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Formation of Explosive Chlorine−Nitrogen Compounds during the Reaction of Ammonium Compounds with Chlorine

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Introduction

It is known that during the reaction of chlorine or hypochloride with ammonium compounds chlorine amines of the composition $NH_{3-n}Cl_n$ ($n = 0-3$) may be formed as unstable intermediate compounds. Of them, NCl_3 is especially explosive.[1] The following systems are considered to be dangerous:[2] (i) amounts of ≥0.5 mL of liquid NCl_3; (ii) mixtures with ≥10 vol % of NCl_3 in inert solvents, e.g., chlorinated hydrocarbons; (iii) mixtures with ≥0.5 vol % of NCl_3 in the gas phases.

The literature data concerning the formation of NCl_3 during the reaction of NH_4Cl with chlorine

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl \qquad (1)$$

are dispersed and, in part, incomplete.[2]

This especially applies to the dependence of NCl_3 formation upon acidity. In the weakly acidic medium (pH 1−6) NCl_3 is rapidly formed at reaction yields from 30 up to 70%. At pH ≥ 10 and $C_{HCl} > 6$ M, no NCl_3 is formed. As to the acidity range from 0.1 to 6 M there are not sufficient data.

For this range NCl_3 formation was studied with the use of higher NH_4Cl concentration and at different reaction temperatures.

Experimental Section

The experiments were performed with the use of 100−500 mL of solution. Because of the great influence of apparatus conditions on NCl_3 formation the dependence upon relevant experimental parameters was always determined with the same apparatus conditions. *In view of the tendency of NCl_3 to explode, the following precautions were taken:* assembly of the apparatus behind double glass shields; avoidance of critical phase composition by continuously agitating the reaction solution and passing an air flow through the free reaction space.

For a given time chlorine was passed through the reaction solution under intensive agitation with, at the same time, a given air flow maintained in the gas space. The chlorine stream was determined, and from that the chlorine quantity introduced into the system was calculated. The reaction gases were passed through a system of washing bottles. The fractions were processed after the completion of chlorination and a downtime of 5 min.

The quantities of NCl_3 passed from the reaction solution into the gas phase as well as the NCl_3 content in the reaction solution after the experiment had been finished were determined. The total NCl_3 quantity was given in millimoles of NCl_3 as well as in fractions of the added quantities of NH_4Cl and chlorine according to eq 1. In addition, the remaining NH_4Cl content in the reaction solution after the separation of NCl_3 was determined.

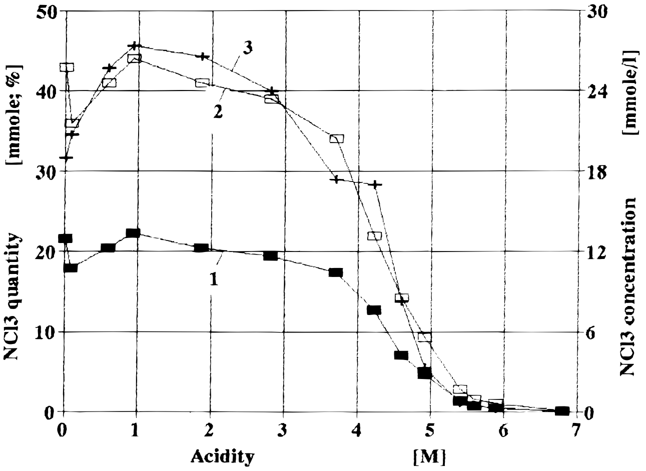

Figure 1. Dependence of NCl_3 formation upon the acidity of reaction solution: (Curve 1) NCl_3 quantity formed (mmol); (curve 2) NCl_3 quantity formed relative to the NH_4Cl quantity used (%); (curve 3) NCl_3 concentration in the reaction solution (mmol/L).

The determination of NCl_3 was based on the selective separation of NCl_3 (a) from the reaction solution by extraction with CCl_4 followed by conversion with hydrochloric acid to NH_4Cl and (b) from the gas phase by absorption in 12 M hydrochloric acid. The final determination of NH_4^+ was performed photometrically.[3] The detection limits for NCl_3 were in the gas phase 0.007 mmol and in the reaction solution 0.0035 mmol of NCl_3. The correctness of the value obtained was verified by determining the blank value and by model tests using a 0.9 M NCl_3 solution in CCl_4.

Results

Preliminary tests have also shown that in clearly acidic solutions relevant quantities of NCl_3 have rapidly formed, being highly dependent on the apparatus conditions and, thereby, on the intensity of interaction between the chlorine and solution phases (during the reaction of 0.5 M NH_4Cl/0.5 M HCl solution with chlorine the yield varied between 30 and 65%). Under equal conditions the formed NCl_3 quantity increased nearly proportionally to the chlorine flow and, thereby, to the chlorine quantity introduced.

Dependence of NCl_3 Formation upon the Acidity of Solution. Under constant conditions (using each time 0.1 L of 0.5 M NH_4Cl solution of different acidity, reaction temperature 20 °C, chlorination time 30 min, chlorine flow 8−9 L/h, and chlorine quantity added 180−206 mmol corresponding to 120−137% according to eq 1) the dependence of NCl_3 formation upon the acidity was determined within the range from pH = 4.6 to 6.8 M. The results are shown in Figure 1.

Influence of NH_4^+ Concentration. Under constant conditions (using 0.1 L of 0.5 M HCl solution, reaction temperature 20 °C, chlorination time 30 min, chlorine flow 8.5 L/h, and chlorine quantity added 185 mmol) the NH_4Cl concentration varied from 0.01 to 2 M. The results are shown in Figure 2.

Influence of Reaction Temperature. Under constant conditions (using 0.1 L of 0.5 M NH_4Cl solution in 1.97 M HCl, chlorination time 30 min) at two different chlorination rates the reaction temperature was varied as follows. Series A: 5 L/h of Cl_2; chlorine quantity 113 mmol corresponding to 73% according to eq 1. Series B: 9.0 L/h of Cl_2; chlorine quantity 203 mmol corresponding to 132% of the theoretical value. The results are shown in Figure 3.

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(1) *Gmelin, Handbuch der anorganischen Chemie*; Verlag Chemie: Weinheim, Germany: (a) System No. 6, *Chlorine* (Hauptband, 1927; Ergänzungsband, 1969); (b) System No. 23, *Ammonium*, 1936.

(2) Dokter, T. *J. Hazard. Mater.* **1985**, *12*, 207.

(3) De Vries, T.; Savariar, C. P.; Chakrabartty, M. M. *J. Am. Water Works Assoc.* **1962**, *54*, 858.

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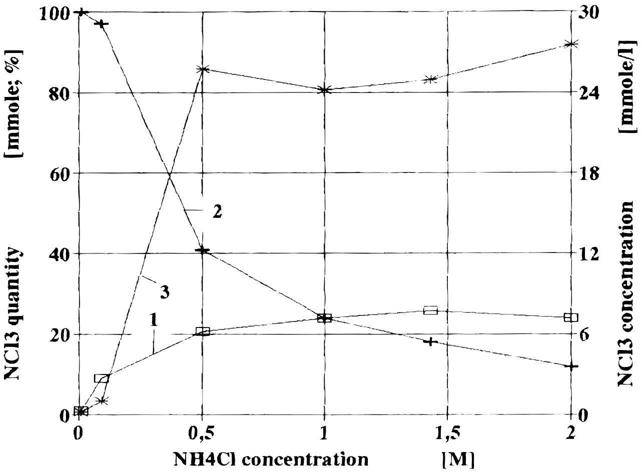

Figure 2. Dependence of NCl_3 formation upon NH_4Cl concentration in the reaction solution: (Curve 1) NCl_3 quantity formed (mmol); (curve 2) NCl_3 quantity formed relative to the NH_4Cl quantity used (%); (curve 3) NCl_3 concentration in the reaction solution (mmol/L).

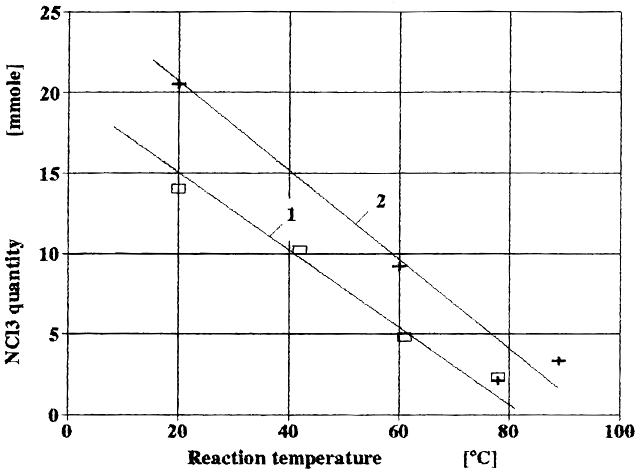

Figure 3. Dependence of NCl_3 formation upon reaction temperature: (Curve 1) chlorine quantity used, 73% of the theoretical value; (curve 2) chlorine quantity used, 132% of the theoretical value.

Time Dependence of the Formation and Decomposition Reactions of NCl_3. With the use of 0.5 M NH_4Cl solution in 0.5 M hydrochloric acid the formation rate of NCl_3 was studied for a period of 45 min. For that, samples were taken and analyzed from both the reaction solution and the absorption solution arranged behind that. After the chlorine flow had been shut off, agitating the chlorine-containing reaction solution and passing the carrier gas flow through the free reaction space were continued.

The results are given in Table 1. From that the following can be seen: (i) In the reaction solution a rapid formation of NCl_3 took place with the greater portion of NCl_3 (93−96%) initially remaining in the aqueous solution. (ii) After the chlorine flow had been shut off, the NCl_3 quantity in the reaction solution decreased. Of that, 77% was recovered in the absorption solution. (iii) Of the NCl_3 quantity removed subsequently from the reaction solution during 21 h, only 16% was recovered in the absorption solution.

Table 1. Dependence of Formation and Decomposition Reaction of NCl_3 upon Time[a]

	reacn solution		abs solution
time, min	C_{NCl_3}, mmol/L	n_{NCl_3}, mmol	n_{NCl_3}, mmol
	Chlorination Reaction		
10	4.4	2.21	0.09
20	12.9	6.33	0.31
30	17.1	8.29	0.67
45	26.4	12.50	2.1
	Decomposition Reaction		
15	22.9	10.50	n.b.[c]
30	12.9	5.71	n.b.
45	11.4	4.93	n.b.
60	8.1	3.41	n.b.
180	1.57	0.64	10.4
24 h	0.019	0.007	0.1[b]

[a] Quantity used: 0.5 L of 0.5 M NH_4Cl/0.5 M HCl. Specific chlorine flow: 5.4 L/(h·L of solution). [b] The absorption solution was changed. [c] No values.

Summary

By the reaction of chlorine with NH_4Cl solutions (investigated concentration range 0.01−2 M NH_4Cl), a rapid formation of NCl_3 took place. The acidities at which the formation of relevant NCl_3 quantities must be expected ranged from neutral values up to a hydrochloric acid concentration of about 5 M. Rising temperatures, indeed, diminished the NCl_3 formation; however, even at about 90 °C noticeable NCl_3 quantities were still formed. The behavior of NCl_3-containing systems was governed by the noticeable, but limited, solubility of the NCl_3 in aqueous solution and its relatively high vapor pressure and remarkable chemical stability against excessive NH_4Cl.

Therefore, during the formation stage the NCl_3 concentration in the reaction solution initially increased which is accompanied with a relatively low transition of the NCl_3 into the gas phase. Then, the NCl_3 concentration in the gas phase distinctly increases when the solubility limit of NCl_3 in the aqueous solution (about 17 mmol/L) is exceeded.

When the flow of chlorine had been shut off, the NCl_3 content in the reaction solution considerably decreases within some hours. The decrease is due, mainly, to the evaporation of NCl_3 and removal by the gas phase, whereas the reaction with water or NH_4Cl present in a large excess contributes only a little to this. The reaction resulting in stable compounds such as N_2 and NO_3^- became decisive only at low NCl_3 contents.

Safety Precautions

From the investigations it follows that during the reaction of NH_4Cl solutions with chlorine the quantity of NCl_3 formed as well as the NCl_3 concentrations in many cases pass beyond the limit of dangerous conditions.

In view of the explosion hazard caused already by small NCl_3 quantities,[2] all reactions in which chlorine and hypochloride, on the one hand, and amines, on the other, are taking part must be tested for the possibility of forming explosive chlorine amines.

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