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Full Papers

Explosion and Decomposition Characteristics of Hydrazoic Acid in the Gas Phase

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Abstract:

The formation of hydrazoic acid HN_3 is inherent to many azide processes due to the presence of small amounts of protic components in the reaction mixtures. Hydrazoic acid is an unstable component which may decompose violently. To ensure safe working conditions during the development or the production of azides, the lower decomposition limit (LDL) of this substance in a nitrogen atmosphere was determined using a 5-L explosion sphere. No decomposition could be observed for HN_3 concentrations below 10%. Moreover, the influence of solvent vapors was investigated to demonstrate that they can be used to inhibit the decomposition reaction of hydrazoic acid.

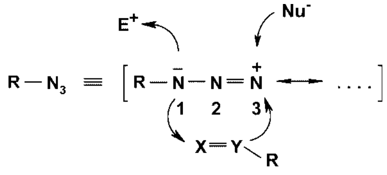
Introduction

Organic azides are extensively used as blowing agents or as functional groups in the chemical and pharmaceutical industries[1] and for the synthesis of heterocycles such as triazoles[2] and tetrazoles.[3–5] In recent times, completely new perspectives have been developed for their use in peptide chemistry and combinatorial chemistry.

Azides can react very differently under different reaction conditions (Scheme 1). In principle, they react with electron-deficient compounds (electrophiles) at N^1 and electron-rich compounds (nucleophiles) at N.[3] There can be retention of the azide unit, but also cleavage of the nitrogen–nitrogen single bond, as in the case of nitrene chemistry. These properties have been used widely in cycloaddition reactions.

The formation of hydrazoic acid is inherent to many azide processes because small amounts of protic components cannot be avoided (impurities in starting materials and presence of some water or of a strong mineral acid such as hydrochloric acid).

Scheme 1. **Reactivity of organic azides**



Scheme 2. **Postulated reaction equation of the formation of hydrazoic acid in the presence of protic components**

$$HX + NaN_3 \rightleftharpoons NaX + HN_3$$

Scheme 3. **Decomposition reaction of hydrazoic acid**

$$2\ HN_3 \longrightarrow H_2 + 3\ N_2$$

This compound was first reported by Curtius in 1890.[6] A postulated reaction equation for the formation of hydrazoic acid from sodium azide is shown in Scheme 2. Hydrazoic acid can also be formed during the sodium azide excess destruction step with sodium nitrite in the presence of hydrochloric acid if not enough sodium nitrite is charged in the reactor.

Hydrazoic acid, as well as sodium azide, is highly toxic.[7] These substances are known to produce hypotension in laboratory animals and humans and to form strong complexes with hemoglobin, consequently blocking oxygen transport in the blood.[8]

Acute inhalation of HN_3 vapor by humans results in lowered blood pressure, bronchitis, eye, nose, throat, and lung irritation, headache, weakness, and collapse.[9] The recommended airborne exposure limit is 0.11 ppm as hydrazoic acid or 0.3 mg/m^3 as sodium azide, which should not be exceeded at any time.[10]

Hydrazoic acid has a boiling point of 36 °C and is therefore considered to be highly volatile under process conditions. It is an unstable component which may decompose violently, forming nitrogen and hydrogen according to Scheme 3 (in the presence of reacting compounds, other decomposition reactions can also occur).

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***Table 1.* Comparison of the explosion characteristics of propane and hydrazoic acid determined in the 5-L explosion sphere**

	propane	hydrazoic acid
initial pressure P_{ini} [bar]	1	0.2
maximum pressure P_{max} [bar]	9.2	6.3
pressure factor	9.2	30
maximum rate of pressure rise $(\mathrm{d}P/\mathrm{d}t)_{\text{max}}$ [bar/s]	651	>9995
K-value [bar·m/s]	111	>1709

Depending on the literature source being consulted, an explosive gas mixture can be formed with air or nitrogen if the hydrazoic acid concentration is higher than 8–15 vol%.[11–13] In the presence of some impurities which are sometimes present in the raw materials, HN_3 concentrations up to 6% were measured during the development of some chemical processes in our laboratories (tetrazole formation). In order to ensure the process safety, too high concentrations of gaseous hydrazoic acid must be avoided, and the concentration level must be continuously known during the reaction.

To illustrate the violence of the decomposition reaction of hydrazoic acid, this compound was compared with mixtures of propane and air which also explode violently. The explosion severity can be characterized with the following parameters:

(1) The maximum explosion (over)pressure (P_{max}) is the maximum pressure occurring during the explosion of a flammable mixture in a closed vessel. The factor between the final and the initial pressure is an important information for the assessment of the explosion severity.

(2) The maximum rate of pressure rise[$(\mathrm{d}P/\mathrm{d}t)_{\text{max}}$] is the maximum value of the pressure rise per unit time in a closed vessel occurring during the explosion of a flammable mixture. In other words, this pressure rise is the maximum speed at which the maximum explosion pressure is reached during the explosion.

(3) The *K*-value (K_g for gases) is a volume-normalized rate of pressure rise and is expressed by the cubic law: $K_g = [(\mathrm{d}P/\mathrm{d}t)_{\text{max}} \cdot V^{1/3}]$. It relates the maximum rate of pressure rise to the volume of the vessel in which the explosion occurs.

The measured data for propane and hydrazoic acid are summarized in Table 1. The rate of pressure rise is shown in Figures 1 and 2. Hydrazoic acid explodes much more violently than propane in air. Moreover, the minimum ignition energy is very low (<1 mJ).

A maximum allowable concentration should be determined during the process risk analysis. Therefore, the conditions to induce an exothermal decomposition in the gas phase must be known. The aim of this paper is to determine the lower decomposition limit (LDL) of hydrazoic acid more accurately to guarantee safe process conditions during the development phase and in the production plant. Moreover, the influence of solvent vapors must be investigated to check if they could be used as inhibitors of the decomposition reaction of hydrazoic acid.

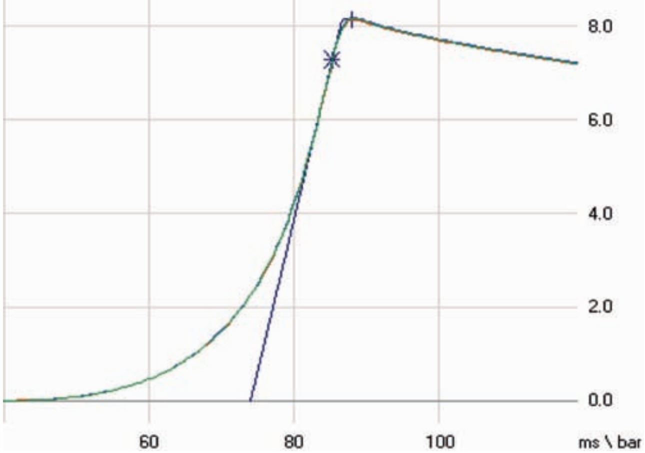

***Figure 1.* Pressure variation during the decomposition of propane in air in the 5-L explosion sphere.**

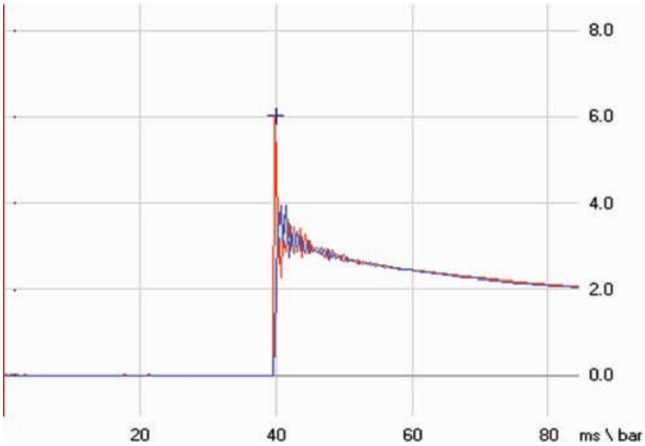

***Figure 2.* Pressure variation during the decomposition of hydrazoic acid in air in the 5-L explosion sphere.**

In parallel to this work, an online method for the determination of the hydrazoic acid concentration in the gaseous phase using NIR spectroscopy was developed (the concentration determination in the gaseous phase was done in the past by using UV spectrometry or by ionic chromatography after absorption of a gas sample in a dilute solution of sodium hydroxide). Due to the dangerous properties of hydrazoic acid, any sampling and contact with this substance should be avoided for the analytics. Therefore, an online monitoring of the HN_3 concentration is more appropriate to avoid any hazardous excessive concentration. The measured data are used to take actions against further unwanted release of HN_3, such as cooling of the reaction mixture or flushing the reactor headspace with nitrogen. The description of this online concentration measurement was published in a separate article.[14] Using this technique, an accurate monitoring of the HN_3 concentration in the reactor headspace in the production plant leads to a significant improvement of the process safety and of the hygiene conditions for the operators.

Experimental Section

Explosion Sphere. The explosion and decomposition behavior of hydrazoic acid in the gas phase has been investigated

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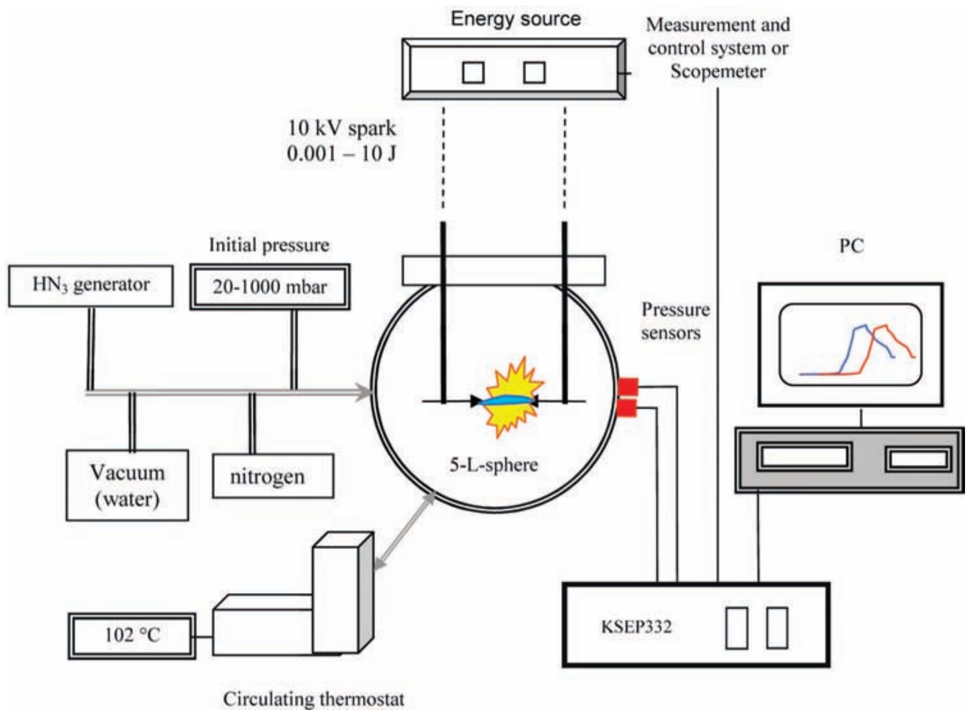

Figure 3. **Five-liter explosion sphere with electrical ignition.**

in a 5-L explosion sphere equipped with an ignition source (see Figure 3). For the determination of the LDL and for the measurement of the explosion/decomposition pressure and rate of pressure rise, a continuous spark with an energy of ~10 J was used. On the other hand, capacitor spark discharges of different energies were used for the determination of the minimum ignition energy required to initiate the explosion/decomposition reaction. The temperature was varied between 50 and 150 °C, the partial HN_3 pressure between 40 and 200 mbar and the absolute initial pressure of the gas mixture between 57 and 1000 mbar.

Some features of the experimental equipment are listed below:

- Ignition energy and spark duration can be varied
- Pressure and temperature are monitored in the millisecond range
- Optimal precision monitoring with an oscilloscope
- Automatic documentation of key test results (dp/dt)

Generation of Hydrazoic Acid. Several methods to prepare hydrazoic acid are described in the literature:

- Reaction of solid sodium azide with a solution of aqueous sulfuric acid or phosphoric acid (50%);[15]

- Reaction of an aqueous sodium azide solution (25%) with a solution of aqueous sulfuric acid (50%);[16]

- Reaction of solid sodium azide with melted stearic acid at 80–90 °C.[15]

In the two first methods, water vapors could be carried in the gaseous phase containing nitrogen and hydrazoic acid and influence the explosion limit (stabilization effect). A heating of the reaction mass is required to avoid the condensation of the highly explosive hydrazoic acid. This problem can be avoided by using the third synthesis method. The mechanism for this formation of hydrazoic acid is shown in Scheme 4.

Scheme 4. **Synthesis of hydrazoic acid**

$$CH_3(CH_2)_{16}CO_2H + NaN_3 \rightleftharpoons CH_3(CH_2)_{16}CO_2Na + HN_3$$

Experimental Equipment. The objective is to prepare HN_3 amounts comprised between 0 and 1-L (i.e., up to 0.05 mol per experiment) which corresponds to a concentration of up to 20 vol% under normal atmospheric pressure in the 5-L explosion sphere. The experimental equipment is shown in Figure 4. It consists of a 1-L steel reactor (for the production of hydrazoic acid) and a 5-L steel sphere (explosion sphere, Figure 3). The connecting pipes are made of stainless steel. The equipment must not contain any nonferrous heavy metals (such as copper, silver, lead, brass) which can react with hydrazoic acid to form shock- and friction-sensitive azides.

Production of Hydrazoic Acid and Transfer to the Explosion Sphere. One equivalent of sodium azide (0.2 mol, 13 g) and one equivalent of stearic acid (0.2 mol, 57 g) are charged at ambient temperature in the 1-L reactor (the valve V2 for the connection with the 5-L explosion sphere is open). The gas atmosphere is removed using a glass filter pump (vacuum, <30 mbar) and is replaced with nitrogen by opening and closing V3. The equipment is evacuated again to <30 mbar via V1. Then, the temperature of the reaction mixture is slowly increased up to 80–90 °C. Above 80 °C the gas production slowly starts, indicated by a pressure increase at the sensors P1 and P2. When the desired partial pressure of HN_3 has been reached (50–250 mbar absolute), V2 is closed, and V1 is opened to remove the excess hydrazoic acid, using the glass filter pump. Then, the total pressure in the explosion sphere is adjusted to the desired value by addition of nitrogen or air. A sample of the gaseous phase is taken with a 2-mL syringe and is extracted with the same volume of 1 N aqueous sodium hydroxide solution. The concentration of the obtained sodium azide

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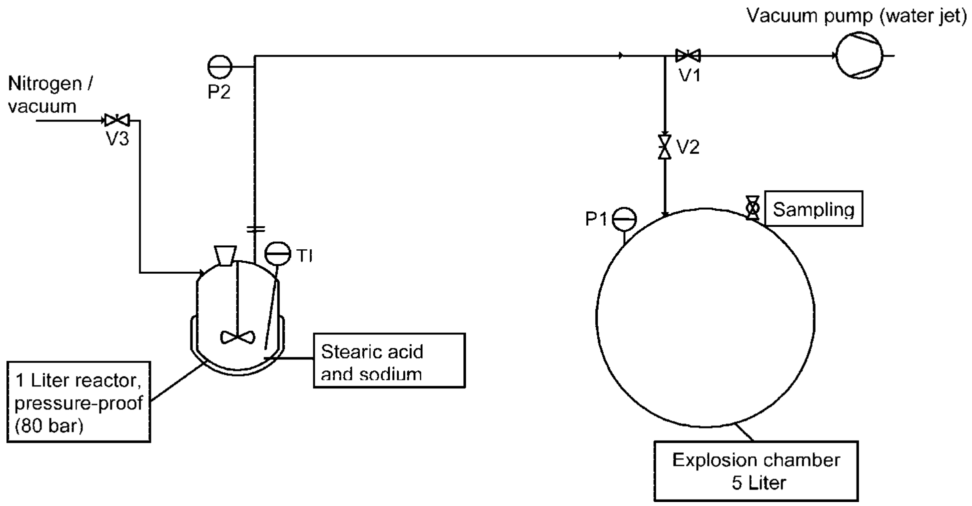

Figure 4. **Experimental equipment for the synthesis of hydrazoic acid and its transfer in the explosion sphere.**

Table 2. **LDL of HN_3 at different pressures and temperatures[a]**

	temperature [°C]									
	50		75		100		125		150	
total initial pressure [mbar]	vol % no ignition	vol % with ignition	vol % no ignit	vol % with ignit	vol % no ignit	vol % with ignit	vol % no ignit	vol % with ignit	vol % no ignit	vol % with ignit
1000	11.5	12.0	12.0	13.0	12.0	13.0	11.0	12.0	10.0	11.0
700	12.1	12.9	–	–	11.0	12.0	–	–	12.0	13.0
400	13.0	13.2	–	–	14.0	15.0	13.0	14.0	12.0	13.0
200	14.0	15.0	–	–	15.0	16.0	–	–	15.0	16.0

[a] Concentration of HN_3 expressed in vol %; ignition source, continuous spark 10 J.

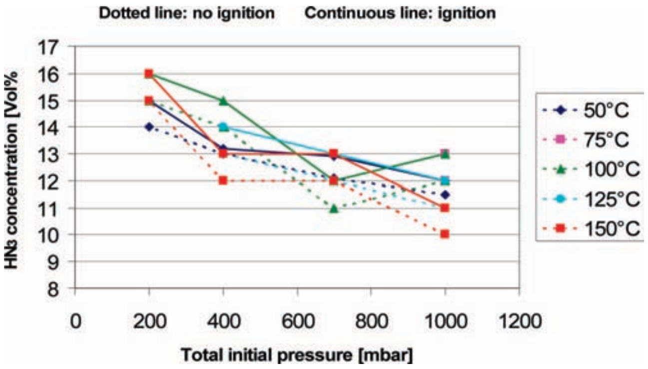

Figure 5. **LDL of hydrazoic acid in nitrogen as a function of total initial pressure.**

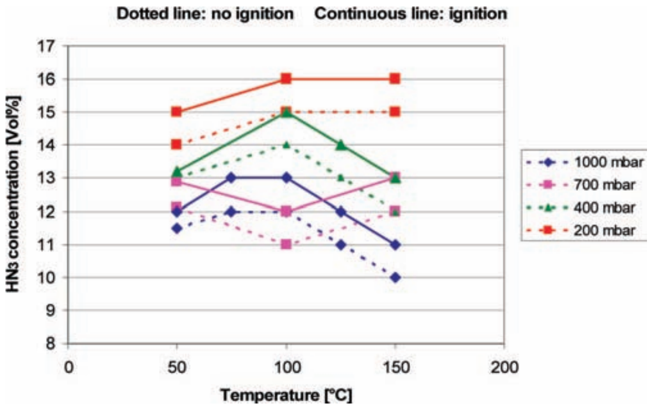

Figure 6. **LDL of hydrazoic acid in nitrogen as a function of the temperature.**

solution is determined afterwards using UV spectroscopy (measurement at 240–260 nm, preferably 250 nm). Prior to experiments the UV analytical method was calibrated with known solutions containing sodium azide. The content of the sphere is ignited with the electrical spark. The pressure increase versus elapsed time is registered. Finally, the remaining gas mixture is decomposed by adding propane and air into the sphere and igniting the sphere contents (elimination of possible hydrazoic acid residues). In the experiments with xylene or ethyl acetate calculated amounts of the liquids were each injected separately into the explosion sphere with a syringe via a septum and allowed to evaporate. The resulting pressure increase was monitored at the pressure gauge.

The variable parameters for the different tests are numerous:

(i) total pressure of the gas mixture before ignition

(ii) temperature

(iii) partial pressure of hydrazoic acid

(iv) partial pressure of xylene or ethyl acetate vapour (solvents for the role of eventual stabilization).

A summary of the results is given in the following tables and figures. Unless stated otherwise, all pressure indications of the total initial pressure (total mixture or components) are given in absolute values (mbar). In the same way, if not stated otherwise, all explosion pressures are overpressures (pressure greater than the initial pressure, which is the pressure just before initiation of the explosion/decomposition reaction). The concentrations in volume percent (vol%) were calculated by assuming an ideal gas.

Lower Decomposition Limit of Hydrazoic Acid in Nitrogen Atmosphere. The value for LDL was determined if at least one successful ignition was observed after five attempts

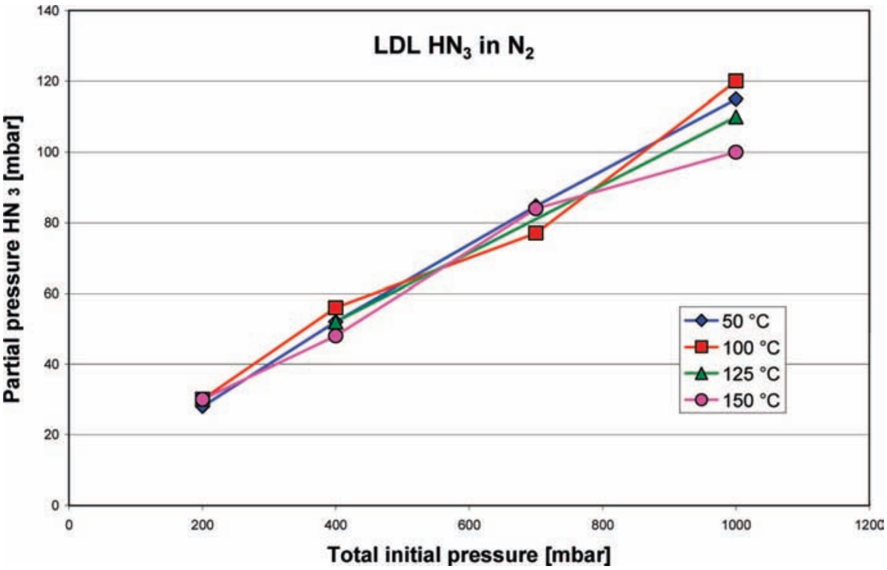

Figure 7. **HN_3 partial pressure as a function of the total initial pressure (data for the LDL of HN_3 in nitrogen).**

Table 3. **Concentration of xylene vapor (and percentage of xylene in total amount of inert gas, in bold italics) required to suppress HN_3 explosion/decomposition at different HN_3 partial pressures, total initial pressures, and temperatures[a]**

			temperature [°C]							
			50		75		140		150	
	HN_3 concentration		xylene concentration[vol %]							
total initial pressure (mbar)	mbar	vol %	no ignition	with ignition	no ignition	with ignition	no ignition	with ignition	no ignition	with ignition
1000	150	15.0	0.30 ***0.35***	0.20 ***0.23***	–	–	–	–	1.5 ***1.76***	1.2 ***1.41***
167	100	59.9	–	–	–	29.94 ***74.66***	–	–	–	–
147	80	54.4	–	–	34.01 ***74.58***	–	–	–	–	–
140	80	57.1	–	–	–	–	–	30.7 ***71.58***	–	–
145	80	55.2	–	–	–	–	33.10 ***73.91***	–	–	–
237	140	59.1	–	–	–	–	–	33.76 ***82.54***	–	–
257	140	54.4	–	–	–	–	38.91 ***85.33***	–	–	–

[a] Ignition source, continuous spark 10 J; residual N_2 pressure, ~17 mbar.

with a spark energy of 10 J (this number of attempts is the standard procedure in our laboratories). Table 2 and Figures 5 and 6 show the LDL of hydrazoic acid in pure nitrogen as a function of pressure and temperature (the dotted line in the figures represents the highest data without ignition, the continuous line, the lowest values with ignition). The LDL of HN_3 drops as a function of increasing the total initial pressure, as can be seen from Figure 5. Within the temperature range investigated (50–150 °C), there is no significant correlation between the LDL of HN_3 in pure nitrogen and the temperature, as can be seen from Figure 6. For a given total initial pressure, the LDL varies moderately as a function of the temperature (±1 °C).

Within a range of the gas pressure from 200 to 1000 mbar and within a range of the gas temperature from 50 to 150 °C no explosion/decomposition could be initiated at a hydrazoic acid concentration equal or lower than 10 vol % in nitrogen.

Figure 7 correlates the variation of the HN_3 partial pressure as a function of the total initial pressure (data for the LDL of HN_3 in nitrogen) and also shows that the influence of the temperature is not significant.

LDL of Hydrazoic Acid in a Mixture of Nitrogen and Vapors of Xylene. Table 3 and Figure 8 show the influence of xylene vapors (isomers mixture) on the LDL of HN_3 for different total initial pressures and temperatures. The LDL of HN_3 strongly increases with increasing the percentage of xylene vapors in the total amount of inert gas for all total initial pressures and temperatures investigated.

LDL of Hydrazoic Acid in a Mixture of Nitrogen and Vapors of Ethyl Acetate. Table 4 and Figure 9 show the influence of ethyl acetate (EtOAc) vapors on the LDL of HN_3 for different total initial pressures at 50 °C. The LDL of HN_3 strongly increases with increasing percentage of EtOAc vapors in the total amount of inert gas at 50 °C and for all total initial pressures.

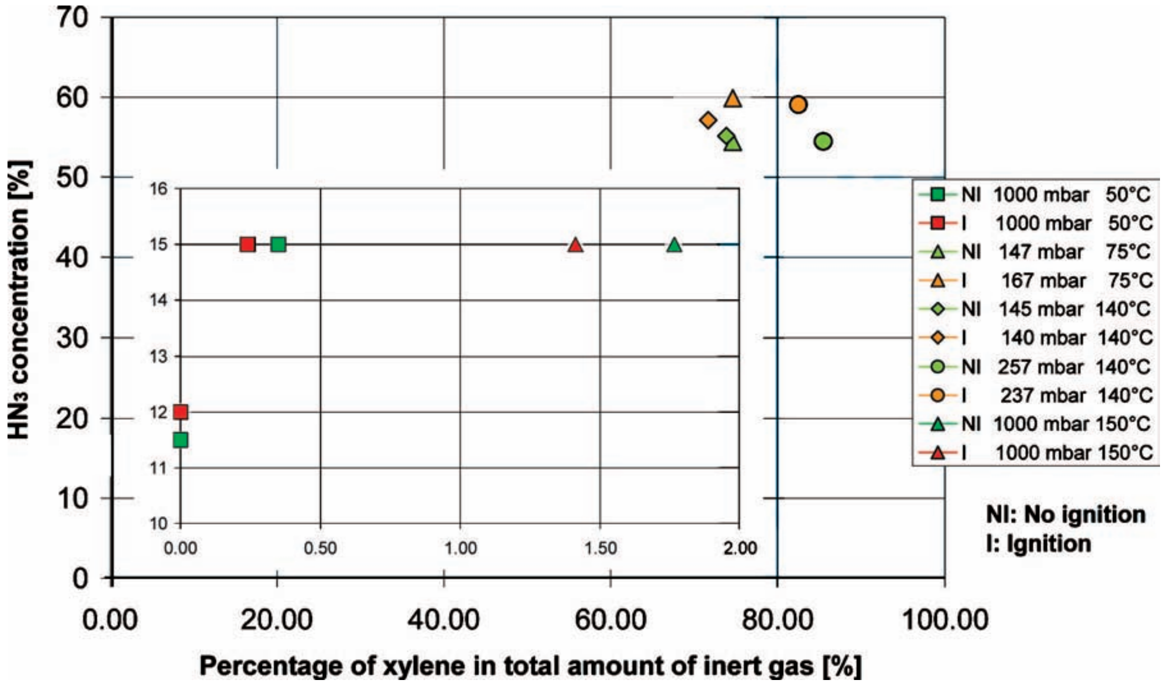

Figure 8. **LDL of hydrazoic acid as a function of the percentage of xylene in total amount of inert gas.**

Table 4. **Concentration of ethyl acetate vapor (and percentage of ethyl acetate in total amount of inert gas in bold italics) required to suppress HN_3 explosion/ decomposition at different HN_3 partial pressures, total initial pressures at 50 °C**[a]

	HN_3 concentration		ethyl acetate concentration	
total initial pressure (mbar)	mbar	vol %	vol % no ignition	vol % with ignition
1000	150	15.0	0.80 ***0.94***	0.60 ***0.71***
1000	200	20.0	4.30 ***5.38***	3.50 ***4.38***
400	80	20.0	2.25 ***2.81***	2.00 ***2.50***
200	40	20.0	1.00 ***1.25***	0.00 ***0.00***
262	150	57.3	–	37.40 ***87.49***
308	150	48.7	46.10 ***89.87***	–
137	80	58.4	–	29.93 ***71.94***
141	80	56.7	31.91 ***73.76***	–

[a] Ignition source: continuous spark, 10 J; residual N_2 pressure, approximately 17 mbar.

Figure 10 shows the effect of the concentration of the inhibitor (xylene or ethyl acetate) as a function of the total initial pressure for a given LDL of HN_3 and temperature. If the influence of temperature is not taken into account, it can be derived from this figure that xylene is, by tendency, a more effective inhibitor than ethyl acetate.

The volume percentage of xylene or ethyl acetate required for a given LDL of HN_3 in a mixture with nitrogen drops as a function of the absolute initial gas pressure (measured for 50 °C and three initial pressures in the case of ethyl acetate and for 140 °C and two initial pressures in the case of xylene).

At an initial pressure of 1000 mbar the LDL of HN_3 in a mixture of nitrogen and xylene is ~15 vol% if the xylene concentration in the gas phase is greater than ~0.5 vol% (5 mbar) at 50 °C and greater than ~2 vol% (20 mbar) at 150 °C. Since these results have been obtained at an initial pressure of 1000 mbar, these limits are also true for lower initial pressures, as can be extrapolated from the previous paragraphs.

At an initial pressure of 1000 mbar, the LDL of HN_3 in a mixture of nitrogen and ethyl acetate is ~15 vol% if the ethyl acetate concentration in the gas phase is greater than ~1.0 vol% (15 mbar) at 50 °C. The corresponding limit at 150 °C is difficult to extrapolate. Most probably it will be between 6 and 10 vol%. Since these results have been obtained at an initial pressure of 1000 mbar, these limits are also true for lower initial pressures, as can be extrapolated from the previous paragraphs.

At an initial pressure of 1000 mbar, the LDL of HN_3 in a mixture of nitrogen and ethyl acetate is ~20 vol% if the ethyl acetate concentration in the gas phase is greater than ~5 vol% (50 mbar) at 50 °C. An extrapolation to higher temperatures is hardly possible. Since these results have been obtained at an initial pressure of 1000 mbar, these limits are also true for lower initial pressures, as can be extrapolated from the previous paragraphs.

Ignition Sensitivity of Hydrazoic Acid with Respect to Sparks and Hot Spots. Table 5 shows the influence of the ignition energy and temperature on the decomposition of hydrazoic acid. The ignition sensitivity characterized by the minimum ignition energy (MIE) at 150 mbar HN_3 and 50 mbar nitrogen is very low (<1 mJ). Even at 150 mbar HN_3 and 850 mbar nitrogen the MIE is below 15 mJ. For comparison, the MIE of hydrogen in air is 0.016 mJ, and the MIE of hydrogen in pure oxygen is 0.0012 mJ. Since the present equipment did not allow measuring values below 1 mJ, it cannot be judged whether the MIE of HN_3 may even be as low as that for hydrogen.

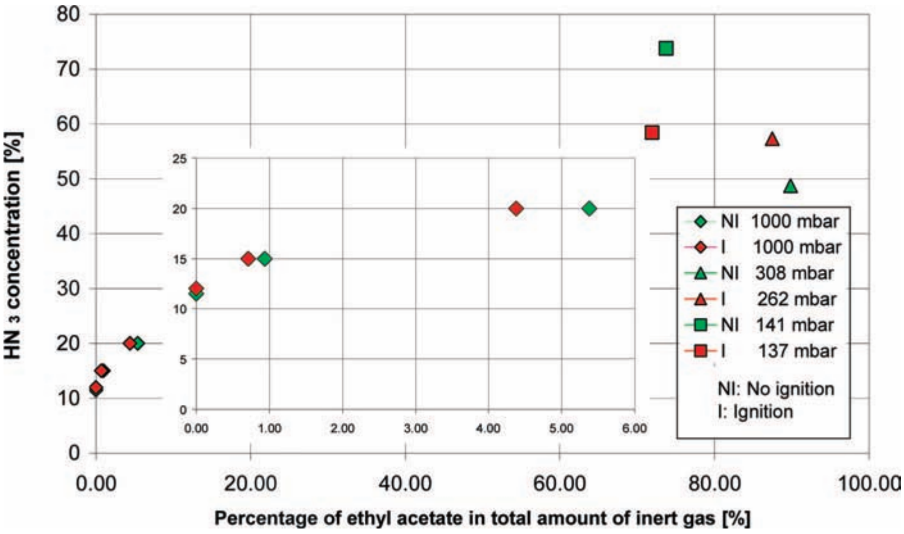

Figure 9. **LDL of hydrazoic acid as a function of the percentage of ethyl acetate in total amount of inert gas at 50 °C.**

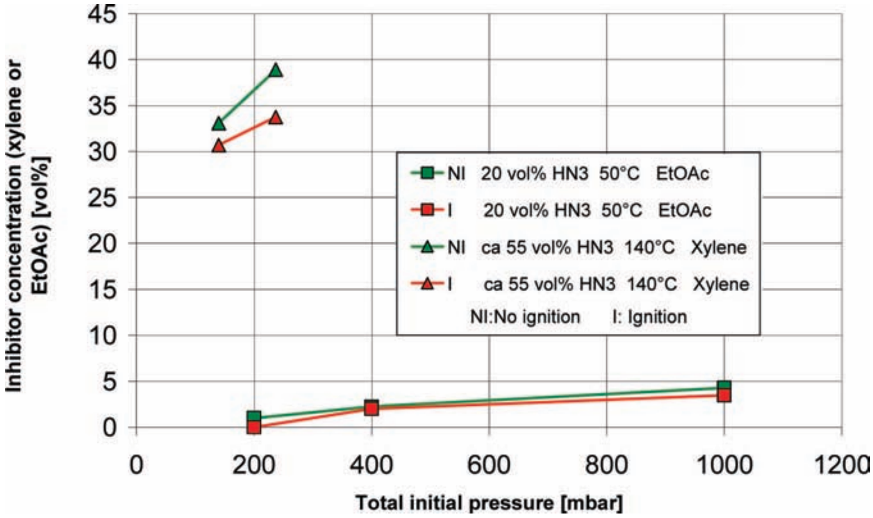

Figure 10. **Effect of concentration of inhibitor (xylene or ethyl acetate) as a function of total initial pressure for a given LDL of HN_3 and temperatures.**

Table 5. **Ignition sensitivity of HN_3 in nitrogen at different initial pressures**[a]

temp, °C	total initial pressure, mbar	concn, vol %, (partial pressure, mbar) of HN_3	ignition occurred at
50	1000	20.0 (200)	15 mJ[b]
50	1000	13.0 (130)	15 mJ[b]
76	157	89.2 (140)	1 mJ[b]
140	167	89.8 (150)	1 mJ[b]
50	1000	15.0 (150)	~50 °C[c]
200	1000	15.0 (150)	~470 °C[b]

[a] Residual N_2 pressure: approximately 17 mbar. [b] Ignition source: spark discharge. [c] Ignition source: glowing wire coil. Ignition occurred at the temperature of the coil indicated in the table (the temperature was determined with an infrared temperature probe through a sight glass in the explosion sphere).

Table 6. **Temperature increase after ignition of HN_3 in vacuum**[a]

initial temp, °C	total initial pressure, mbar	concn, vol %, (partial pressure, mbar) of HN_3	temp increase after ignition, °C
75	162	89.5 (145)	~930
140	167	89.8 (150)	~780

[a] Residual N_2 pressure: approximately 17 mbar.

Table 6 shows the temperature increase due to HN_3 explosion/decomposition. These data show that the decomposition reaction of hydrazoic acid is highly exothermic.

Pressure Increase Due to HN_3 Explosion/Decomposition. Figures 11 and 12 show typical explosion characteristics of HN_3 at 150 mbar in nitrogen at different total initial pressures at 50 and 150 °C. These are the maximum values of the explosion pressure and the *K*-value recorded within the whole test series.

With a HN_3 pressure of 150 mbar and a N_2 pressure of 50 mbar (total absolute pressure of the gas phase is 200 mbar) the maximum explosion pressure is 6.3 bar (absolute), and the *K*-value is higher than 1709 bar·m/s. The explosion pressure drops with increasing temperature and increasing N_2 pressure. The *K*-value drops drastically with increasing N_2 pressure and increases moderately with increasing temperature. For comparison, the explosion pressure of hydrogen in air under atmospheric conditions (~1000 mbar initial pressure) is 7.8 bar absolute, and the *K*-value is 550 bar·m/s.

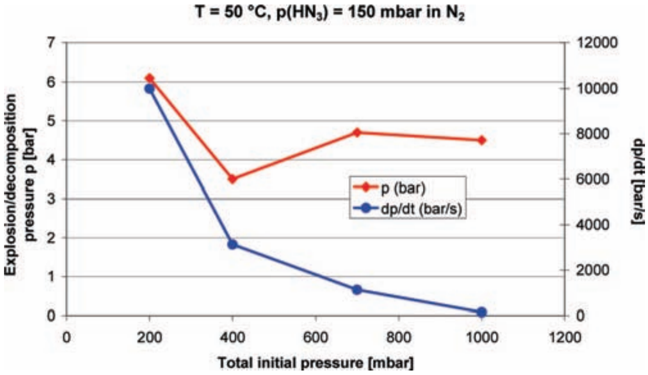

Figure 11. **Explosion characteristics of HN_3 at 50 °C.**

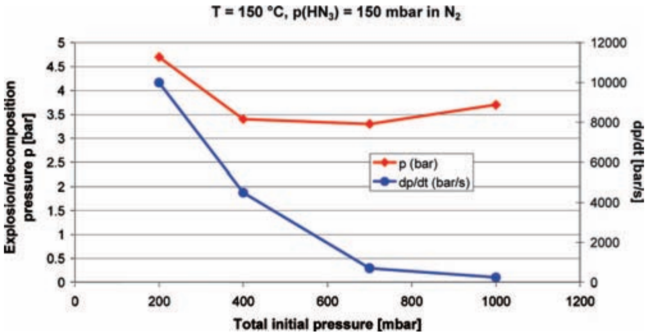

Figure 12. **Explosion characteristics of HN_3 at 150 °C.**

Conclusions

The lower decomposition limit (LDL) of HN_3 in a nitrogen atmosphere was determined under various partial pressures. No decomposition could be observed for HN_3 concentrations below 10%. The influence of the temperature on the LDL is very weak.

The decomposition/explosion of HN_3 is highly violent, and the ignition energy necessary to induce it is very low.

Relatively small partial pressures of solvents efficiently inhibit the explosion. Tests were performed with xylene and ethyl acetate. They show that xylene is by tendency a more effective inhibitor compared to ethyl acetate. Nevertheless, due to the vapour pressure curves of these solvents, efficient xylene vapour concentrations can only be obtained at temperatures higher than those for ethyl acetate.

The data generated during this study are useful for the safety assessment of processes where hydrazoic acid is used or produced. The accumulation of HN_3 in an evacuated head space must absolutely be avoided. Even the weakest ignition source can initiate a very violent decomposition reaction. The solvent vapours which are in most cases present in organic chemical processes can effectively protect the equipment head space against a HN_3 explosion. In all cases, a detailed risk analysis of the involved process is necessary when working with hydrazoic acid.

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