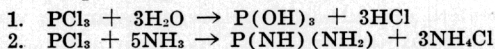


Acid Catalysis in Liquid Ammonia

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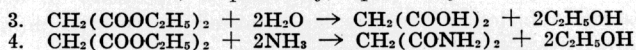
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It has definitely been shown that liquid ammonia possesses unusual properties as a solvent for many inorganic and organic compounds. Like water, it is the parent substance of a system of acids, bases and salts. When dissolved in liquid ammonia, ammonium salts have been shown to behave as acids. Liquid ammonia also acts directly upon many substances to produce solvolytic effects and such reactions are termed "ammonolytic" reactions. Just as phosphorus trichloride is hydrolyzed by water (Equation 1), so it may also be ammonolyzed by ammonia to give the corresponding ammono acid (2).



Many hydrolytic reactions are catalyzed in aqueous solution by acids, or bases. Thus, the inversion of cane sugar is catalyzed by acids and the velocity of the reaction is a function of the concentration of the hydrogen ion. This reaction has been used for the determination of the strength of acids in aqueous solution. Esters also undergo hydrolysis and, in some cases, such reactions have been markedly catalyzed by the hydrogen ion, or in terms of the modern Brönsted concept of acidity, by the solvated proton. It was therefore to be expected that the rate of ammonolysis of esters in liquid ammonia would be accelerated by the presence of ammonium salts.

Preliminary experimental runs indicated that ethyl malonate ammonolyzed at a sufficiently slow rate at 0° to permit of its more extended investigation. Parallel equations, (3) and (4), show the effect of water and ammonia, respectively, upon ethyl malonate.



Weighed samples of ethyl malonate and ammonium chloride were placed in tubes which were cooled in a solid carbon dioxide-acetone bath. A definite volume of liquid ammonia was then introduced and the tubes sealed off and immersed in an ice bath. When the contents had reached a temperature of 0° C. the tubes were shaken and the initial reaction time specified as such. Tubes were removed from the thermostat at varying time intervals, cooled, opened and emptied into filter flasks. The ammonia was allowed to evaporate, the residue washed with ether to remove unchanged ester and the product weighed to determine the yield of malonamide.

The preliminary results of this investigation may be summarized as follows:

(1) The ammonolysis of the pure malonic ester is an auto-catalytic reaction, since both of the products, malonamide and ethanol, behave as acids in liquid ammonia. Addition of either of these substances to the initial reaction mixture greatly speeds up the rate of formation of the amide.

(2) The rate of formation of amide is tremendously accelerated by the addition of ammonium chloride. The yield of amide at the end of a ten hour interval is a linear function of the concentration of the catalyst.

(3) Equivalent concentrations of various ammonium salts exert approximately the same catalytic effect.

(4) Neutral salts, such as NaCl, NaBr and NaI, also markedly accelerate the conversion of ester into amide.