THE REACTION OF DIOXANE WITH HYDROGEN BROMIDE[1]

By A. B. Van Cleave and R. I. Blake[2]

Abstract

Dioxane reacted slowly at room temperature with anhydrous, bromine free hydrogen bromide to form 2, 2′-dibromodiethyl ether as a principal product. The 2, 2′-dibromodiethyl ether was characterized by comparison with a known sample, analysis, molecular weight determination, and by conversion to divinyl ether which was subsequently brominated to yield 1, 1′, 2, 2′-tetrabromodiethyl ether. When refluxed with constant boiling hydrobromic acid 2, 2′-dibromodiethyl ether was partially converted to ethylene dibromide. An intermediate compound in the formation of 2, 2′-dibromodiethyl ether from dioxane and hydrogen bromide was isolated by solvent extraction using petroleum ether. Its properties indicated that it was probably an oxonium salt.

Introduction

In studying the kinetics of the hydrolysis of cyanogen halides in dioxane solution (7), it was found that solutions of anhydrous hydrogen bromide in dioxane showed a steady disappearance of hydrogen bromide with time. A survey of the literature revealed that no work on the reaction of dioxane with hydrogen bromide had been reported; consequently, the present work was undertaken to establish the nature of the products formed.

Paterno and Spallino (6) reacted bromine and iodine with dioxane and obtained addition products $(C_2H_4O)_2Br_2$ and $(C_2H_4O)_2I_2$. They also studied the reaction between dioxane and hydrogen iodide in sealed tubes at 140°C., and identified iodine, acetic acid, and ethyl iodide among the products. They concluded that dioxane behaved in a manner similar to compounds containing a double bond, and that it conforms in some ways to the character of compounds containing basic oxygen.

The present investigation has shown that 1,4-dioxane reacts slowly with anhydrous hydrogen bromide at 25°C. and that the principal product isolated on fractional distillation was a high boiling point liquid with characteristics resembling those reported for 2, 2′-dibromodiethyl ether by McCusker and Kroeger (5). A sample of this ether was prepared by treating diethylene glycol dissolved in pyridine with phosphorus tribromide as described by Ali-Zade and Arbuzov (4). The product isolated from the dioxane – hydrogen bromide reaction was characterized as 2, 2′-dibromodiethyl ether by analysis, molecular weight determination, and by conversion to divinyl ether which was subsequently brominated to yield symmetrical tetrabromoethyl ether.

One might expect to obtain some ethylene dibromide when dioxane is treated with hydrogen bromide. Starting with anhydrous hydrogen bromide no evi-

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[2] *Present address: Consolidated Mining and Smelting Co., Ltd., Trail, B.C.*

dence for the formation of ethylene dibromide was obtained. However, when a sample of 2, 2′-dibromodiethyl ether was refluxed with constant boiling hydrobromic acid it was partially converted to ethylene dibromide.

What appeared to be an intermediate compound in the formation of 2, 2′-dibromodiethyl ether from dioxane and hydrogen bromide was isolated by solvent extraction with petroleum ether. This product was a brown colored liquid freezing below −79°C. It was water soluble and possessed acidic properties. On neutralization with alkali it yielded a light colored precipitate which was not identified. The brown colored liquid was unstable and when an attempt was made to purify it by fractional crystallization it appeared to decompose into dioxane and hydrogen bromide. When some of it was refluxed for a time it was possible to isolate some 2, 2′-dibromodiethyl ether from the mixture. It was presumed that the intermediate compound was an oxonium salt similar to that known to be formed between dioxane and sulphuric acid (6). The yield of the supposed oxonium compound was found to be considerably greater when anhydrous, bromine free hydrogen bromide was bubbled into refluxing dioxane at 101°C. than was obtained on prolonged contact of hydrogen bromide with dioxane at room temperature.

Experimental

Materials

1,4-Dioxane, Eastman Kodak, practical grade, stabilized with *p*-benzylaminophenol was purified by the method of Fieser (2).

Anhydrous, bromine free hydrogen bromide was prepared by admitting liquid bromine to a reaction flask containing red phosphorus and water. The gas was passed through a solution of phenol in carbon tetrachloride, a cold trap at −55°C., a tube filled with glass beads coated with red phosphorus, and finally through drying tubes containing calcium chloride and calcium bromide.

Solutions of hydrogen bromide in dioxane were prepared by bubbling the hydrogen bromide into 400 ml. of dioxane through a sintered glass disk until the mixture was approximately 1 *N*.

The Rate of Disappearance of Hydrogen Bromide in Dioxane Solution

The progress of the reaction between dioxane and hydrogen bromide at 25°C. was followed for one month by daily removal of 1.0 ml. samples which were diluted with 10 ml. of water and titrated with standard potassium hydroxide using methyl red as an indicator. A solution with an initial normality of 0.821 showed a decrease in normality to 0.301 in 30 days. Packing the reaction vessel with Pyrex glass wool did not affect the reaction rate. Another solution with an initial normality of 0.875 showed a decrease to 0.209 in seven months on standing at room temperature. The rate of the reaction was not linear but was greater in the initial stages, that is, during the first few days at 25°C.

Isolation and Identification of 2, 2′-Dibromodiethyl Ether

2, 2′-Dibromodiethyl ether was first isolated from a dioxane – hydrogen bromide mixture that had been maintained at 25°C. for one month. This mixture was fractionally distilled at atmospheric pressure into fractions boiling above and below 105°C. After repeated distillations to remove dioxane these fractions boiled above 110°C. and below 92°C., respectively. Further investigation showed the lower boiling fraction to be largely a mixture of dioxane and water.

The portion boiling above 110°C. was distilled under reduced pressure and a fraction boiling between 94° and 101°C. at 13 mm. was taken, washed with water, dried over anhydrous sodium sulphate, and redistilled to give a fraction boiling from 90°-94°C. at 9 mm. This material was fractionated in a packed column at 1 mm. pressure, the middle fraction being retained for subsequent work.

It was later found that the same material could be isolated by solvent extraction from a dioxane – hydrogen bromine mixture that had been allowed to stand for several months at room temperature. The reaction mixture was neutralized with sodium bicarbonate, then petroleum ether and water were added to form a double layer. The solvent layer was separated and distilled yielding a residue boiling above 110°C. (atm. press.). This residue was washed with water and dried over sodium sulphate. The maximum yield of 2, 2′-dibromodiethyl ether obtained in this way was 38.7% based on the amount of hydrogen bromide that was no longer titratable in the original mixture. The low yield was probably mainly due to inefficient recovery but it is possible that some other bromine containing compounds were formed and not isolated.

2, 2′-Dibromodiethyl ether was first characterized as a reaction product by analysis. Carbon and hydrogen were determined by standard micro procedure* and bromine by a modified micro Carius method. Considerable difficulty was experienced with the latter as the sealed tubes invariably exploded unless the amount of nitric acid used was reduced to somewhat less than 0.30 ml. for 10 mgm. samples. The results of the analyses are shown in Table I.

TABLE I
ANALYSES OF REACTION PRODUCT

	% Carbon	% Hydrogen	% Bromine
Sample 1	22.37	4.01	69.55
Sample 2	22.26	4.00	65.65
Sample 3	....	....	66.25
Mean	22.31	4.00	67.15
Theoretical for 2, 2′-dibromodiethyl ether	20.72	3.48	68.93

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The molecular weights of the reaction product and of 2, 2′-dibromodiethyl ether prepared by the method of Ali-Zade and Arbuzov (1) were determined by the Beckman cryoscopic method using benzene as the solvent. The cyroscopic constant for benzene was determined using twice recrystallized naphthalene at several concentrations and extrapolating to infinite dilution. A similar procedure was employed in obtaining corrected freezing point depressions for the unknowns. The known sample of 2, 2′-dibromodiethyl ether was found to have a molecular weight of 231.5 (theoretical 232) whereas the product isolated from the dioxane – hydrogen bromide reaction had a molecular weight of 225. This result was taken to indicate that there was still a small percentage of lower molecular weight material contaminating the product; probably some β-bromoethyl ether of ethylene glycol ($BrCH_2$-CH_2-O-CH_2-CH_2-OH, mol. wt. 169) the boiling point of which is very close to that of 2, 2′-dibromodiethyl ether.

Derivatives of 2, 2′-Dibromodiethyl Ether

Divinyl ether was prepared from the reaction product by the method used by Hibbert *et al.* (4) for dichlorodiethyl ether. Thirty-five grams of 2, 2′-dibromodiethyl ether, isolated from the reaction, were slowly dropped into molten potassium hydroxide in a copper pot over the course of two hours. The copper pot was provided with a reflux condenser at 40°C. to permit the escape of divinyl ether but not of intermediate or unreacted products. A second condenser connected to the first was maintained at 6°C. The refluxing was continued for three hours yielding 2.6 gm. (24%) of a product boiling at 34.5° to 35.5°C. The reported boiling point for divinyl ether is 34°-35°C. (4).

The same experiment was repeated using alcoholic potassium hydroxide but no divinyl ether was obtained.

One gram of divinyl ether prepared as indicated above was dissolved in chloroform and a bromine–chloroform solution was slowly added, the reaction flask being immersed in ice. On evaporation of the solvent a crystalline product was obtained. After recrystallization from ether this product melted at 63°C. and analysis showed it to contain 12.36% carbon and 1.64% hydrogen. The reported melting point for 1, 1′, 2, 2′-tetrabromodiethyl ether is 63°-64°C. (4) and the theoretical carbon is 12.33% and hydrogen 1.55%.

From the above evidence it was concluded that the product which had been isolated from the dioxane – hydrogen bromide mixture was fairly pure 2, 2′-dibromodiethyl ether.

Cleavage of 2, 2′-Dibromodiethyl Ether

2, 2′-Dibromodiethyl ether (4.58 gm.) isolated from the dioxane – hydrogen bromide reaction was refluxed with constant boiling hydrobromic acid (50 ml.) for several hours. The excess acid was neutralized with sodium bicarbonate and the mixture extracted with ether. The ether layer was washed with water, dilute sulphuric acid, 10% sodium bicarbonate solution, and then with water again. The extract was dried over sodium sulphate and on fractional distillation yielded 4.1 gm. of a product b.p. 130°-131°C., m.p. 10.0°C. The reported values for ethylene dibromide are b.p. 131.6°C., m.p. 9.97°C. (3). The product was therefore identified as ethylene dibromide.

Evidence for the Formation of an Oxonium Compound

Anhydrous, bromine free hydrogen bromide was bubbled into 200 ml. of refluxing dioxane at 101°C. The solution changed from colorless to dark brown and its normality was observed to be 0.214 on titration against standard alkali. Petroleum ether was added to the mixture to bring about separation into two layers. The lower dark brown colored layer (13.6 ml.) was separated off for further tests. This material had an odor resembling that of hydrogen bromide, was practically all soluble in water, and had a normality of 2.39 as an acid. When a similar procedure to that outlined above was applied to 200 ml. of dioxane – hydrogen bromide solution that had been standing for several months at room temperature (normality decrease 0.875 to 0.209), only 1.6 ml. of the dark brown colored lower layer having a normality of 2.89 was obtained.

In all cases when portions of the brown colored material were neutralized with sodium hydroxide a light colored precipitate formed. Unfortunately, time did not permit the identification of this solid.

An attempt was made to purify the brown colored liquid by fractional freezing. The material which crystallized out appeared to be mainly dioxane, and eventually a fraction which would not freeze in a dry ice – acetone bath was obtained; 2.4 gm. of this partially purified material was refluxed for three hours in an atmosphere of nitrogen, then washed with water, dried over sodium sulphate, and fractionally distilled to yield about 0.7 gm. of 2, 2′-dibromodiethyl ether.

It was concluded that in all probability the brown colored liquid was an oxonium salt of dioxane and hydrogen bromide of limited stability. It may decompose to dioxane and hydrogen bromide, or it may undergo cleavage and subsequent reaction to give 2, 2′-dibromodiethyl ether. It appeared almost certain to be an intermediate compound in the formation of the latter from dioxane and hydrogen bromide.

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