PREPARATION OF GUANIDINE FROM UREA, SULPHUR DIOXIDE, AND AMMONIA UNDER PRESSURE[1]

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ABSTRACT

It has been found that guanidine can be prepared in good yield from urea, sulphur dioxide, and ammonia under pressure over a wide range of conditions. A study of the effect of concentration, temperature, time, and pressure has been made. A part of the sulphur dioxide introduced into the reaction vessel can be recovered as elemental sulphur. Guanidine nitrate is easily prepared by treating the reaction product with dilute nitric acid. The mechanism of this synthesis has been found to proceed through the formation of ammonium sulphamate from sulphur dioxide and ammonia. Guanidine was present as the sulphamate when synthesized at low temperatures and as the sulphate at high temperatures.

Ammonia and sulphur trioxide react under suitable conditions to yield ammonium sulphamate (Eq. 1) with some triammonium imidosulphonate (Eq. 2) and sulphamide (Eq. 3).

$$SO_3 + 2NH_3 \rightarrow H_2NSO_3NH_4 \qquad [1]$$

$$2SO_3 + 3NH_3 \rightarrow NH_4N(SO_3NH_4)_2 \qquad [2]$$

$$SO_3 + 2NH_3 \rightarrow NH_2SO_2NH_2 + H_2O \qquad [3]$$

The complex product, obtained from ammonia and sulphur trioxide, is known to yield guanidine sulphamate when heated under pressure with urea and ammonia (3). For convenience of description, only the ammonium sulphamate will be considered, since analogous reactions can be inferred for the other two compounds.

The reaction of sulphur dioxide and ammonia, although not clearly understood, is believed to be similar to that with sulphur trioxide and ammonia.

$$SO_2 + 2NH_3 \rightarrow H_2NSO_2NH_4 \qquad [4]$$

$$2SO_2 + 3NH_3 \rightarrow H_4N—N(SO_2NH_4)_2 \qquad [5]$$

$$SO_2 + 2NH_3 \rightarrow H_2NSONH_2 + H_2O \qquad [6]$$

In the actual preparation of this complex, an excess of ammonia is reacted with sulphur dioxide. The reaction is exothermic. A nearly white product is obtained, but there is always present a red substance which is reported to be triammonium imidosulphinate (1).

When urea, sulphur dioxide, and ammonia are reacted in the molar ratio of 1:3:7 under suitable conditions, urea is converted into guanidine in yields exceeding 80%. It has been found, however, that in all cases one third of the sulphur dioxide taken is recovered in the form of elemental sulphur, which is easily filtered. The filtrate, after evaporation to small volume and treatment with excess of dilute nitric acid, yields guanidine nitrate while some sulphur dioxide is evolved.

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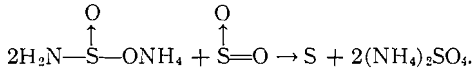
In view of the presence of sulphur in the reaction mixture, it appears that an oxidoreduction process takes place, possibly according to the over-all equation



$$2H_2N-\overset{O}{\overset{\uparrow}{S}}-ONH_4 + \overset{O}{\overset{\uparrow}{S}}=O \rightarrow S + 2(NH_4)_2SO_4. \qquad [7]$$

However, an alternative mechanism could be considered for the formation of sulphur. The amount of sulphur found in the present synthesis of guanidine was nearly constant at one mole when three moles of sulphur dioxide was used; this equation accounts for formation of sulphur and sulphate.

A preliminary investigation of the factors involved in this synthesis of guanidine from urea has been made. In all cases, the ammonia - sulphur dioxide complex was formed below −30° C. in the glass liner of an ordinary Parr bomb, and urea was added to the mixture. After the mixture was heated to the desired temperature over a period of time under ammonia pressure, the mass, which was still liquid at 150° C., was boiled in water. Sulphur was removed by filtration and the filtrate was analyzed for guanidine and melamine contents.

TABLE I

EFFECT OF TEMPERATURE

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; ammonia: 0.7 mole; pressure: 200 p.s.i.g.; heating time: 1 hr.

Temp., °C.	Yield based on urea guanidine, %	Melamine, %
215	1	0
235	64	0
245	80	0
265	81	0
275	76	6.1
285	51	17
295	46	35
305	42	44

Effect of Temperature

It can be seen that 80% yield of guanidine (Table I) can be obtained between 245° C. and 265° C. under the present conditions without the production of melamine which is due to the decomposition of the guanidine formed. The guanidine formation increased with temperature, reached a maximum value, and then decreased when melamine appeared in the mixture.

TABLE II

EFFECT OF CONCENTRATION OF UREA

Sulphur dioxide: 0.3 mole; ammonia: 0.7 mole; temp.: 275°C.; pressure: 200 p.s.i.g.; heating time: 1 hr.

Urea, mole	Yield based on urea guanidine, %	Melamine, %
0.05	60	0
0.10	74	0
0.15	56	0
0.20	43	10.3
0.30	26	8.1

Effect of Concentration of Urea

The optimum amount of urea seemed to be one tenth of a mole under the actual conditions (Table II). At high concentrations of urea, a considerable amount of cyanuric acid was found in addition to unreacted urea.

Effect of Time

The effect of the period of heating has been studied at 255°, 275°, and 305° C. The reaction time given is measured from the attainment of the stated temperature.

TABLE III

EFFECT OF TIME

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; pressure: 200 p.s.i.g.; ammonia: 0.7 mole

Temp., °C.	Time, min.	Yield based on urea guanidine, %
255	30	73
255	60	81
255	90	72
275	30	82
275	60	74
275	90	70
305	5	51
305	10	57
305	15	55
305	60	42

It can be noted that a higher temperature decreases the heating time (Table III). The reaction seems to proceed twice as fast when temperature is increased by 20° C. However, at 305° C. optimum yield is low and it seems that this reaction could not be effected with good yields at high temperature with the equipment used.

Effect of Pressure

From the point of view of equipment design and operation, pressure requirements frequently have a major influence on cost and safety. In the reaction, the effect of pressure is negligible from 200 to 3000 p.s.i.g., as can be seen in Table IV. Even under a pressure of 75 p.s.i.g., a 74% yield could be obtained.

TABLE IV

EFFECT OF PRESSURE

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; temp.: 275°C.; heating time: 30 min.

NH_3, mole	Pressure, p.s.i.g.	Guanidine, %
2.0	3000*	83
2.0	1000*	82
0.7	200*	82
0.7	75*	74
0.7	0	46

**Vented to this pressure, after attaining prescribed temperature.*

Good yields may be obtained over a wide range of conditions. Pressures as low as 75 p.s.i.g. are capable of giving 75% yield. This would simplify the construction of a reaction vessel. An important feature is ready isolation of guanidine in the form of its nitrate. In view of the good yields obtained and the cheap starting materials used, special attention was devoted to elucidate the mechanism of the synthesis.

A review of the literature dealing with ammonium amidosulphinate was not too conclusive for the elucidation of the mechanism. Divers and Ogawa (1) found that ammonium amidosulphinate when heated yields ammonia and ammonium imidosulphinate, a reaction similar to the formation of ammonium imidosulphonate from ammonium sulphamate. They also explain that the reaction between ammonia and sulphur dioxide yields mainly ammonium imidosulphinate, the latter decomposing on heating into volatile matter, sulphur, ammonium sulphate, and ammonium imidosulphinate. In spite of the numerous products isolated from the decomposition of the ammonia – sulphur dioxide complexes, the reaction under ammonia pressure is less intricate because of the recovery of sulphur which has always been made in 33% yield based on sulphur dioxide used. Guanidine was produced in high yields from urea under various conditions of temperature and pressure.

In the following discussion of the explanation of this reaction mechanism, experiments have been made as quantitative as possible considering the difficulties encountered when working with gaseous products and heating them in a bomb at high temperatures.

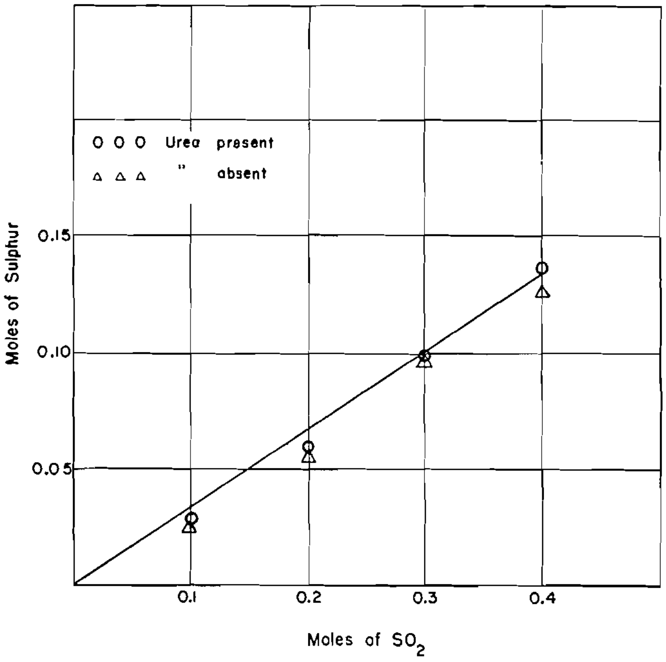


FIG. 1. Formation of sulphur.

Sulphur Formation

By heating together a mixture of urea, sulphur dioxide, and ammonia at 275° C. for half an hour, the yield of guanidine from urea was nearly constant at 80%, when the molar ratio of urea: sulphur dioxide: ammonia was 1:3:9. The variation of the amount of sulphur dioxide used resulted in a variation in the yield of guanidine from urea (Table V). It should also be noted that the formation of sulphur increased with the amount of sulphur dioxide added to the reaction mixture, the yield being nearly constant at 33%. If a graph is made by plotting the molar amounts of sulphur produced against the molar quantities of sulphur dioxide used, a straight line is obtained (Fig. 1).

To prove that urea had no participation in the reaction involving the production of sulphur, the same series of experiments were effected in its absence (Table VI). It was found that sulphur was produced in nearly the same yield as when urea was present.

It was also thought that the formation of sulphur might be an equilibrium reaction. An experiment was made (No. 84, Table V) in which sulphur was added to the reaction mixture. The total amount of sulphur was nearly equal to the sulphur added and the sulphur usually produced from sulphur dioxide.

TABLE V

SULPHUR BALANCE IN THE FUSION OF UREA, SULPHUR DIOXIDE, AND AMMONIA

Run No.	SO_2, mole	Urea, mole	NH_3, mole	Sulphur produced, mole	$BaSO_4$(O), mole *A*	$BaSO_4$(HCl) mole *B*	*A*−*B*	Guanidine, mole	Pressure, p.s.i.g.	Sulphur balance, mole
83	0.1	0.1	0.9	0.0293	0.080	0.058	0.022	0.042	2400	0.109
82	0.2	0.1	0.9	0.061	0.142	0.076	0.066	0.069	1850	0.203
81	0.3	0.1	0.9	0.098	0.212	0.128	0.084	0.083	1400	0.310
85	0.4	0.1	0.9	0.132	0.260	0.118	0.142	0.073	800	0.392
84	0.3– 0.1255*	0.1	0.9	0.196	0.209	0.133	0.076	0.076	200 (vented)	0.405

**Elemental sulphur added.*

NOTE: *The bomb was heated at 275°C. for 30 min. in all the above experiments.*

Thus the addition of sulphur does not appreciably depress its formation; therefore, in the actual synthesis the formation of sulphur does not result from an equilibrium reaction.

Sulphate Formation

Since sulphates were present in the reaction mixture, experiments were carried out to determine the effect of urea on the ammonia – sulphur dioxide complex. After the ingredients had been heated in the same way as mentioned in Tables I and II, the reaction products were dissolved in water and the solution filtered free of sulphur. The filtrate was analyzed for sulphate ion content. It was to be expected that the reaction mixture might contain reducing sulphur compounds like sulphites and thiosulphates, and that a determination of the actual sulphate would be of value. The method involved the cold treatment of a portion of this solution with barium chloride in hydrochloric acid. Results are given in Tables V and VI and shown graphically in Figs. 2 and 3. It can be seen that the molar quantities of sulphate produced from sulphur dioxide are nearly linear in the absence of urea.

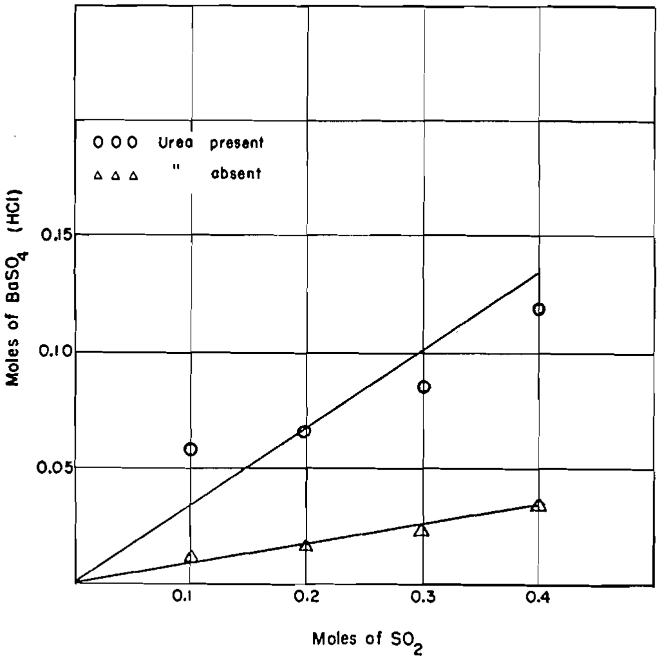


FIG. 2. Formation of barium sulphate (HCl).

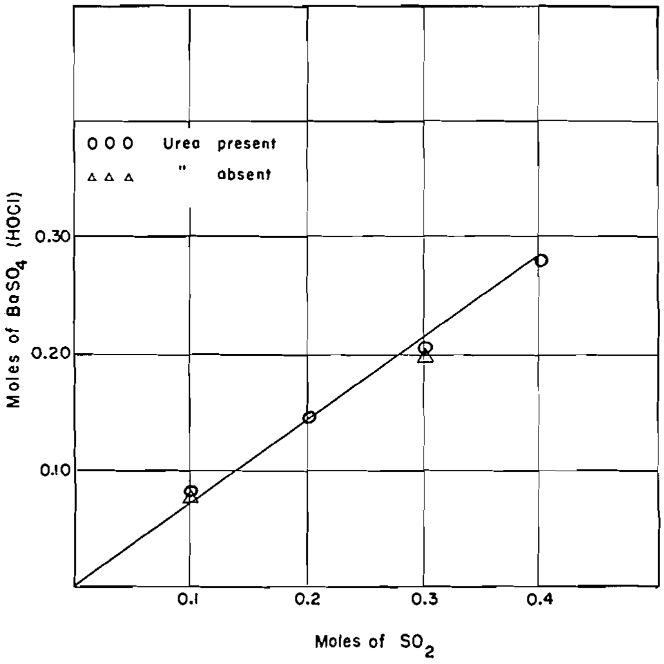


FIG. 3. Formation of barium sulphate (HOCl).

However, what is important in these experiments is the marked increase of sulphate formed when urea is present, i.e. when guanidine is produced.

TABLE VI

SULPHUR BALANCE IN THE REACTION OF SULPHUR DIOXIDE AND AMMONIA

Batch No.	SO_2, mole	NH_3, mole	Pressure, p.s.i.g.	NH_3 recovered in moles	NH_3 used	Sulphur produced in moles	$BaSO_4(O)$, mole A	$BaSO_4(HCl)$, mole B	$A-B$	Sulphur balance, mole
86	0.1	0.9	2800	0.62	0.28	0.025	0.072	0.013	0.059	0.097
87	0.2	0.9	2200	0.55	0.35	0.057	0.143	0.019	0.124	0.201
88	0.3	0.9	1700	0.35	0.55	0.102	0.200	0.024	0.176	0.302
89	0.4	0.9	950	0.25	0.65	0.123	0.278	0.037	0.241	0.401

NOTE: *The bomb was heated at 275°C. for 30 min.*

The determination of total sulphur-containing compounds in the form of sulphate was thought to be of interest in view of obtaining a good sulphur balance. The estimation was made by oxidizing the reducing sulphur compounds present in the solution to sulphate by means of sodium hypochlorite. Fig. 3 shows that the sulphate content, expressed in moles of barium sulphate, increases linearly with increasing amounts of sulphur dioxide, with or without urea, the molar values of sulphate being the same.

Ammonium Sulphamate

If subtraction is made between the molar value of sulphate present after the oxidation of the solution ($BaSO_4(O)$) and the molar quantity of true sulphate ($BaSO_4(HCl)$) when urea was present, values are obtained which are nearly proportional to the quantities of sulphur dioxide present up to 3 moles per mole of urea (Fig. 4).

$$BaSO_4(O) - BaSO_4(HCl) = C$$

This value "C" was found to be equal to the molar quantities of guanidine produced from urea. For instance, in Table V, run No. 81 shows the molar quantity of sulphates formed. This value "C" is: $0.212 - 0.128 = 0.084$. Hence this value "C" is related to the formation of guanidine.

Results also show that the amount of oxidized sulphur-containing compounds as barium sulphate (Tables V and VI), either in the presence of urea or in its absence, is proportional to the amount of sulphur dioxide present in the reaction mixture (Fig. 3).

Moreover, if summation of molar quantities of elemental sulphur and total sulphates formed is made, a good sulphur balance is obtained, as for instance in run No. 82 of Table V and in run No. 87 of Table VI.

From the data of Tables V and VI, proportionality of production of sulphur has been observed in respect to sulphur dioxide in the presence or absence of urea; the same fact has been observed of the actual sulphate present when urea was added to the ammonia – sulphur dioxide complex. In its absence, this value "C" was proportional to the amount of sulphur dioxide used (Fig. 4).

Therefore, there is a relationship between the formation of sulphates, sulphur, and guanidine. It was thought that the ammonium sulphamate

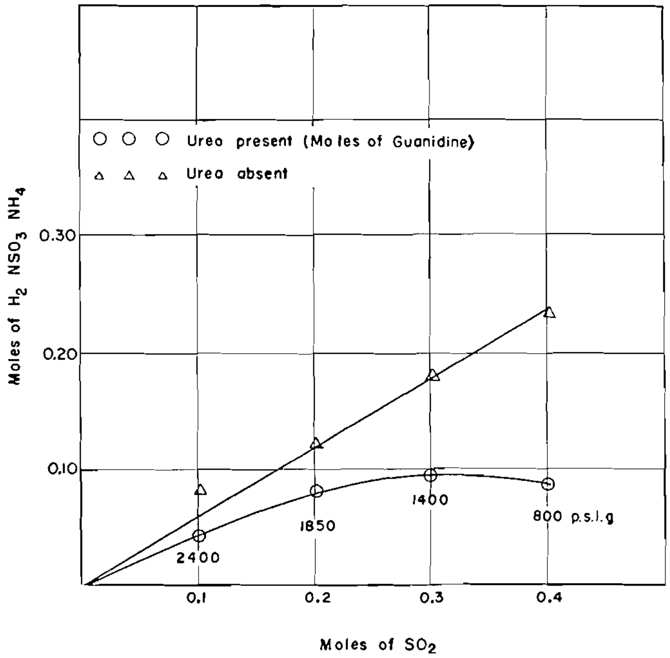


FIG. 4. Formation of ammonium sulphamate.

isolated in low yields by Divers and Ogawa (1) when they heated the ammonia – sulphur dioxide complex was probably the predominant compound under the actual conditions where excess of ammonia is used. If so, guanidine should be present as the sulphamate or sulphate. Guanidine sulphamate is soluble in liquid ammonia and slightly soluble in ethanol whereas guanidine sulphate is insoluble in both solvents. By extraction of the reaction products with liquid ammonia, guanidine sulphamate was identified and isolated in good yields.

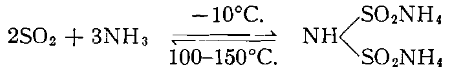
After the isolation of guanidine sulphamate, there was evidence that the actual synthesis was a sulphamate synthesis of guanidine from urea. Therefore, the heating of sulphur dioxide with excess of ammonia under pressure should yield ammonium sulphamate and sulphur as the main products, ammonium sulphate being present in quantities equivalent to the guanidine formed.

When sulphur dioxide and ammonia were heated at 275° C. for half an hour (Table VI), the reaction mixture contained molten products at 125° C. The melt was extracted with liquid ammonia and the solution filtered. After evaporation, a crystalline product was obtained which was found to be ammonium sulphamate. The yields of ammonium sulphamate were excellent.

Mechanism of the Synthesis

The mechanism of the formation of ammonium sulphamate can be thus explained. At low temperature an ammonia – sulphur dioxide complex will be formed consisting of ammonium amidosulphinate (Eq. 8) and ammonium imidosulphinate (Eq. 9).

$$SO_2 + 2NH_3 \underset{100\text{–}150^\circ C.}{\overset{-10^\circ C.}{\rightleftharpoons}} H_2N\text{—}SO_2NH_4 \qquad [8]$$



$$2SO_2 + 3NH_3 \underset{100\text{–}150^\circ C.}{\overset{-10^\circ C.}{\rightleftharpoons}} NH\begin{cases} SO_2NH_4 \\ SO_2NH_4 \end{cases} \qquad [9]$$

But by heating these two compounds in excess of ammonia, they should dissociate incompletely yielding ammonia and sulphur dioxide.

It is known that sulphur dioxide activated by light (2) dissociates into colloidal sulphur and sulphur trioxide according to the following equilibrium reaction:

$$3SO_2 \rightleftharpoons S + 2SO_3. \qquad [10]$$

If so, the formation of ammonium sulphamate will be readily explained from sulphur dioxide and ammonia:

$$SO_3 + 2NH_3 \longrightarrow H_2NSO_3NH_4. \qquad [11]$$

In this synthesis the formation of sulphur has been found to take place at about 150° C. It may be deduced that, owing to thermal activation of the sulphur dioxide molecule, it should dissociate in the presence of ammonia, as above, yielding sulphur and sulphur trioxide. Thus the over-all reaction of sulphur dioxide and ammonia will be represented by the following equation:

$$3SO_2 + 4NH_3 \longrightarrow S + 2NH_2SO_3NH_4. \qquad [12]$$

The isolation of guanidine sulphamate from a mixture of urea, sulphur dioxide, and ammonia in molar ratio 1: 3: 9 is not surprising. From experiments described earlier it has been found that guanidine is produced at a temperature

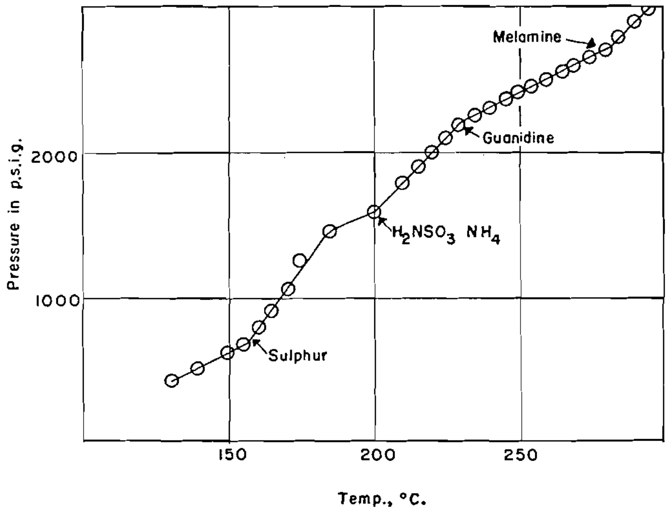


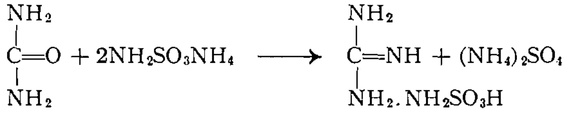
FIG. 5. Pressure–temperature curve.

of about 220° C. Sulphur is formed at a temperature as low as 160° C., therefore sulphamate should be produced. This is shown graphically in Fig. 5 where pressure is plotted against the temperature.

The synthesis of guanidine from urea, sulphur dioxide, and ammonia under pressure proceeds in two main steps. First ammonium sulphamate is produced from sulphur dioxide and ammonia:

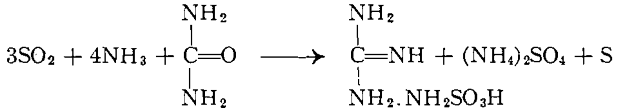
$$3SO_2 + 4NH_3 \longrightarrow 2NH_2SO_3NH_4 + S \qquad [13]$$

then urea reacts with ammonium sulphamate yielding guanidine sulphamate:



$$\begin{array}{c}NH_2\\|\\C{=}O\\|\\NH_2\end{array} + 2NH_2SO_3NH_4 \longrightarrow \begin{array}{l}NH_2\\|\\C{=}NH\\|\\NH_2.NH_2SO_3H\end{array} + (NH_4)_2SO_4$$

[14]



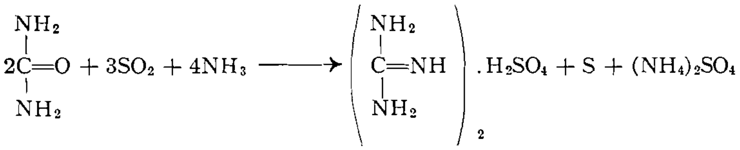
$$3SO_2 + 4NH_3 + \begin{array}{c}NH_2\\|\\C{=}O\\|\\NH_2\end{array} \longrightarrow \begin{array}{l}NH_2\\|\\C{=}NH\\|\\NH_2.NH_2SO_3H\end{array} + (NH_4)_2SO_4 + S$$

[15]

Guanidine Sulphamate and Sulphate

The formation of guanidine increased, as was expected, with the amount of sulphur dioxide used (Fig. 4), but decreased owing to dilution with excess of sulphur dioxide (0.4 mole vs. 0.1 mole urea). When a mixture of urea, sulphur dioxide, and ammonia (molar ratio 1: 3: 9) was heated at 275° C. for an hour at a pressure of 200 p.s.i.g., guanidine was present mainly as the sulphamate. Alternatively, the same reaction mixture heated at 300° C. for two to five minutes and cooled immediately yielded mainly guanidine sulphate. Guanidine sulphamate is soluble in liquid ammonia whereas guanidine sulphate is very insoluble. Therefore a means of separating the two salts of guanidine is suggested.

When urea, sulphur dioxide, and ammonia were used in the molar ratio 2: 3: 7, guanidine sulphate was produced in 43.6% yield, traces of guanidine sulphamate being formed. Melamine was obtained also in good yield owing to the instability of guanidine sulphate under the conditions employed. At a lower temperature of synthesis, for instance at 275° C., less melamine is produced, but the yield of guanidine sulphate is decreased. The reactions involved when two moles of urea are used are as follows:



$$2\begin{array}{c}NH_2\\|\\C{=}O\\|\\NH_2\end{array} + 3SO_2 + 4NH_3 \longrightarrow \left(\begin{array}{c}NH_2\\|\\C{=}NH\\|\\NH_2\end{array}\right)_2 .H_2SO_4 + S + (NH_4)_2SO_4$$

Guanidine Nitrate

A series of runs were made at 275° C. from urea, sulphur dioxide, and ammonia (molar ratio 1: 3: 7) under which conditions 80% yield of guanidine or better was obtained. The reaction products were dissolved in boiling water, sulphur was filtered, and the filtrate treated with various quantities of nitric acid. Table VII shows the proportions and the amounts of guanidine nitrate

TABLE VII

GUANIDINE NITRATE

Run[1] No.	HNO_3 (70%), gm.	Molar ratio, urea: HNO_3	Crude G.N.[2]		Recrystallized G.N.[3] from 20 ml. of water		% Yield of G.N. from urea
			gm.	m.p., °C.	gm.	m.p., °C.	
1	9.0	1:1	9.5	190–195	8.4	204–206	69
2	10.8	1:1.2	10.0	192–196	8.9	205–207	73
3	12.6	1:1.4	10.0	190–195	8.8	204–206	72
4	14.4	1:1.6	8.6	196–199	7.6	204–206	62
5	16.2	1:1.8	8.2	195–198	7.2	205–207	59

[1] *All runs were prepared by heating at 275°C. for half an hour at 200 p.s.i.g., urea:SO_2:NH_3 molar ratio being 1:3:9.*

[2] *Crystallization at 0°C. from 50 ml. of solution. G.N. = guanidine nitrate.*

[3] *Recrystallization at 0°C. from 20 ml. of water.*

isolated. The yields are very good if correction is made for solubility. It should be noted that a maximum yield of guanidine nitrate is obtained when the guanidine – nitric acid ratio is 1: 1.35. Thus a yield of guanidine nitrate of 73% based on urea is obtained.

Conclusion

The synthesis of guanidine from urea, using sulphur dioxide and ammonia as dehydrating agent, is promising in that the starting materials are cheap and easily accessible. The ease of handling of sulphur dioxide and the large amount of this chemical distributed as sulphur or pyrites could render this synthesis applicable to continuous production of guanidine. This can be achieved by feeding an ammonia solution of urea and sulphur dioxide in a suitable reactor maintained at the desired temperature. The reaction products are molten at a temperature as low as 120° C.

EXPERIMENTAL

General Procedure

A 100 ml. autoclave was charged with urea, sulphur dioxide frozen in liquid air, and liquid ammonia. The bomb was heated at the desired temperature for a period of time. After the bomb was cooled, the contents of the glass liner was dissolved in water, sulphur was filtered off, and the clear solution used for analytical work.

Estimation of Sulphur

The crude sulphur obtained by filtration was dissolved in carbon disulphide and the solution evaporated in a weighed dish. Sulphur is reported in moles (Tables V and VI).

Estimation of Sulphates

(*a*) A 10 ml. aliquot portion of the solution made up to 500 ml. was diluted with 200 ml. of water and treated at room temperature with 50 ml. of 10% $BaCl_2$ solution in 2% hydrochloric acid. $BaSO_4$(HCl) is reported in moles (Tables V and VI).

(*b*) A 10 ml. aliquot portion was diluted with 100 ml. of water; 10 ml. of sodium hypochlorite (5% available chlorine) was added and the solution boiled. Hydrochloric acid was added until pH of 1–2 and then 50 ml. of 10% barium chloride added at the boiling point. The precipitate was filtered and weighed. $BaSO_4(O)$ is reported in moles (Tables V and VI).

Isolation of Guanidine Sulphamate

A mixture of urea (6.0 gm., 0.1 mole), sulphur dioxide (19.2 gm., 0.3 mole), and ammonia (15.3 gm., 0.9 mole) was heated at 275° C. for half an hour. The bomb was vented to 200 p.s.i.g. The contents of the glass liner was dissolved in water and sulphur was filtered off. The filtrate, after evaporation to dryness under reduced pressure, was treated with liquid ammonia (200 ml.) and the mixture filtered free of insoluble sulphates. The residue was washed well with ammonia. Analysis of the residue insoluble in liquid ammonia showed only traces of guanidine, presumably the sulphate. The liquid ammonia solution was allowed to evaporate and a residue was left which melted at 80–100° C. This material was recrystallized from alcohol and melted at 127° C. Further crystallizations raised the melting point to 128.5° C. A mixed melting point determination with guanidine sulphamate was not depressed.

Guanidine Sulphate

A similar batch was made by heating continuously to 300° C. and allowing the bomb to cool to 275° C. At this temperature the bomb was cooled with hot water and finally cold water. By working up the reaction products as above, it was found that the material insoluble in liquid ammonia contained 1.96 gm. of guanidine as sulphate and the liquid ammonia soluble material, 0.190 gm. of guanidine as sulphamate, thus giving a ratio of guanidine sulphamate to guanidine sulphate of 1: 10.

When the amount of urea was doubled leaving the quantities of other ingredients the same as above, all the guanidine was present as sulphate. A 43.6% yield of guanidine based on urea was obtained. The other part of urea was transformed into melamine.

Guanidine Nitrate

A series of batches from urea, sulphur dioxide, and ammonia (molar ratio 1: 3: 9) was prepared by heating at 275° C. for half an hour. The reaction products were dissolved in water and the sulphur was removed by filtration. The filtrate was treated with a known amount of 70% nitric acid (Table IV) and the solution evaporated on the hot plate to a volume of 50 ml. The solution was cooled to 0° C. and allowed to stand at this temperature for 10 min. The solid was filtered and washed once with water at 0° C. The melting point of guanidine nitrate was taken. The guanidine nitrate obtained was usually contaminated with urea nitrate. A recrystallization from 20 ml. of water gave a guanidine nitrate melting above 200° C. In Table VII it is seen that the optimum ratio of HNO_3 to guanidine is 1.35 to 1.

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