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ETHYLENEUREA. II. SYNTHESES FROM ETHYLENE GLYCOL OR ETHANOLAMINE AND UREA (OR CARBON DIOXIDE AND AMMONIA)

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Of the several routes to ethyleneurea, explored in 1941 at the request of the National Defense Research Committee[1] and summarized briefly in the initial report of this work,[2] those based on ethylene glycol and urea (or carbon dioxide and ammonia) or ethanolamine and urea are the subject of this paper.

Urea can react with glycols to produce carbamate esters without formation of a C—N bond. Thus at 100–200°, urea and 1,3-butylene glycol yield the corresponding mono- and di-carbamates (1). Similarly, urea and ethanolamine produce 2-hydroxyethylurea without amination of the carbon skeleton (2).

During this investigation, however, conditions were found under which urea, or carbon dioxide and ammonia, could be made to aminate either ethylene glycol or ethanolamine to produce satisfactory yields of ethyleneurea. This work represents an extension of urea chemistry and is reported here in detail. Patents have been granted which pertain to certain aspects of the problem.[3] Of the reactants cited above, urea and ethylene glycol were selected for most thorough study because these raw materials were readily available at low cost and could be made to react at atmospheric pressure.

ETHYLENE GLYCOL AND UREA AT ONE ATMOSPHERE

The synthesis of ethyleneurea from urea and ethylene glycol was achieved most satisfactorily in two steps. In the first step, ethylene glycol and a several molar excess of urea were heated gradually from 150 to 240° during a period of several hours. Ammonia and carbon dioxide were evolved and the product was a liquid which set to a brittle resinous solid when cool. Pyrolysis of this resin at 240–270° under reduced pressure resulted in the formation of some ethyleneurea (yield, based upon ethylene glycol, 25%), but a substantial portion decomposed to a carbonaceous product. If, as the second step, the resinous intermediate was hydrolyzed at about 250°, the yield of ethyleneurea was more than doubled (55%).

Course of the reaction. In Table I, data are presented from two typical experiments which show the relative rates of formation of ammonia and carbon dioxide. These data serve to indicate a possible course of the urea-ethylene glycol reaction. Clearly, the synthesis of ethyleneurea did not proceed through simple elimination of two moles of water from an equimolar mixture of reactants for there

[1] OSRD Contract No. OEmsr-373.

[2] Ethyleneurea I. (Preceding paper).

[3] Dittmar and Loder, U. S. Patent 2,416,046; Larson and Loder, U. S. Patent 2,416,057; Loder, U. S. Patent 2,425,627; Larson, Loder, and Dittmar, U. S. Patent 2,436,311; Loder, U. S. Patent 2,474,004.

was no evidence that water *per se* was obtained from the reaction. Indeed, it did not appear to be even a primary product since, if it had been and if it had reacted with urea, then the quantity of carbon dioxide relative to ammonia would have been much higher in the early stages of the reaction. From the very large quantity of ammonia evolved it appeared that the primary product was a carbamate. This carbamic acid ester of ethylene glycol subsequently lost carbon dioxide with formation of the desired C—N bond as indicated by the following equations:

$$HOCH_2CH_2OH + 2\ NH_2CONH_2 \rightarrow NH_2COOCH_2CH_2OCONH_2 + 2\ NH_3$$
$$NH_2COOCH_2CH_2OCONH_2 \rightarrow NH_2CH_2CH_2NH_2 + 2\ CO_2$$

TABLE I

RATES OF FORMATION OF AMMONIA AND CARBON DIOXIDE

MOLE RATIO: UREA/GLYCOL	TOTAL TIME, HOURS	TEMP., °C.	VARIATION WITH TIME OF COMPOSITION IN MOLES			MOLES CO_2/ GLYCOL CHARGED	MOLES NH_3/ GLYCOL CHARGED	MOLES NH_3/ UREA CHARGED
			Urea	Glycol	Biuret			
3.5	0	156	21.0	6.0	0.0	0.0	0.0	0.0
	1.0	162	14.5	2.75	1.71	.14	0.96	.28
	2.0	169	10.2	1.51	2.04	.36	1.74	.50
	3.0	171	8.45	0.79	2.06	.67	2.38	.68
	4.0	176	6.1	.43	2.10	.94	2.86	.82
	5.0	181	4.65	.20	1.94	1.13	3.36	.96
	6.0	222	0.96	.03	1.85	1.53	4.20	1.20
	7.0	275	.13	.02	0.91	1.87	4.84	1.38
	8.0	260	.13	.01	.0	1.84	4.86	1.39
4.15	0	160				0.0	0.0	0.0
	1.0	170				.16	1.41	.34
	2.0	172				.53	2.34	.56
	3.0	175				.88	3.41	.82
	4.0	181				1.13	3.72	.89
	5.0	200				1.53	4.35	1.04
	6.0	240				1.81	5.28	1.27
	7.0	240				1.98	5.40	1.30

Once ethylenediamine had been formed, it could react with urea to produce the resinous ethyleneurea intermediate.

The data of Table I were obtained in typical experiments in which the evolved gases were analyzed continuously. This was accomplished by passing them through standard sulfuric acid to remove ammonia and then through soda-lime or through standard sodium hydroxide to absorb carbon dioxide. Aliquots of the liquid charge were removed periodically and subjected to analyses for *urea* by a method using urease (3), *biuret* by a colorimetric method based upon the purple copper complex formed in alkaline solution (4), and *free ethylene glycol* by either the periodate method (5) or by titration with Karl Fischer reagent of the water released on esterification (6).

During early stages of the reaction biuret accumulated. This, of course, arose

from rapid reaction of urea with itself, but it accounted for a relatively small portion of the ammonia liberated early in the reaction. As the reaction progressed this biuret was consumed.

Ratio of urea to glycol. Variations in the mole ratio of urea to glycol, as might be expected, have a pronounced effect upon the yield of ethyleneurea and upon the character of the resinous intermediate. As shown in Table II, the intermediate changes from a clear, viscous liquid to a porous, opaque solid as the quantity of urea is increased. Yields of ethyleneurea, based upon ethylene glycol, increase

TABLE II

EFFECTS PRODUCED BY CHANGES IN THE RATIO OF UREA TO GLYCOL

RATIO MOLES UREA: MOLE GLYCOL	YIELD OF ETHYLENEUREA, %		APPEARANCE OF INTERMEDIATE
	Based on glycol	Based on urea	
1.0	2	2	Clear viscous syrup
2.0	23	11.5	Tacky, clear resin
3.0	38	12.7	Clear, brittle glass
3.5	39	11.1	Clear, somewhat porous glass
4.0	55	12.5	Opaque, porous, white solid
5.0	57	11.4	Opaque, porous, white solid

TABLE III

EFFECT OF TIME AND TEMPERATURE ON YIELD

UREA/GLYCOL MOLE RATIO	OVER-ALL TIME AND TEMPERATURE RANGE	YIELD OF ETHYLENEUREA BASED UPON GLYCOL, %
3.0	"Standard"*	38
3.0	4.5 hrs.; 150–240°	26
3.0	9.5 hrs.; 175–215°	15
3.5	"Standard"	39
3.5	4.5 hrs.; 150–240°	10
5.0	"Standard"	57
5.0	3.5 hrs.; 160–240°	56

* "Standard" schedule: Six hours at 160–180°, three hours at 180–240°, one hour at 240°.

with increase in urea, the sharpest rise occurring as the mole ratio changes from 3.5 to 4. The yield, based upon urea, remains about the same if the mole ratio is two or greater.

Time and temperature. Changes in these variables have a pronounced effect upon the yield of ethyleneurea which may be derived from ethylene glycol and urea (after hydrolysis of resinous intermediates) and typical data are presented in Table III. Most satisfactory results—chemically, judged by yields, and physically, judged by freedom from mechanical difficulties such as excessive foaming—were obtained with charges which were heated at 160° to 240° for about ten hours. The temperature was raised from 160° to 180° during six hours, 180° to 240° during three hours and then maintained at 240° for one hour; this was the

"standard" schedule. If the same temperature range was observed but if the over-all time was reduced to three or four hours, yields were lower than those obtained with "standard" schedules and often there was troublesome foaming. A final temperature near 240° was essential to effect complete evolution of carbon dioxide and to obtain maximum yields.

Attempted catalysis. A number of experiments were carried out to test the possible catalytic activity of substances such as potassium carbonate, cupric carbonate, ammonium chloride, ammonium sulfate, potassium silicate, boron phosphate, and silica gel, but in no case was there any indication that the reaction could be catalyzed.

Water treatment of the intermediate. In order to recover the maximum quantity of ethyleneurea, it was necessary to treat the resinous polymeric intermediate with water. If the resin was reasonably fluid at 234–270° it was possible to recover ethyleneurea in high yield simply by passing superheated steam through it at these temperatures.

Resins obtained as products from mixtures in which the ratio of urea to glycol was greater than 3.5 to 1 could not be steam-distilled readily because their viscosities were too high. However, it was found that any of the intermediate resins could be cleaved if they were heated with approximately an equal weight of water to about 270° under autogenous pressures for twenty minutes to one hour. If water treatment was carried out at 300° or higher, ethyleneurea itself was hydrolyzed quite extensively and ethylenediamine was obtained.

ETHYLENE GLYCOL AND UREA UNDER PRESSURE

Investigation of the synthesis of ethyleneurea from glycol and urea under pressure demonstrated that higher temperatures and therefore shorter reaction times could be employed than at one atmosphere. Also, less urea was required for a given yield of product, based upon glycol. Thus in three hours at 275° and about 400 atmospheres pressure, the yield of ethyleneurea was 47%; reducing the reaction time resulted in lower yields. An increase in temperature permitted a reduction in reaction time, but at 360°, for example, substantial amounts of ethanolamine and ethylenediamine formed at the expense of ethyleneurea. Increasing the ratio of urea to glycol above four did not improve the ethyleneurea yield.

ETHYLENE GLYCOL, AMMONIA, AND CARBON DIOXIDE[4]

The direct synthesis of ethyleneurea from ethylene glycol, ammonia, and carbon dioxide under pressure was investigated until it became evident that rather high pressures probably would be required. Best results (58% yield) were obtained from a charge consisting of 1 mole of glycol, 8 moles of ammonia, 4 moles of carbon dioxide, and $1\frac{1}{3}$ moles of water, which was heated for 30 minutes at 250°

[4] Similarly, ethyleneurea was obtained when ethanolamine was used in place of ethylene glycol. However, only a limited number of experiments were carried out so that optimum conditions probably were not found. Maximum yield was about 20% from a charge composed of one mole of carbon dioxide, one mole of ethanolamine, and five moles of ammonia which was processed at 250° for 70 minutes under a pressure of 330 atmospheres.

under a pressure of 900 atmospheres. If water was eliminated from a similar charge the yield declined to 52%. Decreasing the pressure to 400 atmospheres resulted in a yield of only 30%.

ETHANOLAMINE AND UREA AT ONE ATMOSPHERE

Major attention was devoted to syntheses of ethyleneurea based upon ethylenediamine or ethylene glycol, but reactions of ethanolamine were explored briefly. In general, there seemed to be no advantage over using ethylene glycol, considering availability of raw materials and their costs. Best results were obtained when a mixture of three moles of urea and one mole of ethanolamine was heated for about nine hours at 110° to 245° and the resinous intermediate hydrolyzed under pressure. The yield of ethyleneurea was 55%, based upon ethanolamine, and compared favorably to that obtained from four moles of urea and one mole of ethylene glycol.

ETHANOLAMINE AND UREA UNDER PRESSURE

The reaction under pressure of ethanolamine and urea, preferably in excess ammonia, was investigated only briefly. It was found to proceed rapidly to produce yields of approximately 38%, based upon the alkanolamine, at 300° and about 900 atmospheres pressure.

EXPERIMENTAL

Ethylene glycol and urea at atmospheric pressure. A typical preparation of the intermediate resin was carried out as follows: A mixture composed of 360 g. (6.0 moles) of urea and 93 g. (1.5 moles) of ethylene glycol was placed in a three-neck, two-liter, round-bottom Pyrex flask fitted with a ten-bulb reflux condenser, a thermometer, and an oil-sealed stirrer. The stirrer was started and the temperature of the mixture was raised slowly from 160 to 180° during 3 hrs., 180–240° during 3 hrs., and finally was maintained at 240° for 1 hr. Ammonia and carbon dioxide liberated by the reaction were allowed to escape through the reflux condenser which was heated by steam to prevent formation of dangerous plugs of ammonium carbonate. The product, a faintly cloudy, colorless white liquid, was poured into a large evaporating dish while still hot. Upon cooling it set to a porous, opaque white solid which weighed 172 g.

Ethyleneurea was obtained from this resinous intermediate by (a) direct thermal decomposition or (b) water treatment. (a) *Thermal decomposition.* The product prepared above (172 g.) was placed in a 500-cc. round-bottom Pyrex flask fitted with an air-condenser of 20-mm. glass tubing bent at a 60° angle, in the manner of a glass retort. The air condenser was connected to a water-cooled receiver attached to a vacuum pump. After the system had been evacuated to about 1 mm. the polymer was heated to 240–270°. Ethyleneurea distilled from the polymer as it decomposed. Pyrolysis was continued until a rise in pressure ndicated the formation of permanent gases. A total of 32.1 g. of ethyleneurea melting at 125–132° was obtained; yield, based on ethylene glycol, 25%.

(b) *Water treatment.* A mixture of 150 g. of the intermediate resin, prepared as described above, and 100 g. of water was charged into a silver-lined bomb of about 300-cc. capacity and heated at 250° under an autogenous pressure of 585 atm. for 2 hrs. The bomb was allowed to cool and the liquid product was discharged. This was distilled at reduced pressure through a 20 mm. × 60 cm. Vigreux column. Water and a small quantity of ammonia were removed at about 100 mm. pressure. The pressure was reduced and 76.5 g. of ethyleneurea distilling at 160–170°/2–3 mm. was obtained. The crude product, which melted at 118–125°, was recrystallized from chloroform giving 60 g. of ethyleneurea, m.p. 128–131°. Yield, based upon glycol, 55%.

Ethylene glycol and urea under pressure. Two charges, each composed of 60 g. (1 mole) of urea and 62 g. (1 mole) of ethylene glycol, were processed in similar silver-lined bombs of 325-cc. capacity at 275° and a pressure estimated to have been 400 atm. for 3 hrs. The bombs were allowed to cool to room temperature and discharged. The combined products were distilled under reduced pressure and 35% of the ethylene glycol was recovered. Ethyleneurea, b.p. 150–170°/1–2 mm., was obtained which, after crystallization from chloroform, amounted to 51 g. for a net yield of 47%, based on ethylene glycol.

Ethylene glycol, ammonia, and carbon dioxide. Two charges, each composed of 46.6 g. (0.75 mole) of ethylene glycol, 102 g. (6.0 moles) of ammonia, 132 g. (3.0 moles) of carbon dioxide, and 18 g. (1.0 mole) of water were processed in silver-lined bombs at 250° for 30 min. under a pressure of 900 atm. The products were combined and distilled at reduced pressure to give crude ethyleneurea which was purified by crystallization from dioxane. The final product weighed 74.8 g. Yield, based upon glycol, 58%.

Ethanolamine and urea at atmospheric pressure. Equipment described above for the reaction of ethylene glycol and urea at atmospheric pressure was used in this experiment. A mixture of 720 g. (12 moles) of urea and 244 g. (4 moles) of ethanolamine was heated with stirring according to the following schedule: 1 hr., 110–150°; 1 hr. 150–160°; 1.5 hrs. 160–195°; 1.25 hrs., 195°; 2 hrs., 195–224°; and 2 hrs., 224–240°. Ammonia and carbon dioxide were permitted to escape through the steam-heated reflux condenser and were passed through a scrubber containing 200–400 cc. of water. The scrubber was made from a 1-liter, 3-neck, round-bottom Pyrex flask fitted with a stirrer and a gas inlet tube which dipped just below the surface of the water. Ethanolamine (35 g.) which escaped with the gases was collected in the scrubber and recovered by distillation. The product remaining in the reaction flask weighed 465 g. When cool it was a very viscous clear, amber liquid.

This liquid (370 g.) was hydrolyzed by heating it with an equal weight of water to 250° for 2 hrs. in an agitated 800-cc. silver-lined bomb under an autogenous pressure of 925 atm. The resulting product was distilled. Ethylenediamine in 10% yield, based upon ethanolamine, was obtained in the first fraction. The pressure was reduced and 155 g. of ethyleneurea, m.p. 126–129°, distilling at 170–180°/4 mm. was obtained; crude yield, 55%, based upon ethanolamine.

Ethanolamine and urea under pressure. A mixture consisting of 60 g. (1.0 mole) of urea, 61 g. (1.0 mole) of ethanolamine, and 85 g. (5.0 moles) of ammonia was processed in a silver-lined bomb at 300° under a pressure of 930 atm. for 10 min. The product was distilled; 12.0 g. of ethanolamine was recovered together with 59 g. of crude ethyleneurea. One recrystallization from chloroform gave 35 g., m.p. *ca.* 123°. Assuming this product to be 75% pure, the net yield, based upon ethanolamine, was 38%.

SUMMARY

Procedures are reported for the synthesis of ethyleneurea from ethylene glycol or ethanolamine either with urea or with ammonia and carbon dioxide. Pressure and other variables affecting the reactions are discussed and a mechanism is suggested by which amination of the carbon skeleton takes place.

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