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SYNTHESIS OF GLYCINE BY THE AMMONOLYSIS OF TETRACHLOROETHANE AND TRICHLOROETHYLENE

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Glycine was obtained selectively by heating of tetrachloroethane with an excess amount of aqueous ammonia. Trichloroethylene which is separated as an intermediate compound in the early period of the ammonolysis also formed glycine. The yield increased by the addition of sodium carbonate and reached 54.6 mole% at 170° for 2 hr.

In the synthesis of glycine the Strecker reaction[1,2,3] is an important process in the chemical industry although hydrocyanic acid is an undesirable material from the view point of the difficulty in its elimination from the waste solution. Another method using monochloroacetic acid with an excess amount of ammonia[4,5] is also well known. Recently, the amination of acetic acid in the presence of Cu(II)-ammine complex catalyst has been reported from this laboratory.[6] In present paper are investigated a new preparative system of glycine from tetrachloroethane and from trichloroethylene in the presence of aqueous ammonia and sodium carbonate. It was found that two chlorine-substituted ethane isomers, 1,1,2,2- and 1,1,1,2-tetrachloroethane, produce glycine in the presence of an excess amount of ammonia.

One ml of tetrachloroethane and a 30-40 ml solution of aqueous ammonia(7-28%) was put in an autoclave(SUS-32, 100 ml volume) equipped with an electromagnetic stirrer. The autoclave was heated at 120-180° under nitrogen pressure(30 kg/cm^2) for prescribed hour. The reaction products were analyzed using a KLA-5 Hitachi ion-exchange type amino acid analyzer.

The yield of glycine under the various conditions using 1,1,2,2- and 1,1,1,2-tetrachloroethane was shown in Table I. A molar ratio of seventeen times of ammonia to tetrachloroethane gave 28 mole% of glycine at 160° for 15 hr. Ammonium carbonate in place of ammonia also gave glycine with a similar yield. Addition of sodium

Table I. Yield of glycine in the ammonolysis of tetrachloroethane in the presence of aqueous ammonia and sodium carbonate under various conditions

Exp.No.	Tetrachloroethane (mmol)	Material added on ammonolysis	Temp. (°C)	Time (hr)	Yield (mmol)
1	1,1,2,2-TCE(9.47)	7%-NH_4OH(40 ml)	160	15	2.62
2	1,1,2,2-TCE(9.47)	28%-NH_4OH(30 ml)	160	6	3.22
3	1,1,2,2-TCE(9.47)	$(NH_4)_2CO_3$(5g)+H_2O(40 ml)	160	16	2.42
4	1,1,2,2-TCE(9.47)	Na_2CO_3(3g)+28%-NH_4OH(30 ml)	170	1	4.43
5	1,1,2,2-Tce(9.47)	Na_2CO_3(3g)+28%-NH_4OH(30 ml)	170	2	5.17
6	1,1,1,2-TCE(9.17)	7%-NH_4OH(40 ml)	160	16	2.44
7	1,1,1,2-TCE(9.17)	Na_2CO_3(3g)+28%-NH_4OH(30 ml)	170	2	5.02

carbonate increased the yield; 50-55 mole% of glycine was obtained from 1 ml of tetrachloroethane, 30 ml of aqueous ammonia(28%), and 3g of sodium carbonate. A similar glycine yield found by the ammonolysis of 1,1,2,2- and 1,1,1,2-tetrachloroethane suggests that both compounds pass through a common intermediate state.

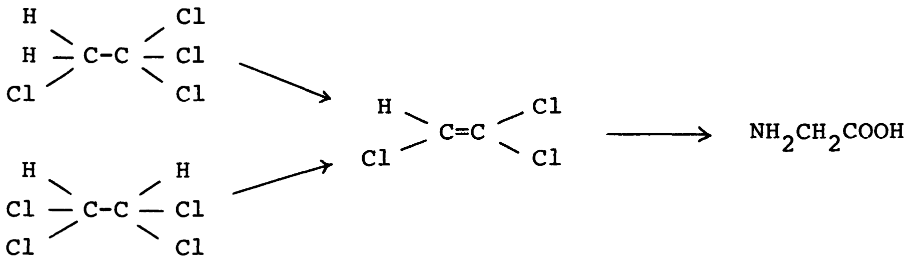
On the other hand, an oily product which was obtained under the mild reaction conditions, at 100° for 3 hr with aqueous ammonia, was separated from the product. The compound was identified as trichloroethylene using NMR and GC analyses. The results of the ammonolysis of trichloroethylene are shown below.

Table II. Yield of glycine in the ammonolysis of trichloroethylene in the presence of aqueous ammonia and various carbonates

Exp.No.	Material added on ammonolysis	Temp. (°C)	Time (hr)	Yield (mmol)
1	7%-NH_4OH(40 ml)	160	6	2.44
2	$(NH_4)_2CO_3$(5g)+28%-NH_4OH(30 ml)	120	17	3.14
3	Na_2CO_3(3g)+28%-NH_4OH(30 ml)	120	15.5	5.37
4	Na_2CO_3(3g)+28%-NH_4OH(30 ml)	170	2	5.51
5	Na_2CO_3(3g)+28%-NH_4OH(30 ml)	180	1	5.86
6	Li_2CO_3(3g)+28%-NH_4OH(30 ml)	180	1	6.44

One ml(11.15 mmol) of trichloroethylene was used.

The yield of glycine from trichloroethylene corresponds to the result of the ammonolysis of tetrachloroethane under the same reaction conditions, and reached 52.6 mole% in the presence of sodium carbonate at 180° for 1 hr. From these results it was considered that the initial product from tetrachloroethane is trichloroethylene which is formed by the elimination of hydrochloric acid in the presence of ammonia and basic catalyst.[7] Then, the reaction scheme is denoted as follows:



[I] [II]

As for the ammonolysis of trichloroethylene in step [II], two possible intermediate compounds are considered, monochloroacetic acid and aminoacetnitrile. Of these,aminoacetnitrile was more sensitive to sodium carbonate than monochloroacetic acid at 160° as shown in Table III. Furthermore, the amount of glycine obtained was almost the same as that from the ammonolysis of trichloroethylene.

All these experimental results indicates that the reaction proceeds successively by way of dehydrochlorination from tetrachloroethane to trichloroethylene, the ammonolysis from trichloroethylene to aminoacetnitrile, and the hydrolysis of aminoacetnitrile to glycine in the presence of basic catalyst such as sodium carbonate.

Table III. Effect of sodium carbonate in the ammonolysis of monochloroacetic acid and aminoacetnitrile with aqueous ammonia at 160° for 3 hr

Exp.No.	Compound (mmol)	Material added on ammonolysis	Yield (mmol)
1	$ClCH_2COOH$(10.58)	7%-NH_4OH(40 ml)	5.68
2	$ClCH_2COOH$(10.58)	Na_2CO_3(3g)+7%-NH_4OH(40 ml)	6.03
3	$NH_2CH_2CN\cdot H_2SO_4$(9.73)	7%-NH_4OH(40ml)	2.63
4	$NH_2CH_2CN\cdot H_2SO_4$(9.73)	Na_2CO_3(3g)+7%-NH_4OH(40 ml)	5.07

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