THE DEHYDRATION OF UREA, BENZAMIDE, AND PHENYLUREA BY THIONYL CHLORIDE IN THE PRESENCE OF AMMONIA[1]

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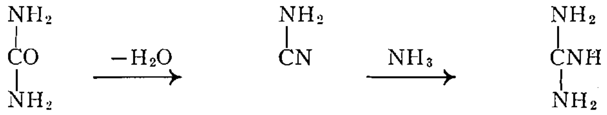
ABSTRACT

The decomposition of thionyl chloride in the presence of ammonia was found to give sulphur, ammonium sulphate, and ammonium sulphamate besides ammonium chloride. Heating urea and the reaction products of thionyl chloride and ammonia under pressure yielded guanidine hydrochloride and melamine, under different conditions of temperature, time, and pressure. Under similar conditions, benzamide was transformed into benzonitrile, and phenylurea into aniline or aniline black and diphenylurea, guanidine being absent.

INTRODUCTION

Guanidine has been synthesized from urea using various dehydrating agents, such as sulphur trioxide (1), sulphur dioxide (2), ammonium sulphamate (1), aluminum metal, or aluminum chloride (3) in the presence of ammonia or ammonium salts. In all cases, the highest yields of guanidine were obtained when the reaction was carried out under pressure (4). Since thionyl chloride is a good dehydrating agent, which reacts with water giving sulphur dioxide and hydrochloric acid, it is of interest to study its potentiality with respect to the dehydration of urea, benzamide, and phenylurea.

As the formation of guanidine is considered as an ammoniation of cyanamide, which in turn is produced by dehydration of urea:



$$\begin{array}{c}\mathrm{NH_2}\\|\\\mathrm{CO}\\|\\\mathrm{NH_2}\end{array}\xrightarrow{-\mathrm{H_2O}}\begin{array}{c}\mathrm{NH_2}\\|\\\mathrm{CN}\end{array}\xrightarrow{\mathrm{NH_3}}\begin{array}{c}\mathrm{NH_2}\\|\\\mathrm{CNH}\\|\\\mathrm{NH_2}\end{array}$$

there is an indication that guanidine would be unstable if thionyl chloride reacted alone with urea. It is known that ammonium salts or ammonia under pressure stabilize the molecule, and the effect of both will be necessary at high temperatures to prevent its decomposition into melamine (5).

Preliminary experiments carried out by heating, in a pressure vessel, urea, thionyl chloride, and ammonia which had been frozen separately in liquid air proved to be hazardous and unreliable. Therefore, to study the dehydrating properties of thionyl chloride with respect to urea and benzamide, a solution of thionyl chloride in anhydrous benzene was treated with an excess of ammonia. The yellow solid was collected and dried over calcium chloride and used without further purification. It will be called a thionyl chloride – ammonia complex since it is an ill-defined material (6, 7, 8, 9).

Thermal Stability of the Thionyl Chloride – Ammonia Complex

Since the synthesis of guanidine is best carried out under pressure, the thermal stability of the thionyl chloride – ammonia complex was studied under various conditions of temperature and pressure. It was observed that sulphur, ammonium sulphate, and ammonium sulphamate were the reaction products obtained, besides the normally

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present ammonium chloride under different conditions. At atmospheric pressure over a range of temperature of 150–325° C, the yield of sulphur was nearly constant to 7.5% and there was an increase of ammonium sulphate from 0.9% at 150° C to 7.5% at 300° C and a decrease to 5.2% at 325° C, as shown in Table I. Ammonium sulphamate was obtained in maximum yield at 250° C, which decreased from 12.6 to 3.1% at 325° C.

Under an ammonia pressure of 100 and 300 p.s.i., the results were similar, but it was observed that ammonium sulphate was present in larger quantities from 275 until 350° C.

TABLE I
Decomposition products of the thionyl chloride – ammonia complex at atmospheric pressure

Temp., ° C	% Composition of solid products			
	S	NH_4Cl	$(NH_4)_2SO_4$	$NH_2SO_3NH_4$
150	7.2	65.7	0.9	8.2
175	7.2	64.4	1.3	9.2
200	7.3	64.7	1.1	10.8
225	7.8	65.2	1.3	11.9
250	7.8	64.1	2.1	12.6
275	7.8	65.7	3.9	11.9
300	7.5	61.8	7.5	4.2
325	7.3	62.4	5.2	3.1

Guanidine from Urea and Thionyl Chloride – Ammonia Complex

As ammonium sulphamate is present in the decomposition products of the complex, it is expected that it could transform urea into guanidine (1). The reaction of the thionyl chloride – ammonia complex with urea was studied under various conditions of temperature, pressure, time, and ratio of reactants.

The method used consisted of mixing thoroughly urea with the dry thionyl chloride – ammonia complex and heating the mixture under normal pressure or under ammonia pressure in the autoclave. The reaction products were analyzed for sulphur, ammonium sulphate, ammonium sulphamate, guanidine, and melamine. Results are given in Table II for the reaction under 300 p.s.i. for a 30-minute period of heating.

TABLE II
Guanidine formation at 300 p.s.i. pressure for a 30-minute period of heating

Temp., ° C	% Composition of reaction products				
	S	$(NH_4)_2SO_4$	$NH_2SO_3NH_4$	$H_2NC(NH)NH_2$	$C_3H_6N_6$
150	6.8	2.0	4.9	—	—
175	6.9	0.6	6.4	—	—
200	7.2	1.2	4.7	—	—
225	7.6	3.8	4.5	—	—
250	7.6	28.6	3.5	19.4	2.8
275	6.9	38.0	2.3	33.8	3.9
300	5.8	38.5	2.5	35.1	4.1
325	5.7	23.5	2.1	31.2	4.5
350	5.6	7.5	1.3	17.5	3.7

At atmospheric pressure, urea was transformed into guanidine between 225° C and 250° C. The conversion of urea into guanidine reached a maximum at 275° C and then fell off sharply at higher temperatures so that no guanidine was found when the experiment was carried out above 325° C. The fact that melamine was found in place of guanidine at the higher temperatures indicates that the guanidine decomposed into cyanamide which trimerized into melamine. Ammonia pressure had a stabilizing effect, and the yield of guanidine was increased from 17 to 35% at 275–300° C when the pressure was either 100 or 300 p.s.i.

In the solid products, sulphur was present to a practically constant proportion of about 7.0% which, however, decreased with increasing temperatures to 5.6%. Ammonium sulphate increased proportionally with the amount of guanidine formed while the ammonium sulphamate content decreased.

With different ratios of urea at a temperature of 275° C and an ammonia pressure of 300 p.s.i., the yield of sulphur was practically constant and the production of ammonium sulphate varied directly with increasing quantity of urea used, whereas the yield of ammonium sulphamate varied inversely with the urea. When the reaction time was limited to 30 minutes, the yield of sulphur was about 7%. Between 60 and 150 minutes, it fell to 5%, but with longer periods of heating it decreased sharply and was less than 1% after 210 minutes. The proportion of ammonium sulphate in the reaction products remained constant for heating periods longer than 60 minutes. Although ammonium sulphate decomposed at temperatures above 300° C (10) during a reaction time of 30 minutes, it was quite stable at 275° C, even when heated for periods up to 3½ hours. Only traces of ammonium sulphamate were found in the reaction products under these conditions.

Guanidine and ammonium sulphate increased continuously with the reaction time up to a maximum yield of about 44%, and further heating had no apparent effect. The increase in the reaction time was unfavorable for the formation of melamine and the yield was reduced from 14.4% after 60 minutes to 10.5% after 210 minutes.

Benzonitrile from the Thionyl Chloride – Ammonia Complex and Benzamide

Since the thionyl chloride – ammonia complex was a dehydrating agent by way of the formation, on heating, of ammonium sulphamate, amides should be converted into the corresponding nitriles (11, 12). By heating the thionyl chloride – ammonia complex and benzamide under pressure, benzonitrile was obtained in only 5% yield at 175° C and more was formed as the temperature was increased until a maximum yield of 57.4% was reached at 325° C. The production of ammonium sulphate increased to a maximum of about 30% at 275° C and then decreased with increasing temperatures. A maximum yield of ammonium sulphamate was obtained at 150° C, but decreased continuously with the increase in temperature.

Products of the Reaction of Phenylurea with the Thionyl Chloride – Ammonia Complex

The reaction of the thionyl chloride – ammonia complex with phenylurea at different pressures led to a mixture of salts where aniline was present at the lower temperatures and aniline black at temperatures above 250° C. When the experiments were performed at atmospheric pressure, the highest yield of ammonium sulphate obtained was about 4% whereas the quantity of ammonium sulphamate for temperatures above 200° C was much lower. The yield of aniline, constant up to a temperature of 275° C, increased slightly at higher temperatures and was accompanied by an increase in the pressure.

An ammonia pressure of 100 p.s.i. gave rise to larger amounts of ammonium sulphamate at 150° C which decreased as the temperature was raised. Again fairly large amounts of aniline black were present up to 300° C. The ammonia pressure caused an increase in the yield of ammonium sulphate and a much higher yield of aniline which, however, decreased from 63.3% at 150° C to 22.0% at 325° C, while that of ammonium sulphate increased from 0.2% at 150° C to 7.9% at 325° C.

A higher ammonia pressure of 300 p.s.i. favored the production of larger quantities of ammonium sulphate, the maximum yields being obtained at 200° and 275° C. Higher temperatures led to reduced yields. Ammonium sulphamate production was highest at the lower temperatures although the amount was a good deal lower. The maximum yield of aniline, 63.3%, was also obtained at the lower temperatures. Ammonia pressure stabilized aniline particularly at the higher temperatures where the minimum yield was found to be about 37%.

Also diphenylurea was obtained between 150 and 250° C at 300 p.s.i., in yields varying from 0.1 to 4.0%, depending on the temperature used. At pressure lower than 300 p.s.i., diphenylurea could not be isolated.

DISCUSSION OF RESULTS

The ill-defined thionyl chloride – ammonia complex was decomposed at ordinary pressure or under an ammonia pressure into sulphur, ammonium sulphate, and ammonium sulphamate. While it is difficult to account specifically for all these products, this behavior should be similar to that of sulphur dioxide and ammonia which give, by heating under pressure, ammonium sulphamate and sulphur and no ammonium sulphate (2). The fact that ammonium sulphate is present indicates that a similar oxidoreduction has taken place where ammonia reduced the chloro derivative of sulphur dioxide into sulphur giving water, which then hydrolyzed part of ammonium sulphamate into ammonium sulphate.

When urea is present, the mechanism of formation of the products sulphur, ammonium sulphate, ammonium sulphamate, guanidine, and melamine is easily explained by reactions similar to the synthesis of guanidine from urea, sulphur dioxide, and ammonia (2). In this case, urea is dehydrated into cyanamide and ammonolyzed into guanidine. Guanidine is present in the actual synthesis as the hydrochloride because of the greater solubility of this salt in liquid ammonia than the sulphamate salt, whereas guanidine sulphate is completely insoluble (5).

When monophenylurea was heated with ammonium sulphamate, aniline, guanidine, and cyanuric acid were produced (12). On heating thionyl chloride and ammonia with monophenylurea, ammonium chloride, sulphate, sulphamate, aniline, aniline black, and diphenylurea were formed. It was assumed that monophenylurea underwent ammonolysis to give urea and aniline, and also diphenylurea. It is well known that aniline, in the presence of an oxidizing agent, forms a polymer, or better a variety of polymers, grouped together under the generic name of aniline blacks, the exact constitution of which is still unknown; since free sulphur was absent, it was concluded that it had oxidized the aniline to form aniline black, sulphur being transformed into hydrogen sulphide.

The absence of urea or guanidine derivatives in the reaction products was explained by the inhibition of hydrogen sulphide to form ammonium sulphamate from the chloro derivative of sulphur dioxide.

EXPERIMENTAL

Thionyl Chloride – Ammonia Complex

Thionyl chloride (20.0 g) was added to a 1-l. flask containing anhydrous benzene (400 ml), and anhydrous ammonia was bubbled through the solution until there was no further evolution of heat. The light yellow solid which precipitated out was separated by filtration on a Büchner funnel, washed with anhydrous benzene, and dried in a vacuum desiccator over calcium chloride (yield, 30.4 g).

The dried yellow starting material (8.0 g) was added to the removable Pyrex glass liner of a pressure vessel which had a volume of 183 ml without the liner, and 108 ml with the liner in place. The liner was fitted with a glass wool plug, and air was displaced by the evaporation of several drops of liquid ammonia in the autoclave. The reaction vessel was then heated at the desired temperature for 30 minutes, removed from the heating jacket, and cooled rapidly.

The solid products were analyzed for sulphur, ammonium chloride, sulphate, and sulphamate (2). Ammonium sulphamate was extracted from the mixture by means of absolute alcohol in which it is slightly soluble and recrystallized to give a melting point of 131° C, which was not depressed by admixing an authentic sample.

Since it would be impracticable to give all the results obtained, the data were omitted.

Thionyl Chloride – Ammonia Complex and Urea

The yellow starting material (5.5 g), made from thionyl chloride and ammonia, and urea (3.0 g, 0.05 mole) were intimately mixed and heated as in the above method. The products were analyzed for sulphur, ammonium sulphate, ammonium sulphamate, guanidine hydrochloride, and melamine (2). Guanidine hydrochloride was isolated by absolute ethanol extraction of the dried products and recrystallized from a mixture of alcohol and acetone. It had a melting point of 184–185° C, which was not depressed by mixing with an authentic sample.

Reaction with Benzamide

The yellow starting material (5.5 g) was added to a glass liner containing benzamide (6.1 g, 0.06 mole, m.p. 130° C) which had been recrystallized. The two solid compounds were then thoroughly mixed and heated in the autoclave and cooled overnight. Caution was exercised in reducing the internal pressure to atmospheric pressure since benzonitrile could be entrained out.

Benzonitrile was determined by extraction with ether and weighing the residue. It boiled at 188–191° C and gave benzoic acid, m.p. 121° C, by hydrolysis with alcoholic sodium hydroxide. The residue which was insoluble in ether was analyzed for ammonium sulphate and sulphamate (2).

Reaction with Monophenylurea

The yellow starting material (5.5 g) and monophenylurea (6.8 g, 0.05 mole) were placed in a Pyrex liner, thoroughly mixed together, and heated in the autoclave. The solid products were analyzed for aniline, ammonium sulphate, ammonium sulphamate, and diphenylurea by extraction or precipitation with barium chloride (2).

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