THE PREPARATION OF GUANIDINE FROM UREA, AMMONIUM CHLORIDE, ALUMINUM SULPHATE, AND AMMONIA UNDER PRESSURE[1]

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ABSTRACT

Guanidine has been synthesized by heating under ammonia pressure an intimate mixture of finely powdered urea, ammonium chloride, and aluminum sulphate. Good yields of guanidine as the hydrochloride salt have been obtained over a wide range of conditions. The mechanism of this synthesis is briefly discussed.

INTRODUCTION

If urea is heated under ammonia pressure, it is much more stable at high temperature because of the stabilizing effect of ammonia (1). The preparation of guanidine about to be described makes use of aluminum sulphate to assist the removal of water from the reaction. This starting material can be produced cheaply from bauxite, clay, and similar materials containing aluminum.

DESCRIPTION OF METHOD

By heating urea, ammonium chloride, and aluminum sulphate together under ammonia pressure at 300° C. for some time, yields of guanidine as high as 70% have been obtained. The reaction product was boiled with ammoniacal water in order to precipitate aluminum hydroxide (Diagram 1). The clear filtrate, which contained guanidine hydrochloride, ammonium sulphate, and unreacted urea and ammonium chloride, was evaporated to dryness. The residue was treated with liquid ammonia and the mixture filtered free from ammonium sulphate. By evaporation of the liquid ammonia solution, a residue was left containing guanidine hydrochloride together with unreacted urea and ammonium chloride. This crude guanidine hydrochloride was transformed into guanidine nitrate by treating its saturated aqueous solution with a quantity of ammonium nitrate equivalent to its guanidine content. After guanidine nitrate was removed the filtrate was evaporated to dryness and the residue heated to 250° C. This material was nearly pure ammonium chloride, suitable for use in a subsequent cycle.

The aluminum hydroxide and ammonium sulphate, individually isolated from the reaction products as indicated above, were heated together at 350° C. to regenerate aluminum sulphate (5) according to the following equation:

$$2\text{Al(OH)}_3+3(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3+6\text{H}_2\text{O}+6\text{NH}_3. \qquad [1]$$

The ammonia evolved during heating can be dried and returned to the reactor.

EFFECT OF TEMPERATURE

In order to explore the effect of the temperature of heating, mixtures consisting of equimolar quantities of urea and ammonium chloride and various

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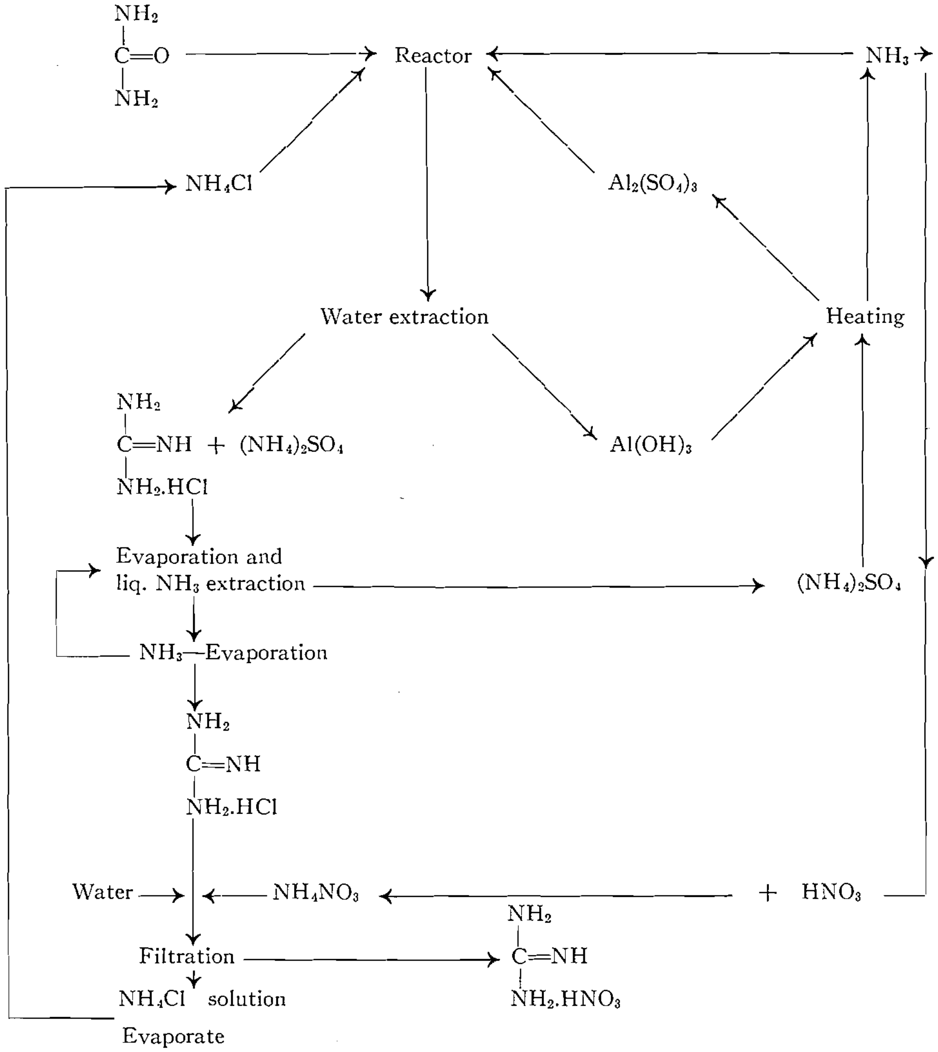


Diagram 1

amounts of aluminum sulphate were heated together under ammonia pressure. Table I shows the compositions of the mixtures and the conditions of the reaction. At high temperature, melamine is produced at the expense of guanidine. The yields of guanidine increase with temperature up to a maximum value, beyond which the formation of melamine becomes increasingly significant. The low yields shown here are ascribed to the fact that the ingredients were coarse and not thoroughly mixed. However, the table shows that increasing yields of guanidine were obtained with increasing amounts of aluminum sulphate.

TABLE I

EFFECT OF TEMPERATURE

Urea: 0.10 mole; NH_4Cl: 0.10 mole; time: 30 min.; pressure: 1000 p.s.i.g.

$Al_2(SO_4)_3$, mole	Temp., ° C.	Yield from urea, %	
		Guanidine	Melamine
0.0166	225	4	Nil
	250	10	Nil
	275	17	Nil
	300	36	10
	325	41	28
	350	29	35
0.033	250	14	Nil
	275	32	Nil
	300	45	Nil
	325	48	16
	350	38	20
0.05	225	Traces	Nil
	250	26	Nil
	275	40	Nil
	300	55	Nil
	325	63	37
	350	45	42

EFFECT OF CONCENTRATION OF UREA

By varying the molar quantities of urea added to a constant mixture of ammonium chloride and aluminum sulphate, as can be seen in Table II, the optimum yield was attained from equimolar amounts of urea and ammonium chloride. When urea was added in excess of this value, melamine was formed together with cyanuric acid.

TABLE II

EFFECT OF CONCENTRATION OF UREA

NH_4Cl: 0.10 mole; $Al_2(SO_4)_3$: 0.05 mole; temp.: 300° C.; time: 30 min.; pressure: 1000 p.s.i.g.

Urea, mole	Yield from urea, %	
	Guanidine	Melamine
0.05	43	Nil
0.10	55	Nil
0.15	34	23
0.20	31	22
0.30	22	20

EFFECT OF CONCENTRATION OF AMMONIUM CHLORIDE

It has been found (Table III) that increasing quantities of ammonium chloride give increasing yields of guanidine, melamine being absent under these conditions. There is a great increase in yield as ammonium chloride increases from 0.05 mole to the stoichiometric amount of 0.10 mole. The better yields obtained here are attributed to thorough mixing of solid ingredients before reaction took place.

TABLE III

EFFECT OF AMMONIUM CHLORIDE

Urea: 0.10 mole; $Al_2(SO_4)_3$: 0.033 mole; temp.: 300° C.; time: 30 min.; pressure: 1000 p.s.i.g.

NH_4Cl, mole	Guanidine yield from urea, %
0.05	39
0.10	68
0.15	70
0.20	75
0.25	68
0.30	65

EFFECT OF TIME OF HEATING

This reaction is dependent on the period of heating (Table IV). It is more complete when the reaction time is longer. The yields increase with time and also with temperature.

TABLE IV

Urea: 0.10 mole; NH_4Cl: 0.10 mole; $Al_2(SO_4)_3$: 0.033 mole; pressure: 1000 p.s.i.g.

Temp., ° C.	Time, min.	Guanidine yield from urea, %
275	30	58
	60	62
	90	64
	120	68
300	30	68
	45	70
	60	72
	90	79

EFFECT OF PRESSURE

The pressure factor is quite important in this reaction. There is evidence (Table V) that the yields are better at higher pressure. At atmospheric pressure, neither guanidine nor melamine was produced. At high pressure, yields were improved very significantly.

TABLE V

EFFECT OF PRESSURE

Urea: 0.10 mole; NH_4Cl: 0.10 mole; $Al_2(SO_4)_3$: 0.033 mole; temp.: 300° C.; time: 30 min.

Pressure, p.s.i.g.	Guanidine yield from urea, %
0	0
100	33
200	37
400	57
1000	68
2000	72

MECHANISM OF THE REACTION

Although the mechanism of this reaction, involving four starting materials, is not fully understood, some suggestions may be offered as to the possible intermediate compounds. In the absence of ammonium chloride, the heating of urea with aluminum sulphate and ammonia failed to give guanidine under the same conditions. Likewise, urea, ammonium chloride, and ammonia gave low yields of guanidine under these conditions of temperature and time; even with the long period of heating employed by Blair (1), these reactants gave only 23% guanidine. When both ammonium chloride and aluminum sulphate are present, however, yields as high as 75% can be obtained in a period of only an hour or so.

It is believed that in the presence of ammonia vapor, as in the present reaction, ammonium chloride and aluminum sulphate react as in the following reaction:

$$6NH_4Cl+Al_2(SO_4)_3 \longrightarrow 2AlCl_3+2(NH_4)_2SO_4. \qquad [2]$$

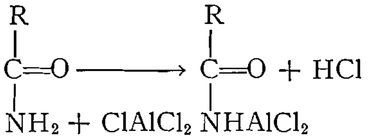
If then urea is present (6) and a small conversion to guanidine takes place, liberating water, the latter can react with aluminum chloride:

$$2AlCl_3+3H_2O \longrightarrow Al_2O_3+6HCl. \qquad [3]$$

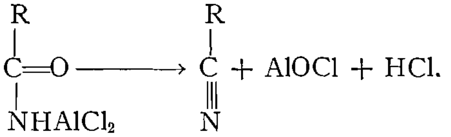
Accordingly, reaction is displaced towards the right, i.e. formation of guanidine is facilitated.

By analogy with the sulphamate synthesis of guanidine from urea (3) and also with the preparation of nitriles from amides by the action of sulphamates (2), it might be expected that an intermediate compound, comprising a substituted urea, could be involved.

Norris and Klemka (4) have shown that nitriles are obtained from amides and aluminum chloride through the formation of an intermediate compound, according to the following equation:

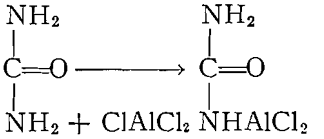


$$\begin{array}{l}R\\ |\\ C{=}O\\ |\\ NH_2 + ClAlCl_2\end{array} \longrightarrow \begin{array}{l}R\\ |\\ C{=}O + HCl\\ |\\ NHAlCl_2\end{array} \qquad [4]$$

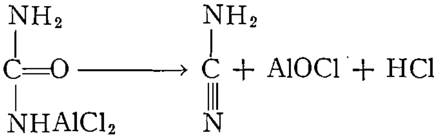


$$\begin{array}{l}R\\ |\\ C{=}O\\ |\\ NHAlCl_2\end{array} \longrightarrow \begin{array}{l}R\\ |\\ C + AlOCl + HCl.\\ |||\\ N\end{array} \qquad [5]$$

Urea, which is an amide, could react similarly giving cyanamide:



$$\begin{array}{l}NH_2\\ |\\ C{=}O\\ |\\ NH_2 + ClAlCl_2\end{array} \longrightarrow \begin{array}{l}NH_2\\ |\\ C{=}O\\ |\\ NHAlCl_2\end{array} \qquad [6]$$

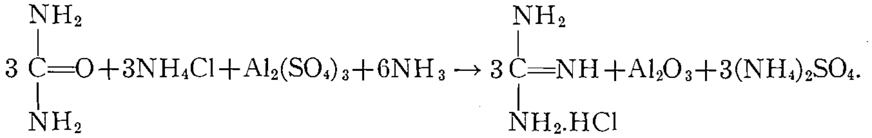


$$\begin{array}{l}NH_2\\ |\\ C{=}O\\ |\\ NHAlCl_2\end{array} \longrightarrow \begin{array}{l}NH_2\\ |\\ C + AlOCl + HCl\\ |||\\ N\end{array} \qquad [7]$$

which under the actual condition should yield guanidine or melamine.

The above suggestions, though tentative, seem to offer an explanation of the observation that whereas neither ammonium chloride nor aluminum sulphate alone is effective, the two together produce a high yield of guanidine from urea and ammonia in a relatively short time of reaction.

It is believed that guanidine hydrochloride is formed from urea according to the following over-all equation:



$$3\,\overset{\displaystyle NH_2}{\underset{\displaystyle NH_2}{C}}{=}O + 3NH_4Cl + Al_2(SO_4)_3 + 6NH_3 \rightarrow 3\,\overset{\displaystyle NH_2}{\underset{\displaystyle NH_2.HCl}{C}}{=}NH + Al_2O_3 + 3(NH_4)_2SO_4. \qquad [8]$$

EXPERIMENTAL

Starting Materials

The urea used was commercial material previously dried at 110° C. Ammonium chloride used was Merck Reagent. Aluminum sulphate was the anhydrous material which had been heated at 500° C.

Procedure

An intimate mixture of finely powdered urea, ammonium chloride, and aluminum sulphate was placed in a glass liner. Enough ammonia (liquid) was added to the mixture to build the desired pressure. After the bomb was closed and the necessary connections were made, the reaction mixture was heated to the temperature of synthesis and in most cases vented to 1000 p.s.i.g. The period of heating was recorded from the time when the temperature of reaction was attained. After the mixture was cooled, the solid products were boiled with ammoniacal water. Aluminum hydroxide was filtered off and the filtrate was analyzed for guanidine and melamine contents.

Identification of Guanidine

(*A*) The picrate obtained from the solution presumed to contain guanidine was treated with an excess of dilute nitric acid and boiled. Then the mixture was exhaustively extracted with benzene to remove picric acid. By evaporation of the aqueous layer, a residue was obtained, m.p. 203–205° C. Recrystallizations from ethanol raised the melting point to 212–213° C. A mixed melting point with an authentic sample of guanidine nitrate was not depressed.

(*B*) A portion of the filtrate was evaporated to dryness and the residue dissolved in the minimum amount of water. Then ammonium nitrate was added, and the solution was heated to boiling and allowed to cool. Crystals separated out, m.p. 202–205° C. Recrystallizations from ethanol raised the melting point to 212–213° C.

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