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TECHNICAL MEMORANDUM No. 1/M/51

A Process for the Manufacture of Nitroguanidine from Urea: The Amination Stage

E. Roberts and J. V. Griffiths

Waltham Abbey,
Essex.

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CORRIGENDUM TO TECHNICAL MEMORANDUM No. 1/M/51

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It is regretted that a portion was omitted from the last paragraph of Section 6.4., page 4. This should read:

"The solution was made up to 250 ml. and free acidity determined by titrating 25 ml. portions against N sodium hydroxide to methyl red indicator. From this titration the residual ammonia in the reaction mixture was calculated.

10 ml. portions of the solution, after being neutralised to methyl red with aqueous ammonia were analysed for guanidine in the usual way".

Please amend your copy and attach this notice.

H.T. Lester

for C.S., E.R.D.E.

Waltham Abbey, Essex.
13th February, 1951

E.R.D.E. 1/M/51.

MINISTRY OF SUPPLY.

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This report does not contain classified information of overseas origin.

Approved: A.FORSTER
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Reference: XR.441/102

1. ABSTRACT.

1.1. Object of Investigation.

To examine the effect of proportion of ammonia, using aqueous solutions, in the amination of O-ethylisourea, i.e. in the amination stage of the process for the manufacture of nitroguanidine from urea, using the molar ratio, urea: diethyl sulphate, 1:1.

1.2. Scope of Investigation.

The formation of guanidine from O-ethylisourea, more strictly 'ethylation product', has been studied using the molar ratio, urea: diethyl sulphate, 1:1, varying (a) the molar ratio of O-ethylisourea: NH_3, (b) concentration of ammonia, and (c) time of reaction at a temperature of 60°C.

1.3. Conclusions.

The rate and extent of formation of guanidine, in aqueous solution at 60°C, from O-ethylisourea, contained in the 'ethylation product' prepared using urea (1 mole) and diethyl sulphate (1 mole), is determined by the proportion of ammonia used for amination.

A constant and optimum yield, based on urea of 75 to 76 per cent guanidine is obtained using 1.33 to 1.70 moles NH_3, contained in 4.5 moles H_2O per mole urea. No further increase in yield is obtained using a higher proportion of ammonia.

The rate of amination increases with increase in proportion of ammonia. Using 1.33, 1.52, 1.70 and 2.34 moles NH_3 respectively in 4.5 moles H_2O, per mole urea or diethyl sulphate, the reaction times for attainment of optimum yield of guanidine are 2.0, 1.0, 0.75 and 0.50 hour respectively.

The yield of guanidine, now recorded, viz. 75 to 76 per cent, is 2 to 3 per cent higher than that, viz. 72 to 73 per cent, previously recorded using 1.14 moles NH_3 in 4.5 moles H_2O after 3 hours at 60°C. Using 1.33 and 1.52 moles NH_3 a yield of 72 to 73 per cent guanidine can be obtained in 1.0 and 0.50 hours respectively.

The increase in yield of guanidine now recorded, viz. 2 to 3 per cent, is equivalent to an increase in output of 3 to 4 per cent nitroguanidine in the process.

1.4. Recommendations.

The use of at least 1.33 moles NH_3, contained in 4.5 moles H_2O per mole diethyl sulphate, or urea, is recommended for amination of the product of ethylation obtained in the first stage of the process for the manufacture of nitroguanidine from urea.

The use of a higher proportion of ammonia would be determined primarily by technical considerations relating to desired throughput.

2. INTRODUCTION.

Early work (1) (2) showed the feasibility of producing nitroguanidine from urea. In later work (3) the elements of a process for the production of nitroguanidine (picrite) from urea were established.

Since, a more critical examination has been made of each stage in the proposed process for the production of nitroguanidine from urea in order to

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introduce possible improvements and define more exact conditions for a continuous process. A full report covering this work is in preparation.

At the U.S. Conference on 'High Nitrogen Compounds' held at Chicago on Sept. 11-13, 1950, a paper (4) was presented outlining the present position and including a flowsheet for the projected process. The optimum conditions for the four stages, viz. alkylation, amination, hydrolysis and nitration, involved in the process were defined. The study of the amination stage was, at the time of presentation, not complete and now the results which are considered of significance, are presented in the form of an E.R.D.E. Technical Memorandum. The issue of this paper will facilitate the work of those now actively engaged in the field whilst the more complete report is being compiled.

3. THE AMINATION STAGE.

The amination of the product of the ethylation stage, using urea (1 mole) and diethyl sulphate (D.E.S., 1 mole) has been studied using gaseous ammonia, under anhydrous conditions, and aqueous ammonia. Only those results referring to the use of aqueous ammonia will be considered in this report as they are considered more relevant to the technical procedure envisaged in the process for the manufacture of nitroguanidine from urea.

It was stated (4) that the conversion of O-ethylisourea, contained in the ethylation product, to guanidine was optimum using about 20 per cent excess ammonia, based on about 74 per cent conversion of urea to O-ethylisourea, and aminating at 60°C. for 3 hours. In the amination, in addition to formation of guanidine, a further quantity of ammonia was fixed in side reactions. Thus, using urea (1 mole) and D.E.S. (1 mole), amount of ammonia used for amination was 0.74 + 50% (0.74) mole = 1.11 mole NH_3; of this, it was found that about 0.22 mole NH_3 was fixed in side reactions, showing real excess, i.e. unreacted, of ammonia used for guanidine formation to be about 0.15 mole NH_3, equivalent to 20 per cent excess on the O-ethylisurea value.

In further discussion of the amination stage it is now preferred to refer to ammonia usage in terms of moles NH_3 used per mole urea, or, per mole 'ethylation product', prepared using urea (1 mole) and D.E.S. (1 mole).

The rate and extent of amination of the product of the ethylation stage, using urea (1 mole) and D.E.S. (1 mole) has been studied in aqueous solution at 60°C. using the following molar proportions of ammonia (per mole urea) respectively: 1.14 (25%), 1.33 (50%) 1.52 (75%), 1.70 (100%) and 2.34 (185%). In brackets are shown the percentage of excess, i.e. unreacted, ammonia used, as defined above, assuming the formation of 0.75 mole O-ethylisourea from 1 mole urea, and 0.20 mole NH_3 fixed in side reactions. In all cases the water introduced in the ammonia solution was that previously found (4) (5) to be optimum for the hydrolysis stage, viz. 4.5 moles H_2O per mole D.E.S. used in ethylation stage. The necessary input of ammonia was achieved by using an aqueous solution of suitable concentration. Thus, in our experiments, since the amount of water present is constant the combined effect of, (a) molar ratio of O-Et-isourea : NH_3 and, (b) concentration of ammonia has been observed.

The experimental results obtained are shown in Section 5.4 (Tables 2 and 3). These show:

(i) A constant and optimum yield, based on urea, of 75 to 76 per cent guanidine is obtained using 1.33 to 1.70 moles NH_3, contained in 4.50 moles H_2O, per mole per urea. No further increase in yield is obtained using a higher proportion of ammonia.
(ii) The rate of amination increases with increase in proportion of ammonia. Using 1.33, 1.52, 1.70 and 2.34 moles NH_3 respectively in 4.5 moles H_2O, per mole or D.E.S. the reaction times for attainment of optimum yield of guanidine are 2,1, 0.75 and 0.50 hour respectively.
(iii) the yield of guanidine now recorded, viz. 75 to 76 per cent, is 2 to 3 per cent higher than that, viz. 72 to 73 per cent, previously recorded.

(3) (4) (5) and obtained using 1.14 moles NH_3 in 4.5 moles H_2O after 3 hours at 60°C. Using 1.33 and 1.52 moles NH_3 a yield of 72 to 73 per cent guanidine can be obtained in 1.0 and 0.5 hour respectively.

(iv) In addition to the ammonia converted to guanidine a further quantity is consumed in side reactions; this had been found to correspond to about 0.25 mole NH_3 per mole 'ethylation product'. The total consumption of ammonia at the amination stage is therefore almost exactly 1 mole NH_3 per mole 'ethylation product, or, per mole urea.

(v) The use of an increased excess, i.e. when using high proportions, of ammonia would necessitate the recovery of correspondingly larger quantities of ammonia. The proportion of ammonia used would be determined primarily by technical considerations relating to throughput desired.

4. CONCLUSION

Conditions have been defined establishing an improvement in yield, based on urea, from 72 to 73 to 75 to 76 per cent guanidine.

The overall yield obtainable of purified nitroguanidine, based on urea, should correspondingly, in the light of this study, be about 2 to 3 per cent higher than that previously recorded (3) (4), which is equivalent to an increase in output of 3 to 4 per cent of final product.

5. BIBLIOGRAPHY

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6. EXPERIMENTAL

6.1. Ethylation of Urea: Preparation of 'Ethylation Product'

Small batches of urea were ethylated with diethyl sulphate using the molar ratio urea: D.E.S., 1:1 and carrying out the reaction at 110°C for 30 min. This product, which will be referred to as 'ethylation product' consists primarily of O-ethylisourea in the form of a salt of ethyl hydrogen sulphate; it solidifies on cooling and was stored prior to use in a desiccator.

6.2. Amination of 'Ethylation Product'

The necessary input of ammonia was achieved by using an aqueous solution of suitable concentration.

The molar proportions of ammonia, per mole urea, or D.E.S. or 'ethylation product', used were respectively: 1.14 (25%), 1.33 (50%), 1.52 (75%), 1.70(100%) and 2.34 (185%), contained in 4.5 moles H_2O per mole D.E.S, or urea, (molar ratio,1:1) used in the ethylation stage: in all cases the water introduced was that previously found to be optimum for the hydrolysis stage. In brackets are shown the percentage excess, i.e. unreacted, ammonia used calculated on the content of O-ethylisourea, assuming that 0.75 mole O-ethylisourea was formed from 1 mole urea, and 0.20 mole NH_3 was fixed in side reactions. In some preliminary experiments

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it had been observed that 0.20 mole NH_3 was fixed, per mole urea, in side reactions, but in the experiments now recorded the amount of ammonia fixed in side reactions would appear to be 0.25 mole NH_3 per mole urea.

6.3. General Method.

'Ethylation product' was melted and 10 g. (approximate) samples poured into weighed boiling tubes fitted with rubber stoppers. The contents of the tubes were quickly cooled to give a supercooled syrup and the tubes reweighed.

The requisite ammonia solution was added from a burette to form a supernatant layer and the tube securely stoppered and weighed. The contents of the tube were well shaken when a clear homogeneous solution was readily obtained. The tube was then reheated in an oil bath at 60°C. for the desired period of time.

When the period of heating had elapsed the tube was removed from the bath, quickly cooled and the contents washed into a 250 ml. standard flask containing a known excess of N sulphuric acid. This served to arrest the amination reaction.

The solution was made up to 250 ml. and free acidity determined by titrating 25 ml. portions against N sodium hydroxide to methyl red with aqueous ammonia, were analysed for guanidine in the usual way.

6.4. Experimental Data.

Two series of experiments were carried out:
Series I Two different batches of 'ethylation product' were used in this series; one batch using 1.33 moles NH_3 (50% excess) and 1.52 moles NH_3 (75% excess), and the other using 1.70 moles NH_3 (100% excess) and 2.34 moles NH_3 (185% excess). The results obtained are therefore not strictly comparable.

Note: Some values of consumption of ammonia, i.e. fixed in side reactions, are probably too high due to experimental losses of ammonia.

The experimental conditions together with the analytical data are shown in Table 1.

Series II All experiments were carried out on a uniform batch of material. Greater care was taken to minimise manipulative losses of ammonia. In these experiments the solution before insertion in the oil bath was allowed to stand 10 min. at room temperature; under these conditions the temperature of the solution rose spontaneously to about 35-40 C.

The experimental conditions together with the analytical data are shown in Table 2.

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Table I.

Molar ratio, urea: D.B.S. = 1:1
(Ethylation carried out at 110°C for 30 min.)
Temperature of Amination, 60°C.
Water used, 4.5 moles H_2O/mole urea.

Ammonia Used											
Moles NH_3/mole Urea	1.33						1.52				
Excess on Isourea, %	50.						75.				
Conc^n of NH_3 Soln., % by Wt.	21.9						24.1				
Time of Amination, hours.	1/2	1	2	3	4	5	1/2	1	2	3	4
% yield Guanidine on Urea.	69.3	72.7 72.7	74.0 75.2	75.6 76.5	76.4	76.4	72.7	74.9	75.8	76.8	77.2
Moles NH_3/mole Urea Fixed as By-products.	0.20	0.21 0.22	0.29 0.21	0.25 0.22	0.24	0.23	0.22	0.30	0.26	0.23	0.23

Ammonia Used											
Moles NH_3/mole Urea	1.70					2.34					
Excess on Isourea, %	100					185					
Conc^n of NH_3 Soln. % by Wt.	26.3					33.0					
Time of Amination, hours.	1/2	1	2	3	4	1/4	1/2	3/4	1	2	3
% Yield of Guanidine on Urea.	73.9	74.5	75,3	75.1	75.1	73.6	75.9	76.0	75.3	75.9	75.4 76.3
Moles NH_3/mole Urea Fixed as By-products.	0.21	0.27	0.26	0.27	0.27	0.43	0.44	0.40	0.41	0.40	0.32 0.42.

Table 2.

Molar ratio, urea: D.E.S. 1:1
(Ethylation carried out at 110°C for 30 min.)
Temperature of Amination, 60°C.
Water used, 4.5 moles H_2O/mole urea.

Ammonia Used												
Moles NH_3/mole Urea	1.14						1.33					
Excess on Isourea, %	25						50					
Conc^n of NH_3 Soln., % by Wt.	19.4						21.9					
Time of Amination, hours.	1/4	1/2	3/4	1	2	3	1/4	1/2	3/4	1	2	3
% Yield Guanidine on Urea	59.7	64.0	67.2	29.3	71.5	73.0	64.1	68.9	71.6	73.0	74.6	75.1
Moles NH_3/mole Urea Fixed as By-Products.	0.14	0.17	0.17	0.18	0.19	0.20	0.20	0.23	0.22	0.23	0.24	0.24

Ammonia Used												
Moles NH_3/mole Urea	1.52						1.70					
Excess on Isourea, %	75.						100					
Conc^n of NH_3 Soln. % by Wt.	24.1						26.3					
Time of Aminating, hours.	1/4	1/2	3/4	1	2	3	1/4	1/2	3/4	1	2	3
% Yield Guanidine on Urea.	68.8	72.5	73.6	74.1	74.6	74.9	70.8	73.8	74.4	71.2	74.7	74.5
Mole NH_3/mole Urea Fixed as By-products.	0.20	0.22	0.22	0.23	0.23	0.23	0.21	0.23	0.25	0.24	0.23	0.24

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