constant melting range 103–119°, yield 87 g. (37% over-all) of red needles.

Anal. Calcd. for $C_{16}H_{16}\cdot C_{13}H_5N_3O_7$: TNF, 60.2. Found:[22] TNF, 59.5.

Chromatographic dissociation of the molecular compound by the preceding method produced nearly colorless VI, b.p. 139–140° (1.4 mm.).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.83; H, 7.89.

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[22] Determined spectrophotometrically by a procedure to be described elsewhere.

[CONTRIBUTION FROM THE POLYCHEMICALS RESEARCH DEPARTMENT, DOW CHEMICAL CO.]

Reaction of Ethylene Oxide with Urea

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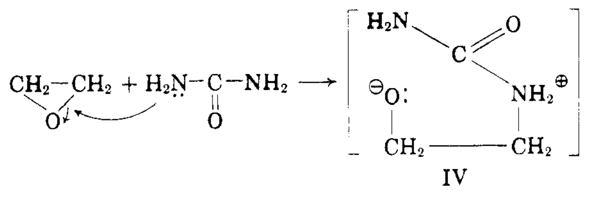
The reaction of equimolar amounts of ethylene oxide and urea gives as a main product β-aminoethylcarbamate, rather than the expected β-hydroxyethylurea. The reaction mechanism can be compared with an N → O acyl migration.

Pacquin[1] reported that a high molecular weight, water soluble product is obtained by reaction of ethylene oxide with urea at temperatures above 90°. However, the intermediates and the final product were ill defined.

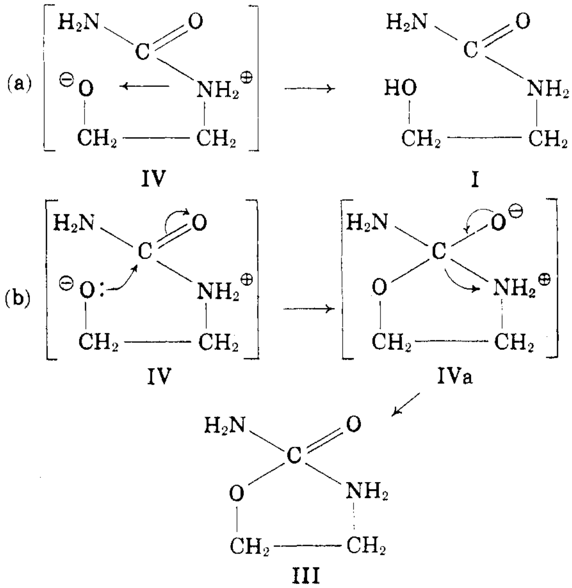
The purpose of this paper is to present a study of the reaction products obtained by passing ethylene oxide into molten urea. It was shown that small amounts of β-hydroxyethylurea (I) and 2-oxazolidinone (II) were produced along with the main reaction product, β-aminoethylcarbamate (III).

The various products isolated and characterized in the experimental section are in conformity with a mechanism involving as a first step a nucleophilic attack by urea on ethylene oxide. This would give the transient intermediate (IV):



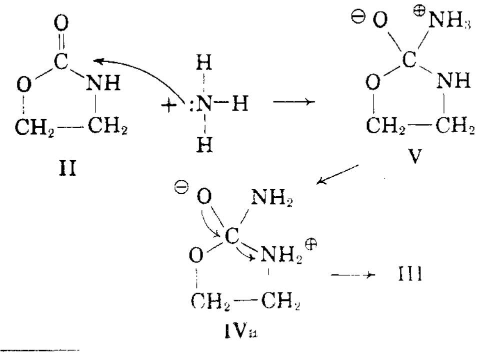
The intermediate could be stabilized by a proton transfer from nitrogen to oxygen to form β-hydroxyethylurea (I). An alternative method of stabilization could be an intramolecular nucleophilic attack of the negatively charged oxygen on the carbonyl carbon to form the cyclic intermediate (IVa), which subsequently dissociates into β-aminoethylcarbamate (III).

The latter mechanism is similar to that proposed by Van Tamelen[2,3] for the formation of *cis*-2-aminocyclopentyl (*p*-nitrobenzoate) by the action of hydrogen chloride on *cis* or *trans*-*N*-(*p*-nitrobenzoyl)-2-aminocyclopentanol.



The formation of 2-oxazolidinone (II) conceivably occurs by an elimination reaction involving the removal of ammonia from either (I) or (III). Close,[4,5] for example, converted β-hydroxyethylurea into 2-oxazolidinone by heating at 190–200°. By analogous treatment we were able to transform β-aminoethylcarbamate (III) into 2-oxazolidinone (II).

Finally it is of interest that 2-oxazolidinone (II) may be converted into β-aminoethylcarbamate



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[1] A. Pacquin, *Kunststoffe*, **37**, 165 (1947).

[2] Van Tamelen, *J. Am. Chem. Soc.* **73**, 5773 (1951).

[3] Van Tamelen, Tousignant, Peckham, *J. Am. Chem. Soc.* **75**, 1297 (1953).

[4] Close, *J. Am. Chem. Soc.* **73**, 95 (1951).

[5] Close, *J. Org. Chem.* **15**, 1131 (1951).

(III) by reaction with aqueous ammonia. This probably proceeds by a nucleophilic attack of ammonia on the 2-oxazolidinone (II) to form the cyclic intermediate (V) which isomerizes into (IVa).

EXPERIMENTAL

Ethylene-oxide-urea reaction. A 10-gal. water-jacketed stainless steel reaction vessel was charged with 13.6 kg. (227 moles) of urea. The system was rapidly heated to about 136° under a nitrogen atmosphere. At this temperature, urea was molten. Nine and nine-tenths kg. (227 moles) of ethylene oxide was added with stirring over an 8-hr. period. The addition was at such a rate as to maintain a pressure of 50–70 p.s.i.g. The container was then cooled to 65°, evacuated gradually to approximately 10 mm., and, while under vacuum, reheated to 100°. This technique served to remove ammonia and residual amounts of ethylene oxide. The reaction residue was a viscous, water-soluble liquid, which changed into a semicrystalline solid on standing. Attempted vacuum distillation of this material resulted in decomposition and evolution of ammonia.

Isolation of the reaction products was therefore effected by the following treatment: A 2-kg. sample of the residue was diluted with 400 ml. of water to which was added gradually, with stirring, 2 kg. of Dowex 50 (acid form). Stirring was continued for 24 hr. to insure complete liberation of carbon dioxide. The Dowex 50 resin was removed by filtration and the filtrate treated with Norite and refiltered. The 400 ml. of water was removed by vacuum distillation at 2–5 mm. at room temperature.

After this treatment, 800 g. of the above residue was allowed to stand until partial solidification had occurred. The sample was then centrifuged and the solid residue containing 80 gr. (10%) of crude β-hydroxyethylurea (I) was collected and purified by recrystallization from 95% ethanol. The recrystallized product melted at 94–95°. Morgan reported a melting point of 95°.[6] This compound, when mixed with an authentic sample, prepared by the procedure of Morgan,[6] failed to depress the melting point. The compound was further identified by an infrared analysis which compared identically with the known sample of β-hydroxyethylurea.

One hundred grams of the viscous liquid remaining after centrifuging was extracted with 52 100-ml. portions of hot chloroform. The chloroform was evaporated on a steam bath. The residual oil (23.5 g.) was allowed to stand approximately a week, whereupon crystals settled out and were filtered. Recrystallization from chloroform gave 10 g. of a product melting at 87–89°. This compound was identified as 2-oxazolidinone (II) by a mixed melting point with an authentic sample prepared by the method of Homeyer[7] and by an infrared comparison with an authentic sample.

The chloroform insoluble fraction constituted the major portion of the reaction product, which amounted to 76.0 g. This residue decomposed upon attempted distillation. It was identified without further purification by the following means: The infrared spectrum indicated a carbamate linkage. A likely structure that corresponds to these facts would be β-aminoethylcarbamate (III). Since this compound had not been previously characterized in the literature it was prepared by treatment of β-chloroethylcarbamate with ammonium hydroxide as described below. A comparison of the infrared spectra of this compound and the residue remaining after chloroform extraction indicated that they were identical.

Two molecular weight determinations, by boiling point elevation in methanol, gave 105 and 89 (theoretical 104).

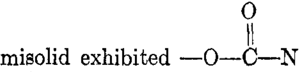
Anal. Calcd. for $C_3H_8N_2O_2$: C, 34.61; H, 7.69; N, 26.29. Found: C, 35.12; H, 7.74; N, 26.20.

A potentiometric titration was carried out on this material. The resulting titration curve gave a *p*H end point at 4.45. This corresponded to an equivalent weight of 99.0 (theoretical eq. wt. 104).

Hydrolysis of β-aminoethylcarbamate (III) with a 10% solution of sodium hydroxide, by refluxing for a period of 18 hr. gave the expected degradation products. Ammonia was collected in an acetone dry ice trap, carbon dioxide was obtained as sodium carbonate, and the corresponding alcohol, namely, 2-aminoethanol, was obtained in 45% yield. The identification of 2-aminoethanol was made by preparation of the dibenzoate derivative melting at 88–89° (lit. m.p. 88–89°[8]).

β-Chloroethylcarbamate. One hundred g. (0.7 mole) of β-chloroethylchloroformate was added dropwise with cooling and stirring, to 43.0 g. of 28% aqueous ammonia. The addition required 2.5 hr. and stirring was continued for an additional 0.5 hr. The white precipitate that formed was filtered and amounted to 75 g. (87%) of β-chloroethylcarbamate. The carbamate was recrystallized from hot water to the constant m.p. 73–75° (lit. m.p. 76°.[9]).

β-Aminoethylcarbamate (III). A mixture of 24.6 g. (0.2 mole) of β-chloroethylcarbamate and 360.0 g. of 28% aqueous ammonia (6.0 mole ammonia) was kept at 50–60° with continuous stirring for 24 hr. The course of the reaction was followed by Volhard titrations until the conversion of organic chloride to ionic chloride was 93%.

After cooling, ammonia and water were evaporated from the reaction product by placing in an open dish at room temperature. A viscous oil resulted which contained crystals of ammonium chloride. The latter was removed by filtration, and the oil became semicrystalline. Infrared spectrum of this semisolid exhibited  $-O-\overset{\overset{O}{\|}}{C}-NH_2$ absorption at 6.0 μ and N—H stretching band at 3.0 μ.

Anal. Calcd. for $C_3H_8N_2O_2$: N, 26.92. Found: N, 26.46.

2-Oxazolidinone (II) conversion into β-aminoethylcarbamate (III). Into a 1.5-l. stainless steel rocking autoclave were placed 21.7 g. (0.25 mole) of 2-oxazolidinone and 250 g. of 28% aqueous ammonia (4.1 mole ammonia). This mixture was held at 130–135° for 1 hr. under 150 p.s.i.g. Ammonia and water were removed under vacuum from the resulting solution. This gave an oil which became semisolid upon standing for an extended period of time. The infrared spectrum was similar to the previously obtained spectrum of β-aminoethylcarbamate (III).

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[6] Morgan, U.S. Patent **2,501,788**.

[7] Homeyer, U.S. Patent **2,399,118**.

[8] Gabriel, *Ber.* **38**, 2412 (1905).

[9] Gattermann, *Ann.* **244**, 41 (1888).