CHEMISTRY

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1961

SovietRxiv

Abstract

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ON THE INTERACTION OF ETHYLENE OXIDE WITH CARBON DISULFIDE

In continuation of work on the reactions of certain alkene oxides with carbon dioxide, we have carried out a study of the interaction of ethylene oxide with another analogue of carbonic anhydride—carbon disulfide.

The reaction between ethylene oxide and carbon disulfide was used by Darden and co-workers to obtain ethylene trithiocarbonate ([1]). It was carried out under nitrogen pressure in the presence of tertiary amines. The greatest yield of ethylene trithiocarbonate was obtained at a molecular ratio of carbon disulfide : ethylene oxide equal to 2.5, with heating to 150°. As by-products, CO_2 and COS were detected. According to the mechanism proposed by the authors, the intermediate formation of ethylene sulfide is assumed; however, the latter was not isolated from the reaction products. We used, as catalyst, tetramethylammonium bromide, which we had previously employed ([2]). The reaction was carried out by heating equivalent amounts of the reagents in sealed ampoules at 90-100°.

The conversion of ethylene oxide was 54-55%. The unreacted substances were distilled off from the reaction mixture in equimolecular amounts. As a result of the reaction, ethylene carbonate and ethylene trithiocarbonate (ETTC) were isolated in a molecular ratio of 1 : 2, which corresponds to the reaction equation:

$$3\ CH_2{-}CH_2O + 3CS_2 \rightarrow OCH_2{-}CH_2{-}O{-}CO + 2SCH_2{-}CH_2{-}S{-}CS \qquad (1)$$

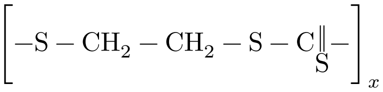
No gas formation was observed.

To separate the mixture of ethylene carbonate and ethylene trithiocarbonate we used the method of washing out the ethylene carbonate with water. The remaining ethylene trithiocarbonate, after recrystallization from alcohol, was obtained in the pure state. We also attempted to separate the mixture of ethylene carbonate and ethylene trithiocarbonate by vacuum distillation. However, in this case, after the ethylene carbonate had been distilled off, during distillation of the ethylene trithiocarbonate formation of volatile substances was observed; these condensed in a trap cooled in a mixture of solid carbon dioxide and acetone.

We assumed that the volatile substances are formed as a result of partial decomposition of ethylene trithiocarbonate. Indeed, ethylene trithiocarbonate obtained by us by the washing method, upon distillation, likewise gave a volatile fraction. Meanwhile, the volatile fractions obtained in the first and in the second cases, although according to analysis they consist of a mixture of carbon disulfide and ethylene sulfide, behaved differently.

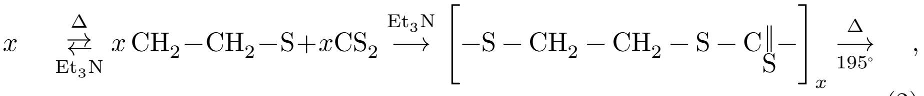
In the first case, on standing at ordinary temperature the mixture was converted into a bright-yellow powder insoluble in organic solvents. In composition it corresponds to $C_3H_4S_3$. The volatile fraction obtained in the second case, on standing, separated white flakes of a polymer of composition C_2H_4S, while carbon disulfide remained.

We assume that in the first case a copolymer of ethylene sulfide and carbon disulfide of the composition



$$\left[-S-CH_2-CH_2-S-\underset{\underset{S}{\|}}{C}-\right]_x$$

is formed, according to the reaction:



$$x \quad \underset{Et_3N}{\overset{\Delta}{\rightleftarrows}} x\,CH_2-CH_2-S+xCS_2 \xrightarrow{Et_3N} \left[-S-CH_2-CH_2-S-\underset{\underset{S}{\|}}{C}-\right]_x \xrightarrow[195^\circ]{\Delta} , \qquad (2)$$

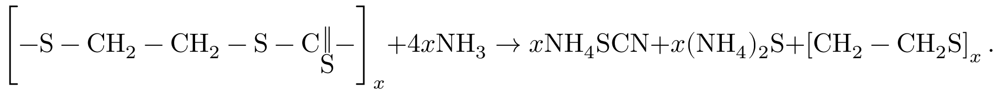
whereas in the second, a polymer of ethylene sulfide is formed. To explain this difference, it was suggested that in one case volatile products are formed which catalyze the copolymerization of ethylene sulfide and carbon disulfide. Such a product could be triethylamine, formed through the decomposition of tetraethylammonium bromide remaining in the mixture of ethylene carbonate and ethylene trithiocarbonate. (The bath temperature during distillation was 200–220°.) In the other case the catalyst was washed out together with the ethylene carbonate; therefore, the mixture of ethylene sulfide and carbon disulfide did not give a copolymer, and on standing only polymerization of ethylene sulfide was observed.

To test our assumption, we mixed equimolecular amounts of ethylene sulfide and carbon disulfide in the presence of triethylamine. At room temperature the mixture gradually turned into a yellow powder. From it, ethylene trithiocarbonate was isolated by treatment with chloroform. In its properties, the remaining polymer is analogous to that obtained by distillation of ethylene trithiocarbonate in the presence of a catalyst.

When tetraethylammonium bromide is used as the catalyst, the reaction between carbon disulfide and ethylene sulfide begins, but quickly ceases because of the insolubility of tetraethylammonium bromide in the ethylene sulfide—carbon disulfide system.

The elemental composition of the polymer obtained coincides with the elemental composition of ethylene trithiocarbonate. Upon heating to 195–200°, decomposition of the polymer is observed with formation of ethylene trithiocarbonate according to equation (2). The structure of the macromolecule was proved by cleavage of the polymer with ammonia, as a result of which ammonium rhodanide, ammonium sulfide, and polyethylene sulfide were obtained.

The polymer reacts with liquid ammonia in a sealed ampoule already at room temperature. Ammonium rhodanide could be formed only at the expense of the group $-\mathrm{C}(=\mathrm{S})-\mathrm{S}$:



$$\left[-\mathrm{S}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{S}-\underset{\mathrm{S}}{\mathrm{C}\|}-\right]_x + 4x\mathrm{NH_3} \rightarrow x\mathrm{NH_4SCN} + x(\mathrm{NH_4})_2\mathrm{S} + [\mathrm{CH_2}-\mathrm{CH_2S}]_x\,.$$

Apparently, under the action of ammonia, cleavage of the polymer occurs into ethylene sulfide, which polymerizes, and carbon disulfide, which in turn reacts with ammonia.

Experimental Part

Ethylene oxide and carbon disulfide in the presence of 0.5% tetraethylammonium bromide, based on the weight of the ethylene oxide taken, were sealed in glass ampoules and heated for 10 hours at 90–100°.

The reaction mixture was worked up by two methods:

Method I. After the ampoules were opened and the unreacted products were distilled off, the reaction mixture was fractionated in vacuo. Two fractions were thereby isolated, with b.p. 72–94°/4 mm and 114–130°/4 mm.

The 1st fraction is a pale-yellow liquid, which crystallizes on cooling. After three recrystallizations from chloroform, white crystals with m.p. 38° were obtained. The substance contains no sulfur. A mixed sample with ethylene carbonate melted without depression. Yield based on reacted oxide: 18.4%.

The 2nd fraction is an orange liquid, which also crystallizes on cooling. By two recrystallizations from alcohol, yellow crystals with m.p. 37° were obtained. A mixed sample with ethylene trithiocarbonate melted without depression. Yield based on the oxide taken: 48.6%.

The light, volatile liquid collected in the cooled trap amounted to as much as 24% of the mixture taken for distillation. It quickly turns yellow and then is converted into a bright-yellow solid substance. After washing with benzene, chloroform, and carbon disulfide, it had the following elemental composition:

$C_3H_4S_3$.	Found, %:	C 26.82; H 3.07; S 70.00
	Calculated, %:	C 26.40; H 2.94; S 70.50

On heating this substance with ammonia and alcohol in a sealed ampoule, polyethylene sulfide, ammonium rhodanide, and ammonium sulfide were obtained.

Method II. After distillation of the unreacted substances, the mixture was diluted with chloroform and washed repeatedly with water. Ethylene carbonate was isolated from the water. The residue, after removal of the chloroform, was distilled in vacuo to obtain ethylene trithiocarbonate. From the liquid that collected in the trap, white flakes of polyethylene sulfide precipitated in this case. Found, %: S 53.27 C_2H_4S. Calculated, %: S 53.40.

On standing at room temperature, an equimolecular mixture of ethylene sulfide and carbon disulfide in the presence of triethylamine gave the yellow polymer described above. Together with it, ethylene trithiocarbonate was also obtained. In the course of four days the reaction proceeded to 63%. From 7.4 g of ethylene sulfide and 9.37 g of carbon disulfide, 5.2 g of polymer and 5.35 g of ethylene trithiocarbonate were obtained.

Received
8 VI 1961

REFERENCES CITED

1. J. Durden, U. Stansbury, W. Catlette, *J. Am. Chem. Soc.*, **82**, 3082 (1960).
2. G. A. Razuvaev, V. S. Etlis, L. N. Grobov, *ZhOKh*, **31**, 1328 (1961).

Note: Figure translations are in progress. See original paper for figures.

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