicals has no other option than to dimerize to form N_2H_4 .

In an attempt to elucidate whether hydrazine is formed inside the cavitation bubbles or at the bubble liquid interface, phenol was added into the solution as a radical scavenger. Phenol has a high boiling point (182°C) and a low vapor pressure (0.2 mmHg at 20°C), making it improbable its diffusion inside the cavitation bubble, as demonstrated in other reports.^[18] Hence, phenol is a suitable radical scavenger to selectively trap radicals at the bubble-liquid interface. Interestingly, in the presence of phenol (0.1 mol/L) in an aqueous NH_3 solution (5 wt%), no hydrazine was formed, suggesting that hydrazine is more likely to be formed at the bubble-liquid interface. To further support this claim, sodium benzoate was also tested as another radical scavenger, as it reacts slower with radical species than phenol, allowing a better monitoring of the reaction.^[16, 19] In addition, as a salt, the vapor pressure of sodium benzoate is negligible at 30°C. As expected, an incremental increase of the amount of sodium benzoate led also a gradual decrease of the amount of hydrazine, confirming the results obtained with phenol (Fig. S16). Altogether, these results strongly suggest that the formation of hydrazine occurred at the bubble-liquid interface. Beside, hydrazine hydrate (64 wt%) has a boiling point of 114°C and a vapor pressure of 7.5 mmHg at 30°C. Hence, its diffusion inside the cavitation bubbles is negligible and thus hydrazine dominantly remains compartmented into the bulk solution at 30°C, where its thermal decomposition is drastically limited. (Fig. 5).

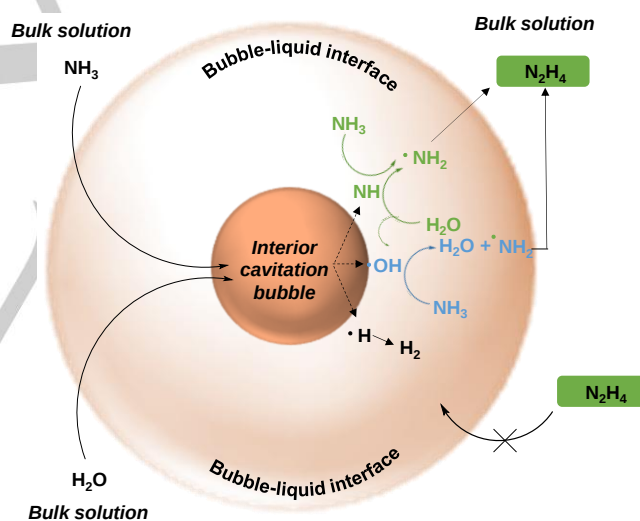


Figure 5. Proposed reaction pathway. For the sake of clarity, only reactions taking place at the cavitation bubble-liquid interface are shown.

As the selectivity to hydrazine is governed by the concentration of NH_3 and N_2H_4 into the reactor, one may question the maximum concentration of hydrazine this technology may support. Using a simple statistical model, and with the approximations that (1) the rate of each radical reactions is similar and (2) the NH/OH ratio is 1, aqueous solution of hydrazine of 3.5 and 7.3 wt% could be theoretically obtained with this technology from a 5 and 10 wt% of aqueous NH_3 solution, respectively (more information is provided in the SI, Fig. S17–S19). If the NH/OH ratio now varies from 0.01 to 100, the N_2H_4 is expected to be produced within a concentration range of 2.32–3.91 wt% and 4.72–8.08 wt% from a 5 and 10 wt% of

aqueous NH_3 solution, respectively, which are typical concentrations routinely handled in industry. The highest amount of N_2H_4 is obtained at the highest NH_3/OH ratio (Fig. S20). It is noteworthy that at these concentration ranges, and in our conditions (atmospheric pressure and 30°C), the risk of detonation/flammability is very unlikely (no flash point of aqueous hydrazine at these concentrations), water acting as an inerting agent in this case.^[20] More information on safety is discussed in the supporting information.

With the reactor design in our hands, we are limited by the low formation rate of N_2H_4 , making it very long, and even not realistic, the formation of 2–8 wt% aqueous solution of hydrazine. However, the formation rate of hydrazine could be largely increased by working in a continuous flow reactor, as the acoustic power density will be locally much higher than in our reactor. To demonstrate this possibility, the acoustic power density was varied from 0.1 to 0.23 W/mL (Fig. 6). As expected, the formation rate of hydrazine was directly impacted by the acoustic power and the formation rate of hydrazine exponentially increased with the acoustic power. This last result demonstrates that switching from a batch to a continuous flow reactor could be a promising perspective for this work to investigate the conversion of NH_3 to more concentrated solutions of hydrazine hydrate, but also to reduce the energy expenditure of this pathway.

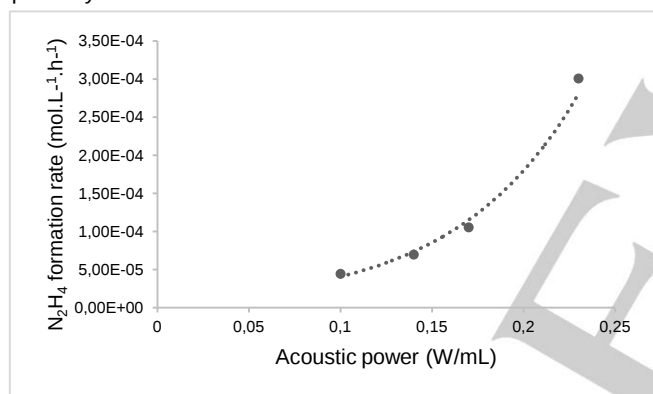


Figure 6. Effect of the absorbed acoustic power on the formation rate of hydrazine (30 ml/min NH_3 , 525 kHz, 30°C).

In conclusion, these preliminary results suggest that high frequency ultrasound is a potential disruptive technology for the direct, salt-free conversion of NH_3 to hydrazine. Cavitation bubbles act as micro-reactors to activate NH_3 , resulting in the formation of NH species that are further recombined to hydrazine at the bubble-liquid interface. One of the advantage of this technology is the compartmentation of hydrazine into the bulk solution where the temperature is maintained at 30°C , thus avoiding its thermal degradation, a recurrent problem faced with previous technologies. In addition, we showed that adjusting the concentration of NH_3 allowed a rapid scavenging of $\bullet\text{OH}$ by NH_3 , thus limiting the oxidative degradation of hydrazine at the bubble liquid-interface.

Two perspectives are under investigation in our groups (1) a switch from a batch to a continuous flow reactor to improve the efficiency of this transformation, in particular in terms of reaction time (i.e. energy efficiency), and (2) the exploration of this technology for the activation and utilization of NH_3 in organic

reactions to produce chemicals with higher added value than N_2H_4 .

Acknowledgements

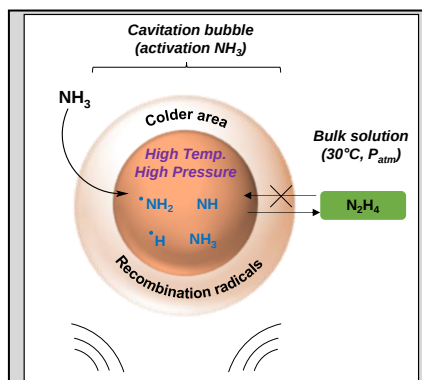
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Keywords: Ammonia • Cavitation bubbles • Hydrazine • Radicals • Ultrasound

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