Previous Page

The first example of a tris-N_2 complex is the yellow crystalline compound *mer*-$[Mo(\eta^1\text{-}N_2)_3(PPr^n_2Ph)_3]$.(39)

X-ray structural studies have shown that for N_2 complexes with structure (1), the M–N–N group is linear or nearly so (172–180°); the N–N internuclear distance is usually in the range 110–113 pm, only slightly longer than in gaseous N_2 (109.8 pm). Such complexes have a strong sharp, infrared absorption in the range 1900–2200 cm^{-1}, corresponding to the Raman-active band at 2331 cm^{-1} in free N_2. Similarly, in complexes with structure (2), when both transition metals have a closed d-shell, the N–N distance falls in the range 112–120 pm and ν(N–N) often occurs near 2100 cm^{-1}, i.e. little altered from that of the corresponding complexes of structure (1). On the other hand, if one of the M is a transition metal with a closed d-shell and the other is either a main-group metal such as Al in $AlMe_3$ or an open-shell transition metal such as Mo in $MoCl_4$, then the N–N bond is greatly lengthened and the N–N stretching frequency is lowered even to 1600 cm^{-1}. Compounds with structure (3) have N–N ~134–136 pm, and this very substantial lengthening has been attributed to interaction with the Li atoms in the structure.(33)

As implied above, N_2 is isoelectronic with both CO and C_2H_2, and the detailed description of the bonding in structures 1–4 follows closely along the lines indicated on pp. 927 and 932 though there are some differences in the detailed sequences of orbital energies. Crystallographic and vibrational spectroscopic data have been taken to indicate that N_2 is weaker than CO in both its σ-donor and π-acceptor functions. Theoretical studies suggest that σ donation is more important for the formation of the M–N bond than is π back-donation, which mainly contributes to the weakening of the N–N bond, and end-on (η^1) donation is more favourable than side-on (η^2).(40)

The chemical reactivity of coordinated N_2 has been extensively studied because of its potential relevance to the catalytic and biological fixation of N_2 to NH_3 (p. 1035). For other recent work on the reactions of coordinated dinitrogen see refs. 41–44

To conclude this section on the chemical reactivity of nitrogen it will be helpful to compare the element briefly with its horizontal neighbours C and O, and also with the heavier elements in Group 15, P, As, Sb and Bi. The diagonal relationship with S is vestigial. Nitrogen resembles oxygen in its high electronegativity and in its ability to form H bonds (p. 52) and coordination complexes (p. 198) by use of its lone-pair of electrons. Catenation is more limited than for carbon, the longest chain so far reported being the N_8 unit in PhN=N—N(Ph)—N=N—N(Ph)—N=NPh.

Nitrogen shares with C and O the propensity for multiple bonding via p_π–p_π interactions both with another N atom or with a C or O atom. In this it differs sharply from its Group 15 congeners which have no analogues of the oxides of nitrogen, nitrites, nitrates, nitro-, nitroso-, azo- and diazo-compounds, azides, cyanates, thiocyanates or imino-derivatives. Conversely, there are no nitrogen analogues of the various oxoacids of phosphorus (p. 510).

11.3 Compounds

This section deals with the binary compounds that nitrogen forms with metals, and then describes the extensive chemistry of the hydrides, halides, pseudohalides, oxides and oxoacids of the element. The chemistry of P–N compounds is deferred until Chapter 12 (p. 531) and S–N

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[39] S. N. ANDERSON, D. L. HUGHES and R. L. RICHARDS, *J. Chem. Soc., Chem. Commun.*, 958–9 (1984).

[40] T. YAMABE, K. HORI, T. MINATO and K. FUKUI, *Inorg. Chem.* **19**, 2154–9 (1980).

[41] M. HIDAI and Y. MIZOBE, in P. S. BRATERMAN (ed.) *Reactions of Coordinated Ligands*, Vol. 2, Plenum Press, New York, 1989, pp. 53–114 (202 refs.)

[42] T. A. GEORGE, L. M. KOCZON and R. C. TISDALE, *Polyhedron* **9**, 545–51 (1990).

[43] J. O. DZIEGIELEWSKI and R. GRZYBEK, *Polyhedron* **9**, 645–51 (1990).

[44] S. NIELSON-MARSH, R. J. CROWTE and P. G. EDWARDS, *J. Chem. Soc., Chem. Commun.*, 699–700 (1992).

compounds are discussed in Chapter 15 (p. 721). Compounds with B (p. 207) and C (p. 319) have already been treated.

11.3.1 Nitrides, azides and nitrido complexes

Nitrogen forms binary compounds with almost all elements of the periodic table and for many elements several stoichiometries are observed, e.g. MnN, Mn_6N_5, Mn_3N_2, Mn_2N, Mn_4N and Mn_xN ($9.2 < x < 25.3$). Nitrides are frequently classified into 4 groups: "salt-like", covalent, "diamond-like" and metallic (or "interstitial"). The remarks on p. 64 concerning the limitations of such classifications are relevant here. The two main methods of preparation are by direct reaction of the metal with N_2 or NH_3 (often at high temperatures) and the thermal decomposition of metal amides, e.g.:

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

$$3Mg + 2NH_3 \xrightarrow{900^\circ} Mg_3N_2 + 3H_2$$

$$3Zn(NH_2)_2 \longrightarrow Zn_3N_2 + 4NH_3$$

Common variants include reduction of a metal oxide or halide in the presence of N_2 and the formation of a metal amide as an intermediate in reactions in liquid NH_3:

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

$$2ZrCl_4 + N_2 + 4H_2 \longrightarrow 2ZrN + 8HCl$$

$$3Ca + 6NH_3 \xrightarrow{-3H_2} \{3Ca(NH_2)_2\} \longrightarrow Ca_3N_2 + 4NH_3$$

Metal nitrides have also been prepared by adding KNH_2 to liquid-ammonia solutions of the appropriate metal salts in order to precipitate the nitride, e.g. Cu_3N, Hg_3N_2, AlN, Tl_3N and BiN.

"Salt-like" nitrides are exemplified by Li_3N (mp 548°C, decomp) and M_3N_2 (M = Be, Mg, Ca, Sr, Ba). It is possible to write ionic formulations of these compounds using the species N^{3-} though charge separation is unlikely to be complete, particularly for the corresponding compounds of Groups 11 and 12, i.e. Cu_3N, Ag_3N, and M_3N_2 (M = Zn, Cd, Hg). The N^{3-} ion has been assigned a radius of 146 pm, slightly larger than the value for the isoelectronic ions O^{2-} (140 pm) and F^- (133 pm), as expected. Stability varies widely; e.g. Be_3N_2 melts at 2200°C whereas Mg_3N_2 decomposes above 271°C. The existence of Na_3N is doubtful and the heavier alkali metals appear not to form analogous compounds, perhaps for steric reasons (p. 76). However the azides NaN_3 and KN_3 are well characterized as colourless crystalline salts which can be melted with little decomposition; they feature the symmetrical linear N_3^- group as do $Sr(N_3)_2$ and $Ba(N_3)_2$. The corresponding "B subgroup" metal azides such as AgN_3, $Cu(N_3)_2$, and $Pb(N_3)_2$ are shock-sensitive and detonate readily; they are far less ionic and have more complex structures. Further discussion of azides is on p. 433. Other stoichiometries are also known, e.g. Ca_2N (anti-$CdCl_2$ layer structure), Ca_3N_4, and $Ca_{11}N_8$.

The covalent binary nitrides are more conveniently treated under the appropriate element. Examples include cyanogen $(CN)_2$ (p. 320), P_3N_5 (p. 531), S_2N_2 (p. 725) and S_4N_4 (p. 722). The Group 13 nitrides MN (M = B, Al, Ga, In, Tl) are a special case since they are isoelectronic with graphite, diamond, SiC, etc., to which they are structurally related (p. 255). Their physical properties suggest a gradation of bond-type from covalent, through partially ionic, to essentially metallic as the atomic number increases. Si_3N_4 and Ge_3N_4 are also known and have the phenacite (Be_2SiO_4)-type structure. Si_3N_4, in particular, has excited considerable interest in recent years as a ceramic material with extremely desirable properties: high strength and wear resistance, high decomposition temperature and oxidation resistance, excellent thermal-shock properties and resistance to corrosive environments, low coefficient of friction, etc. Unfortunately it is extremely difficult to fabricate and sinter suitably shaped components, and considerable efforts have therefore been spent on developing related nitrogen ceramics by forming solid solutions between Si_3N_4 and Al_2O_3 to give the "sialons" (SiAlON) of general formula $Si_{6-0.75x}Al_{0.67x}O_xN_{8-x} (0 < x < 6)$.(45)

The most extensive group of nitrides are the metallic nitrides of general formulae MN, M_2N, and M_4N in which N atoms occupy some or all of the interstices in cubic or hcp metal lattices (examples are in Table 11.1, p. 413). These compounds are usually opaque, very hard, chemically inert, refractory materials with metallic lustre and conductivity and sometimes having variable composition. Similarities with borides (p. 145) and carbides (p. 297) are notable. Typical mps (°C) are:

TiN	ZrN	HfN	VN	NbN	TaN
2950	2980	2700	2050	2300	3090
CrN	ThN	UN			
d1770	2630	2800			

Hardness on the Mohs scale is often above 8 and sometimes approaches 10 (diamond). These properties commend nitrides for use as crucibles, high-temperature reaction vessels, thermocouple sheaths and related applications. Several metal nitrides are also used as heterogeneous catalysts, notably the iron nitrides in the Fischer-Tropsch hydriding of carbonyls. Few chemical reactions of metal nitrides have been studied; the most characteristic (often extremely slow but occasionally rapid) is hydrolysis to give ammonia or nitrogen:

$$2AlN + (n+3)H_2O \longrightarrow Al_2O_3.nH_2O + 2NH_3$$

$$2VN + 3H_2SO_4 \longrightarrow V_2(SO_4)_3 + N_2 + 3H_2$$

The crystal chemistry of metal nitrides has been reviewed(45a) and there have recently been some intriguing developments in our understanding of the stoichiometries and structures of ternary and quaternary metal nitrides.(45b)

The nitride ion N^{3-} is an excellent ligand, particularly towards second- and third-row transition metals.(46) It is considered to be by far the strongest π donor known, the next strongest being the isoelectronic species O^{2-}. Nitrido complexes are usually prepared by the thermal decomposition of azides (e.g. those of phosphine complexes of V^V, Mo^{VI}, W^{VI}, Ru^{VI}, Re^V) or by deprotonation of NH_3 (e.g. $[OsO_4 \rightarrow OsO_3N]^-$). Most involve a terminal $\{\equiv N\}^{3-}$ group as in $[VCl_3N]^-$, $[MoO_3N]^-$, $[WCl_5N]^{2-}$, $[ReN(PR_3)_3X_2]$ and $[RuN(OH_2)X_4]^-$. The M–N distance is much shorter (by 40–50 pm) than the "normal" σ-(M–N) distance, consistent with strong multiple bonding. Other bonding modes feature linear symmetrical bridging as in $[(H_2O)Cl_4Ru{-}N{-}RuCl_4(OH_2)]^{3-}$, trigonal planar μ_3 bridging as in $[\{(H_2O)(SO_4)_2Ir\}_3N]^{4-}$, and tetrahedral coordination as in $[(MeHg)_4N]^+$ (Fig. 11.3). The nitrido ligand has a strong *trans* influence, e.g. in $[Os^{VI}NCl_5]^{2-}$ (p. 1085); likewise, in the octahedral complex. $[Tc^VNCl_2(PMe_2Ph)_3]$, the Tc–Cl distance *trans* to N is 266.5 pm whereas that *cis* to N is only 244.1 pm.(47)

Azidotrifluoromethylmethane, CF_3N_3, (mp −152°, bp −285°) is a colourless gas which is thermally stable at room temperature. It can be prepared in 90% yield by reacting CF_3NO with hydrazine in MeOH at −78° and then treating the product with HCl gas.(48)

$$CF_3NO + H_2NNH_2 \longrightarrow CF_3{-}N{=}NNH_2 \longrightarrow CF_3NNN$$

The molecule has an almost linear N_3 group and an angle C–N–N of 112.4° (Fig. 11.4a).(49) The (linear) azide ion, N_3^-, is isoelectronic with N_2O, CO_2, OCN^-, etc. and forms numerous coordination complexes by standard ligand replacement reactions. Various coordination modes have been established, including end-on η^1, bridging

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[45] K. H. Jack, *Trans. J. Br. Ceram. Soc.* **72**, 376–84 (1973). F. L. Riley (ed.), *Nitrogen Ceramics*, Noordhoff-Leyden, 1977, 694 pp.

[45a] N. E. Brese and M. O'Keefe, *Structure and Bonding*, **79**, 307–78 (1992).

[45b] R. Kniep, *Pure Appl. Chem.* **69**, 185–91 (1997).

[46] W. P. Griffith, *Coord. Chem. Revs.* **8**, 369–96 (1972).

[47] A. S. Batsanov, Yu. T. Struchkov, B. Lorenz and B. Olk, *Z. anorg. allg. Chem.* **564**, 129–34 (1988).

[48] K. O. Christe, and C. J. Schack, *Inorg. Chem.* **20**, 2566–70 (1981).

[49] K. O. Christe, D. Christen, H. Oberhammer and C. J. Schack, *Inorg. Chem.* **23**, 4283–8 (1984).

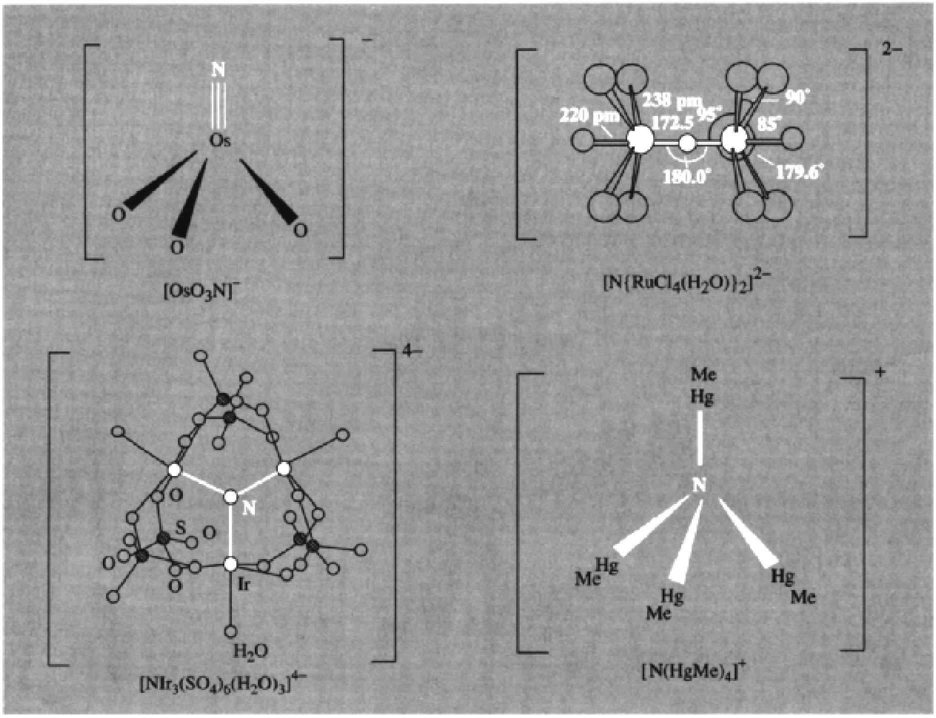


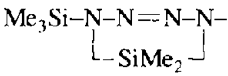
Figure 11.3 Structures of some nitrido complexes.(24)

μ,η^1 and bridging $\mu,\eta^1{:}\eta^1$ (Fig. 11.4).(50,51) The binuclear complex $[Mo_2Cl_2N_{20}]^{2-}$ features a terminal nitrido ligand, N≡⁻, as well as terminal and bridging azido ligands, i.e. $[\{(MoCl(N)(\eta^1\text{-}N_3)_2(\mu,\eta^1\text{-}N_3)\}_2]^2$.(52)

Concatenations larger than N_3 are rare. The planar bridging $N_4{}^{4-}$ occurs in the binuclear W^{VI} dianion, $[Cl_5W(\mu,\eta^1{:}\eta^1\text{-}N_4)WCl_5]^{2-}$; this is formed during the thermolytic interconversion of $[W(N_3)Cl_5]$ to the corresponding nitrido complex $WNCl_3$ in the presence of Ph_4AsCl, the nitride reacting as it is formed with unreacted azide still present according to the simple stoichiometry:(53)

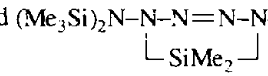
$$2Ph_4AsCl + WNCl_3 + W(N_3)Cl_5 \longrightarrow [Ph_4AsCl]_2[Cl_5W(\mu\text{-}N_4)WCl_5]$$

It will be noted that $N_4{}^{4-}$ is isosteric with the tetradeprotonated urea molecule, $(H_2N)_2C{=}O$, and is also isoelectronic and isostructural with $CO_3{}^{2}$ and $NO_3{}^-$. An X-ray analysis of the red single crystals shows that N(central)-N_μ is long (149 pm) and that N(central)-N_t is short (123 pm). Unbranched N-catenation is observed in 2-tetrazenes such as $(Me_3Si)_2N\text{-}N{=}N\text{-}N(SiMe_3)_2$ (mp 46°) and its derivatives, e.g.



$$Me_3Si\text{-}\underbrace{N\text{-}N{=}N\text{-}N}_{SiMe_2}\text{-}N(SiMe_3)_2 \qquad (\text{mp } 40°)$$

and



$$(Me_3Si)_2N\text{-}\underbrace{N\text{-}N{=}N\text{-}N}_{SiMe_2}\text{-}N(SiMe_3)_2$$ (54)

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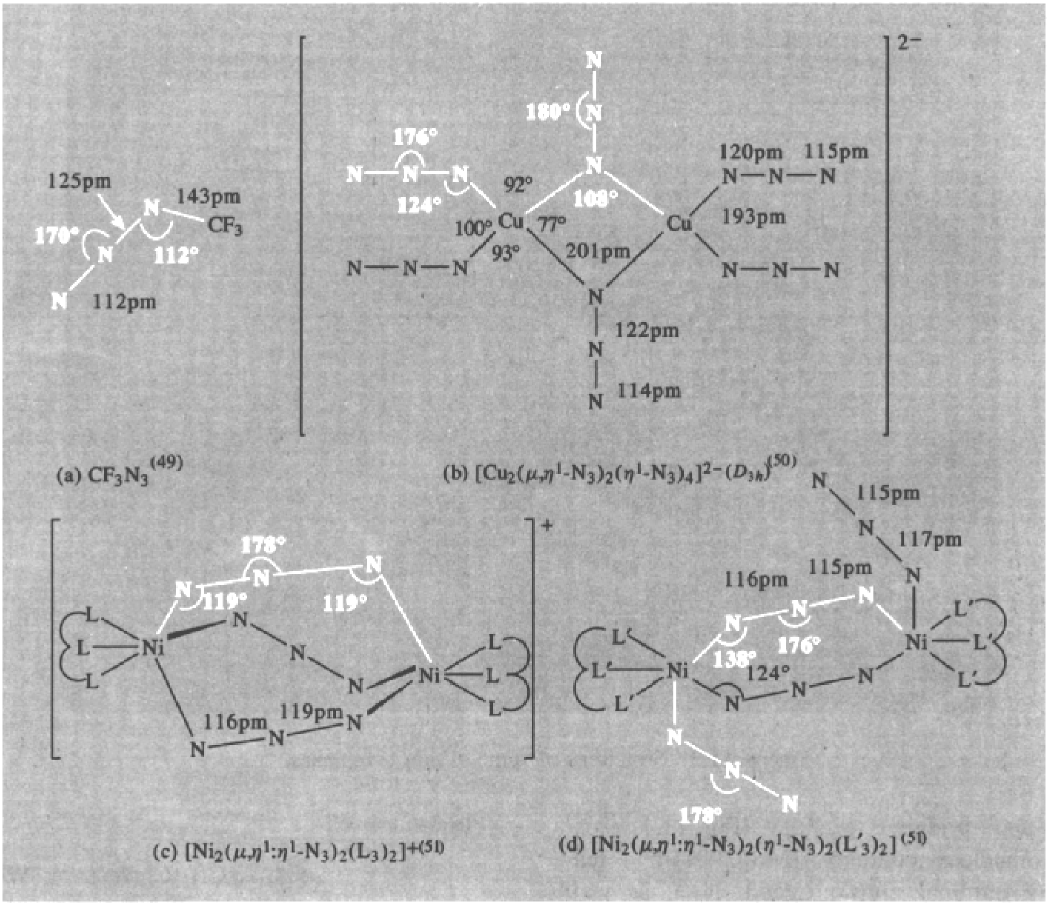
[50] D. Fenske, K. Steiner and K. Dehnicke, *Z. anorg. allg. Chem.* **553**, 57-63 (1987).

[51] P. Chaudhuri, M. Guttmann, D. Ventur, K. Wieghardt, B. Nuber and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1618-20 (1985).

[52] K. Jansen, J. Schmitte and K. Dehnicke, *Z. anorg. allg. Chem.* **552**, 201-9 (1987).

[53] W. Massa, R. Kujanek, G. Baum and K. Dehnicke, *Angew. Chem. Int. Edn. Engl.* **23**, 149 (1984).

[54] N. Wiberg and G. Ziegleder, *Chem. Ber.* **111**, 2123-9 (1978).



(a) CF_3N_3 (49)

(b) $[Cu_2(\mu,\eta^1\text{-}N_3)_2(\eta^1\text{-}N_3)_4]^{2-}(D_{3h})$ (50)

(c) $[Ni_2(\mu,\eta^1{:}\eta^1\text{-}N_3)_2(L_3)_2]^{+}$ (51)

(d) $[Ni_2(\mu,\eta^1{:}\eta^1\text{-}N_3)_2(\eta^1\text{-}N_3)_2(L'_3)_2]$ (51)

Figure 11.4 Structures of some azido complexes.

11.3.2 Ammonia and ammonium salts

NH_3 is a colourless, alkaline gas with a unique, penetrating odour that is first perceptible at concentrations of about 20–50 ppm. Noticeable irritation to eyes and the nasal passages begins at about 100–200 ppm, and higher concentrations can be dangerous.(55) NH_3 is prepared industrially in larger amounts (number of moles) than any other single compound (p. 407) and the production of synthetic ammonia is of major importance for several industries (see Panel).

In the laboratory NH_3 is usually obtained from cylinders unless isotopically enriched species such as $^{15}NH_3$ or ND_3 are required. Pure dry $^{15}NH_3$ can be prepared by treating an enriched $^{15}NH_4{}^+$ salt with an excess of KOH and drying the product gas over metallic Na. Reduction of $^{15}NO_3{}^-$ or $^{15}NO_2{}^-$ with Devarda's alloy (50% Cu, 45% Al, 5% Zn) in alkaline solution provides an alternative route as does the hydrolysis of a nitride, e.g.:

$$3Ca + {}^{15}N_2 \longrightarrow Ca_3{}^{15}N_2 \xrightarrow{6H_2O} 2{}^{15}NH_3 + 3Ca(OH)_2$$

ND_3 can be prepared similarly using D_2O, e.g.:

$$Mg_3N_2 + 6D_2O \longrightarrow 2ND_3 + 3Mg(OD)_2$$

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[55] T. A. Czuppon, S. A. Knez and J. M. Rovner, Ammonia, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 2, pp. 638–91, Wiley, New York, 1992

Industrial Production of Synthetic Ammonia(55–57)

The first industrial production of NH_3 began in 1913 at the BASF works in Ludwigshaven-Oppau, Germany. The plant, which had a design capacity of 30 tonnes per day, involved an entirely new concept in process technology; it was based on the Haber-Bosch high-pressure catalytic reduction of N_2 with H_2 obtained by electrolysis of water. Modern methods employ the same principles for the final synthesis but differ markedly in the source of hydrogen, the efficiency of the catalysts, and the scale of operations, many plants now having a capacity of 1650 tonnes per day or more. Great ingenuity has been shown not only in plant development but also in the application of fundamental thermodynamics to the selection of feasible chemical processes. Except where electricity is unusually cheap, reduction by electrolytic hydrogen has now been replaced either by coke/H_2O or, more recently, by natural gas (essentially CH_4) or naphtha (a volatile aliphatic petrol-like fraction of crude oil). The great advantages of modern hydrocarbon reduction methods over coal-based processes are that, comparing plant of similar capital costs, they occupy one-third the land area, use half the energy, and require one-tenth the manpower, yet produce 4 times the annual tonnage of NH_3.

The operation of a large synthetic ammonia plant based on natural gas involves a delicately balanced sequence of reactions. The gas is first *desulfurized* to remove compounds which will poison the metal catalysts, then compressed to ~30 atm and reacted with steam over a nickel catalyst at 750°C in the *primary steam reformer* to produce H_2 and oxides of carbon:

$$CH_4 + H_2O \xrightleftharpoons{\text{Ni/750}^\circ} CO + 3H_2; \quad CH_4 + 2H_2O \xrightleftharpoons{\text{Ni/750}^\circ} CO_2 + 4H_2$$

Under these conditions the issuing gases contain some 9% of unreacted methane; sufficient air is injected via a compressor to give a final composition of 1 : 3 N_2 : H_2 and the air burns in the hydrogen thereby heating the gas to ~1100°C in the *secondary reformer:*

$$2H_2 + \underset{\text{air}}{(O_2 + 4N_2)} \xrightleftharpoons{1100^\circ} 2H_2O + 4N_2; \quad CH_4 + H_2O \xrightleftharpoons{\text{Ni/1000}^\circ} CO + 3H_2$$

The emerging gas, now containing only 0.25% CH_4, is cooled in heat exchangers which generate high-pressure steam for use first in the turbine compressors and then as a reactant in the primary steam reformer. Next, the CO is converted to CO_2 by the *shift reaction* which also produces more H_2:

$$CO + H_2O \xrightleftharpoons{\text{(a) + (b)}} CO_2 + H_2$$

Maximum conversion occurs by equilibration at the lowest possible temperature so the reaction is carried out sequentially on two beds of catalyst: (a) iron oxide (400°C) which reduces the CO concentration from 11% to 3%; (b) a copper catalyst (200°) which reduces the CO content to 0.3%. Removal of CO_2 (~18%) is effected in a *scrubber* containing either a concentrated alkaline solution of K_2CO_3 or an amine such as ethanolamine:

$$CO_2 + H_2O + K_2CO_3 \xrightleftharpoons[\text{regeneration (heat)}]{\text{absorption}} 2KHCO_3$$

Remaining trace quantities of CO (which would poison the iron catalyst during ammonia synthesis) are converted back to CH_4 by passing the damp gas from the scrubbers over a Ni *methanation catalyst* at 325°: $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$. This reaction is the reverse of that occurring in the primary steam reformer. The *synthesis gas* now emerging has the approximate composition H_2 74.3%, N_2 24.7%, CH_4 0.8%, Ar 0.3%, CO 1–2 ppm. It is *compressed* in three stages from 25 atm to ~200 atm and then passed over a *promoted iron catalyst* at 380–450°C:

$$N_2 + 3H_2 \xrightleftharpoons{\text{Fe/400}^\circ\text{/200 atm}} .2NH_3$$

The gas leaving the catalyst beds contains about 15% NH_3; this is condensed by refrigeration and the remaining gas mixed with more incoming synthesis gas and recycled. Variables in the final reaction are the synthesis pressure,

Panel continues

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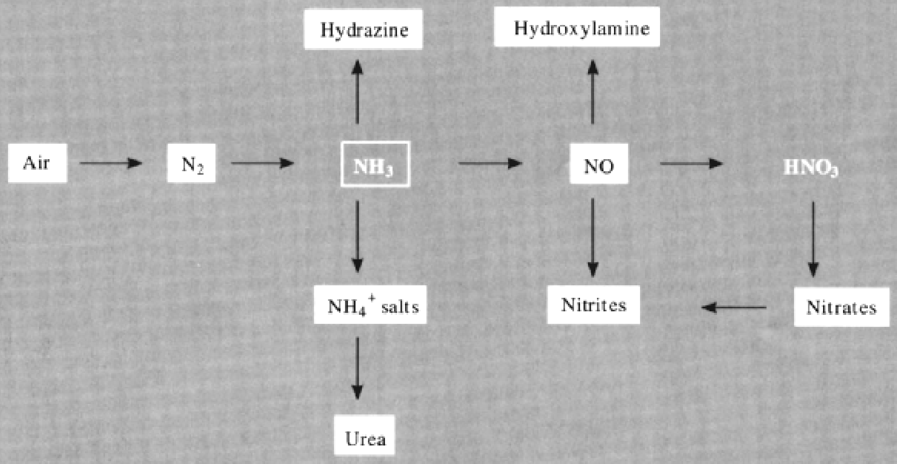
[56] S. P. S. Andrew, in R. Thompson (ed.), *The Modern Inorganic Chemicals Industry*, pp. 201–31, The Chemical Society, London, 1977.

[57] S. D. Lyon, *Chem. Ind.* 731–9 (1975).

synthesis temperature, gas composition, gas flow rate[†] and catalyst composition and particle size. Since the earliest days the "promoted" Fe catalysts have been prepared by fusing magnetite (Fe_3O_4) on a table with KOH in the presence of a small amount of mixed refractory oxides such as MgO, Al_2O_3 and SiO_2; the solidified sheet is broken up into chunks 5–10 mm in size. These chunks are then reduced inside the ammonia synthesis converter to give the active catalyst which consists of Fe crystallites separated by the amorphous refractory oxides and partly covered by the alkali promotor which increases its activity by at least an order of magnitude.

World production of synthetic ammonia has increased dramatically particularly during the period 1950–80. Production in 1950 was little more than 1 million tonnes; though this was huge when compared with the production of most other compounds, it is dwarfed by today's rate of production which exceeds 120 million tonnes pa. In 1990 world production capacity was 119.6 million tonnes distributed as follows: Asia 35.4%, the former Soviet Union 21.5%, North America 13.8%, Western Europe 11.3%, Eastern Europe 9.7% Latin America 5.3%, Africa 3.0%. The price of NH_3 (FOB Gulf Coast plants, USA) was $107/tonne in 1990.

The applications of NH_3 are dominated (over 85%) by its use in various forms as a fertilizer. Of these, direct application is the most common (28.7%), followed by urea (22.4%), NH_4NO_3 (15.8%), ammonium phosphates (14.6%), and $(NH_4)_2SO_4$ (3.4%). Industrial uses include (a) commercial explosives — such as NH_4NO_3, nitroglycerine, TNT and nitrocellulose, which are produced from NH_3 via HNO_3 — and (b) fibres/plastics e.g. in the manufacture of caprolactam for nylon-6, hexamethylenediamine for nylon-6,6, polyamides, rayon and polyurethanes. Other uses include a wide variety of applications in refrigeration, wood pulping, detinning of scrap-metal and corrosion inhibition; it is also used as a rubber stabilizer, pH controller, in the manufacture of household detergents, in the food and beverage industry, pharmaceuticals, water purification and the manufacture of numerous organic and inorganic chemicals. Indeed, synthetic ammonia is the key to the industrial production of most inorganic nitrogen compounds, as indicated in the subjoined Scheme.



[†] Flow rate is usually quoted as "space velocity", i.e. the ratio of volumetric rate of gas at STP to volume of catalyst; typical values are in the range 8000–60 000 h^{-1}.

The chemical fixation of N_2 to NH_3 under less extreme conditions than those used industrially is a continuing area of active research and considerable progress has been made in elucidating mechanisms involving N_2 coordinated to Mo, W, V and other centres.(5,6,58–63)

Some physical and molecular properties of NH_3 are in Table 11.2. The influence of H

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[58] T. A. George and R. C. Tisdale, *J. Am. Chem. Soc.* **107**, 5157–9 (1985).

[59] K. Alka, *Angew. Chem. Int. Edn. Engl.* **25**, 558–9 (1986).

[60] R. L. Richards, *Chem. in Britain*, Feb. 1988, pp. 133–6.

[61] M. Y. Mohammed and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1119–21 (1988).

[62] R. R. Eady, *Polyhedron* **8**, 1695–1700 (1989).

[63] G. J. Leigh, R. Prieto-Alcón and J. R. Sanders, *J. Chem. Soc., Chem. Commun.*, 921–2 (1991).

Table 11.2 Some properties of ammonia, NH_3

Physical properties		Molecular properties	
MP/K	195.42	Symmetry	C_{3v} (pyramidal)
BP/K	239.74	Distance (N–H)/pm	101.7
Density(l; 239 K)/g cm^{-3}	0.6826	Angle H–N–H	107.8°
Density(g; rel. air = 1)	0.5963	Pyramid height/pm	36.7
η(239.5 K)/centipoise[(a)]	0.254	μ/Debye[(b)]	1.46
Dielectric constant ε(239 K)	22	Inversion barrier kJ mol^{-1}	24.7
κ(234.3 K)/ohm^{-1} cm^{-1}	1.97×10^{-7}	Inversion frequency/GHz[(c)]	23.79
ΔH_f°(298 K)/kJ mol^{-1}	−46.1	D(H–NH_2)/kJ mol^{-1}	435
ΔG_f°(298 K)/kJ mol^{-1}	−16.5	Ionization energy/kJ mol^{-1}	979.7
S°(298 K)/J K^{-1} mol^{-1}	192.3	Proton affinity (gas)/kJ mol^{-1}	841

(a) 1 centipoise = 10^{-3} kg m^{-1} s^{-1}. (b) 1 Debye = 10^{-18} esu = $3.335\ 64\times10^{-30}$ C m. (c) 1 GHz = 10^9 s^{-1}.

bonding on the bp and other properties has already been noted (p. 53). It has been estimated that 26% of the H bonding in NH_3 breaks down on melting, 7% on warming from the mp to the bp, and the final 67% on transfer to the gas phase at the bp. The low density, viscosity and electrical conductivity, and the high dielectric constant of liquid ammonia are also notable. Liquid NH_3 is an excellent solvent and a valuable medium for chemical reactions (p. 424); its high heat of vaporization (23.35 kJ mol^{-1} at the bp) makes it relatively easy to handle in simple vacuum flasks. The molecular properties call for little comment except to note that the rapid inversion frequency with which the N atom moves through the plane of the 3 H atoms has a marked effect on the vibrational spectrum of the molecule. The inversion itself occurs in the microwave region of the spectrum at 23.79 GHz (corresponding to a wavelength of 1.260 cm) and was, in fact, the first microwave absorption spectrum to be detected (C. E. Cleeton and N. H. Williams, 1934). The associated energy ($hc\bar{\nu}$) is 0.7935 cm^{-1} i.e. 9.49 J mol^{-1}. Inversion also occurs in ND_3 at a frequency of 1.591 GHz, i.e. less than for NH_3 by a factor of 14.95. The inversion can be stopped in NH_3 by increasing the pressure to ~2 atm. The corresponding figure for ND_3 is ~90 mmHg (i.e. again a factor of about 15).

Ammonia is readily absorbed by H_2O with considerable evolution of heat (~37.1 kJ per mol of NH_3 gas). Aqueous solutions are weakly basic due to the equilibrium

$$NH_3(aq) + H_2O \overset{H_2O}{\rightleftharpoons} NH_4{}^+(aq) + OH^-(aq);$$

$$K_{298.2} = [NH_4{}^+][OH^-]/[NH_3] = 1.81\times10^{-5}\ \text{mol l}^{-1}$$

The equilibrium constant at room temperature corresponds to $pK_b = 4.74$ and implies that a 1 molar aqueous solution of NH_3 contains only 4.25 mmol l^{-1} of $NH_4{}^+$ (or OH^-). Such solutions do not contain the undissociated "molecule" NH_4OH, though weakly bonded hydrates have been isolated at low temperature:

$NH_3.H_2O$ (mp 194.15 K) and $2NH_3.H_2O$ (mp 194.32 K)

These hydrates are not ionically dissociated but contain chains of H_2O molecules cross-linked by NH_3 molecules into a three-dimensional H-bonded network.

Ammonia burns in air with difficulty, the flammable limits being 16–25 vol%. Normal combustion yields nitrogen but, in the presence of a Pt or Pt/Rh catalyst at 750–900°C, the reaction proceeds further to give the thermodynamically less-favoured products NO and NO_2:

$$4NH_3 + 3O_2 \xrightarrow{\text{burn}} 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 \xrightarrow{\text{Pt/800}^\circ} 4NO + 6H_2O$$

$$2NO + O_2 \xrightarrow{\text{Pt/800}^\circ} 2NO_2$$

These reactions are very important industrially in the production of HNO_3 (p. 466). See also the industrial production of HCN by the Andrussov process (p. 321): $2NH_3 + 3O_2 + 2CH_4 \longrightarrow 2HCN + 6H_2O$.

Gaseous NH_3 burns with a greenish-yellow flame in F_2 (or ClF_3) to produce NF_3 (p. 439). Chlorine yields several products depending on conditions: NH_4Cl, NH_2Cl, $NHCl_2$, NCl_3, $NCl_3.NH_3$, N_2 and even small amounts of N_2H_4. The reaction to give chloramine, NH_2Cl, is important in urban and domestic water purification systems. Reactions with other nonmetals and their halides or oxides are equally complex and lead to a variety of compounds, many of which are treated elsewhere (pp. 497, 501, 506, 535, 723, etc.). At red heat carbon reacts with NH_3 to give $NH_4CN + H_2$, whereas phosphorus yields PH_3 and N_2, and sulfur gives H_2S and N_4S_4. Metals frequently react at higher temperature to give nitrides (p. 417). Of particular importance is the attack on Cu in the presence of oxygen (air) at room temperature since this precludes the use of this metal and its alloys in piping and valves for handling either liquid or gaseous NH_3. Corrosion of Cu and brass by moist NH_3/air mixtures and by air-saturated aqueous solutions of NH_3 is also rapid. Contact with Ni and with polyvinylchloride plastics should be avoided for the same reason.

Liquid ammonia as a solvent[64–67]

Liquid ammonia is the best-known and most widely studied non-aqueous ionizing solvent. Its most conspicuous property is its ability to dissolve alkali metals to form highly coloured, electrically conducting solutions containing solvated electrons, and the intriguing physical properties and synthetic utility of these solutions have already been discussed (p. 77). Apart from these remarkable solutions, much of the chemistry in liquid ammonia can be classified by analogy with related reactions in aqueous solutions. Accordingly, we briefly consider in turn, solubility relationships, metathesis reactions, acid-base reactions, amphoterism, solvates and solvolysis, redox reactions and the preparation of compounds in unusual oxidation states. Comparison of the physical properties of liquid NH_3 (p. 423) with those of water (p. 623) shows that NH_3 has the lower mp, bp, density, viscosity, dielectric constant and electrical conductivity; this is due at least in part to the weaker H bonding in NH_3 and the fact that such bonding cannot form cross-linked networks since each NH_3 molecule has only 1 lone-pair of electrons compared with 2 for each H_2O molecule. The ionic self-dissociation constant of liquid NH_3 at $-50°C$ is $\sim 10^{-33}\,mol^2\,l^{-2}$.

Most ammonium salts are freely soluble in liquid NH_3 as are many nitrates, nitrites, cyanides and thiocyanates. The solubilities of halides tend to increase from the fluoride to the iodide; solubilities of salts of multivalent ions are generally low suggesting that (as in aqueous systems) lattice-energy and entropy effects outweigh solvation energies. The possibility of H-bond formation also influences solubility and, in the case of NH_4I, an X-ray single-crystal analysis of the monosolvate shows the presence of an H-bonded cation $N_2H_7^+$ with an $N-H\cdots N$ distance of 269 ± 5 pm.[68] Some typical solubilities at 25°C expressed as g per 100 g solvent are: NH_4OAc 253.2, NH_4NO_3 389.6, $LiNO_3$ 243.7, $NaNO_3$ 97.6, KNO_3 10.4, NaF 0.35, NaCl 3.0, NaBr 138.0, NaI 161.9, NaSCN 205.5. Some of these solubilities are astonishingly high, particularly when expressed as the number of moles of solute per 10 mol

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[64] W. L. JOLLY and C. J. HALLADA, Chap. 1 in T. C. WADDINGTON (ed.), *Non-Aqueous Solvent Systems*, pp. 1–45, Academic Press, London. 1965.

[65] G. W. A. FOWLES, Chap. 7, in C. B. COLBURN (ed.), *Developments in Inorganic Nitrogen Chemistry*, pp. 522–76, Elsevier, Amsterdam, 1966.

[66] J. J. LAGOWSKI and G. A. MOCZYGEMBA, Chap. 7 in J. J. LAGOWSKI (ed.), *The Chemistry of Non-aqueous Solvents*, Vol. 2, pp. 320–71, Academic Press, 1967.

[67] D. NICHOLLS, *Inorganic Chemistry in Liquid Ammonia: Topics in Inorganic and General Chemistry*, Monograph 17, Elsevier, Amsterdam, 1979, 238 pp.

[68] H. J. BERTHOLD, W. PREIBSCH and E. VONHOLDT, *Angew. Chem. Int. Edn. Engl.* **27**, 1524–5 (1988).

NH_3, e.g.: NH_4NO_3 8.3, $LiNO_3$ 6.1, NaSCN 4.3. Further data at 25° and other temperatures are in ref. 69.

Metathesis reactions are sometimes the reverse of those in aqueous systems because of the differing solubility relations. For example because AgBr forms the complex ion $[Ag(NH_3)_2]^+$ in liquid NH_3 it is readily soluble, whereas $BaBr_2$ is not, and can be precipitated:

$$Ba(NO_3)_2 + 2AgBr \xrightarrow{\text{liq } NH_3} BaBr_2\downarrow + 2AgNO_3$$

Reactions analogous to the precipitation of AgOH and of insoluble oxides from aqueous solution are:

$$AgNO_3 + KNH_2 \xrightarrow{\text{liq } NH_3} AgNH_2\downarrow + KNO_3$$

$$3HgI_2 + 6KNH_2 \xrightarrow{\text{liq } NH_3} Hg_3N_2\downarrow + 6KI + 4NH_3$$

Acid-base reactions in many solvent systems can be thought of in terms of the characteristic cations and anions of the solvent (see also p. 831)

$$\text{solvent} \rightleftharpoons \text{characteristic cation (acid)} + \text{characteristic anion (base)}$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$2NH_3 \rightleftharpoons NH_4{}^+ + NH_2{}^-$$

On this basis $NH_4{}^+$ salts can be considered as solvo-acids in liquid NH_3 and amides as solvo-bases. Neutralization reactions can be followed conductimetrically, potentiometrically or even with coloured indicators such as phenolphthalein:

$$\underset{\text{solvo-acid}}{NH_4NO_3} + \underset{\text{solvo-base}}{KNH_2} \xrightarrow{\text{liq } NH_3} \underset{\text{salt}}{KNO_3} + \underset{\text{solvent}}{2NH_3}$$

Likewise, amphoteric behaviour can be observed. For example $Zn(NH_2)_2$ is insoluble in liquid NH_3 (as is $Zn(OH)_2$ in H_2O), but it dissolves on addition of the solvo-base KNH_2 due to the formation of $K_2[Zn(NH_2)_4]$; this in turn is decomposed by $NH_4{}^+$ salts (solvo-acids) with reprecipitation of the amide:

$$K_2[Zn(NH_2)_4] + 2NH_4NO_3 \xrightarrow{\text{liq } NH_3} Zn(NH_2)_2 + 2KNO_3 + 4NH_3$$

Solvates are perhaps less prevalent in compounds prepared from liquid ammonia solutions than are hydrates precipitated from aqueous systems, but large numbers of ammines are known, and their study formed the basis of Werner's theory of coordination compounds (1891–5). Frequently, however, solvolysis (ammonolysis) occurs (cf. hydrolysis).(65) Examples are:

$$M^IH + NH_3 \longrightarrow MNH_2 + H_2$$

$$M^I_2O + NH_3 \longrightarrow MNH_2 + MOH$$

$$SiCl_4 \xrightarrow[\text{temp}]{\text{low}} [Si(NH_2)_4] \xrightarrow{0^\circ} Si(NH)(NH_2)_2 \xrightarrow{1200^\circ} Si_3N_4$$

Amides are one of the most prolific classes of ligand and the subject of metal and metalloid amides has been extensively reviewed.(70)

Redox reactions are particularly instructive. If all thermodynamically allowed reactions in liquid NH_3 were kinetically rapid, then no oxidizing agent more powerful than N_2 and no reducing agent more powerful than H_2 could exist in this solvent. Using data for solutions at 25°:(64)

Acid solutions (1 M $NH_4{}^+$)

$$NH_4{}^+ + e^- = NH_3 + \tfrac{1}{2}H_2 \qquad E^\circ = 0.0\text{ V}$$

$$3NH_4{}^+ + \tfrac{1}{2}N_2 + 3e^- = 4NH_3 \qquad E^\circ = -0.04\text{ V}$$

Basic solutions (1 M $NH_2{}^-$)

$$NH_3 + e^- = NH_2{}^- + \tfrac{1}{2}H_2 \qquad E^\circ = 1.59\text{ V}$$

$$2NH_3 + \tfrac{1}{2}N_2 + 3e^- = 3NH_2{}^- \qquad E^\circ = 1.55\text{ V}$$

Obviously, with a range of only 0.04 V available very few species are thermodynamically stable. However, both the hydrogen couple and the nitrogen couple usually exhibit "overvoltages" of ~1 V, so that in acid solutions the practical range of potentials for solutes is from +1.0 to −1.0 V. Similarly in basic solutions the practical range

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[69] K. JONES, Nitrogen, Chap. 19 in *Comprehensive Inorganic Chemistry* Vol. 2, pp. 147–388, Pergamon Press, Oxford, 1973.

[70] M. F. LAPPERT, P. P. POWER, A. R. SANGER and R. C. SRIVASTAVA, *Metal and Metalloid Amides*, Ellis Horwood Ltd., Chichester, 1980, 847 pp. (approximately 3000 references).

extends from 2.6 to 0.6 V. It is thus possible to work in liquid ammonia with species which are extremely strong reducing agents (e.g. alkali metals) and also with extremely strong oxidizing agents (e.g. permanganates, superoxides and ozonides; p. 609). For similar reasons the NO_3^- ion is effectively inert towards NH_3 in acid solution but in alkaline solutions N_2 is slowly evolved:

$$3K^+ + 3NH_2^- + 3NO_3^- \longrightarrow 3KOH\downarrow + N_2 + 3NO_2^- + NH_3$$

The use of liquid NH_3 to prepare compounds of elements in unusual (low) oxidation states is exemplified by the successive reduction of $K_2[Ni(CN)_4]$ with Na/Hg in the presence of an excess of CN^-: the dark-red dimeric Ni^I complex $K_4[Ni_2(CN)_6]$ is first formed and this can be further reduced to the yellow Ni^0 complex $K_4[Ni(CN)_4]$. The corresponding complexes $[Pd(CN)_4]^{4-}$ and $[Pt(CN)_4]^{4-}$ can be prepared similarly, though there is no evidence in these latter systems for the formation of the M^I dimer. A ditertiaryphosphine complex of Pd^0 has also been prepared:

$$[Pd\{1,2\text{-}(PEt_2)_2C_6H_4\}_2]Br_2 \xrightarrow{Na/NH_3} [Pd\{1,2\text{-}(PEt_2)_2C_6H_4\}_2] + 2NaBr$$

$[Co^{III}(CN)_6]^{3-}$ yields the pale-yellow complex $[Co^I(CN)_4]^{3-}$ and the brown-violet complex $[Co_2^0(CN)_8]^{8-}$ (cf. the dimeric carbonyl $[Co_2(CO)_8]$).

Liquid NH_3 is also extensively used as a preparative medium for compounds which are unstable in aqueous solutions, e.g.:

$$2Ph_3GeNa + Br(CH_2)_xBr \xrightarrow{\text{liq } NH_3} Ph_3Ge(CH_2)_xGePh_3 + 2NaBr$$

$$Me_3SnX + NaPEt_2 \xrightarrow{\text{liq } NH_3} Me_3SnPEt_2 + 2NaX$$

Alkali metal acetylides M_2C_2, MCCH and MCCR can readily be prepared by passing C_2H_2 or C_2HR into solutions of the alkali metal in liquid NH_3, and these can be used to synthesize a wide range of transition-element acetylides,$^{(71)}$ e.g.:

$$Ni(SCN)_2.6NH_3 + 5KC_2Ph \xrightarrow{\text{liq } NH_3} K_2[Ni(C_2Ph)_4].2NH_3 + 2KSCN + 4NH_3$$

$$K_2[Ni(C_2Ph)_4].2NH_3 \xrightarrow{\text{vac}} \underset{\text{yellow}}{K_2[Ni^{II}(C_2Ph)_4]} + 2NH_3$$

Other examples are orange-red $K_3[Cr^{III}(C_2H)_6]$, rose-pink $Na_2[Mn^{II}(C_2Me)_4]$, dark-green $Na_4[Co^{II}(C_2Me)_6]$, orange $K_4[Ni^0(C_2H)_4]$, yellow $K_6[Ni_2^I(C_2Ph)_6]$. Such compounds are often explosive, though the analogues of Cu^I and Zn^{II} are not, e.g. yellow $Na[Cu(C_2Me)_2]$, colourless $K_2[Cu(C_2H)_3]$, and colourless $K_2[Zn(C_2H)_4]$.

Ammonium halides have been used as versatile reagents in low-temperature solid-state redox and acid-base reactions.$^{(72)}$ For example, direct reaction with the appropriate metal at 270–300° yields the ammonium salts of $ZnCl_4^{2-}$, $LaCl_5^{2-}$, YCl_6^{3-}, YBr_6^{3-}, $CuCl_3^{2-}$, etc., whereas Y_2O_3 yields either $(NH_4)_3YBr_6$ or YOBr depending on the stoichiometric ratio of the reagents. Solid-state reactions of ammonium sulfate, nitrate, phosphates and carbonate have also been studied.

11.3.3 Other hydrides of nitrogen

Nitrogen forms more than 20 binary compounds with hydrogen$^{(73)}$ of which ammonia (NH_3, p. 420), hydrazine (N_2H_4, p. 427) and hydrogen azide (N_3H, p. 432) are by far the most important. Hydroxylamine, $NH_2(OH)$, is closely related in structure and properties to both ammonia, $NH_2(H)$, and hydrazine, $NH_2(NH_2)$ and it will be convenient to discuss this compound in the present section also (p. 431). Several protonated cationic species such as NH_4^+, $N_2H_5^+$, etc, and deprotonated anionic species such as NH_2^-, $N_2H_3^-$, etc. also exist but ammonium hydride, NH_5, is unknown. Among

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(71) R. NAST and coworkers; for summary of results and detailed refs., see pp. 568–71 of ref. 65.

(72) G. MEYER, T. STAFFEL, S. DÖTSCH and T. SCHLEID, *Inorg. Chem.* **24**, 3504–5 (1985).

(73) *Gmelin Handbook of Inorganic and Organometallic Chemistry*, 8th Edition, Nitrogen, Supplement B1, 280 pp., Supplement B2, 188 pp., Springer Verlag, Berlin, 1993.

Table 11.3 Some physical and thermochemical properties of hydrazine

MP/°C	2.0	Dielectric constant $\varepsilon(25°)$	51.7
BP/°C	113.5	$\kappa(25°)/\text{ohm}^{-1}\ \text{cm}^{-1}$	$\sim 2.5\times 10^{-6}$
Density/(solid at $-5°$)/g cm^{-3}	1.146	$\Delta H_{\text{combustion}}/\text{kJ mol}^{-1}$	621.5
Density (liquid at 25°)/g cm^{-3}	1.00	$\Delta H_f^\circ(25°)/\text{kJ mol}^{-1}$	50.6
$\eta(25°)$/centipoise[(a)]	0.9	$\Delta G_f^\circ(25°)/\text{kJ mol}^{-1}$	149.2
Refractive index n_D^{25}	1.470	$S^\circ(25°)/\text{J K}^{-1}\,\text{mol}^{-1}$	121.2

[(a)] 1 centipoise = $10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1}$.

the less familiar (and less stable) neutral radicals which have been well characterized are the imidogen (NH), amidogen (NH_2), diazenyl (N_2H) and hydrazyl (N_2H_3) radicals. Such species are important in atmospheric chemistry and in combustion reactions. Of the neutral compounds the following can be mentioned:[(73)]

N_2H_2: *trans*-diazene, HN=NH (yellow), and its 1:1 isomer, $H_2N{=}N$
N_3H: hydrogen azide (p. 432) and cyclotriazene (triazairine). $\overline{N{=}N{-}N}H$
N_3H_3: triazene, $HN{=}N{-}NH_2$ and cyclotriazane (triaziridene) c-$(NH)_3$
N_3H_5: triazane (aminohydrazine), $H_2NN(H)\text{-}NH_2$
N_4H_4: *trans*-2-tetrazene, $H_2N{-}N{=}N{-}NH_2$, (colourless, low-melting crystals, N–N 143 pm, N=N 121 pm). and ammonium azide, NH_4N_3 (white crystals, subl. 133°C, *d* 1.350 g cm^{-3})
N_4H_6: tetrazane, $H_2NN(H)N(H)NH_2$, (bright yellow solid)
N_5H_5: hydrazinium azide, $N_2H_5N_3$, (explosive white crystals)
N_6H_2: Probably a cyclic dimer of N_3H
N_7H_9: hydrazinium azide monohydrazinate, $N_2H_5N_3.N_2H_4$
N_9H_3: cyclic trimer of N_3H, i.e. 1,3,5-$N_6(NH)_3$

Hydrazine[(74)]

Anhydrous N_2H_4 is a fuming, colourless liquid with a faint ammoniacal odour which is first detectable at a concentration of 70–80 ppm. Many of its physical properties (Table 11.3) are remarkably similar to those of water (p. 623); comparisons with NH_3 (p. 423) H_2O_2 (p. 634) are also instructive, and the influence of H bonding is apparent. In the gas phase four conformational isomers are conceivable (Fig. 11.5) but the large dipole (1.85 D) clearly eliminates the staggered *trans*-conformation; electron diffraction data (and infrared) indicate the *gauche*-conformation with an angle of rotation of 90–95° from the eclipsed position.

The most effective preparative routes to hydrazine are still based on the process introduced by F. Raschig in 1907: this involves the reaction of ammonia with an alkaline solution of sodium hypochlorite in the presence of gelatin or glue. The overall reaction can be written as

$$2NH_3 + NaOCl \xrightarrow{\text{aqueous alkali}} N_2H_4 + NaCl + H_2O \tag{1}$$

but it proceeds in two main steps. First there is a rapid formation of chloramine which proceeds to completion even in the cold:

$$NH_3 + OCl^- \longrightarrow NH_2Cl + OH^- \tag{2}$$

The chloramine then reacts further to produce N_2H_4 either by slow nucleophilic attack of NH_3 (3a) and subsequent rapid neutralization (3b), or by preliminary rapid formation of the chloramide ion (4a) followed by slow nucleophilic attack of NH_3 (4b):

$$NH_2Cl + NH_3 \xrightarrow{\text{slow}} N_2H_5{}^+ + Cl^- \tag{3a}$$

$$N_2H_5{}^+ + OH^- \xrightarrow{\text{fast}} N_2H_4 + H_2O \tag{3b}$$

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[74] E. W. Schmidt, *Hydrazine and its Derivatives, Preparation, Properties, Application* Wiley, Chichester, 1984, 1059 pp. (over 4400 references).

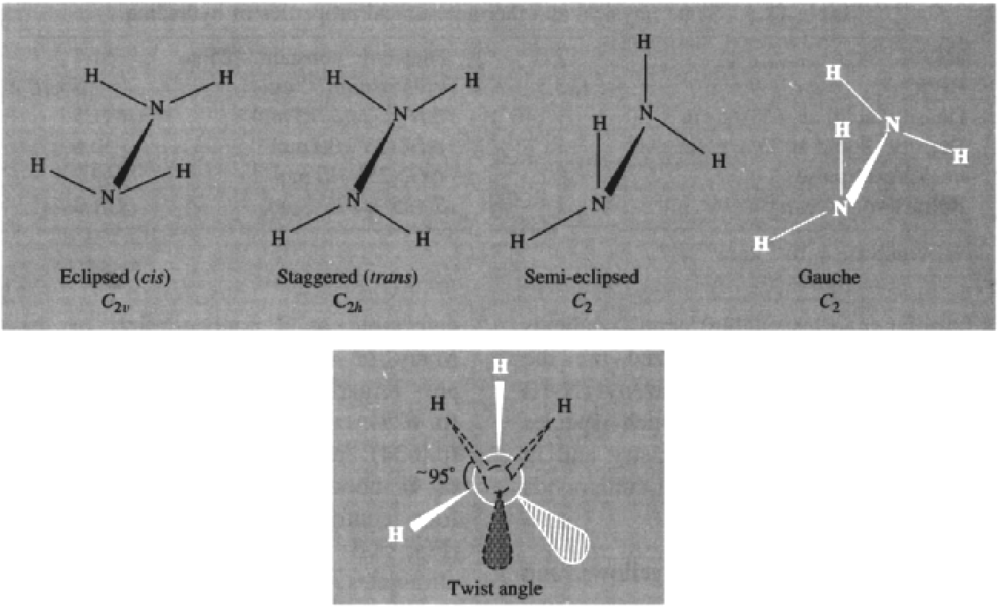

Figure 11.5 Possible conformations of N_2H_4 with pyramidal N. Hydrazine adopts the gauche C_2 form with N–N 145 pm, H–N–H 108°, and a twist angle of 95° as shown in the lower diagram.

$$NH_2Cl + OH^- \xrightarrow{\text{fast}} NHCl^- + H_2O \qquad (4a)$$

$$NHCl^- + NH_3 \xrightarrow{\text{slow}} N_2H_4 + Cl^- \qquad (4b)$$

In addition there is a further rapid but undesirable reaction with chloramine which destroys the N_2H_4 produced:

$$N_2H_4 + 2NH_2Cl \xrightarrow{\text{fast}} 2NH_4Cl + N_2 \qquad (5)$$

This reaction is catalysed by traces of heavy metal ions such as Cu^{II} and the purpose of the gelatin is to suppress reaction (5) by sequestering the metal ions; it is probable that gelatin also assists the hydrazine-forming reactions between ammonia and chloramine in a way that is not fully understood. The industrial preparation and uses of N_2H_4 are summarized in the Panel.

At room temperature, pure N_2H_4 and its aqueous solutions are kinetically stable with respect to decomposition despite the endothermic nature of the compound and its positive free energy of formation:

$$N_2(g) + 2H_2(g) \longrightarrow N_2H_4(l); \ \Delta H_f^\circ = 50.6\,\text{kJ mol}^{-1}$$
$$\Delta G_f^\circ = 149.2\,\text{kJ mol}^{-1}$$

When ignited, N_2H_4 burns rapidly and completely in air with considerable evolution of heat (see Panel):

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O;$$
$$\Delta H = -621.5\,\text{kJ mol}^{-1}$$

In solution, N_2H_4 is oxidized by a wide variety of oxidizing agents (including O_2) and it finds use as a versatile reducing agent because of the variety of reactions it can undergo. Thus the thermodynamic reducing strength of N_2H_4 depends on whether it undergoes a 1-, 2-, or 4-electron oxidation and whether this is in acid or alkaline solution. Typical examples in acid solution are as follows:†

1-electron change (e.g. using Fe^{III}, Ce^{IV}, or MnO_4^-):

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† See p. 435 for discussion of standard electrode potentials and their use. It is conventional to write the half-reactions as (oxidized form) + ne^- = (reduced form). Since $\Delta G = -nE^\circ F$ at unit activities, it follows that the reactions will occur spontaneously in the reverse direction to that written when E° is negative, i.e. hydrazine is oxidized by the reagents listed.

Industrial Production and Uses of Hydrazine[75]

Hydrazine is usually prepared in a continuous process based on the Raschig reaction. Solutions of ammonia and sodium hypochlorite (30:1) are mixed in the cold with a gelatin solution and then passed rapidly under pressure through a reactor at 150° (residence time 1 s). This results in a 60% conversion based on hypochlorite and produces a solution of ~0.5% by weight of N_2H_4. The excess of NH_3 and steam are stripped off in stages and the solution finally distilled to give pure hydrazine hydrate $N_2H_4.H_2O$ (mp −51.7°, bp 118.5°, d 1.0305 g cm^{-3} at 21°). In the Olin Mathieson variation of this process, NH_2Cl is preformed from $NH_3 + NaOCl$ (3:1) and then anhydrous NH_3 is injected to a ratio of ~30:1; this simultaneously raises the temperature and pressure in the reactor. An alternative industrial route, which is economical only for smaller plants, uses urea instead of ammonia in a process very similar to Raschig's:

$$(NH_2)_2CO + NaOCl + 2NaOH \xrightarrow[\text{protein inhibitor}]{\text{rapid heat/}} N_2H_4.H_2O + NaCl + Na_2CO_3$$

Hydrazine hydrate contains 64.0% by weight of N_2H_4 and is frequently preferred to the pure compound not only because it is cheaper but also because its much lower mp avoids problems of solidification. Anhydrous N_2H_4 can be obtained from concentrated aqueous solutions by distillation in the presence of dehydrating agents such as solid NaOH or KOH. Alternatively, hydrazine sulfate can be precipitated from dilute aqueous solutions using dilute H_2SO_4 and the precipitate treated with liquid NH_3 to liberate the hydrazine:

$$N_2H_4(aq) + H_2SO_4(aq) \longrightarrow N_2H_6SO_4 \xrightarrow[\text{(anhydr)}]{2NH_3} N_2H_4 + (NH_4)_2SO_4$$

World production capacity of hydrazine solutions in 1995 (expressed as N_2H_4) was about 40 000 tonnes, predominantly in USA 16 500 t, Germany 6400 t, Japan 6600 t and France 6100 t. In addition some 3200 t of anhydrous N_2H_4 was manufactured in USA for rocket fuels.

The major use (non-commercial) of anhydrous N_2H_4 and its methyl derivatives $MeNHNH_2$ and Me_2NNH_2 is as a rocket fuel in guided missiles, space shuttles, lunar missions, etc. For example the Apollo lunar modules were decelerated on landing and powered on blast-off for the return journey by the oxidation of a 1:1 mixture of $MeNHNH_2$ and Me_2NNH_2 with liquid N_2O_4; the landing required some 3 tonnes of fuel and 4.5 tonnes of oxidizer, and the relaunching about one-third of this amount. Other oxidants used are O_2, H_2O_2, HNO_3, or even F_2. Space vehicles propelled by anhydrous N_2H_4 itself include the Viking Lander on Mars, the Pioneer and Voyager interplanetary probes and the Giotto space probe to Halley's comet.

The major commercial applications of hydrazine solutions are as blowing agents (~40%), agricultural chemicals (~25%), medicinals (~5%), and — increasingly — in boiler water treatment now as much as 20%. The detailed pattern of usage, of course, depends to some extent on the country concerned.

Aqueous solutions of N_2H_4 are versatile and attractive reducing agents. They have long been used to prepare silver (and copper) mirrors, to precipitate many elements (such as the platinum metals) from solutions of their compounds, and in other analytical applications. A major application as noted above is now in the treatment of high-pressure boiler water: this was first introduced in about 1945 and has the following advantages over the previously favoured Na_2SO_3:

(a) N_2H_4 is completely miscible with H_2O and reacts with dissolved O_2 to give merely N_2 and H_2O:
$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$
(b) N_2H_4 does not increase the dissolved solids (cf. Na_2SO_3) since N_2H_4 itself and all its reaction and decomposition products are volatile.
(c) These products are either alkaline (like N_2H_4) or neutral, but never acidic.
(d) N_2H_4 is also a corrosion inhibitor (by reducing Fe_2O_3 to hard, coherent Fe_3O_4) and it is therefore useful for stand-by and idle boilers.

The usual concentration of O_2 in boiler feed water is ~0.01 ppm so that, even allowing for a twofold excess, 1 kg N_2H_4 is sufficient to treat 50 000 tonnes of feed water (say ~4 days' supply at the rate of 500 tonnes per hour).

Hydrazine and its derivatives find considerable use in the synthesis of biologically active materials, dyestuff intermediates and other organic derivatives. Reactions of aldehydes to form hydrazides ($RCH{=\!=}NNH_2$) and azines ($RCH{=\!=}NN{=\!=}CHR$) are well known in organic chemistry, as is the use of hydrazine and its derivatives in the synthesis of heterocyclic compounds.

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[75] Hydrazine and its derivatives, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 13, pp. 560–606 (1995).

$$NH_4^+ + \tfrac{1}{2}N_2 + H^+ + e^- = N_2H_5^+; \quad E^\circ = -1.74\,V$$

2-electron change (e.g. using H_2O_2 or HNO_2):

$$\tfrac{1}{2}NH_4^+ + \tfrac{1}{2}HN_3 + \tfrac{5}{2}H^+ + 2e^- = N_2H_5^+; \quad E^\circ = +0.11\,V$$

4-electron change (e.g. using IO_3^- or I_2):

$$N_2 + 5H^+ + 4e^- = N_2H_5^+; \quad E^\circ = -0.23\,V$$

For basic solutions the corresponding reduction potentials are:

$$NH_3 + \tfrac{1}{2}N_2 + H_2O + e^- = N_2H_4 + OH^-; \quad E^\circ = -2.42\,V$$

$$\tfrac{1}{2}NH_3 + \tfrac{1}{2}N_3^- + \tfrac{5}{2}H_2O + 2e^- = N_2H_4 + \tfrac{5}{2}OH^-; \quad E^\circ = -0.92\,V$$

$$N_2 + 4H_2O + 4e^- = N_2H_4 + 4OH^-; \quad E^\circ = -1.16\,V$$

In the 4-electron oxidation of acidified N_2H_4 to N_2, it has been shown by the use of N_2H_4 isotopically enriched in ^{15}N that both the N atoms of each molecule of N_2 originated in the same molecule of N_2H_4. This reaction is also the basis for the most commonly used method for the analytical determination of N_2H_4 in dilute aqueous solution:

$$N_2H_4 + KIO_3 + 2HCl \xrightarrow{H_2O/CCl_4} N_2 + KCl + ICl + 3H_2O$$

The IO_3^- is first reduced to I_2 which is subsequently oxidized to ICl by additional IO_3^-; the end-point is detected by the complete discharge of the iodine colour from the CCl_4 phase.

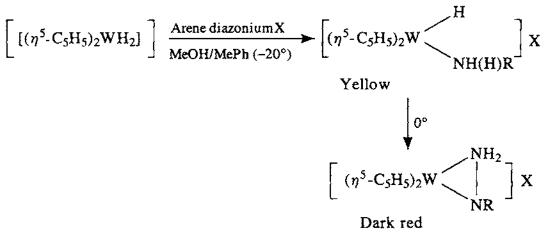
As expected, N_2H_4 in aqueous solutions is somewhat weaker as a base than is ammonia (p. 423):

$$N_2H_4(aq) + H_2O = N_2H_5^+ + OH^-; \quad K_{25^\circ} = 8.5 \times 10^{-7}\,mol\,l^{-1}$$

$$N_2H_5^+(aq) + H_2O = N_2H_6^{2+} + OH^-; \quad K_{25^\circ} = 8.9 \times 10^{-16}\,mol\,l^{-1}$$

The hydrate $N_2H_4.H_2O$ is an H-bonded molecular adduct and is not ionically dissociated. Two series of salts are known, e.g. N_2H_5Cl and $N_2H_6Cl_2$. (It will be noticed that $N_2H_6^{2+}$ is isoelectronic with ethane.) H bonding frequently influences the crystal structure and this is particularly noticeable in $N_2H_6F_2$ which features a layer lattice similar to CdI_2 though the structure is more open and the fluoride ions are not close packed. Sulfuric acid forms three salts, $N_2H_4.nH_2SO_4$ ($n = \tfrac{1}{2}$, 1, 2), i.e. $[N_2H_5]_2SO_4$, $[N_2H_6]SO_4$ and $[N_2H_6][HSO_4]_2$.

Hydrazido(2−)-complexes of Mo and W have been prepared by protonating dinitrogen complexes with concentrated solutions of HX and by ligand exchange.(76) For example several dozen complexes of general formulae $[MX_2(NNH_2)L_3]$ and *trans*-$[MX(NNH_2)L_4]$ have been characterized for M = Mo; X = halogen; L = phosphine or heterocyclic-N donor. Similarly, *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ afforded *trans*-$[WF(NNH_2)(PMe_2Ph)_4][BF_4]$ when treated with HF/MeOH in a borosilicate glass vessel. Side-on coordination of a phenylhydrazido(1−) ligand has also been established in compounds such as the dark-red $[W(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}H_2NNPh)][BF_4]$;(77) these are synthesized by the ready isomerization of the first-formed yellow η^1-arylhydrazido(2−) tungsten hydride complex above −20° (X = BF_4, PF_6):



In these reactions R = Ph, *p*-$MeOC_6H_4$, *p*-MeC_6H_4 or *p*-FC_6H_4. Further bonding modes are as an isodiazene (i.e. $M \leftarrow N{=}NMe_2$ rather than $M{=}N{-}NMe_2$)(78) and as a bridging diimido

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(76) J. Chatt, A. J. Pearman and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1766–76 (1978).

(77) J. A. Carroll, D. Sutton, M. Cowie and M. D. Gauthier, *J. Chem. Soc., Chem. Commun.*, 1058–9 (1979).

(78) J. R. Dilworth, J. Zubieta and J. R. Hyde, *J. Am. Chem. Soc.* **104**, 365–7 (1982).

group (M=N–N=M).(79) Both hydrazine itself and its dianion, $HNNH^{2-}$, act as bridging ligands in the pale yellow dinuclear tungsten(VI) complex shown in Fig. 11.6.(80) A selection of further recent work on the various coordination modes of substituted hydrazido, diazenido and related ligands is appended.(81)

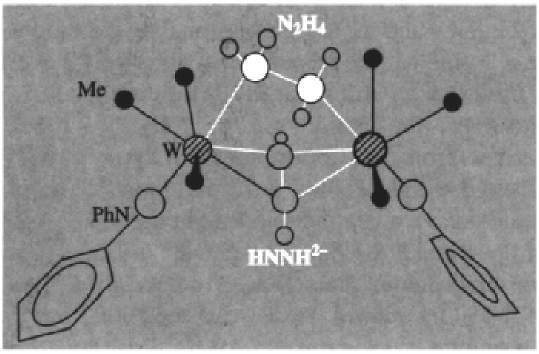

Figure 11.6 Structure of $[\{W(NPh)Me_3\}_2(\mu\text{-}\eta^1,\eta^1\text{-}NH_2NH_2)(\mu\text{-}\eta^2,\eta^2\text{-}NHNH)]$.

Hydroxylamine

Anhydrous NH_2OH is a colourless, thermally unstable hygroscopic compound which is usually handled as an aqueous solution or in the form of one of its salts. The pure compound (mp 32.05°C, d 1.204 g cm^{-3} at 33°C) has a very high dielectric constant (77.63–77.85) and a vapour pressure of 10 mmHg at 47.2°. It can be regarded as water in which 1 H has been replaced by the more electronegative NH_2 group or as NH_3 in which 1 H has been replaced by OH. Aqueous solutions are less basic than either ammonia or hydrazine:

$$NH_2OH(aq) + H_2O = NH_3OH^+ + OH^-;$$
$$K_{25^\circ} = 6.6 \times 10^{-9}\ \mathrm{mol\,l^{-1}}$$

Hydroxylamine can be prepared by a variety of reactions involving the reduction of nitrites, nitric acid or NO, or by the acid hydrolysis of nitroalkanes. In the conventional Raschig synthesis, an aqueous solution of NH_4NO_2 is reduced with HSO_4^-/SO_2 at 0° to give the hydroxylamido-N,N-disulfate anion which is then hydrolysed stepwise to hydroxylammonium sulfate:

$$NH_4NO_2 + 2SO_2 + NH_3 + H_2O \longrightarrow [NH_4]_2[N(OH)(OSO_2)_2]$$

$$[NH_4]^+{}_2[N(OH)(OSO_2)_2]^{2-} + H_2O \longrightarrow [NH_4][NH(OH)(OSO_2)] + [NH_4][HSO_4]$$

$$2[NH_4]^+[NH(OH)(OSO_2)]^- + 2H_2O \longrightarrow [NH_3(OH)]_2[SO_4] + [NH_4]_2[SO_4]$$

Aqueous solutions of NH_2OH can then be obtained by ion exchange, or the free compound can be prepared by ammonolysis with liquid NH_3; insoluble ammonium sulfate is filtered off and the excess of NH_3 removed under reduced pressure to leave solid NH_2OH.

Alternatively, hydroxylammonium salts can be made either (a) by the electrolytic reduction of aqueous nitric acid between amalgamated lead electrodes in the presence of H_2SO_4/HCl, or (b) by the hydrogenation of nitric oxide in acid solutions over a Pt/charcoal catalyst:

$$\text{(a)}\ HNO_3(aq) + 6H^+(aq) \xrightarrow{6e^-} 2H_2O + NH_2OH \xrightarrow{HCl(g)} [NH_3(OH)]Cl(s)$$

$$\text{(b)}\ 2NO(g) + 3H_2(g) + H_2SO_4(aq) \xrightarrow{Pt/C} [NH_3(OH)]_2SO_4$$

A convenient laboratory route involves the reduction of an aqueous solution of nitrous acid or potassium nitrite with bisulfite under carefully

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[79] M. R. Churchill and H. J. Wasserman, *Inorg. Chem.* **20**, 2899–904 (1981).

[80] L. Blum, I. D. Williams and R. R. Schrock, *J. Am. Chem. Soc.* **106**, 8316–7 (1984).

[81] M. D. Fitzroy, J. M. Frederiksen, K. S. Murray and M. R. Snow, *Inorg. Chem.* **24**, 3265–70 (1985). J. Bultitude, L. F. Larkworthy, D. C. Povey, G. W. Smith, J. R. Dilworth and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 1748–50 (1986). J. R. Dilworth, R. A. Henderson, P. Dahlstrom, T. Nicholson and J. S. Zubieta, *J. Chem. Soc., Dalton Trans.*, 529–40 (1987). T. Nicholson and J. Zubieta, *Polyhedron* **7**, 171–85 (1988). F. W. Einstein, X. Yan and D. Sutton, *J. Chem. Soc., Chem. Commun.*, 1466–7 (1990).

controlled conditions: The hydroxylamidodisulfate first formed, though stable in alkaline solution, rapidly hydrolyses to the monosulfate in acid solution and this can then subsequently be hydrolysed to the hydroxylammonium ion by treatment with aqueous HCl at 100° for 1 h:

$$HNO_2 + 2HSO_3^- \longrightarrow [N(OH)(OSO_2)_2]^{2-} + H_2O$$

$$\xrightarrow{\text{fast}} [NH(OH)(OSO_2)]^- + [HSO_4]^-$$

$$[NH(OH)(OSO_2)]^- + H_3O^+ \xrightarrow{100°/1\,h} [NH_3(OH)]^+ + [HSO_4]^-$$

Anhydrous NH_2OH can be prepared by treating a suspension of hydroxylammonium chloride in butanol with NaOBu:

$$[NH_3(OH)]Cl + NaOBu \longrightarrow NH_2OH + NaCl + BuOH$$

The NaCl is removed by filtration and the NH_2OH precipitated by addition of Et_2O and cooling.

NH_2OH can exist as 2 configurational isomers (*cis* and *trans*) and in numerous intermediate *gauche* conformations as shown in Fig. 11.7. In the crystalline form, H bonding appears to favour packing in the *trans* conformation. The N–O distance is 147 pm consistent with its formulation as a single bond. Above room temperature the compound decomposes (sometimes explosively) by internal oxidation-reduction reactions into a complex mixture of N_2, NH_3, N_2O and H_2O. Aqueous solutions are much more stable, particularly acid solutions in which the compound is protonated, $[NH_3(OH)]^+$. Such solutions can act as oxidizing agents particularly when acidified but are more generally used as reducing agents, e.g. as antioxidants in photographic developers, stabilizers of monomers, and for reducing Cu^{II} to Cu^{I} in the dyeing of acrylic fibres. Comparisons with the redox chemistry of H_2O_2 and N_2H_4 are also instructive (see, for example, pp. 272–3 of ref. 69). The ability of NH_2OH to react with N_2O, NO and N_2O_4 under suitable conditions (e.g. as the sulfate adsorbed on silica gel) makes it useful as an absorbent in combustion analysis. However, the major use of NH_2OH, which derives from its ability to form oximes with aldehydes and ketones, is in the manufacture of caprolactam, a key intermediate in the production of polyamide-6 fibres such as nylon. This consumes more than 97% of world production of NH_2OH, which is at least 650 000 tonnes per annum.

The extensive chemistry of the hydroxylamides of sulfuric acid is discussed later in the context of other H–N–O–S compounds (pp. 740–6).

Hydrogen azide

Aqueous solutions of HN_3 were first prepared in 1890 by T. Curtius who oxidized aqueous hydrazine with nitrous acid:

$$N_2H_5^+ + HNO_2 \longrightarrow HN_3 + H^+ + 2H_2O$$

Other oxidizing agents that can be used include nitric acid, hydrogen peroxide, peroxydisulfate, chlorate and the pervanadyl ion. The anhydrous

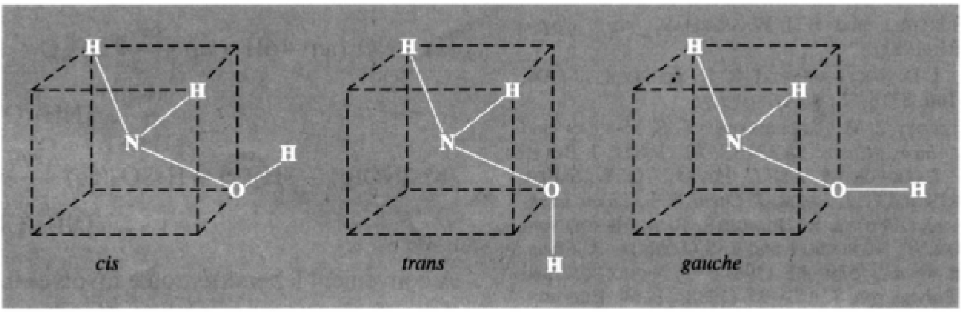
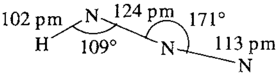
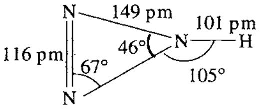


Figure 11.7 Configurations of NH_2OH.

compound is extremely explosive and even dilute solutions should be treated as potentially hazardous. Pure HN_3 is best prepared by careful addition of H_2SO_4 to NaN_3; it is a colourless liquid or gas (mp ~ −80°, estimated bp 35.7°, d 1.126 g cm^{-3} at 0°). Its large positive enthalpy and free energy of formation emphasize its inherent instability: ΔH_f°(1, 298 K) 269.5, ΔG_f° (1, 298 K) 327.2 kJ mol^{-1}. It has a repulsive, intensely irritating odour and is a deadly (though non-cumulative) poison; even at concentrations less than 1 ppm in air it can be dangerous. In the gas phase the 3 N atoms are (almost) colinear, as expected for a 16 valence-electron species, and the angle HNN is 109°; the two N–N distances are appreciably different, as shown in structure (1). The structure and dimensions of the isomeric molecule cyclotriazene are given in (2) for comparison; the N–H bond is tilted out of the plane of the N_3 ring by 74°.



(1)



(2)

Similar differences are found for organic azides (e.g. MeN_3). In ionic azides (p. 417) the N_3^- ion is both linear and symmetrical (both N–N distances being 116 pm) as befits a 16-electron species isoelectronic with CO_2 (cf. also the cyanamide ion NCN^{2-}, the cyanate ion NCO^-, the fulminate ion CNO^- and the nitronium ion NO_2^+).

Aqueous solutions of HN_3 are about as strongly acidic as acetic acid:

$$HN_3(aq) = H^+(aq) + N_3^-(aq);\ K_a\ 1.8 \times 10^{-5},\quad pK_a\ 4.77 \text{ at } 298\text{ K}$$

Numerous metal azides have been characterized (p. 417) and covalent derivatives of non-metals are also readily preparable by simple metathesis using either NaN_3 or aqueous solutions of HN_3[82,83]. In these compounds the N_3 group behaves as a pseudohalogen (p. 319) and, indeed, the unstable compounds FN_3, ClN_3, BrN_3, IN_3 and NCN_3 are known, though potential allotropes of nitrogen such as $N_3{-}N_3$ (analogous to Cl_2) and $N(N_3)_3$ (analogous to NCl_3) have not been isolated. More complex heterocyclic compounds are, however, well established, e.g. cyanuric azide $\{-NC(N_3)-\}_3$, *B,B,B*-triazidoborazine $\{-NB(N_3)-\}_3$ and even the azidophosphazene derivative $\{-NP(N_3)_2-\}_3$.

Most preparative routes to HN_3 and its derivatives involve the use of NaN_3 since this is reasonably stable and commercially available. NaN_3 can be made by adding powdered $NaNO_3$ to fused $NaNH_2$ at 175° or by passing N_2O into the same molten amide at 190°:

$$NaNO_3 + 3NaNH_2 \longrightarrow NaN_3 + 3NaOH + NH_3$$

$$N_2O + 2NaNH_2 \longrightarrow NaN_3 + NaOH + NH_3$$

The latter reaction is carried out on an industrial scale using liquid NH_3 as solvent; a variant uses Na/NH_3 without isolation of the $NaNH_2$:

$$3N_2O + 4Na + NH_3 \longrightarrow NaN_3 + 3NaOH + 2N_2$$

A remarkable new covalent azide is the pale yellow nitrosyl NNNNO, prepared by reacting gaseous NOCl (p. 441) with solid NaN_3 at low temperature.[84] $NNNN(SO_2F)_2$ has also very recently been made by a similar route from $(SO_2F)_2NCl$; it is a volatile yellow liquid which sometimes decomposes explosively.[84a]

The major use of inorganic azides exploits the explosive nature of heavy metal azides. $Pb(N_3)_2$ in particular is extensively used in detonators because of its reliability, especially in damp conditions; it is prepared by metathesis between $Pb(NO_3)_2$ and NaN_3 in aqueous solution.

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[82] Pp. 276–93 of ref. 69.

[83] A. D. YOFFE, Chap. 2 in C. B. COLBURN (ed.), *Developments in Inorganic Nitrogen Chemistry*, Vol. 1, pp. 72–149, Elsevier, Amsterdam, 1966.

[84] A. SCHULZ, I. C. TORNIEPORTH-OETTING and T. M. KLAPÖTKE, *Angew. Chem. Int. Edn. Engl.* **32**, 1610–12 (1993).

[84a] H. HOLFTER, T. M. KLAPÖTKE and A. SCHULZ, *Polyhedron* **15**, 1405–7 (1996).

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