NON-AQUEOUS SOLVENTS FOR PREPARATION AND REACTIONS OF NITROGEN HALOGEN COMPOUNDS

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Abstract - The importance of non-aqueous solvents for the chemistry of haloamines is shown in more recent reaction examples. The solvents must be low-melting because of the general temperature sensitivity of the haloamines. They may take part in the reaction (formation of $CH_3NI_2 \cdot CH_3NH_2$, $(CH_3)_2NI$, $NI_3 \cdot 5\ NH_3$, and $NH_2I \cdot NH_3$) or may be inert (formation of $NI_3 \cdot$quinuclidine, $2\ NI_3 \cdot 1$ triethylenediamine, $[I(quinuclidine)_2]^{\oplus}$ salts, pure NBr_3, and compounds of the type $R_1R_2NClO_3$ with R_1 and R_2 = organic group or hydrogen).

INTRODUCTION

Non-aqueous solvents play an important role in preparation and reactions of nitrogen halogen compounds. Due to the fact, that all haloamines are derivatives of ammonia or amines, liquid ammonia or liquid organic amines are used as solvents very often. Liquid ammonia and the lower organic amines reveal, in addition, the advantage of low melting points (liquid ammonia -78, liquid monomethylamine -93.5, liquid dimethylamine -92, liquid tri-methylamine -124°C); these meet the general temperature sensitivity of the nitrogen halogen compounds, especially of the pure inorganic ones. Ammonia and amines are very seldom inert solvents; they mostly take part in the reaction planned for synthesis or conversion of the haloamine. In case a reaction of the solvent is to be avoided, one has to look for a low melting inert solvent, for example methylene chloride (m.p. -97°C) or a lower hydro-carbon (for instance n-pentane, m.p. -131, or n-hexane, m.p. -94°C).

In this article some examples of more recent nitrogen halogen chemistry in non-aqueous solvents shall be discussed.

1. THE SOLVENT TAKES PART IN THE REACTION

It has been known for some time that the dissolution of iodine in <u>liquid ammonia</u> (m.p. -78, b.p. -33.5°C, dipole moment 0.93 D, dielectric constant 22-26) at temperatures between -35 and -70°C via intermediates, which will be discussed later, finally leads to green iridescent nitrogen triiodide-3-ammonia, $(NI_3 \cdot 3\ NH_3)_n$, which due to its polymeric character is sparingly soluble and by this may be easily seperated from ammonium iodide (1).

$$3\ I_2 + 7\ NH_3 \xrightarrow[-35\ \text{to}\ -70°C]{\text{liq. } NH_3} NI_3 \cdot 3\ NH_3 \downarrow + 3\ NH_4I \qquad (1)$$
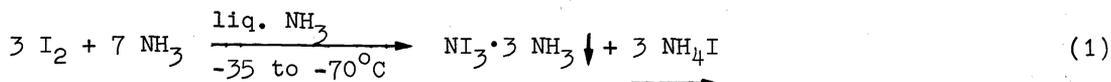
An attempt to dissolve iodine in <u>liquid methylamine</u> (m.p. -93.5, b.p. -6°C, dipole moment 1.23 D, dielectric constant 10) or <u>dimethylamine</u> (m.p. -92, b.p. -7°C, dipole moment 1.02 D, dielectric constant 5-6) for isolating di-iodo methylamine, CH_3NI_2, or iododimethylamine, $(CH_3)_2NI$, fails because of the abundant solubility of these compounds as well as the corresponding ammonium iodides.

$$2\ I_2 + 3\ CH_3NH_2 \xrightarrow{\text{liq. } CH_3NH_2} CH_3NI_2 + 2[CH_3NH_3]I \qquad (2)$$

$$I_2 + 2(CH_3)_2NH \xrightarrow{\text{liq. } (CH_3)_2NH} (CH_3)_2NI + [(CH_3)_2NH_2]I \qquad (3)$$
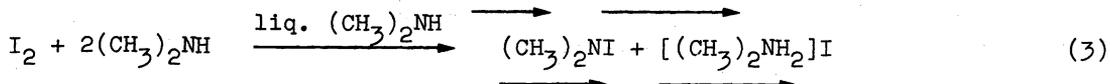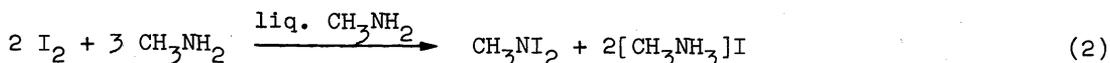
In these cases, however, the experiment is successful if one dissolves nitrogen triiodide-1-ammonia, $(NI_3 \cdot NH_3)_n$, in the liquid amines at temperatures below $-15°C$.

$$2\ NI_3 \cdot NH_3 + 6\ CH_3NH_2 \xrightarrow[\ <-15°C\ ]{liq.\ CH_3NH_2} 3\ CH_3NI_2 \cdot CH_3NH_2 + 4\ NH_3 \uparrow \qquad (4)$$

$$NI_3 \cdot NH_3 + 3(CH_3)_2NH \xrightarrow[\ <-15°C\ ]{liq.\ (CH_3)_2NH} 3(CH_3)_2NI + 2\ NH_3 \uparrow \qquad (5)$$
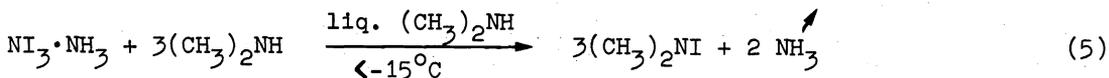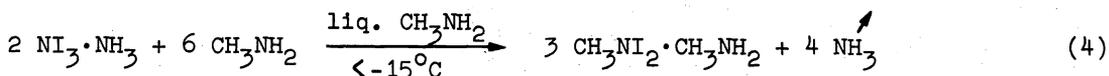
After evaporation of the solvent at low temperature reddish yellow diiodo-methylamine-1-methylamine, $CH_3NI_2 \cdot CH_3NH_2$, and yellow iododimethylamine, $(CH_3)_2NI$, is obtained, respectively (2,3).

To come back to the dissolution of iodine in liquid ammonia, it has been observed some time ago, that at temperatures below $-70°C$, that means between -70 and the freezing point of ammonia, $-78°C$, the solid product is not green iridescent, but brown, brown-red or red (1). To study this phenomenon further   one should carry out experiments in liquid ammonia at temperatures below $-78°C$. Unfortunately, this is not possible because of the freezing point of ammonia. It was tried, therefore, to lower the freezing point of ammonia by dissolving big amounts of <u>chloroform</u> (m.p. -63.5, b.p. $61°C$, dipole moment 1.18 D, dielectric constant $\underline{5-7}$) in it. It was found that a mixture of two parts by volume of chloroform with one of liquid ammonia remains liquid to $-95°C$ (4).

If one dissolves iodine - or better iodine bromide - in this mixed solvent at temperatures between -75 and $-85°C$, a red precipitate is obtained with a nitrogen: iodine ratio of about 2:1. Besides the precipitate, ammonium iodide or ammonium bromide is formed, respectively; both are soluble in the mixed solvent and by this are easily separated from the red precipitate. Its low temperature IR spectrum corresponds almost exactly with that of the polymeric green nitrogen triiodide-3-ammonia, the identical position of the intense NI skeletal vibrations being especially noteworthy (red precipitate: 579, 506, 385, $(NI_3 \cdot 3\ NH_3)_n$: 579, 506, 385 cm^{-1} (4)).

Wherefrom does one know that the green nitrogen triiodide-3-ammonia has a polymeric structure? To explain this, first of all one must discuss the structure of the black brown nitrogen triiodide-1-ammonia. It has long been known and contains a polymeric NI framework rather than isolated NI_3 units. This is made up of NI_4 tetrahedra with infinite zig-zag NINI chains along the <u>b</u> axis. The zig-zag chains of tetrahedra are built into sheets of tetrahedra by iodine-iodine contacts between the zig-zag chains which lie above one another along the <u>c</u> axis. One iodine atom of each tetrahedron is loosely attached to an ammonia molecule which projects into the corrugated space between the zig-zag chains of tetrahedra. A further characteristic of this structure is the linear groups NIN; this illustrates the tendency of covalently bonded iodine atoms to form a second bond. The bond is best described in terms of MO theory as a 3 centre 4 electron bond without participation of d orbitals. It is notable that the NIN groups within the zig-zag NINI chains are completely symmetrical, that is, there is no longer a difference between the intramolecular and the intermolecular bond (5).

Secondly, by IR spectroscopic work one knows very well the IR absorptions which belong to the polymeric NI skeleton of this compound (558, 488, 382 cm^{-1} (6)). And from the striking fact, that these intense skeleton vibrations are present and show a similar position also in the low temperature IR spectrum of the green nitrogen triiodide-3-ammonia (579, 506, 385 cm^{-1}), one is lead to the view that NI_4 tetrahedra are again present in this compound and that they resemble those in the monoammoniate in structure and dimensions: in all probability the NI_3 molecules form infinite chains of linked NI_4 tetrahedra as they do in nitrogen triiodide-1-ammonia (7).

And finally, the correspondence of the IR spectrum of the red precipitate with that of the green nitrogen triiodide-3-ammonia, especially with regard to the intense NI skeletal vibrations, leads to the view that the red precipitate is also a polymeric nitrogen triiodide; both compounds differ with respect to the number of ammonia molecules per unit NI_3: The green compound contains three, the red compound about five molecules of ammonia, $(NI_3 \cdot 5\ NH_3)_n$. Both compounds are convertible into each other conditional on the temperature (4).

It is extremly interesting, that the dissolution of iodine bromide in the mixed solvent below -85°C does not lead to nitrogen triiodide-5-ammonia just referred to, but to a second red compound which has likewise a nitrogen: iodine ratio of about 2:1, though the low temperature IR spectrum is different from that of the red pentammine. It does not show the three intense NI skeletal vibrations, but one intense IR band at 480 cm^{-1} in the NI stretching region. We suppose this second red compound to be monoiodamine-1-ammonia, $H_2NI \cdot NH_3$. Above -85°C it is transformed into the first red compound, nitrogen triiodide-5-ammonia (4).

2. THE SOLVENT DOESN'T TAKE PART IN THE REACTION

Many successful experiments have been carried out in the past to replace the ammonia in nitrogen triiodide by other N-bases, for instance pyridine, the picolines, lutidine, collidine or quinoline (4). In all these cases no significant alteration of the NI framework takes place. The sheets of NI_4 tetrahedra built parallel to the bc plane remain unchanged and, according to X ray structure determinations, just enlarge their distances from one another by introduction of the more voluminous N-base (8).

However, the way of preparation usually applied to these adducts doesn't work in case of nitrogen triiodide-1-quinuclidine. The adducts are usually formed by direct reaction of preformed nitrogen triiodide-1-ammonia with excess of N-base in aqueous suspension, ammonia being set free. The new adduct, then, results as a black precipitate. In the case of quinuclidine, no such reaction takes place (4); apparently the consumption of energy for elimination of ammonia and enlargement of the distances of the sheets of NI_4 tetrahedra is greater than the profit of energy for adding quinuclidine.

A convenient way of preparation has now been found with the aid of non-aqueous solvents. The most important point of the new way is that one adds quinuclidine already to the reaction mixture in which nitrogen triiodide is being synthesized. By reacting bis-trimethylsilyl-iodamine with quinu-

$$[(CH_3)_3Si]_2NI + N\bigcirc \xrightarrow[-30°C]{\text{n-pentane}} [(CH_3)_3Si]_2NIN\bigcirc \qquad (6)$$

$$[(CH_3)_3Si]_2NIN\bigcirc + 2 \, ICl \xrightarrow[-40°C]{\text{n-pentane}} I_2NIN\bigcirc + 2(CH_3)_3SiCl \qquad (7)$$

$$NI_3 \cdot N\bigcirc$$
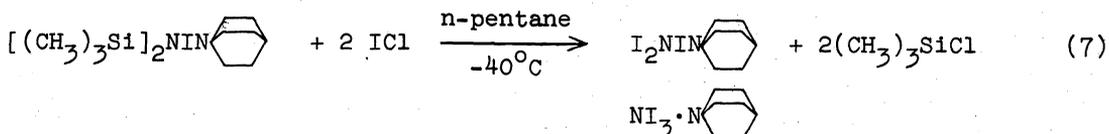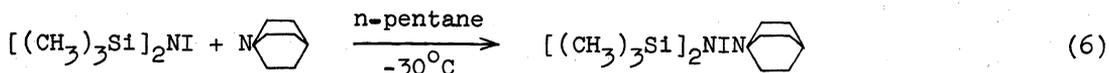
clidine in n-pentane (m.p. -131, b.p. +36°C, dipole moment 0 D, dielectric constant 2.33) at -30°C, a white precipitate is formed which can be easily identified as an adduct of quinuclidine to bis-trimethylsilyl-iodamine. If one cleaves this adduct with iodine chloride in n-pentane at -40°C, brown nitrogen triiodide-1-quinuclidine is formed besides soluble trimethylsilyl-chloride (9).

In an analogous experiment, bis-trimethylsilyl iodamine was reacted with triethylenediamine, $N(-CH_2-CH_2-)_3N$, in n-pentane at low temperature with a molar ratio 2:1. Again a white precipitate is formed as expected which can

$$[(CH_3)_3Si]_2NI + N\bigcirc N + IN[Si(CH_3)_3]_2 \xrightarrow[-30°C]{\text{n-pentane}}$$

$$[(CH_3)_3Si]_2NIN\bigcirc NIN[Si(CH_3)_3]_2 \qquad (8)$$

$$[(CH_3)_3Si]_2NIN\bigcirc NIN[Si(CH_3)_3]_2 + 4 \, ICl \xrightarrow[-40°C]{\text{n-pentane}}$$

$$NI_3 \cdot N\bigcirc N \cdot I_3N$$

$$I_2NIN\bigcirc NINI_2 + 4(CH_3)_3SiCl \qquad (9)$$
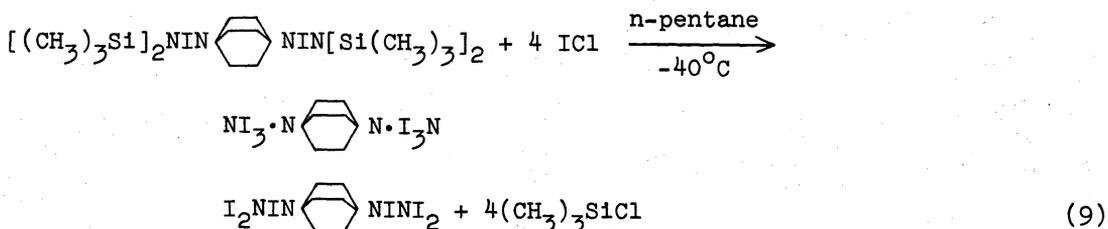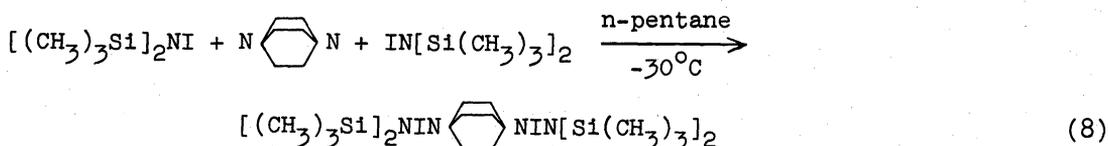
be easily identified as an adduct of one mole triethylenediamine to two

moles bis-trimethylsilyl-iodamine. Reaction of the new compound with iodine chloride in pentane at -40°C gives indeed brown 2-nitrogentriiodide-1-tri-ethylenediamine (9).

Although no structure investigations have been carried out, the NIN groups in the new compounds referred to in all probability are linear as they were found in nitrogen triiodide-1-ammonia. Furthermore, for the first time iodonium salts stabilized by quinuclidine have been prepared, for which the linear structure has been proved. These experiments were carried out in

$$I_2 + AgNO_3 \quad \xrightarrow[\text{0°C}]{\text{dimethylformamide}} \quad I^{\oplus} + NO_3^{\ominus} + AgI \qquad (10)$$
$$ClO_4 \qquad\qquad\qquad\qquad\qquad ClO_4^{\ominus}$$

$$I^{\oplus}(solv)_x + 2\ N\!\!\bigcirc \quad \xrightarrow[\text{0°C}]{\text{dimethylformamide}} \quad [\ \bigcirc\!\!N\,I\,N\!\!\bigcirc\ ]^{\oplus} + x\ solv \qquad (11)$$
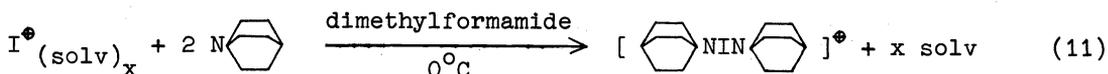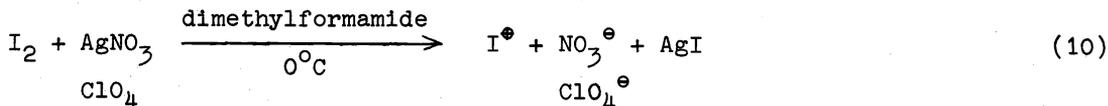
dimethylformamide (m.p. -61, b.p. +158°C, dielectric constant 37-38). In the first step iodine reacts with silver nitrate or perchlorate at 0°C, silver iodide being precipitated. In the second step which follows immediately without separation of silver iodide, quinuclidine is added to form the bis-quinuclidine iodonium cation. The nitrate or perchlorate of this cation, after filtration and removal of silver iodide, may be precipitated by addition of petroleum ether (10).

The aprotic solvent dimethylformamide with its dipole is well suitable for carrying out reactions of this kind. By its solvating properties (donor number about 27) it stabilizes the iodonium cation first formed and keeps it in solution. On the other hand, the basic properties cannot compete with those of quinuclidine, and by addition of this base bis-quinuclidine iodonium cation is formed in a nucleophilic substitution reaction.

In a number of nitrogen iodine compounds the linear twofold coordination of iodine towards nitrogen is proved by X ray structure determinations. Besides the adducts of nitrogen triiodide and some other compounds also the iodonium salts of pyridine, 3-picoline, and urotropin show this type of coordination. The latter N-base shows a NI distance of 230 pm. The bis-quinuclidine iodonium nitrate, the X ray structure of which was investigated by Pritzkow (11), shows a linear NIN group as well and a NI distance in the same order of magnitude, that is about 230 pm.

In the field of nitrogen-bromine and nitrogen-chlorine compounds, the most simple compounds which contain only nitrogen and halogen, nitrogen tri-bromide and nitrogen trichloride, one cannot prepare in the same way as nitrogen triiodide by dissolving the halogen in liquid ammonia. In these cases one obtains monobromamine and monochloramine, respectively (12,13,14). For nitrogen trichloride a good preparation method in aqueous solution is well known since long: When introducing chlorine in an aqueous solution of ammonium sulfate with $p_H \sim 4$ one obtaines an aqueous solution of nitrogen trichloride, from which the compound may be extracted by tetrachlormethane or other solvents or may be driven out by nitrogen gas and - after drying - condensed on a cool finger as a yellow solid (12,15). An attempt was made to apply this reaction principle for the preparation of nitrogen tribromide. This was shown to be not possible because of the temperature sensitivity of nitrogen tribromide which makes it impossible to work in aqueous solution. One needs at least -60 to -70°C to prevent the decomposition of nitrogen tribromide.

So one is forced to look for a low melting non-aqueous solvent. In dichloro-methane (m.p. -97, b.p. 40°C, dipole moment 1.58 D, dielectric constant 9) at -85°C several possibilities for the direct bromination of ammonia were found: One may use bromine, bromine chloride, N-bromosuccinimide, dibromo-isocyanuric acid, acetyl hypobromite and tertiary butylhypobromite, respectively. One obtains solid, orange coloured nitrogen tribromide, which is contaminated with different by-products depending on the brominating agent. By dissolving nitrogen tribromide from this orange solid with an excess of dichloromethane pure orange yellow solutions of nitrogen tribromide are obtained. They are very diluted - 4×10^{-3} mole/l - and not suitable for taking IR- or Raman spectra.

Pure, solid nitrogen tribromide is obtained by a reaction which is analogous to the preparation of N-iodamines from bis-trimethylsilylamines and iodine chloride. Bis-trimethylsilylbromamine was reacted with bromine chloride, but

$$[(CH_3)_3Si]_2NBr + 2\ BrCl \xrightarrow[-85°C]{\text{n-pentane}} \cdot NBr_3\!\downarrow + 2(CH_3)_3SiCl \qquad (12)$$
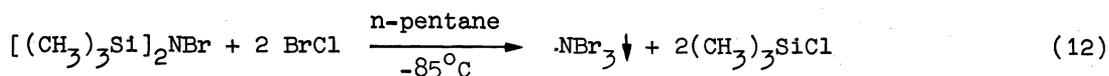
n-pentane was used as solvent instead of chloroform. The reaction temperature is -85°C. Pure nitrogen tribromide is obtained as a deep red solid. In the pure state it is highly explosible, so that again it is impossible to take a spectrum (16).

It was possible to take the Raman spectrum from an impure product prepared from ammonia and acetylhypobromite (17). If one subtracts the frequencies of the impurities - mainly ammonium acetate and ammonium bromide - there are still left so many bands that it is not possible to assume that solid nitrogen tribromide possesses a molecular lattice as nitrogen trichloride does (15). One rather has to assume strong intermolecular contacts, so that solid nitrogen tribromide takes a medium position between polymeric nitrogen triiodide and monomeric nitrogen trichloride.

Finally, a very interesting new group of nitrogen chlorine compounds will be mentioned, the organic amidoperchlorates $R_1R_2NClO_3$, which owe their existence to a new preparation technique in <u>tetrachloromethane</u> (m.p. -23, b.p. 154°C, dipole moment 0 D, dielectric constant 2). Until recently, inorganic amidoperchlorates were prepared via perchlorylfluoride (18) which method caused considerable difficulties. It was found now that inorganic as well as organic amidoperchlorates may easily be prepared by simple mixing tetrachloromethane solutions of dichlorineheptoxide and the amine concerned in the

$$2\ R_1R_2NH + Cl_2O_7 \xrightarrow[+25\ to\ -20°C]{CCl_4} R_1R_2NClO_3 + (R_1R_2NH_2)ClO_4\!\downarrow \qquad (13)$$

$R_1R_2 =$

O$\big\langle\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}\big\rangle$ $R_1=R_2=C_5H_{11}$ $R_1=H,\ R_2=$ $H_2C\big\langle\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}\big\rangle CH-$

$H_2C\big\langle\begin{smallmatrix}CH_2-CH_2\\CH-CH_2\end{smallmatrix}$ C_4H_9 C_6H_{13}
$\quad\quad CH_3$

$CH_3-CH\big\langle\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}\big\rangle$ C_3H_7 C_4H_9

$H_2C\big\langle\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}\big\rangle$ C_2H_5 C_3H_7

$C_2H_5-CH\big\langle\begin{smallmatrix}\\CH_2\end{smallmatrix}$ CH_3 $(CH_3)_2CH-$

$\begin{smallmatrix}H_2C-CH_2\\H_2C-CH_2\end{smallmatrix}\big\rangle$ $(CH_3)_3C-$

temperature range +25 to -20°C (19,20). After filtration of the ammonium salt, a pure tetrachloromethane solution of the wanted amidoperchlorate is obtained. The colourless or, at the most, faintly yellow compounds are not isolated as a rule because of their explosive nature, but are identified in tetrachloromethane solution by ratio analysis as well as IR and H-NMR spectroscopy.

When these compounds still have hydrogen bonded to nitrogen, they are appreciably acidic; more stable solid white potassium, tetramethylammonium

pKa Values for Amidoperchloric Acids

$$H_2NClO_3 \quad pKa_1 \quad 5.5 \qquad H_2C \underset{\underset{H_2C - CH_2}{\bigg\langle}}{\overset{H_2C - CH_2}{\bigg\langle}} CHNHClO_3 \quad pKa \quad 6.9$$

$$pKa_2 \quad 11.9$$

$$(CH_3)_3CNHClO_3 \qquad\qquad pKa \quad 7.0$$
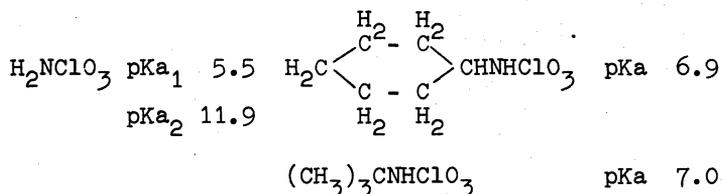
and silver salts may be made.

With regard to the most important IR stretching frequencies of these compounds (19) it can be established that in the series K_2NClO_3 - Ag_2NClO_3 - $KRNClO_3$ - $KHNClO_3$ - $AgRNClO_3$ - R_2NClO_3 - $RHNClO_3$ ν_{N-Cl} decreases from ~ 1260 to 650 cm^{-1} and $\nu_{as\ O-Cl}$ rises from ~ 900 to ~ 1250 cm^{-1}, corresponding with a decrease in the double bond character of the NCl bond and an increase for the OCl bond. The decrease in double bond character for the NCl bond is to be associated well with increase in the electronegativity of nitrogen with change in the atom attached to it: it attracts the π-bonding electron pair of the NCl double bond increasingly to nitrogen. The resulting increasing electron requirement of chlorine is then satisfied in increasing measure by π-electrons from oxygen, which will explain the increase in the double bond character of the OCl bond. A corresponding effect has already been observed and described in a comparison of the IR spectra of amidoperchlorate anion, $NClO_3^{2-}$, and fluorine perchlorate (21).

Some X ray structural investigations were carried out to confirm this interpretation from interatomic distances. In the amidoperchlorate anion (22) the NCl distance is small (141 pm); in this anion there are three pairs of electrons available for π-bonding, and a low electronegativity at nitrogen occurs. The NCl distance becomes bit by bit greater and nearly reaches that for a single bond in proceeding to tetramethylammoniumcyclohexylamidoperchlorate (153 pm) (11), potassiumhydrogenamidoperchlorate (164 pm) (23) and silver cyclohexylamidoperchlorate (161-165 pm) (11); the latter containes no free electron pair because of 2 silver ligands and therefore shows a higher electronegativity at nitrogen. Conversely the ClO distances decrease progressively in the series K_2NClO_3 (150-152 pm) - $[(CH_3)_4N]RNClO_3$ (143-145 pm) - $KHNClO_3$ (143-146 pm) - $AgRNClO_3$ (138-144 pm).

CONCLUSION

In conclusion, it is to be stated that modern chemistry of nitrogen halogen compounds is not imaginable without low melting non-aqueous solutions. An important point is, that it is not sufficient to use only protic or only polar, coordinating or only non-polar, non-coordinating solvents; it is necessary to use - depending on the special case - all the different kinds of solvents to be successful in preparation and reactions of these sensitive compounds.

REFERENCES

1. J. Jander and U. Engelhardt, Z.Anorg.Allgem.Chem. 339, 225 (1965).
2. J. Jander, U. Engelhardt and G. Weber, Angew.Chem. 74, 75 (1962).
3. U. Engelhardt and J. Jander, Fortschr.Chem.Forsch. 5, 663 (1966).
4. J. Jander, Advances Inorg.Chem.Nucl.Chem. 19 (1976), in the press.
5. H. Hartl, H. Bärnighausen and J. Jander, Z.Anorg.Allgem.Chem. 357, 225 (1968).
6. K. Knuth, J. Jander and U. Engelhardt, Z.Anorg.Allgem.Chem. 392, 279 (1972).
7. J. Jander and R. Minkwitz, Z.Anorg.Allgem.Chem. 405, 250 (1974).
8. H. Hartl and D. Ullrich, Z.Anorg.Allgem.Chem. 409, 228 (1974).
9. J. Jander and A. Maurer, unpublished results.
10. J. Jander and A. Maurer, Z.Anorg.Allgem.Chem. 416, 251 (1975).
11. H. Pritzkow, unpublished results, University of Heidelberg, 1976.
12. L. Bayersdorfer, U. Engelhardt, J. Fischer, K. Höhne and J. Jander, Z.Anorg.Allgem.Chem. 366, 169 (1969).
13. J. Jander and C. Lafrenz, Z.Anorg.Allgem.Chem. 349, 57 (1967).

14. J. Jander and U. Engelhardt, in "Developments in Inorganic Nitrogen Chemistry" (C.W. Colburn ed.), Vol. 2, pp. 70-203, Elsevier Scientific Publishing Company, Amsterdam, London, New York, 1973.

15. H. Hartl, J. Schöner, J. Jander and H. Schulz, Z.Anorg.Allgem.Chem. 413, 61 (1975).

16. J. Jander, J. Knackmuss and K.U. Thiedemann, Z.Naturforschg. 30b, 464 (1975).

17. J. Jander and J. Fritsch, unpublished results.

18. A. Engelbrecht and H. Atzwanger, J.Inorg.Nucl.Chem. 2, 348 (1956).

19. D. Baumgarten, E. Hiltl, J. Jander and J. Meussdoerffer, Z.Anorg.Allgem. Chem. 405, 77 (1974).

20. C.D. Beard and K. Baum, J.Am.Chem.Soc. 96, 3237 (1974).

21. J. Goubeau, E. Kilcioglu and E. Jacob, Z.Anorg.Allgem.Chem. 387, 190 (1968).

22. N.I. Golovina, G.A. Klitskaya and L.O. Atovmyan, J.Struct.Chem. (USSR) 9, 919 (1968)

23. L.O. Atovmyan, Izv.Akad. Nauk SSSR (Ser.Chim.), in preparation, 1975.