

Thermal decomposition of ammonia. N_2H_4 - an intermediate reaction product

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Received 12 April 2006; accepted 19 June 2006

Abstract: The paper reports the thermal decomposition of ammonia under dynamic conditions at 800°C in a quartz reactor. Its purpose is to confirm the homogeneous-heterogeneous degenerated branched chain mechanism established in previous studies, which assume the formation of N_2H_4 as a molecular intermediate; this paper identifies hydrazine as a product of thermal decomposition using FT-IR and UV-VIS spectroscopies.

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Keywords: Ammonia decomposition, mechanism reduction, hydrazine, spectroscopy FT-IR, spectroscopy UV-VIS

1 Introduction

The decomposition of NH_3 has been studied under different conditions: thermal [1, 2], catalytic [3, 4], photo-chemical [5], and in plasma [6]. The kinetics and the reaction mechanism - even in the simplest case of thermal decomposition - have not yet been fully elucidated with several matters still in dispute. That is why, this kinetic study of the NH_3 thermal decomposition under dynamic conditions has been undertaken, in order to achieve a better understanding of the reaction mechanism.

In our previous paper [7, 8], a thorough description of the instrumentation used under dynamic conditions is reported, along with the dosage methods of the reactant and of the final reaction products, including the corresponding kinetic curves obtained at 800°C in a 348.831 cm³ quartz reactor with an S/V ratio of 0.85 cm⁻¹.

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The kinetic curves corresponding to the final reaction products, H_2 and N_2 , show obvious induction periods, which demonstrate that, the thermal decomposition of ammonia is not a simple one and suggesting, under such conditions, a chain mechanism. [9]

Consequently, an extended mechanistic pattern has been considered, including all possible homogeneous elementary reactions, as well as heterogeneous processes which satisfactorily describe the experimentally-observed temporal evolution. [8]

For the reduction of the reaction mechanism, the non-important reactions are identified by sensitivity analyses [10], based upon the normalised sensitivity coefficients, and then are eliminated off the pattern; the reduced pattern of the NH_3 thermal decomposition - which also supports the experimental data - is thus obtained. Numerical integration, the fitting of the kinetic pattern to the experimental data and sensitivity analyses are performed in KINTECUS. [11]

The heterogeneous reactions involved in the mechanism support an accumulation of N_2H_4 in the initial period of the reaction (at low contact times), which explains the delayed formation of the final products and the occurrence of the induction period and thus confirming the degenerated, homogeneous-heterogeneous branched chain mechanism for NH_3 thermal decomposition.

The present study provides evidence that N_2H_4 is a reaction intermediate, suggesting a method for hydrazine production.

Hydrazine is a raw material for various organic and inorganic syntheses, plastics, drugs, insecticides and is also a fuel for combustion piles; the literature describes several methods for its production, some as early as 1887. [12] The largest scale procedure for the synthesis of N_2H_4 is the Rasching process, [12] which has several disadvantages, such as numerous reaction stages, low selectivity and yield, a high degree of pollution, and repeated distillation operations, which result in an increased cost of the final product.

Hydrazine produced as an intermediate from NH_3 thermal decomposition, eliminates the short-comings of known production methods; the procedure is simple and non-polluting. The non-reacted ammonia is also liable to be used for the same end, while the hydrogen and the nitrogen - as final reaction products - may be applied in various domains.

2 Experimental

The experimental reactor used for the kinetic study of ammonia thermal decomposition under dynamic conditions is depicted in figure 1. [7]

The quantitative analysis of NH_3 and the reaction products (H_2 , N_2) was carried out by gas-chromatography. The NH_3 content was analysed on a GCHF 18.3-4 type gas chromatograph equipped with a FID (flame ionization detector), using a 2 m long column with Ethoplat 60/25, 15% filling deposited on chromosorb T (30/60 mesh).

The reaction products (H_2 , N_2) were analysed on a Pye type chromatograph (U series 104, England) equipped with a thermal conductivity detector and a 2 m long glass column filled with Merck 80/100 mesh molecular sieves, using argon as a carrier gas

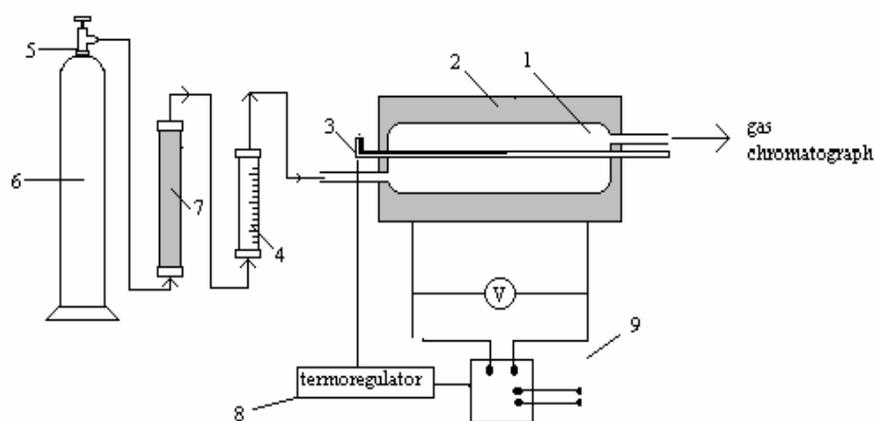


Fig. 1 Block diagram of the experimental installation under dynamic conditions: 1-quartz reaction; 2-electric oven; 3-thermocouple; 4-ammonia flow meter; 5-pressure reducer; 6-liquid ammonia cylinder (99.98% purity); 7- drying vessel with silica gel; 8- temperature regulator; 9- rheostat.

The theoretical curve of N_2H_4 formation, plotted in Figure 2, showed the optimum reaction conditions, namely 800°C with an ammonia flow rate of $580 \text{ cm}^3/\text{min}$, which corresponds to the contact time at which, the N_2H_4 concentration is around the maximum value of $1.4 \times 10^{-4} \text{ mol/L}$.

The gas resulting from the NH_3 thermal decomposition under the above conditions was passed through a U-shaped tube and cooled to $\pm 1^\circ\text{C}$. After 60 minutes, a 1 mL sample of oily liquid was obtained in the tube.

The characterization of hydrazine was made by FT-IR spectroscopy on a JASCO FT-IR plus spectrometer and by UV-VIS spectroscopy on a HITACHI U 2001 spectrometer, using a specific dosing method [13].

3 Results and discussion

The results of the sensitivity analysis [10] for the reduced mechanistic pattern of the NH_3 thermal decomposition is presented in Table 1. Reaction 13 is a heterogeneous reaction forming the molecular intermediate N_2H_4 , while reaction 21 is a reaction of heterogeneous interruption on the surface of the thermally - activated quartz surface. In reactions 13 and 21, the apparent rate constants are obtained by fitting using the Powell method [14], based upon the experimental kinetic curves for NH_3 and the subsequent formation of the final products, H_2 and N_2 .

Superposition of the kinetic curves associated with the reduced mechanism and the experimental kinetic curves demonstrates that the reduced pattern (known as including 21 elementary reactions comparatively with 55 in the extended mechanism) reproduces the experimentally - observed temporary evolution of the system, which confirms the homogeneous-heterogeneous degenerated mechanism in the branched chain.

Table 1 Reduced pattern for the mechanism of NH₃ thermal decomposition.

Nr.	Reaction	A (L/mol·s)	m	E _a (kJ/mol)
1	NH ₃ + M[N ₂ (2);H ₂ (2)] = NH + H ₂ + M	6.30E+11	0	391
2	NH ₃ + NH = 2NH ₂	3.16E+11	0	112.08
3	NH ₂ + NH = NH ₃ + N	1.00E+10	0	8.37
4	NH ₃ + NH ₂ = N ₂ H ₃ + H ₂	1.00E+08	0.5	90.43
5	NH + H ₂ = NH ₂ + H	1.00E+11	0	84.03
6	NH + H = N + H ₂	3.20E+10	0	1.36
7	N ₂ H ₃ + M[N ₂ (2.4);NH ₃ (3);N ₂ H ₄ (4)] = NH ₂ + NH + M	5.00E+13	0	251.21
8	N ₂ H ₃ + M[N ₂ (2.4);NH ₃ (3);N ₂ H ₄ (4)] = N ₂ H ₂ + H + M	1.00E+14	0	138.16
9	N ₂ H ₂ + M[N ₂ (2);H ₂ (2)] = NNH + H + M	5.00E+13	0	209.34
10	NNH + M[N ₂ (2);H ₂ (2)] = N ₂ + H + M	1.00E+10	0.5	12.81
11	N ₂ H ₂ + NH ₂ = NH ₃ + NNH	8.80E-05	4.05	-6.75
12	N ₂ H ₂ + H = NNH + H ₂	85	2.63	-0.963
13	2NH ₂ + Act_Site{s} = N ₂ H ₄ + Act_Site{s}	k = 4.23E+13 (L/mol · s)		
	N ₂ H ₄ + M[N ₂ (2.4);NH ₃ (3);N ₂ H ₄ (4)] = 2NH ₂ + M	5.00E+11	0	251.21
14	Low pressure			
	N ₂ H ₄ + M[N ₂ (2.4);NH ₃ (3);N ₂ H ₄ (4)] = 2NH ₂ + M	1.50E+12	0	163.28
15	N ₂ H ₄ + M[N ₂ (2.4);NH ₃ (3);N ₂ H ₄ (4)] = N ₂ H ₃ + H + M	1.00E+12	0	266.28
16	N ₂ H ₄ + NH = NH ₂ + N ₂ H ₃	1.00E+06	1.5	8.37
17	N ₂ H ₄ + H = N ₂ H ₃ + H ₂	7.00E+09	0	10.47
18	N ₂ H ₄ + N = N ₂ H ₃ + NH	1.00E+07	1	8.37
19	N ₂ H ₄ + NH ₂ = N ₂ H ₃ + NH ₃	1.80E+03	1.71	-5.78
20	NH ₃ + H = NH ₂ + H ₂	5.42E+02	2.4	41.53
21	2H + Act_Site{s} = H ₂ + Act_Site{s}	k = 3.51E+14 (L/mol · s)		

$$k = AT^m e^{-E_a/RT}$$

The FT-IR spectrum of the liquid obtained from the condensation tube, was recorded on KBr between 400 - 4000 cm⁻¹. Table 2 lists the fundamental frequencies characteristic of hydrazine [15–17] and of the liquid.

The fundamental IR frequencies of the liquid from the reactor coincide with those of hydrazine reported in the literature, suggesting that the liquid is hydrazine. In addition, a comparative analysis of the spectra of 98% N₂H₄ and of the liquid from the reactor produce the same characteristic bands, leading to the same conclusion.

For the quantitative determination of hydrazine, a spectrophotometrical dosing method, [13] obtained by plotting a calibration curve for known values of concentration over the 1 – 400 μg/mL domain, is applied. The creation of the calibration curve involves the following steps:

- (1) From a 1 mg/mL stock hydrazine solution, solution volumes between 0.1 – 0.4 mL were taken, which were poured into a 50 mL graduated vial;

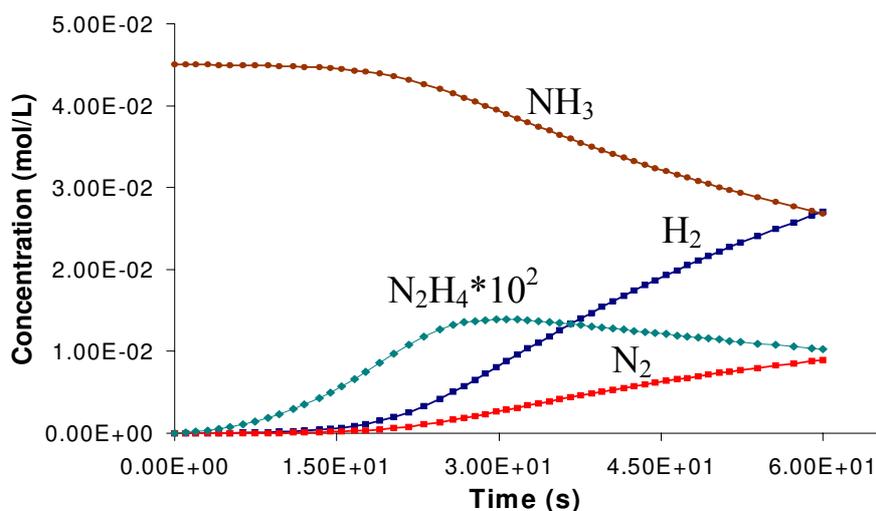


Fig. 2 Superposition of the kinetic curves obtained by numerical integration: symbol (\diamond , \blacksquare , \blacktriangle): reduced model; full line: experimental curves.

Table 2 Fundamental frequencies of N_2H_4 and of the liquid under analysis.

Characteristic bands	Analysed liquid IR liquid (cm^{-1})	N_2H_4 literature IR liquid (cm^{-1})
- NH_2 antisymmetrical stretching (ν_{NH} a)	3347	3332
- NH_2 symmetrical stretching (ν_{NH} a)	3192	3189
- NH_2 deformation (δ_{NH_2})	1627	1608
- NH_2 wagging (ω_{NH_2})	1304	1324
- N-N stretching ($\rho_{\text{NH}_2} + 0.7\nu_{\text{NN}}$)	1083	1103
- NH_2 rocking ($\nu_{\text{NN}} + 0.7\rho_{\text{NH}_2}$)	911	881

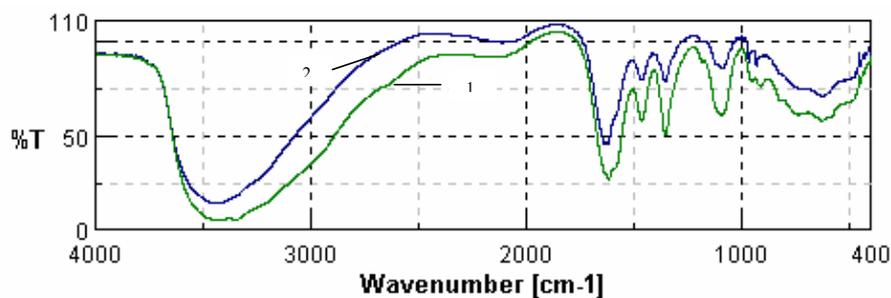


Fig. 3 Superposition of the 98% N_2H_4 (1) and of the analyzed liquid (2) spectra.

- (2) 15 mL of HCl from a 0.1 mol/L stock solution are added into each vial;
- (3) 1 mL of NaOH from a 1.8 mol/L stock solution is added, in order to produce a neutral medium;
- (4) 10 mL of a 0.168 mol/L p-dimethylaminobenzaldehyde solution is added;
- (5) The resulting solution is stirred and left at 20°C for 30 minutes;

(6) A final volume of 50 mL is attained by the addition of glacial acetic acid.

The absorbance of each solution is measured on a HITACHI U-2001 spectrophotometer at a wavelength of 480 nm, a value at which absorbance is maximum, [18] on using as reference a solution prepared following steps 2-6. Figure 4.a illustrates the absorption spectrum of a 0.2 mg/mL hydrazine solution obtained prepared using the above dosing method. [13]

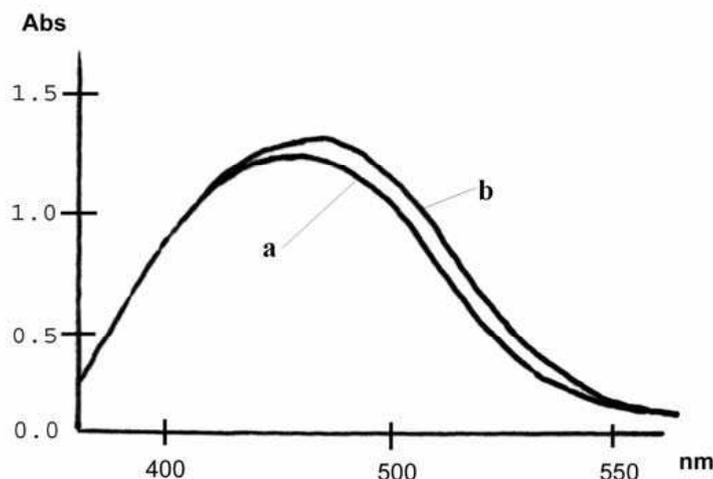


Fig. 4 UV-VIS spectrum of hydrazine: a – standard solution; b – hydrazine obtained from thermal decomposition of NH_3 .

The absorption spectra have been plotted for the four hydrazine solutions of known concentration, while reading of the absorbance corresponding to each solution. The calibration curve was obtained using linear regression ($y = 3.8227 \cdot x$, $R^2 = 0.997$).

From the 1 mL of hydrazine obtained from the condensation tube, a 0.15 mL sample is poured into a 100 mL graduated vial. Steps 2 – 5 are performed and, after 30 minutes, it is diluted to the mark with glacial acetic acid. The absorption spectrum of the resulting solution is shown in Figure 4.b, producing the same absorption maximum as the hydrazine sample of known concentration at 480 nm.

Based upon the absorbance spectrum at 480 nm [13] and comparing to the previously plotted calibration curve, the N_2H_4 concentration from the gaseous reaction mixture is calculated using equation (1).

$$C_{\text{N}_2\text{H}_4} = \frac{C_{c.e.} V_1 V_2}{1000 V_3 t D M} 1000 \quad (1)$$

where:

$C_{c.e.}$ – concentration from the calibration curve (g/L);

V_1 – volume of solution utilised in the analysis (100 mL);

V_2 – volume of hydrazine solution obtained from the reaction of thermal decomposition of NH_3 (mL);

V_3 – volume of hydrazine solution under analysis (mL);

D – ammonia flow rate (cm^3/min);

t – shifting time of the gaseous reaction mixture through the condensation tube (min);

M – molar mass of hydrazine.

Table 3 lists the values of experimental and theoretical N_2H_4 concentrations.

NH_3 flow (cm^3/min)	$C_{\text{N}_2\text{H}_4}$ c.e. (mg/mL)	$C_{\text{N}_2\text{H}_4}$ exp. (mol/L)	$C_{\text{N}_2\text{H}_4}$ theor. (mol/L)
350	0.1260	$1.25 \cdot 10^{-4}$	$0.99 \cdot 10^{-4}$
580	0.2986	$1.87 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$
850	0.3375	$1.31 \cdot 10^{-4}$	$1.22 \cdot 10^{-4}$

Table 3 Values of experimental and theoretical N_2H_4 concentrations.

The values given in the table show good agreement between the optimum theoretical value of the N_2H_4 concentration (Figure 2) and the concentration values calculated from the experimental data. The data provide quantitative confirmation of the presence of hydrazine as a molecular intermediate from which the final reaction products are preponderantly obtained through subsequent elementary reactions.

4 Conclusions

The present study leads us to conclude that N_2H_4 is a molecular intermediate in the thermal decomposition of NH_3 in a quartz reactor;

Hydrazine has been identified qualitatively using FT-IR and quantitatively by UV-VIS spectroscopy, by means of a specific dosing method;

The kinetic curve of N_2H_4 provides an explanation for the occurrence of the induction period [19] during the H_2 and N_2 formation, which confirms that the reaction mechanism is homogeneous-heterogeneous degenerated branched chain for the thermal decomposition of ammonia;

The study proposes a new, simpler method for hydrazine production under the optimum theoretical conditions, which eliminates several of the shortcomings reported in the literature for other procedures.

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