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Elaboration of High-grade Chloramine from Ternary and Quaternary Ammoniacal Combinations and Hypochlorite at 100 Chlorometric Degrees

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High-grade chloramine is prepared in batch and in continuous mode starting from mixed ammoniacal solutions and hypochlorite at hundred chlorometric degrees.

This work indicates, for the first time, the possibility to obtain a chloramine in yield > 11% from hypochlorite solutions with hundred chlorometric degrees. The feasibility of the synthesis was proven in batch (2.35 M) and in continuous mode by the realization of a pilot plant with a final NH_2Cl concentration of *ca.* 2.1 M being achieved. The preparation of hydrazine according to Raschig process leads to, with the same unit volume of hypochlorite, an increase in the productivity of hydrazine and reduction in energy and materials during synthesis, recycling and distillation.

Chloramines are inorganic compounds which have both research and industrial importance. The chemistry of chloramines is diverse not only because nitrogen and chlorine act as reaction sites but also because of the different modes by which these functionalities react.[1,2] Only the monochloramine (NH_2Cl) is of commercial interest. Reaction of NH_2Cl with an excess of NH_3 in alkaline medium[5,6] is the basis of the industrial-scale production of hydrazines [eqn. (1)].[7]

$$NH_2Cl + RR'NH + NaOH \rightarrow RR'NNH_2 + NaCl + H_2O \quad (1)$$

This process, studied in the laboratory, arouses a great interest taking into account its lower polluting nature compared to former preparations involving *N*-nitrosamines.[10,11] However, it presents disadvantages related to the low hydrazine content in the reaction medium, which does not exceed 2–4%. This limitation is due mainly to substantial dilution of the reagents and in particular of hypochlorite, which entails delicate and expensive extraction operations.

A higher chloramine yield requires the use of a new reagent at high chlorometric degree and the investigation of appropriate operating conditions. The synthesis of high-grade chloramine was studied starting from sodium hypochlorite solutions containing 25% NaOCl. The pure reagents are relatively stable and decompose to the extent of *ca.* 1.4% after 24 h at 17 °C. The temperature of crystallisation is 14.2 °C (precipitation of $NaOCl \cdot 5H_2O$) but it is possible to utilise such solutions at −20 °C in a supersaturated state.

Aqueous solutions of monochloramine are unstable and decompose with time. The nature of the formed products and the rate of degradation are influenced by the pH, the total concentration of ammonia ($[NH_3]_T = [NH_4^+] + [NH_3]$) and temperature.[16–25] Analysis of the reaction scheme of decomposition of NH_2Cl enabled us to specify the conditions for the optimisation of preparation of concentrated chloramine solutions.

To obtain a quantitative yield, it is necessary to add an acidic species to the reaction medium in order to instantaneously neutralize hydroxide ions generated by eqn. (2)

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH \quad (2)$$

An ammonium salt of the type $(NH_4{}^+)_\alpha H_\beta^+ A^{(\alpha+\beta)-}$ is the most appropriate reagent since it regenerates ammonia as soon is consumed. This operation, which preserves the concentration of NH_3 kinetically promotes the formation of NH_2Cl to the detriment of its *in situ* oxidation by hypochlorite ions.

The pH of the reaction controlled by the $NH_3/NH_4{}^+$ ratio must be maintained around 10 to stabilize the formed chloramine. This also prevents conversion to $NHCl_2$, NCl_3, NH_2OH, N_2 and NH_3.

The temperature of crystallization of the reactive mixture must be as low as possible because of the exothermicity of the reactions involved (formation, neutralization and degradation). In particular the *in situ* oxidation of chloramine by hypochlorite is very exothermic ($\Delta H = -364.5\,\mathrm{kJ\,mol^{-1}}$)[33] and kinetically favoured upon increasing the temperature.

In the case of continuous preparation, the crystallization point of the ammonia mixture must be lower than −10 °C to counteract the injection of chlorine at 15 °C. We thus sought to limit the temperature of the ammoniacal reagent which permits synthesis in a monophasic medium.

The exploitation of polythermic diagrams involving $NH_4{}^+$ ions imply the use of ammonium nitrate systems: $NH_4NO_3-NH_4Cl-NH_3-H_2O$ or $NH_4NO_3-NH_3-H_2O$.[46–48] These combinations allow use of a homogeneous medium down to −30 °C. In particular, the ternary combination $NH_4NO_3-NH_3-H_2O$ ($[NH_3] = 7.2$ M, $[NH_4NO_3] = 4.76$ M) is compatible and crystallizes at −33.2 °C. These conditions permit synthesis between −15 °C and −20 °C with partial or total substitution of NH_4Cl by ammonium nitrate. In the absence of NH_4NO_3, the preparation of high-grade chloramine can only be performed batchwise. The synthesis of concentrated chloramine is illustrated by the following experiments.

Experimental

$NH_4Cl-NH_3-H_2O$ System: Hypochlorite Reactive at Surfusion State, Discontinuous Synthesis, Heterogeneous Medium.—The reaction is carried out in a double walled cylindrical reactor at −20 °C by thermostatic fluid circulation. The ammoniacal solution contains 7.2 M of NH_3 and 4.76 M of NH_4Cl, which corresponds to the following composition: 12.1% NH_3, 25.2% NH_4Cl, 62.7% H_2O. 30 mL of this mixture was introduced in the vessel under agitation until thermal equilibrium was reached. The sodium hypochlorite solution (104.4 chlorometric degrees, 4.64 M) in a supersaturated state was added in a steady flow for 10 min, so that the temperature in

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the reactor does not exceed $-10\,^{\circ}C$. The representative point of ammoniacal mixture is initially inside the diphasic domain liquid + NH_4Cl region (isotherm at $-20\,^{\circ}C$ of the ternary diagram $NH_4Cl-NH_3-H_2O$ and 29.3% of the initial quantity of ammonium chloride is precipitated. During the addition of NaOCl, the mixture quickly becomes homogeneous upon dilution and removal of hydroxide ions. A 2.18 M chloramine solution is obtained (11.2%), which corresponds to a yield of 98% with respect to hypochlorite. The NH_2Cl formed is relatively stable at $-20\,^{\circ}C$ and decomposes to the extent of only 1.4% after 15 min.

$NH_4NO_3-NH_4Cl-NH_3-H_2O$ System: Discontinuous Synthesis, Hypochlorite Reactive at 15 °C, Homogeneous Medium.—To carry out the preparation in a monophasic medium with hypochlorite solution at 15 °C and to neutralize the hydroxide ions liberated, a quaternary mixture $NH_4Cl-NH_4NO_3-NH_3-H_2O$ has been employed. Its composition of NH_3, NH_4Cl, NH_4NO_3 and H_2O is 13.14 M (22.4%), 3.02 M (16.2%), 1.76 M (14.1%) and 26.2 M (47.3%), respectively. 30 mL of the mixed ammoniacal solution were introduced in a vessel maintained at $-25\,^{\circ}C$. An equivalent volume of hypochlorite solution (98.4 chlorometric degrees, 4.39 M) is added dropwise (over 15 min) so that the temperature in the reactor did not exceed $-15\,^{\circ}C$. A 2.01 M NH_2Cl solution (yield 90%) is obtained with a tenor close to 10.3%.

$NH_4NO_3-NH_4Cl-NH_3-H_2O$ System, Continuous Synthesis, Hypochlorite Reactive at 15 °C, Homogeneous Medium.—The synthesis of chloramine is carried out in an agitated continuous reactor maintained at between -20 and $-30\,^{\circ}C$. The reactants have a composition as above and flows are fixed at $4\,mL\,min^{-1}$. The injection temperatures are maintained respectively at 15 and $-30\,^{\circ}C$ for NaOCl and the quaternary mixture $NH_4NO_3-NH_4Cl-NH_3-H_2O$. The temperature of the reaction mixture is regulated at $-11\,^{\circ}C$. At the reactor exit, one obtains continuously a 2.07 M solution of NH_2Cl (10.6%).

References: 48 Full text in French

Tables: 2 (composition and stability of hypochlorite solutions at hundred chlorometric degrees)

Fig. 1: Continuous synthesis of high-grade chloramine (pilot plant)

Figs. 2 and 3: Rate constants and stability of hypochlorite at high chlorometric degree

Figs. 4 and 5: Ternary systems $NaOCl-NaCl-H_2O$ (10 °C) and $NH_4Cl-NH_3-H_2O$ (−20 °C).

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References cited in this synopsis

1 P. Kovacic, M. K. Lowery and K. W. Field, *Chem. Rev.*, 1970, **70**, 639.

2 J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Co., New York, NY, vol. VIII 1928, vol. VIII, suppl. II, Part II, 1967.

5 M. Anbar and G. Yagil, *J. Am. Chem. Soc.*, 1962, **84**, 1797.

6 F. Raschig, *Schwefel und Stickstoffstudien*, Verlag Chemie, Berlin–Leipzig, 1924.

7 E. W. Schmidt, *Hydrazine and its Derivatives, Preparation, Properties, Application*, John Wiley & Sons, Inc., New York, 1984.

10 J. B. Wright and R. E. Willette, *J. Med. Pharm. Chem.*, 1962, **5**, 815.

11 R. Mauge, *Fr. Pat. 2540110,* 1983.

16 H. Delalu, *Thèse de Doctorat d'État ès Sciences no 77–29*, Université Lyon I, 1977.

17 C. Morris, in *Principles and Applications of Water Chemistry*, eds. S. D. Faust and J. D. Hunter, John Wiley & Sons, Inc., New York, 1967, p. 23.

18 E. T. Gray, D. W. Margerum and R. P. Huffman, in *Organometals and Organometalloids, Occurrence and Fate in the Environment*, ed. F. E. Brinckman and J. M. Bellama, American Chemical Society, Washington, D.C., *ACS Symp. Ser.*, 1978, no. 82, p. 264.

19 E. T. Gray, D. W. Margerum and R. P. Huffman, in *Organometals and Organometalloids, Occurrence and Fate in the Environment*, eds. F. E. Brinckman and J. M. Bellama, American Chemical Society, Washington, D.C., *ACS Symp. Ser.*, 1978, no. 82, p. 278.

20 J. L. S. Saguinsin and J. C. Morris, in *Disinfection, Water and Wastewater,* ed. D. Johnson, Ann Arbor Science, Ann Arbor, MI, 1975, ch. 14.

21 J. C. Morris and R. A. Isaac, *Water Chlorination, Environmental Impact and Health Effects*, Ann Arbor Science, Ann Arbor, MI, 1983, p. 49.

22 C. Colin, M. Brunetto and R. Rosset, *Analusis*, 1987, **15**, 265.

23 R. M. Chapin, *J. Am. Chem. Soc.*, 1929, **51**, 2112.

24 R. E. Corbett, W. S. Metcalf and F. G. Soper, *J. Chem. Soc.*, 1953, 1927.

25 W. C. Bray and C. T. Dowell, *J. Am. Chem. Soc.*, 1917, **39**, 905.

33 R. Abraham, *Thèse de Doctorat de l'Université, no. 81–69*, Université Lyon I, 1981.

46 A. G. Bergman and K. K. Moroz, *Zh. Prikl. Khim.*, 1967, **12**(**2**), 551.

47 C. F. Prutton, J. C. Brosheer and S. H. Maron, *J. Am. Chem. Soc.*, 1935, **57**, 1656.

48 I. R. Krichevskii and G. A. Sorina, *Dokl. Akad. Nauk. SSSR*, 1991, **317**(**1**), 137.