

LIQUID AMMONIA AS A SOLVENT*

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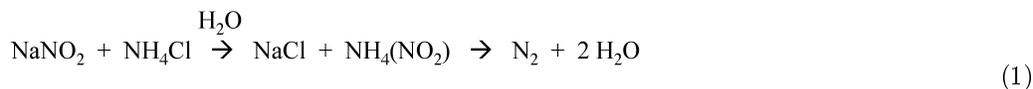
Ammonia has a reasonable liquid range (-77 to -33 °C), and as such it can be readily liquefied with dry ice (solid CO₂, T_{sub} = -78.5 °C), and handled in a thermos flask. Ammonia's high boiling point relative to its heavier congeners is indicative of the formation of strong hydrogen bonding, which also results in a high heat of vaporization (23.35 kJ/mol). As a consequence ammonia can be conveniently used as a liquid at room temperature despite its low boiling point.

Liquid ammonia is a good solvent for organic molecules (e.g., esters, amines, benzene, and alcohols). It is a better solvent for organic compounds than water, but a worse solvent for inorganic compounds. The solubility of inorganic salts is highly dependant on the identity of the counter ion (Table 1).

Soluble in liquid NH ₃	Generally insoluble in liquid NH ₃
SCN ⁻ , I ⁻ , NH ₄ ⁺ , NO ₃ ⁻ , NO ₂ ⁻ , ClO ₄ ⁻	F ⁻ , Cl ⁻ , Br ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , O ²⁻ , OH ⁻ , S ²⁻

Table 1: General solubility of inorganic salts in liquid ammonia as a function of the counter ion.

The difference in solubility of inorganic salts in ammonia as compared to water, as well as the lower temperature of liquid ammonia, can be used to good advantage in the isolation of unstable compounds. For example, the attempted synthesis of ammonium nitrate by the reaction of sodium nitrate and ammonium chloride in water results in the formation of nitrogen and water due to the decomposition of the nitrate, (1). By contrast, if the reaction is carried out in liquid ammonia, the sodium chloride side product is insoluble and the ammonium nitrate may be isolated as a white solid after filtration and evaporation below its decomposition temperature of 0 °C, (2).



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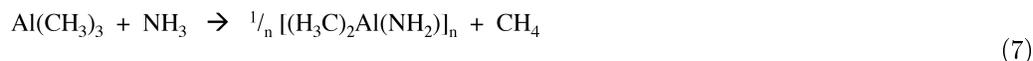
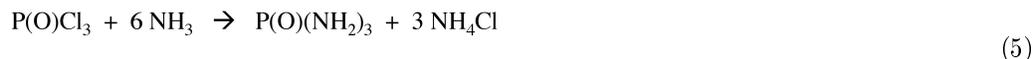
1 Ammonation

Ammonation is defined as a reaction in which ammonia is added to other molecules or ions by covalent bond formation utilizing the unshared pair of electrons on the nitrogen atom, or through ion-dipole electrostatic interactions. In simple terms the resulting *ammine* complex is formed when the ammonia is acting as a Lewis base to a Lewis acid, (3) and (4), or as a ligand to a cation, e.g., $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, and $[\text{Co}(\text{NH}_3)_6]^{3+}$.



2 Ammonolysis

Ammonolysis with ammonia is an analogous reaction to hydrolysis with water, i.e., a dissociation reaction of the ammonia molecule producing H^+ and an NH_2^- species. Ammonolysis reactions occur with inorganic halides, (5) and (6), and organometallic compounds, (7). In both case the NH_2^- moiety forms a substituent or ligand.



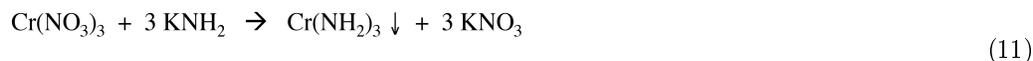
The reaction of esters, (8), and aryl halides, (9), are also examples of ammonolysis reactions.



3 Homoleptic amides

A homoleptic compound is a *compound with all the ligands being identical*, e.g., $\text{M}(\text{NH}_2)_n$. A general route to homoleptic amide compounds is accomplished by the reaction of a salt of the desired metal that is soluble in liquid ammonia (Table 1) with a soluble Group 1 amide. The solubility of the Group 1 amides is given in Table 2. Since all amides (except those of the Group 1 metals) are insoluble in liquid ammonia, the resulting amide may be readily isolated, e.g., (10) and (11).





Amide	Solubility in liquid ammonia
LiNH ₂	Sparingly soluble
NaNH ₂	Sparingly soluble
KNH ₂	Soluble
RbNH ₂	Soluble
CsNH ₂	Soluble

Table 2: Solubility of Group amides in liquid ammonia.

4 Redox reactions

Ammonia is poor as an oxidant since it is relatively easily oxidized, e.g., (12) and (13). Thus, if it is necessary to perform an oxidation reaction ammonia is not a suitable solvent; however, it is a good solvent for reduction reactions.



Liquid ammonia will dissolve Group 1 (alkali) metals and other electropositive metals such as calcium, strontium, barium, magnesium, aluminum, europium, and ytterbium. At low concentrations (ca. 0.06 mol/L), deep blue solutions are formed: these contain metal cations and solvated electrons, (14). The solvated electrons are stable in liquid ammonia and form a complex: $[\text{e}^-(\text{NH}_3)_6]$.



The solvated electrons provide a suitable and powerful reducing agent for a range of reactions that are not ordinarily accomplished, e.g., (15) and (16).

