[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT—CHEMICALS OF E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

ETHYLENEUREA. I. SYNTHESIS FROM UREA AND ETHYLENEDIAMINE

CARL E. SCHWEITZER

Received August 15, 1949

Starting in December, 1941, at the request of the National Defense Research Committee, methods were developed for the synthesis of ethyleneurea, 2-imidazolidone.[1] Results of this investigation indicated several possibilities for commercial scale production, and removal of security restrictions has made it possible to describe these developments in a series of papers of which this is the first.

When this investigation of an ethyleneurea synthesis was begun, there were several preparative methods in the literature (1–5), but each of these was subject to certain limitations, judged by the requirements of a commercial process. However, other theoretically possible routes were apparent and of these, four were developed which were based upon the reactions of:

(A) Ethylenediamine with carbon dioxide
(B) Ethylenediamine with urea
(C) Ethylene glycol with urea or with ammonia and carbon dioxide
(D) Ethanolamine with urea

Starting with ethylenediamine and carbon dioxide as indicated in (A) above, excellent yields (*ca.* 98%) of ethyleneurea were obtained at elevated temperatures and pressures. However, this reaction, studied independently at about the same time by others (6), has already been described. Results were comparable with those obtained in this laboratory.

The reaction of ethylenediamine with urea, which is the subject of this paper, likewise proved to be a highly satisfactory method for synthesizing ethyleneurea. It may be carried out in one step at atmospheric pressure with yields of 98% or better. Because operation by this route is relatively simple, it is of interest both commercially and as an especially attractive laboratory procedure. After this work had been completed, it was found that the ethylenediamine-urea reaction had been tried, but the yield of ethyleneurea was less than 10% (7). Here the important role of water as a moderator for the reaction was not recognized. This probably accounts for the marked difference.

Using ethylene glycol and urea (or carbon dioxide and ammonia in place of urea) or ethanolamine and urea (C or D) it was possible to obtain ethyleneurea in good yields and the results of these phases of the study will be presented in papers to follow.[2]

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[1] OSRD contract No. OEMsr-373.

[2] The following patents have been granted which pertain to certain aspects of the ethyleneurea problem: Dittmar and Loder, U. S. Patent 2,416,046; Larson and Loder, U. S. Patent 2,416,057; Loder, U. S. Patent 2,245,627; Larson, Loder, and Dittmar, U. S. Patent 2,436,311; Loder, U. S. Patent 2,474,004.

ETHYLENEDIAMINE-UREA REACTION

Urea undergoes reaction with a variety of amines to produce alkyl-substituted ureas (8), and with diamines to yield polyalkylureas (9). It has now been found that urea and ethylenediamine will react to give ethyleneurea in high yields provided water is present as a moderator.

$$NH_2CH_2CH_2NH_2 + NH_2CONH_2 \rightarrow \underline{NHCH_2CH_2NHCO} + 2\,NH_3$$

Thus, an equimolar mixture of urea and aqueous ethylenediamine (68% diamine, 32% water by weight) was permitted to reflux while water was removed slowly and ammonia, liberated by the reaction, was allowed to escape. The mixture changed from a liquid to a thick pasty mass and finally again to a clear melt of substantially pure ethyleneurea in nearly quantitative yield. With no sacrifice in yield it was possible to maintain a reasonably fluid charge if a 5–20% molar excess of the diamine-water azeotrope was used. This excess diamine was separated by vacuum-distillation from the final product.

If water is not removed as the reaction proceeds, the relatively low reflux temperature retards the desired reaction but permits a partial hydrolysis of urea. This reduces the yield of ethyleneurea. Under these conditions the chief product appears to be crude 2-aminoethylurea which upon further heating is converted partly to ethylenediamine and partly to a white unidentified high-melting solid.

If water is omitted from an equimolar charge of ethylenediamine and urea, the anhydrous materials react slowly to liberate ammonia until a temperature of about 140° is attained. At this point an extremely vigorous reaction occurs which produces a white solid melting near 270°. In one case the reaction was violent enough to eject the thermometer and part of the solid from the flask.

Attempts to accelerate the reaction by replacing water with higher-boiling liquids such as *n*-butyl alcohol, dimethylformamide or methoxymethoxyethanol resulted in high-melting, unidentified products rather than ethyleneurea. If, however, the desired higher temperature is attained by operating under pressure, the reaction is accelerated and satisfactory yields of ethyleneurea may be obtained in an aqueous system. At 245–275° the reaction is complete within an hour.

At ordinary temperatures ethyleneurea is a white, neutral solid which is odorless when pure. It melts at 133.7° (corr.); [lit., 131° (1, 6)] and may be distilled at 163°/3 mm.; 187°/10 mm.; 192°/16 mm. The last value is in good agreement with the one published boiling point (6). Crystallized from a water solution, it is obtained as the hemihydrate which at room temperature effloresces slowly to the anhydrous form.

There are two crystalline modifications with a transition temperature of about 80°. Optical constants, obtained under the petrographic microscope by the method of Bryant (10), are as follows:

ETHYLENEUREA (anhydrous)

Biaxial (+). Refractive indices (25 ± 3°; 5461 Å): $\alpha = 1.537$, $\beta = 1.563$, $\gamma = 1.694$; all ± 0.003. Optic Axial Angles: $2H_a = 57°$ (4358 Å); 59° (5461 Å); 60°

(6908 Å); all ±1°. Second anhydrous modification (unstable at room temperature) is uniaxial (+).

ETHYLENEUREA HEMIHYDRATE

Uniaxial (+). Refractive indices (25 ± 3°; 5461 Å): *omega* = 1.521 ±0.003, *epsilon* > 1.56.

Solubilities in several solvents at different temperatures are given in Table I.

EXPERIMENTAL

Synthesis of ethyleneurea at one atmosphere. A mixture composed of 732 g. of the ethylenediamine-water azeotrope [498 g. (8.3 moles) of ethylenediamine and 234 g. (13 moles) of water] plus 498 g. (8.3 moles) of urea, was charged into a two-liter, three-necked, round-bottom flask. The flask was fitted with a sturdy stirrer, a thermometer, and a 20 mm. × 60 cm. Vigreux column carrying a condenser which could be set for various reflux ratios. Contents of the flask were stirred and heated to vigorous reflux. During a four-hour period, liberated ammonia was allowed to escape and water was slowly removed from the top of the column so that the temperature of the reaction mixture rose from 110° to 240–250°. At the end of approximately three hours, when the temperature had reached 160–180°, the mixture became quite pasty and rather difficult to stir, but during the final hour it changed to a clear, pale amber liquid. This, upon cooling, solidified to give 710 g. of ethyleneurea, m.p. 127–131° (yield, 99+%). One recrystallization from chloroform brought the melting point to 130–131° and by repeated recrystallizations from chloroform and from dioxane the melting point was raised to 133.7° (corr.).

TABLE I

SOLUBILITIES OF ETHYLENEUREA

SOLVENT	TEMP., °C.	SOLUBILITY[a]
Water	8	41
	35	60
	56	75
Methanol	64	79
Ethanol	25	*ca.* 23
n-Butanol	25	<10
Chloroform	61	20
Acetone	0	<0.2
	25	2
	56	3–4

[a] Expressed as grams of anhydrous ethyleneurea per 100 grams of solution.

Synthesis of ethyleneurea under pressure. A charge comprising 87.9 g. of the water-ethylenediamine azeotrope [containing 60 g. (1.0 mole) of diamine] plus 60 g. (1.0 mole) of urea, was heated at 250° in an agitated, silver-lined, steel bomb of 325-cc. capacity at a pressure of 160 atmospheres for one hour. The resulting product was distilled at reduced pressure to remove volatiles, including water and 10% of the charged ethylenediamine. Ethyleneurea, 66.6 g., remaining as the residue melted at 119–125° and represented a yield of 85% based upon the diamine and 77% based upon urea. When recrystallized from chloroform it had m.p. 129–131°.

SUMMARY

A practical laboratory procedure is reported for the synthesis of ethyleneurea in nearly theoretical yield from urea and ethylenediamine in the presence of water as a moderator. Variables affecting yields are discussed and certain physical properties of ethyleneurea are recorded.

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REFERENCES

(1) FISHER AND KOCH, *Ann.*, **232**, 277 (1886).
(2) KLUT, *Arch. Pharm.*, **240**, 677 (1902).
(3) TAFEL AND REINDL, *Ber.*, **34**, 3286 (1901).
(4) PIERRON, *Ann. chim.*, [9] **11**, 361 (1919).
(5) PUSCHIN AND MITIC, *Ann.*, **532**, 300 (1937).
(6) MULVANEY AND EVANS, *Ind. Eng. Chem.*, **40**, 393 (1948).
(7) HANSEN, Master's Thesis, Massachusetts Institute of Technology, 1939.
(8) DAVIS, U. S. Patent 1,785,730; OLIN, U. S. Patents 2,257,717 and 2,253,528.
(9) ARNOLD, U. S. Patent 2,145,242.
(10) BRYANT, *J. Am. Chem. Soc.*, **60**, 1394 (1938); *J. Am. Chem. Soc.*, **63**, 511 (1941).