

FORMATION OF NCl_3 AND N_2O IN THE REACTION OF NaOCl AND NITROGEN COMPOUNDS

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Summary

This paper deals with the problems that can arise when a nitrogen-containing compound, in this case ammonium chloride, is present in a solution which is to be chlorinated. The chlorination can be performed with chlorine itself, or with a compound capable of forming active chlorine, such as sodium hypochlorite. A short literature review is given concerning this subject, and the reactions of nitrogen compounds with active chlorine are discussed. The formation of nitrogen, nitrogen trichloride and dinitrogen monoxide in these systems is explained and proven in experiments. It is shown that, especially in acidic circumstances, free nitrogen trichloride can be formed which at higher temperatures is able to evaporate from the solution. The amount of nitrogen trichloride recovered exceeds 30% of the theoretical value. The nitrogen trichloride formed detonates very easily upon rapid heating, even in quantities of one gram. Upon the chlorination of acidic ammonium ion containing solutions ($\text{pH} < 8$) nitrogen trichloride is formed; therefore these circumstances are to be avoided. This can be done, for example, by the addition of sufficient alkali or by intensive stirring. When the formation of nitrogen trichloride cannot be avoided stringent safety measures are necessary.

Introduction

In the literature a number of publications is devoted to the formation and decomposition of nitrogen trichloride; most of them concern the appearance of nitrogen trichloride in chlorinated waste water or the safety problems in chlorine manufacture, and some deal with the analysis of the compound.

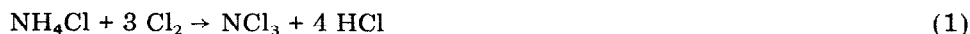
During an investigation of reactions between a nitrogen-containing compound and sodium hypochlorite we suspected the formation of nitrogen trichloride. The reaction conditions in our investigations were above the known atmospheric boiling point of nitrogen trichloride and at various pH values. As there was an obvious lack of knowledge, we started an investigation into the pH dependence of nitrogen trichloride formation from a solution of ammonium chloride at temperatures of 70–80°C.

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Formation and reactions of nitrogen trichloride

From the literature [1—5] a number of reactions between ammonium chloride (as a representative of organically and inorganically bound nitrogen) and a chlorinating agent, such as chlorine, hypochlorous acid or sodium hypochlorite, are known. In these reactions, products are formed such as chloroamine, dichloroamine, nitrogen trichloride and nitrogen. The following review is not intended to be, and therefore will not be, complete. Various reactions are presented below:

Nitrogen trichloride is formed in the reaction of chlorine with ammonium salt solutions of strong acids (e.g. sulfate, phosphate, chloride) [6—8]:



The formation of nitrogen trichloride results from reactions in which chlorine is dissociated into positive and negative chlorine ions (the same type of chlorine ions play a role in the decomposition of nitrogen trichloride to ammonia by hydrogen chloride):



Concentrated hydrochloric acid reacts with a concentrated nitrogen trichloride solution in carbon tetrachloride in the following manner [9, 10]:

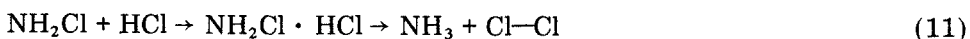
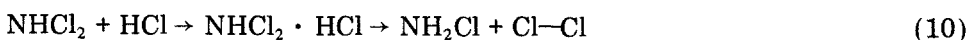
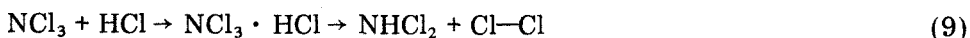


In Ref. [1] Szeliwanow states that the evolution of chlorine is preceded by hydrolysis giving hypochlorous acid (reactions 5 and 6) so that the nitrogen trichloride should be regarded as the amidanhydride of hypochlorous acid.

A number of investigators [6, 11] report the reaction



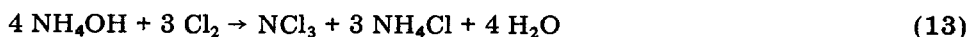
which essentially is the result of reactions (5), (6) and (7). The same route is given by Noyes [6] and Chapin [9], as being the reverse of reactions (2), (3) and (4):



In the reaction of ammonium salts of weak acids with chlorine, nitrogen is evolved together with nitrogen trichloride. The same is true in case of an ammonia solution:



This reaction can be considered a combination of the two reactions:



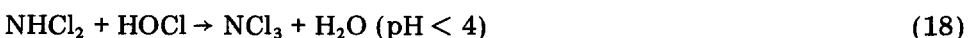
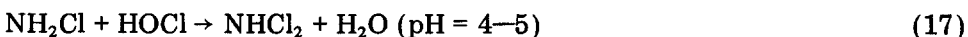
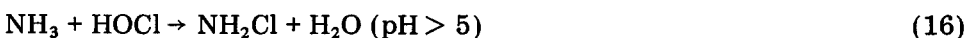
In most of the decomposition reactions the result is acidification of the solution. Reaction (14) is also reported in Ref. [12].

In the reaction between hypochlorous acid and ammonium salts, nitrogen trichloride is formed [13]:

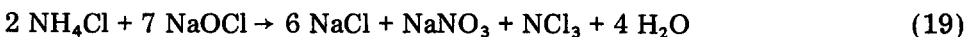


Many non-salt organic nitrogen compounds react in the same way forming nitrogen trichloride.

Depending on the reaction conditions the three chloroamines are formed [9, 14]:



Sodium hypochlorite can be used instead of hypochlorous acid. In this case sodium nitrate can be formed as well:



Excess ammonia, ammonium chloride or ammonium hydroxide gives a slow decomposition reaction in which nitrogen is evolved:



If insufficient ammonia is present for the decomposition, the nitrogen trichloride reacts with ammonium chloride. The reaction of ammonium trichloride with ammonium chloride is said not to be very likely as it is expected to be of the ninth order [20], but this expectation seems to be incorrect and is probably based only on consideration of overall reactions. To reduce decomposition, the solution must be weakly acid. Under strongly alkaline conditions nitrogen formation is the dominant reaction:



Under strongly alkaline conditions the reaction is as follows:



and decomposition takes place according to:



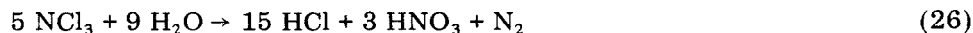
Electrolysis of an ammonium chloride solution gives nitrogen trichloride droplets at the anode.

Temperatures of 32°C and over are said to favour nitrogen trichloride production, whereas below 0°C no nitrogen trichloride is formed. The presence of ammonium sulphide, sulphur or carbon (charred wood) prevents the formation of nitrogen trichloride. It is not known whether this is solely the prevention of the formation, or a combination with catalysis of the decomposition. When the chlorine used is mixed with 1/3% (v/v) of air or carbon dioxide, or with the same volume of hydrogen, no nitrogen trichloride formation is reported. This is in contrast to the regular preparation method [15] where air can be sucked in together with the chlorine.

In general, all organic nitrogen compounds and most of the inorganic compounds behave like ammonium chloride (e.g. Ref. [16]) in the formation of nitrogen trichloride.

Decomposition of nitrogen trichloride usually takes place by the reactions mentioned above, giving nitrogen and chlorine.

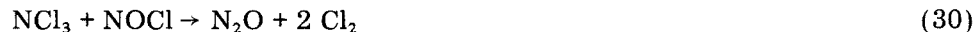
Nitrogen trichloride is very slightly soluble in water, so the reaction between water and nitrogen trichloride is believed to be only of minor interest when high levels of nitrogen trichloride are present. In hot water the decomposition takes place much faster than in cold water, according to Davy [1]. In water at ambient temperature the decomposition of dissolved nitrogen trichloride is completed quantitatively in 24 hours, partly by the reactions mentioned above and partly by the formation of hydrogen chloride and nitric acid:



Alkaline compounds decompose nitrogen trichloride. Sodium hydroxide gives an evolution of nitrogen. A potassium hydroxide solution gives nitrogen, potassium nitrate and potassium chloride. The evolution of heat in these reactions accelerates the decomposition. Concentrated ammonia reacts slowly with nitrogen trichloride. According to Clark and Cline [17, 18] the following radical reactions occur:



Nitrosyl chloride reacts with nitrogen trichloride with the formation of dinitrogen monoxide [19]:



Anhydrous ammonia and chlorine (possible also dissolved in carbon tetrachloride, chloroform or pentane) form nitrogen trichloride at temperatures

of -90 to -180°C in the above-mentioned steps. The nitrogen trichloride formed decomposes directly into nitrogen and chlorine (reaction 14) or to nitrogen and hydrogen chloride, according to Ref. [20] :



At ambient temperature, nitrogen trichloride is also formed from dry ammonia and chlorine in the gas phase in absolute darkness. The pressure has to be less than 25 Torr for safe handling as spontaneous explosions are very likely to occur (Griffiths and Norrisch [21]).

With completely dry hydrogen chloride, ammonium chloride and chlorine are produced quantitatively.

Nitrogen trichloride reacts violently, and in some cases explosively, with most organic chemicals and it detonates upon contact with fats or greases. A solution of 18% nitrogen trichloride in benzene, cooled in ice, was reported to produce flames of 5 to 10 metres in length.

When in contact with nitrogen trichloride, small amounts of mercury produce nitrogen, mercurous chloride and mercuric chloride. Large amounts react explosively.

Properties of NCl_3

Nitrogen trichloride is a very unstable, explosive, oily, yellow liquid. Dulong, who discovered nitrogen trichloride in 1811, lost the sight of one eye and three fingers during his experiments. The compound is very sensitive to heat or shock. Spontaneous explosions are observed with the pure component upon contact with organic chemicals or catalytic surfaces, by impact, by supersonic sound waves (shock waves), or simply by selfheating due to the decomposition reactions. Spontaneous ignition is reported at temperatures above 93°C . The concentration of nitrogen trichloride being high, a detonation will easily develop, giving a bright white-bluish flash and a strong shock wave.

Nitrogen trichloride has a melting point of approximately -40°C and a boiling point of 71°C (see Fig. 1 for an estimation of the vapour pressure vs. temperature). The density of the liquid is 1.635 g/cm^3 at ambient temperature. Nitrogen trichloride is hardly soluble in water, but readily soluble in for example carbon tetrachloride, chloroform, benzene and carbon disulphide.

The enthalpy of formation from the elements is -229 kJ/mol (298°C). Upon explosion, a total amount of energy of 230 kJ/mol is evolved (from these figures it is obvious that not all data have been quite accurately determined). The constant volume detonation of nitrogen trichloride gives a maximum temperature of 2128°C and a maximum pressure of approximately 5500 bar.

The ultraviolet spectrum of nitrogen trichloride in anhydrous carbon tetrachloride gives a maximum absorption at wavelengths of 265 and 345 nanometres. Absorption is found in the infrared spectrum at 650 cm^{-1} for the gas and at 645 cm^{-1} for a solution in carbon tetrachloride [17, 18].

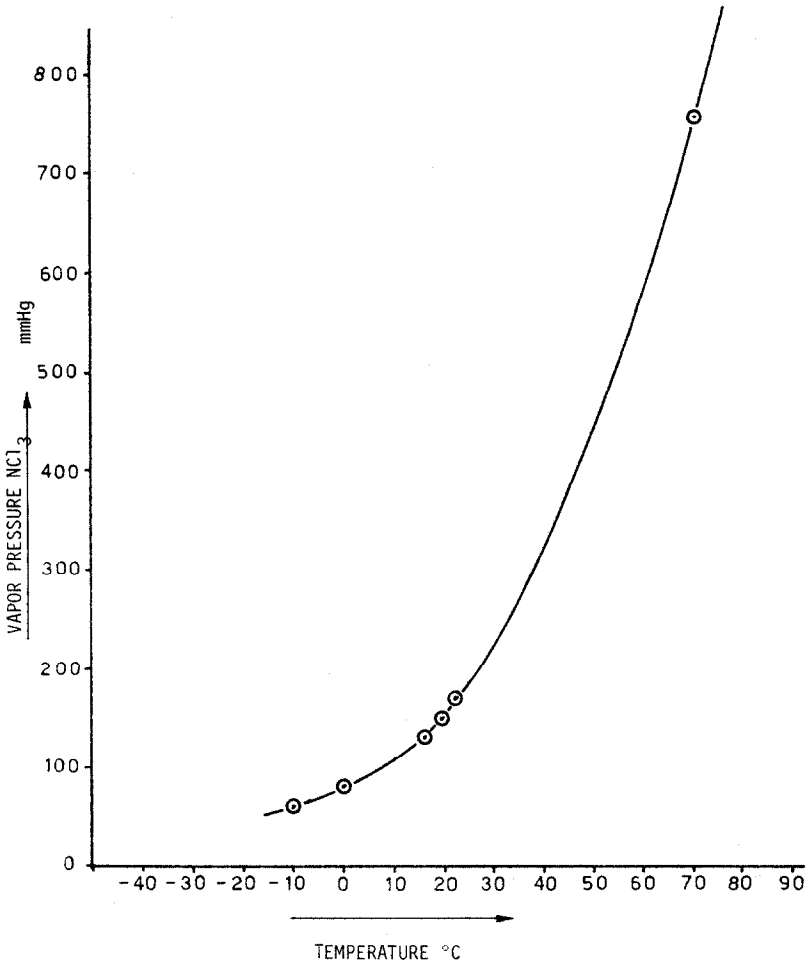


Fig. 1. Vapor pressure of nitrogen trichloride as a function of temperature.

Considerations

In general the experiments reported in the literature were carried out at, or below, ambient conditions and in dilute solutions. It was to be expected that at higher temperatures and higher concentrations a possibly dangerous quantity of nitrogen trichloride would be present in the gaseous phase, this expectation being based on the following considerations:

- When the temperature is above the boiling point or above the temperature at which there is an equilibrium between the nitrogen trichloride concentration in the solution and the concentration in the gas phase, nitrogen trichloride will evaporate from the solution.

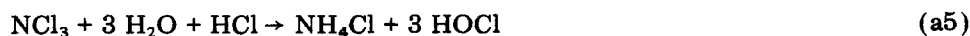
- The evolved gases (mainly nitrogen due to the decomposition of the nitrogen trichloride) will enhance the above-mentioned evaporation.
- Only nitrogen trichloride will evaporate and especially at the higher pH levels all N—Cl bonds formed will be treated as nitrogen trichloride. This means that three monochloroamine equals two ammonia plus one nitrogen trichloride, and that three dichloroamine equals one ammonia plus two nitrogen trichloride.
- The reaction between hypochlorite and ammonium chloride will take place immediately, so that when the hypochlorite solution is flowing (dripping) in the top layer of the fluid the nitrogen trichloride formed will easily enter the gas phase.
- The liquid phase only contains ammonium chloride, hydrochloric acid, sodium hydroxide, sodium chloride, hypochlorous acid or sodium hypochlorite in water. Although nitric acid is one of the possible decomposition products of nitrogen trichloride, it is assumed that it is present in minor amounts (this was analytically confirmed) and does not influence the experiments.

As can be seen, some authors use elementary step reactions, while others simply consider the overall reactions in the presentation of their results. Based on the information presented in the literature the following reaction scheme was developed for the reaction between ammonium chloride and sodium hypochlorite. (It should be kept in mind that most of the reactions can be reversed.):

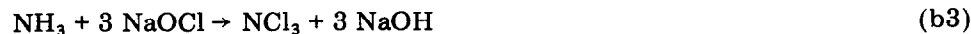
General reactions (pH independent):

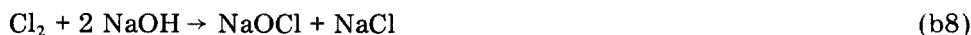
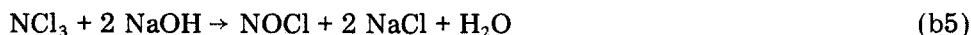
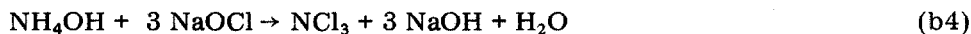


For *strongly acidic conditions* the following reactions are assumed:



Strongly alkaline conditions:

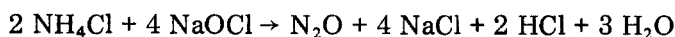
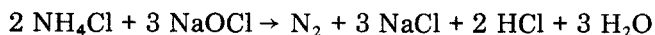
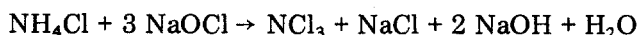




In our experiments we found considerable amounts of dinitrogen oxide, and the formation of nitrogen oxychloride is believed to be the precursor (reaction 30). Reaction (b5) is postulated here as there is no other source for the formation of nitrogen oxychloride from the solution. Another possibility is the reaction between ammonium chloride or ammonium hydroxide and hypochlorite, but this reaction can be regarded as a combination of for example (b1), (b4) and (g2):

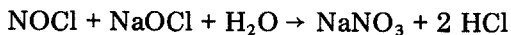
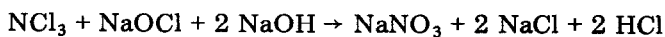


From these reactions the following overall possibilities remain using ammonium chloride as the starting material:



These reactions show that in the case of the production of nitrogen trichloride, sodium hydroxide is formed, while the decomposition reactions give an equal number of moles of hydrochloric acid compared to ammonium chloride, so that the solution will be less alkaline or become acidified, a condition favouring the formation of nitrogen trichloride. Under strongly alkaline conditions the evolution of nitrogen and dinitrogen oxide is more likely as the hydrogen chloride formed is neutralised by the excess sodium hydroxide. In a neutral or acidic solution the formation of nitrogen trichloride is probable and as the decomposition reactions produce hydrogen chloride, acidification of the solution is a direct result giving more nitrogen trichloride formation.

For the reactions in the liquid phase the following reactions are possible:



It will, however, be assumed that the formation of sodium nitrate will not play an important role in these reactions, as was confirmed in the experiments.

Experimental

The hypothesis that at higher temperatures nitrogen trichloride could be present in the gaseous phase over an ammonium chloride solution, and even that liquid nitrogen trichloride could condense from the gas, was checked by performing a series of experiments.

General experimental procedure

Into a double-walled flanged vessel of 1 litre, fitted with a stirrer, thermometer, pH-electrode, reflux condenser, and inlet and outlet facilities, 500 ml of a molar ammonium chloride solution were added. The pH was controlled by means of a potentiostat (addition of sodium hydroxide or hydrochloric acid solution) during the complete test.

A sodium hypochlorite solution (fresh) was pumped at a constant rate into the vessel, at a temperature of approximately 75°C. The off-gas was in some cases analysed for nitrogen trichloride and dinitrogen oxide, while for a number of experiments the total volume of gases evolved was determined. The gas was led through a scrubber to collect all the nitrogen trichloride.

In some experiments the condenser was removed and replaced by an off-gas line that led to a cooling device to condense the nitrogen trichloride from the gas. The condensate was collected and the gases from the collecting vessel were scrubbed with carbon tetrachloride to wash the nitrogen trichloride.

Due to safety reasons there is some uncertainty in the amount of nitrogen trichloride recovered. The amount of liquid is determined on the screen of a television monitor by measuring the height of the liquid level in the receiver tube that was calibrated prior to the experiments. The amount of gaseous nitrogen trichloride was measured by absorption of the component into carbon tetrachloride, but in this case there was no correction for the amount of carbon tetrachloride that possibly evaporated and therefore was lost. The maximum deviation in this amount is 3.5 g (75°C), although the actual value will be lower due to the combination of analysis of the off-gas and the gravimetric determination. The maximum amount of nitrogen trichloride that could be formed is theoretically approximately 60 g; the amount of evolved gases, calculated as nitrogen, is at maximum approximately 6.25 l. The nitrogen trichloride collected, mainly from the experiments carried out at a pH of 1, i.e. an acidic solution, was in the first experiments heated by means of a 10 kV spark bridge on the outside of the receiver to permit safe disposal of the material by igniting it. In some cases the material was allowed to self-heat with or without thermal insulation around the receiver. The diameter of the receiver lower part was approximately 5 mm internally.

As the experiments were carried out at different pH levels and the reactions are in general acid forming, the ammonia—ammonium ion equilibrium is of importance. This equilibrium is given by the equation (derived from the thermodynamics):

$$\ln K = -0.78 + 6280/T$$

The calculated and experimental values of the amount of hydrochloric acid or sodium hydroxide to reach the pH level desired are in good agreement. The results show that for pH levels above about 6, a considerable concentration of ammonia is present in the solution, and at levels above about 10, the ammonia will be evolved from the solution.

Analysis

The nitrogen trichloride was determined by means of IR spectroscopy in the gas phase and by means of titrimetry according to Ref. [10] in carbon tetrachloride. Dinitrogen oxide and ammonia were determined via infra-red spectroscopy and also by gas-liquid chromatography (GLC). The other gaseous compounds were determined by GLC analysis. The volume of the off-gas was measured with a gas burette (accuracy approximately 3%). In a number of cases the liquid phase was analysed for nitrates, but these were only present below the detectable limit of 150 mg/kg.

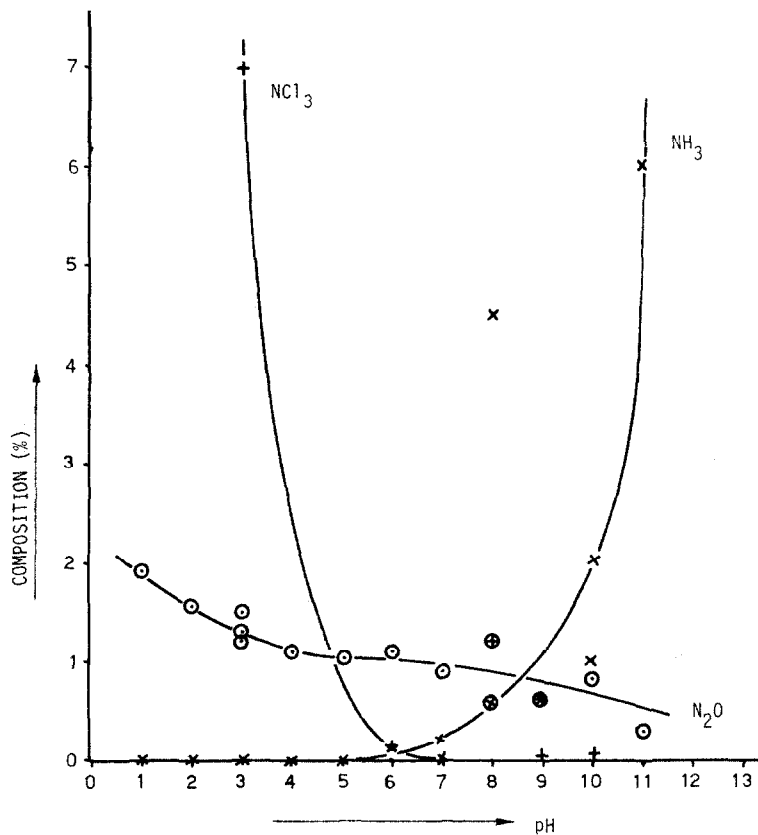


Fig. 2. Concentration of components in the off-gas.

Experimental results

Figures 2 to 7 summarize the results of the experiments that were carried out at different temperatures, pH and addition rates.

In Fig. 2 the composition of the off-gas is given for temperatures of 70–80°C and addition rates of 7.7 mmol active chlorine per minute. As can be seen, there is a very sharp pH region for the nitrogen trichloride formation. Therefore, it is quite clear that the amount of dinitrogen monoxide is partly related to the amount of nitrogen trichloride and/or to the presence of the ammonium ion in the liquid phase. Nitrogen trichloride is not found above a pH of 7–8, although the smell of the off-gas did suggest the presence of nitrogen trichloride. As was expected, ammonia was found in the gas phase at higher pH levels. The analysis of the gas phase was made by infra-red spectroscopy and by means of a gas chromatograph. The IR analysis was performed once during the experiment and the GC samples were taken at the end of the test. The total amount of gases evolved ranged from 5.6 to 6.0 l.

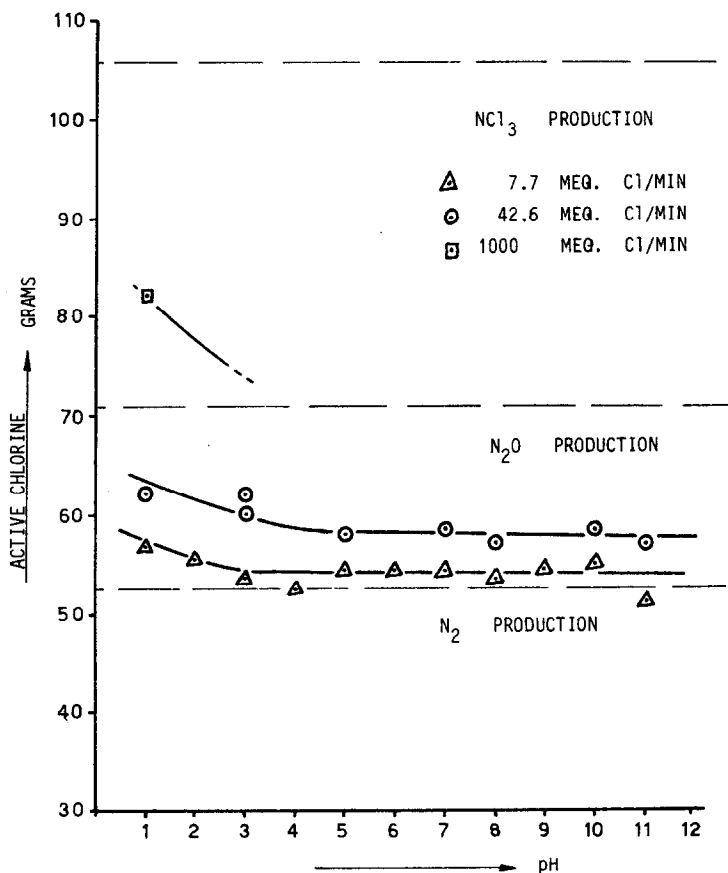


Fig. 3. Active chlorine needed to complete the decomposition of the ammonium chloride.

Figure 3 shows the amount of active chlorine needed to complete the decomposition of the ammonium chloride to either of the products mentioned. The degradation reaction of sodium hypochlorite was not taken into account, but the presence of at a maximum of 5% oxygen is indicative of this reaction. As was expected, the rate of active chlorine addition is very important to the formation of nitrogen trichloride. At higher addition rates the decomposition, especially in the gas phase, is of the same order, so net production is higher.

The expectation that the amount of sodium hydroxide needed to maintain the pH constant is a function of the pH and the addition rate, proved to be correct. The ratios of the number of moles of sodium hydroxide and active chlorine are presented in Fig. 4. The amount of sodium hydroxide needed to bring the solution to the desired pH level is incorporated in the diagram. The influence of the addition rate on the formation of hydrogen chloride in the solution is obvious.

These results suggest that the decomposition of nitrogen trichloride takes place mainly in the liquid phase.

In order to investigate the temperature influence on the formation of nitrogen trichloride several experiments were carried out at different temperatures at pH = 1. The results are shown in Fig. 5. As the gas was cooled,

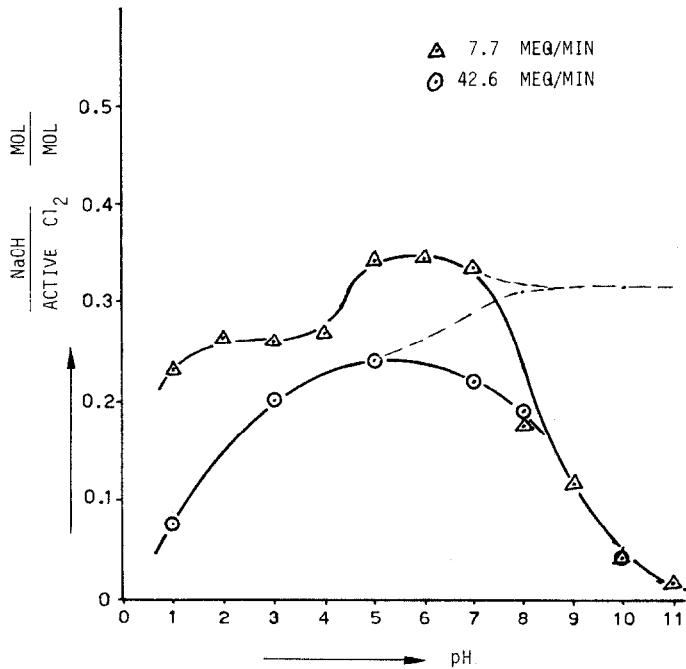


Fig. 4. Total amount of sodium hydroxide needed to maintain the pH level constant during destruction.

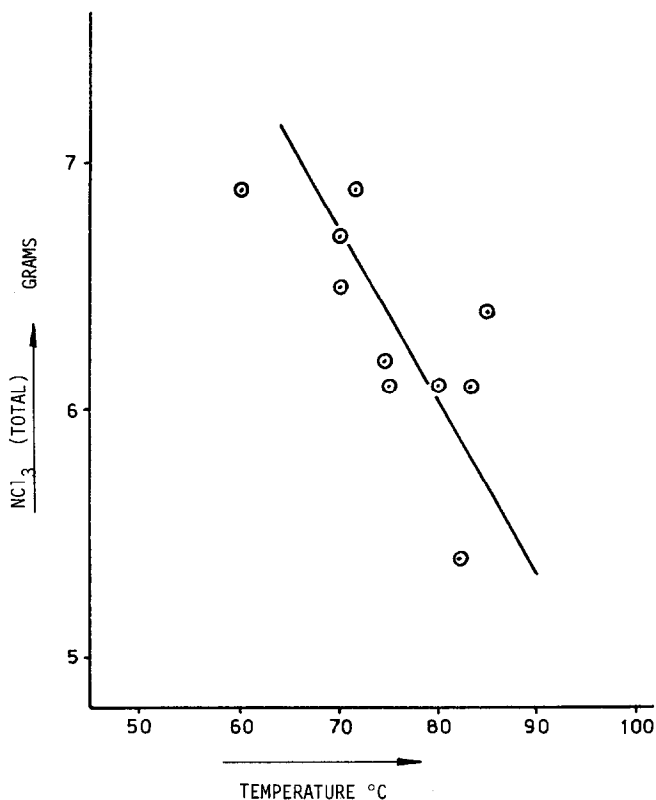


Fig. 5. Temperature influence on the formation of nitrogen trichloride.

liquid nitrogen trichloride was collected in a small glass tube and the level was read for safety reasons by means of a videocamera (which introduced an uncertainty into the quantity measured). During all absorption experiments in carbon tetrachloride no correction was made for the evaporated amount of tetra, which means that the quantity of nitrogen trichloride formed could be as much as 4.2 g higher (assuming that 5.6 l of off-gas are evolved and that it is completely saturated with carbon tetrachloride at 80°C).

The concentration calculated from the measured quantities of nitrogen trichloride in the gas phase is given as a function of the pH in Fig. 6. At low pH values the amount of nitrogen trichloride in the gas phase can be as high as 30% at an addition rate of 42.6 mmol/min, giving a very dangerous gas phase, as was experienced during the experiments.

The unstable nature of nitrogen trichloride inspired us to take extensive safety precautions, such as the use of a concrete cubicle, television cameras and remotely controlled apparatus. Strict regulations were given for entering the cubicle during and after the experiments.

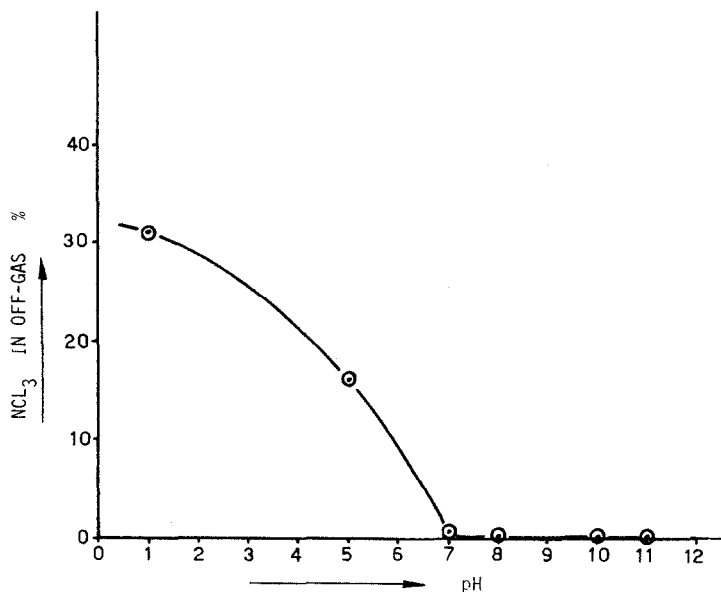


Fig. 6. Calculated concentration of nitrogen trichloride in the gas phase as a function of the pH.

The necessity of these safety measures was proven during the following case history. Just after the start of one of the experiments a leakage of the first drop of nitrogen trichloride was noticed at a ball joint in the off-gas tube. The experiment was stopped, the joint was cleaned and clamped together again. When the clamp was placed over the joint, the gas (there was no liquid nitrogen trichloride left) exploded (detonated) and destroyed the whole apparatus. Due to personal protection methods there was no injury, apart from a small cut in the hand caused by flying debris.

The rate of production of liquid nitrogen trichloride was measured in a number of experiments, the results of which have been summarized in Fig. 7. At first there is a delayed start due to the hold-up of the apparatus, but the production rate is fairly constant. Towards the end of the reaction the production ends and visually the amount of nitrogen trichloride formed in the last phase of the reaction seems to be negligible. The maximum amount of liquid nitrogen trichloride that was collected in the receiver was approximately 11 g, while the total amount measured in this experiment (at the highest addition rate) was 19 g, i.e. a yield of 32% of theoretical.

During the self-heating experiments a maximum temperature of 53°C was measured at the outer side of the vessel, not only when no insulation was present, but also when a Rockwool insulating mantel was used and the whole placed completely in a Dewar flask. A water layer was present on top of the nitrogen trichloride in all experiments.

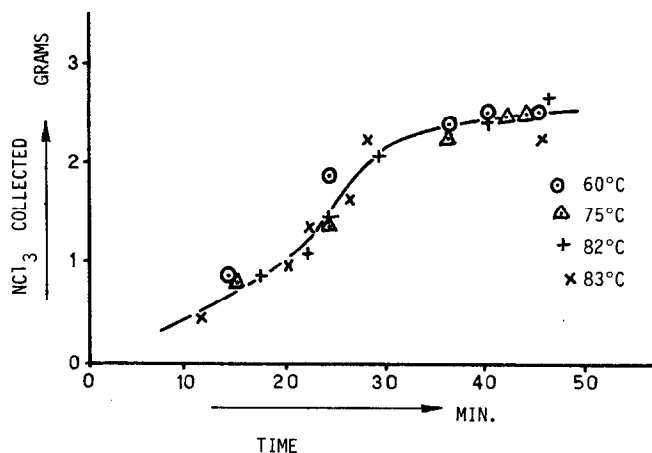


Fig. 7. Amount of liquid nitrogen trichloride collected as a function of time.

Full scale test

To check the results of the laboratory experiments, one full scale experiment was performed. About 2000 l of a solution containing inorganic chlorides and 1.5 kg of nitrogen (110 mol) as a nitrogen compound (mainly ammonium chloride) were pumped into a tank of approximately 4750 l. In approximately 4 hours a total of 270 mol of sodium hypochlorite was added, mixed with the same amount of sodium hydroxide (total volume approximately 100 l), while the pH was monitored and kept at a value of not less than 10. In the gas phase of the tank no nitrogen chloride was detected and the nitrogen content of the liquid was greatly reduced, indicating that this procedure is a safe operation provided that the addition rate (in this case approximately 0.7 mol/min m³) is kept low.

Discussion

From the experiments the following conclusions can be derived:

When an ammonium compound containing solution is treated with a chlorinating agent such as sodium hypochlorite at pH levels of 7 and lower (acidic situation) and at temperatures of 70 to 80°C there will be an evolution of gaseous nitrogen trichloride.

The nitrogen trichloride formation rate is highest during the first period of the reaction, as can be expected due to the decreasing amount of ammonium chloride.

When the chlorination is carried out at fairly high rates (above approximately 7.7 mmol/min), there is a serious danger of condensation of nitrogen trichloride from the gaseous phase.

When liquid nitrogen trichloride is heated locally by a hot spot, even in quantities of 0.5 ml or less, a detonation is observed.

A maximum amount of 19 g was found, being 32% of theoretical, while a maximum of 11 g of liquid nitrogen trichloride was collected in the same experiment.

It was observed that when ignition takes place during the evolution of the gas, and especially in the early phases of the reaction, the amount of nitrogen trichloride can be more than 20% and the gas phase will explode. It was not clear whether this explosion was or could have been a detonation, but in larger installations a detonation is a very real possibility.

Very little energy is needed to obtain ignition of the material, as was shown when the complete apparatus was demolished after a clamp had been placed on a leaking joint after cleaning.

Although there is not sufficient proof, it is expected from the self-heating experiments that there exists an azeotropic mixture of nitrogen trichloride and water, containing only small amounts of water, boiling at a temperature of approximately 53°C. Another possible (though not likely) explanation for this temperature level is that the heat of vaporization equals the heat production rate due to decomposition at exactly 53°C, while the nitrogen evolved gives a total pressure of one bar.

As the decomposition reaction causes acidification of the solution one can never be completely sure of preventing nitrogen trichloride formation, unless the pH is measured, or when additionally a very large quantity of sodium hydroxide is present (at least twice the molar nitrogen content at pH levels of 8 and below).

The risk of liquid nitrogen trichloride formation is greatly reduced when the addition of the chlorinating agent is carried out at a controlled pH, at high temperatures and with a very low addition rate. The introduction of the hypochlorite solution should be well below the liquid surface under vigorous stirring. The residence time of the gas bubbles should be high enough to allow the bulk of the nitrogen trichloride to decompose.

Safety aspects of the handling of nitrogen trichloride

Nitrogen trichloride should be regarded as a very unstable explosive and should never be handled in large quantities. The formation of nitrogen trichloride should be avoided by operating in strongly alkaline solutions when nitrogen compounds and chlorine are involved. If experiments with nitrogen trichloride have to be carried out, it should, whenever possible, be used as a solution in carbon tetrachloride. This solvent has about the same boiling point as nitrogen trichloride, so concentration of the solution is unlikely. The maximum concentration that can be used without stringent safety measures is approximately 10%. In other solvents there is a serious chance of preferential evaporation of the solvent, leaving pure nitrogen trichloride, or evaporation of the nitrogen trichloride giving a possible detonable gaseous phase. Furthermore it is not permitted to use a solvent that is combustible with air, oxygen and/or chlorine, without precautions being taken against a thermal explosion or flash fire due to chlorination of the solvent.

The following recommendations can be made for industrial situations:

The easiest way of handling nitrogen trichloride is to prevent its formation, which means that no nitrogen compounds are allowed in the handling and production of chlorine or compounds capable of generating active chlorine. The safest and the most expensive way is to design the apparatus for gaseous and liquid phase detonations of nitrogen trichloride.

The more practical way to chlorinate an ammonium ion containing solution safely is to follow the procedure given below, provided that it is possible to maintain an alkaline situation:

- (1) Determine the amount of nitrogen that is present in the system under consideration.
- (2) Add twice the molar amount of sodium hydroxide.
- (3) Add the sodium hypochlorite at rates of less than 3 mmol/min l (3 mol Cl/min m³). (This is an arbitrary rate as we did not perform experiments below 15 mmol/min l.)
- (4) Dilute the off-gas, if possible, to reduce the amount of dinitrogen monoxide to below the toxic or narcotic level, or use forced ventilation.
- (5) In case of the suspected presence of nitrogen trichloride (the smell is quite characteristic at very low levels) obtain expert advice immediately and take all precautions needed to prevent injuries or damage from an accidental explosion.

When there is no possibility of operating in an alkaline situation, the addition of active chlorine to a solution containing nitrogen compounds has to be performed at a very low rate and the gas phase above the solution has to be monitored for nitrogen trichloride. This monitoring should be very regular during the first period of addition, and the addition has to be stopped as soon as the concentration exceeds approximately 0.5%.

Conclusion

The hypothesis presented in this paper, predicting the formation of dinitrogen monoxide, could be valid, but sufficient proof was not obtained. The evolution of nitrogen trichloride from a warm solution was proven and the liquid compound was collected. Safe disposal of the unstable nitrogen trichloride is possible, but prevention of its formation in general avoids very serious explosion and detonation hazards.

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