THE REACTION BETWEEN ALCOHOLS AND AQUEOUS SOLUTIONS OF HYDROCHLORIC AND HYDROBROMIC ACIDS. II.

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In previous papers[1] the action of aqueous solutions of hydrochloric, hydrobromic, and hydriodic acids on a variety of alcohols was described. It was shown that the reaction furnished the most convenient method of preparing alkyl bromides and iodides, and that in certain cases chlorides could be made advantageously in this way. Recently Kahn has found that the addition of sulfuric acid to the solution of hydrobromic acid increases the yield of alkyl bromides obtained, especially in the case of alcohols of higher molecular weight.

The previous work was limited to monatomic alcohols and had to do primarily with the effect of the structure of the alcohols on the ease with which the reaction took place, and with the yields obtained. The action of hydrochloric acid was quite different from that of hydrobromic and hydriodic acids. While the latter formed alkyl halides with all alcohols studied, hydrochloric acid reacted in certain cases only. Chlorides were formed from all tertiary and some secondary alcohols. The acid did not react with any primary saturated aliphatic alcohols; it formed, however, chlorides with benzyl alcohol and allyl alcohol. It was shown that the presence of unsaturated radicals and aryl radicals rendered the hydroxyl group active, and that this influence decreased as the position of these radicals was farther from the hydroxyl group. Phenyl and unsaturated radicals are so-called negative groups; it seemed advisable, therefore, to study more fully the reaction between alcohols containing such groups to determine if they in general possessed this activating influence. It was found in certain cases that when the negativity was markedly increased the alcohol containing such a group failed to react with aqueous hydrochloric acid. This was shown to be the case with the nitrobenzyl alcohols.

It seems probable from work which will be reported later that the reaction between an alcohol and a halogen acid consists in the addition of the two compounds and the subsequent elimination of water. The ease with which these two separate steps occur determines whether reaction takes place or not under the conditions used. If this view is correct the difference in the behavior of hydrochloric acid and that of hydrobromic acid can be explained.

The work described below was a study of the behavior of certain polyatomic alcohols with aqueous solutions of hydrochloric acid and hydro-

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[1] *Am. Chem. J.*, **38**, 627 (1907); THIS JOURNAL, **38**, 1071 (1916).

bromic acid; a few monatomic alcohols which contained either negative substituents or belonged to classes not previously investigated were also studied. All the compounds investigated reacted with hydrobromic acid; the results serve, therefore, to strengthen the conclusion previously reached, that the acid may be used as test for the alcoholic hydroxyl group. Aqueous hydrochloric acid replaced hydroxyl groups in certain compounds containing negative substituents, although its failure to act in other cases brought out clearly the fact that other influences than those of negativity serve to activate the hydroxyl group.

Ethylene glycol when heated with aqueous hydrobromic acid (sp. gr. 1.49) yielded a mixture of the bromohydrin and ethylene bromide, the proportions of which varied with the conditions used. When propylene glycol was heated with the acid, profound changes occurred which led to the formation of highly colored oils. From trimethylene glycol a yield of 62% of the bromide along with some bromohydrin was obtained. Glycerol gave 46% of the dibromohydrin and 13% of the monobromohydrin. A detailed study of the conditions under which the reactions are carried out would probably result in larger yields. In a number of cases only very small amounts of the alcohols (3 to 5 g.) were employed so that large yields could not be expected.

The chief interest in the work lay in the behavior of the alcohols with aqueous hydrochloric acid, since it was hoped the results would throw light on the factors which activate the hydroxyl group. When ethylene glycol was heated with a large excess of hydrochloric acid (sp. gr. 1.17) 12% of the alcohol was converted into the chlorohydrin. Since ethyl alcohol does not react with aqueous hydrochloric acid in an open vessel the activation in this case may be due to the added negative hydroxyl group. Ethylene bromohydrin did not, however, react with the acid. In this case if negativity is the cause of the activation, the substituting atom is too negative in character, and the effect is lost. The results recall the fact that while benzyl alcohol reacts readily with hydrochloric acid, the nitrobenzyl alcohols do not.

When propylene glycol was heated with hydrochloric acid, deep-seated changes took place, as might be expected; but 5% of chlorohydrin was obtained. Trimethylene glycol gave a trace of the chloride and about 28% of the chlorohydrin. Trimethylene chlorohydrin was converted to a small extent into the chloride when boiled with hydrochloric acid; the bromohydrin behaved in a similar manner. In these cases the halogen was in the β-position to the hydroxyl group, whereas in ethylene bromohydrin which yielded no chloride the strongly negative halogen atom was in the α-position.

Glycerol reacted to a slight extent only with the acid to form chlorohydrins; a trace of dichlorohydrin and about 9% of monochlorohydrin

were formed. Pinacone hydrate reacted slowly at room temperature with hydrochloric acid (sp. gr. 1.17) and gave the chloride.

A few cyclic alcohols were studied to learn the effect of ring structure on the activity of the hydroxyl group. Cyclohexanol gave a yield of 93% of the corresponding chloride. In its activity the alcohol resembles secondary and tertiary alcohols. Menthol reacted much more sluggishly and gave a yield of 41% of the chloride. The increase in the molecular weight or the radical in the *ortho* position may be the cause of the difference between the activity of cyclohexanol and its derivative. Borneol gave but 30% of chloride. Cumin alcohol resembled in activity benzyl alcohol and gave practically a theoretical yield of the chloride.

Unfortunately so many factors are involved in the reaction between alcohols and aqueous solutions of the halogen acid used that no definite general conclusion can be drawn with the facts at present available. It is planned to continue the work with special attention to the physical conditions which come into play. The fact that the alcohols and their halides vary in solubility and volatility no doubt is an important factor which has not been investigated. Quantitative measurements will be made under conditions which can be used in all cases so that the results obtained are comparable. The qualitative work which has been done was necessary in order to survey the field to determine which compounds would serve best in a detailed quantitative study of the reaction.

The results already obtained have led to practical methods of preparation of halides which have proved of great value. The main problem— the interpretation of the mechanism of the reaction—will be actively investigated, since it is of the greatest importance in organic chemistry to know more about the manner in which molecules interact.

Experimental Part.

Ethylene Glycol.—A mixture of 20.3 g. of the glycol and 271 cc. of conc. hydrochloric acid (one molecule of the glycol to 9 of the acid) was heated at its boiling-point for 4.5 hours. The product was then fractionated with a Le Bel-Henninger tube. The fractions containing the chlorohydrin and the glycol were neutralized and extracted with ether. The ethereal solutions were dried over anhydrous potassium carbonate and distilled. Yield of chlorohydrin was 12%; b. p. 127.6–128.6°; d^{20} 1.194. The glycol recovered weighed 10.5 g.

Ethylene Bromohydrin.—A mixture of 5.7 g. of the hydrin and 22.7 cc. of conc. hydrochloric acid was kept near its boiling-point for 6.5 hours. Some decomposition occurred but there was no evidence of the formation of an insoluble halide.

Trimethylene Glycol.—A mixture of 5 g. of the glycol and 53 cc. of conc. hydrochloric acid was slowly distilled. The distillate was neutralized and extracted with ether. After drying with sodium sulfate

the ethereal solution yielded 1.8 g. of the chlorohydrin, which boiled at 160.5° and contained 36.55% of chlorine, the calculated value for the compound being 37.55%. The yield of chlorohydrin was thus 28%.

A mixture of 3 g. of the glycol and 13.4 cc. of constant-boiling hydrobromic acid (molecular ratio one of glycol to 3 of acid) was heated near its boiling-point for several hours and then distilled. The oil which separated was distilled and shown to be trimethylene bromide. From the aqueous distillate was isolated 0.5 g. of a liquid which had the specific gravity of the bromohydrin. The yields of the bromide and bromohydrin were 62 and 8% respectively.

In another experiment conditions were used which favored the formation of the bromohydrin. Four g. of trimethylene glycol was heated with 7.14 g. of constant-boiling hydrobromic acid (mol. ratio 1 to 1.2) at 70° for an hour. The mixture was then raised to the boiling-point for a few minutes until an insoluble oil began to form; it was then cooled, neutralized, and extracted. The ethereal solution left on evaporation 3.3 g. of a liquid which possesses the properties and solubility in water of ethylene bromohydrin. Since it contained 54% of bromine and the pure compound contains 57.5% the sample was not quite pure. The yield was 43%.

A small sample of trimethylene bromohydrin was distilled with conc. hydrochloric acid. A small amount of an insoluble oil was obtained which was no doubt formed as the result of the displacement of the hydroxyl group by chlorine.

Glycerol.—A mixture of 105.4 g. of 95% glycerol and 898 cc. of hydrochloric acid of sp. gr. 1.178 (molecular ratio 1 to 9.4) was kept at the boiling-point (about 85°) for 4 hours and then slowly distilled through a Le Bel-Henninger column. After the excess of acid had distilled over, the temperature rose to above 110°, the residue in the flask darkened rapidly, and drops of oil appeared in the distillate. The distillation was continued under diminished pressure. At the end of the distillation the flask contained a thick, very viscous residue which weighed 58 g. and contained no chlorine. The distillate was fractionated and yielded 10.8 g. monochlorohydrin, which is a 9% yield.

A number of experiments were carried out to determine the behavior of glycerol with aqueous hydrobromic acid (sp. gr. 1.49). Three molecular weight equivalents of the acid to one of the alcohol were used. The mixtures were distilled slowly until the temperature rose to above 126° when the distillation was continued under diminished pressure. As the temperature increased the material in the flask darkened and finally a tarry residue was left. By fractionating the volatile material obtained when 50 g. of glycerol was used 66 g. of a mixture was obtained which yielded approximately 11 g. of monobromohydrin and 55 g. of dibromohydrin. This corresponds to a yield of 13% of the former and 46% of the

latter. The dibromohydrin had d_{21}^{21} 2.1348; b. p., 87° (corr.) 8.5 mm. pressure and 214.8° (corr.). at 760 mm. The percentage of bromine found was 72.66, that calculated being 73.35%. The constants reported for the symmetrical dibromohydrin are as follows, b. p. 105° at 16 mm., 124° at 38 mm., and 219° at 760 mm., d^{18} 2.11. The constants for the unsymmetrical compound are, b. p. 118° at 17 mm. and 212–214° at 760 mm., d^0 2.1682. It is impossible from these constants to determine which dibromohydrin was formed as the results of the experiment described above. It is possible that the product was a mixture. The solubility of the compound in water makes it appear probable that it was the symmetrical dibromohydrin. It was soluble in about 30 parts of cold water and in a slightly less volume of hot water. The solubility of the unsymmetrical dibromohydrin is reported as one part in 9 parts of water at 19° and 6 parts of water at 72°.

The monobromohydrin was probably the one of the structure $CH_2OH.-CHOH.CH_2Br$. It boiled at 120–123° at 10 mm. pressure. It dissolved 1.5 volumes of cold water, and was soluble in about 50 parts of cold water. It was miscible in all proportions with boiling water. The symmetrical compound $CH_2OH.CHBr.CH_2OH$ has not been described. The boiling-points recorded for the known bromohydrin are as follows, 134° at 16 mm., 138° at 17 mm., 145° at 30 mm. and 160° at 60 mm.

The fractionation of the product was difficult as in the presence of the acid changes took place slowly. It is probable that some of the mono-bromohydrin was being converted into the dibromohydrin or that molecular rearrangements were taking place. The reaction deserves further study.

Pinacone.—It has been shown by previous workers[1] that pinacone is converted into the corresponding dibromides and dichlorides when treated with aqueous solutions of the halogen acid saturated at 0°. After standing at room temperature for some time yields of about 75% of the halides were obtained. When pinacone is distilled with the acids pinacoline and other ill-defined products, some of which contained halogen, were formed.

Cyclohexanol.—When 3 g. of the alcohol was treated with 25 cc. of conc. hydrochloric acid at room temperature it dissolved. The solution soon clouded. On heating, an oil continued to separate and in one hour the reaction appeared to be complete. The oil was separated, washed with a solution of sodium carbonate and dried over calcium chloride. The yield was 3.3 g. or 93%. The oil boiled at 142.7–145° (corr.) at 760 mm. The recorded boiling-point is 143° at 758 mm.

Menthol.—A mixture of 5 g. of menthol and 28 cc. of conc. hydro-

[1] Thiele, *Ber.*, **27**, 455 (1894); Kondakow, *J. prakt. Chem.*, **54**, 429 (1896); **62**, 169 (1901).

chloric acid (mol. ratio 1 : 9) was gently boiled for several hours. The layer of insoluble oil was separated, dried and analyzed. It was found to be a mixture of chloride and unchanged alcohol. The yield of chloride in the mixture was 41.3%.

Borneol.—When 7.5 g. of borneol was heated with 40 cc. of constant-boiling hydrochloric acid the solution soon clouded. After boiling for 4 hours the solid product was separated and dried over sulfuric acid. It melted at 163.5–170°. Borneol melts at 204° and its chloride at 157°. The product was evidently a mixture. A halogen determination showed that it contained about 33% of the chloride. A fractional crystallization of the product from petroleum removed most of the unchanged borneol.

Cumin Alcohol.—When the alcohol was mixed with constant-boiling hydrochloric acid, the acid layer soon clouded showing that reaction was taking place at room temperature. After boiling the mixture for 2 hours it was neutralized and extracted with ether. The product boiled at 227–228°; the recorded temperature is 225–229°. The yield was practically that theoretically possible.

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