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REACTION OF ETHYLENE OXIDE WITH ANTIMONY CHLORIDES

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The reaction of ethylene oxide with several inorganic halides is described in the literature. For example, arsenic trichloride at room temperature yields β-chloroethyl ethers of arsenic chlorides (*e.g.* $Cl\text{-}CH_2\text{-}CH_2\text{-}O\text{-}AsCl_2$) (Malinovskii, 1940) while boron trifluoride, silicon tetrafluoride, and arsenic trifluoride transform ethylene oxide into dioxane (Schmeisser and Jenkner, 1952) Sulfur dichloride and ethylene oxide react with the formation of ethylene dichloride and ethylene chlorohydrin as well as β-chloroethoxy sulfoxide (Malinovskii, 1939).

Similar experiments were carried out in this laboratory with the chlorides of antimony.

Materials and Method

The reaction vessel consisted of a 500-ml., three-necked flask, fitted with a gas dispersion outlet leading to the bottom of the flask, a thermometer and a delivery tube. The delivery tube was provided with a Claissen distilling head, fitted with a thermometer and connected to a water condenser and receiving flask in order to isolate the distillate. An oil trap was attached to the end of the system to provide a slight pressure. Ethylene oxide gas was passed into the dispersing tube along with an alternate feed of nitrogen; the latter was used to displace air and moisture from the system. The reaction vessel was heated with a rheostat-controlled glas-col mantle.

In a typical experiment, the reaction vessel was charged with catalyst which was preheated to 75-100° C. in the inert nitrogen gas. Ethylene oxide gas was then passed through the catalyst so that only a few bubbles escaped through the oil trap. The temperature quickly rose to 180-200° C. and was maintained in that range by the heating mantle as well as by the heat of the reaction. As the reaction progressed the volatile products distilled from 80-130° C. and after 6-8 hours the system was purged with nitrogen to displace the remainder of the volatile materials. The distillate was then fractionated in a heated, 18-inch column, packed with glass helices, and the fractions were identified from their physical properties. The proportion of each product was estimated from the distillation curves.

Results

Antimony pentachloride.—When 250 gms. (0.86 moles) of antimony pentachloride was treated with 250 gms. (5.68 moles) of ethylene oxide, over a period of 7 hours, the evolution of hydrogen chloride gas was noted. The volatile distillate (B.P. 80-130° C.) amounted to 160 ml. along with 10 gms. of sublimed, white crystalline solid. The solid was identified as antimony oxychloride by melting point (170° C.) as well as by antimony (70.14%) and

TABLE 1.—Yields and Physical Constants of Distillate from the Reaction of Ethylene Oxide and Antimony Chlorides.

	Ethylene dichloride	Dioxane	Ethylene chlorohydrin
From antimony pentachloride			
Percent yield*	2.2	23.2	12.9
B.P.° C	80-83	101-102	127-128
N_D^{20}	1.4440	1.4223	1.4423
D_4^{20}	1.2445	1.0305	1.1957
From antimony trichloride			
Percent yield*	8.0	38.3	13.1
B.P.	80-82	101-102	127-129
N_D^{20}	1.4450	1.4213	1.4415
D_4^{20}	1.2535	1.0321	1.1970
Literature values (Heilbron, 1953:502, 398, 501)			
B.P.	83.7	101	128.6
N_D^{20}	1.4443	1.4224	1.4419
D_4^{20}	1.2521	1.0337	1.1988

*Yields based on ethylene oxide used.

chlorine (21.23%) analyses. Theoretical values for SbOCl are 70.29% Sb and 20.47% Cl.

The black tarry residue remaining in the reaction vessel weighed 197 gms. and contained 45.3% antimony and 38.5% chlorine. This corresponds to 89% of the original antimony content of the catalyst. Aside from a small quantity of SbOCl in the residue, attempts to isolate pure compounds proved futile, although the above analyses do correspond to $Cl\text{-}CH_2CH_2\text{-}O\text{-}SbCl_3$ (Sb, 44.7%; Cl, 39.1%).

The volatile liquid from the reaction was then distilled and dioxane, ethylene dichloride, and ethylene chlorohydrin were identified as the chief components. The yields and physical constants used to identify the products are listed in Table 1.

Antimony trichloride.—Two hundred gms. (0.915 moles) of antimony trichloride were treated with 250 gms. (5.68 moles) of ethylene oxide over a period of 8 hours. The reaction did not appear to be as vigorous as with the pentachloride and no evolution of hydrogen choloride was noticed. In addition, no antimony oxychloride sublimed with the distillate. In this experiment, 195 ml. of distillate boiling from 80-130° C. was obtained along with the black residue remaining in the flask. Ethylene dichloride, dioxane, and ethylene chlorohydrin were likewise identified as the chief products of the condensation. The yields and

physical constants of these products are also listed in Table 1.

The black residue (235 gms.) contained 39.1% antimony and 32.3% chlorine, corresponding to $(Cl\text{-}CH_2CH_2\text{-}O)_2\text{-}SbCl$ (Sb, 38.5%; Cl, 33.7%). Vacuum sublimation did not produce any antimony oxychloride and only traces of antimony trichloride from this residue. Purification was unsuccessful.

Discussion and Summary

The reaction of antimony pentachloride with ethylene oxide produced hydrogen chloride, antimony oxychloride, dioxane, ethylene dichloride, and ethylene chlorohydrin. These products indicate that the pentachloride quite possibly decomposes part of the ethylene oxide to oxygen or water, and hydrogen chloride is formed by chlorination of the ethylene oxide. The oxygen or water converts the antimony chloride to the oxychloride. Ethylene chlorohydrin, which may also be converted to the dichloride with hydrogen chloride, is formed from ethylene oxide and hydrogen chloride or by hydrollysis of the chloroethers of antimony chlorides. Dehydrohalogenation of ethylene chlorohydrin would account for the dioxane. The analyses on the organic residue correspond to the β-chloroethyl ether of antimony chloride.

The probable reactions may be represented as follows:

$$CH_2\text{-}CH_2\text{-}O + SbCl_5 \longrightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SbCl_2$$

$$Cl\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SbCl_2 + H_2O \longrightarrow HO\text{-}CH_2\text{-}CH_2\text{-}Cl + SbOCl \text{ (trace)} + HCl$$

$$CH_2\text{-}CH_2\text{-}O + HCl \longrightarrow HO\text{-}CH_2\text{-}CH_2\text{-}Cl$$

$$2HO\text{-}CH_2\text{-}CH_2\text{-}Cl \longrightarrow O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2 + 2HCl$$

$$HO\text{-}CH_2\text{-}CH_2\text{-}Cl + HCl \longrightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}Cl$$

Since the reaction with antimony trichloride does not produce noticeable quantities of hydrogen chloride, the ethylene chlorohydrin is more probably formed by hydrolysis of chloroethylethers of antimony chlorides. This is further indicated by the higher overall yields of the distilled products from the latter reaction and, therefore, less decomposition of the ethylene oxide. In the latter instance the analyses on the residue indicate the formation of $(Cl\text{-}CH_2\text{-}CH_2\text{-}O)_2\text{-}SbCl$.

The reaction of ethylene oxide and antimony chlorides produces dioxane, ethylene chlorohydrin, and ethylene dichloride, as well as hydrogen chloride. With antimony pentachloride a small amount of antimony oxychloride was isolated. The antimony residues apparently contained organic matter, and analyses on the crude material correspond to β-chloroethyl ethers of antimony chloride. However, no purified organic antimony compounds were isolated.

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