CXXVIII.—*The Chlorination of Ethyl Alcohol.*

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THE interaction of two such familiar substances as chlorine and ethyl alcohol has naturally attracted the attention of many chemists (Liebig, *Annalen*, 1832, **1**, 182; Lieben, *ibid.*, 1857, **104**, 114; *Ber.*, 1870, **3**, 907; Personne, *Compt. rend.*, 1869, **69**, 1363; Fritsch, *Annalen*, 1894, **279**, 288), but the complete course of the reactions, which result ultimately in the formation of chloral, has never been satisfactorily settled.

With the intention of making more clear the initial stage of the reaction, the chlorination of alcohol has again been studied. It has been shown that ethyl hypochlorite and hydrogen chloride are first produced, and that acetaldehyde is formed from the hypochlorite by the elimination of hydrogen chloride.

As only an inconsiderable amount of ethyl chloride is formed at this stage, it is probable that the ethyl chloride recognised by Liebig and others is mainly produced by the slow interaction of the hydrogen chloride first formed with the alcohol present in excess.

The course of the reactions which lead to the formation of chloral alcoholate appears to be explained satisfactorily as follows.

When chlorine first acts on alcohol ethyl hypochlorite and hydrogen chloride are produced, the yellow colour of the solution being due to the hypochlorite. In the presence of excess of unchanged alcohol the ethyl hypochlorite very quickly breaks down into acetaldehyde and hydrogen chloride :

$$CH_3\cdot CH_2\cdot OH + Cl_2 \longrightarrow CH_3\cdot CH_2\cdot OCl + HCl.$$
$$CH_3\cdot CH_2\cdot OCl \longrightarrow CH_3\cdot CHO + HCl.$$

Under the influence of the hydrogen chloride present, the aldehyde is polymerised to paracetaldehyde. This is next chlorinated to *s*-trichloroparacetaldehyde, which to a small extent depolymerises under the influence of hydrogen chloride to monochloroacetaldehyde. This, immediately it is set free, combines with some of the still unattacked alcohol to form monochloroacetaldehyde alcoholate.*

$$CH_3\cdot CHO \xrightarrow{HCl} (CH_3\cdot CHO)_3 \xrightarrow{Cl_2} (CH_2Cl\cdot CHO)_3 \xrightarrow{HCl}$$
$$CH_2Cl\cdot CHO \xrightarrow{EtOH} CH_2Cl\cdot CH(OH)\cdot OEt.$$

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* Natterer (*Monatsh.*, 1884, **5**, 497) found that when monochloroacetaldehyde is added to alcohol heat is evolved and monochloroacetaldehyde alcoholate is formed.

This compound now reacts both with alcohol, which is still present, to form monochloroacetal, and with hydrogen chloride, which has now been produced in considerable amount, to form dichloroethyl ether.

$$\begin{tikzcd}
 & \mathrm{CH_2Cl{\cdot}CHCl{\cdot}OEt + H_2O} \\
\mathrm{CH_2Cl{\cdot}CH}{<}\substack{\mathrm{OH}\\ \mathrm{OEt}} \arrow[ur, "\mathrm{HCl}"] \arrow[dr, "\mathrm{EtOH}"'] & \\
 & \mathrm{CH_2Cl{\cdot}CH(OEt)_2 + H_2O}
\end{tikzcd}$$

Further chlorination of each of these compounds leads to the formation of trichloroethyl ether, chlorination of monochloroacetal occurring either before or after its conversion into a chloro-ether by the hydrogen chloride, now present in great excess :

$$\begin{tikzcd}
 & \mathrm{CH_2Cl{\cdot}CHCl{\cdot}OEt} \arrow[dr, "\mathrm{Cl_2}"] & \\
\mathrm{CH_2Cl{\cdot}CH}{<}\substack{\mathrm{OEt}\\ \mathrm{OEt}} \arrow[ur, "\mathrm{HCl}"] \arrow[dr, "\mathrm{Cl_2}"'] & & \mathrm{CHCl_2{\cdot}CHCl{\cdot}OEt} \\
 & \mathrm{CHCl_2{\cdot}CH(OEt)_2} \arrow[ur, "\mathrm{HCl}"'] &
\end{tikzcd}$$

At this stage the liquid separates into an upper layer, consisting chiefly of a saturated solution of hydrogen chloride in water, and a lower layer of trichloroethyl ether. On warming, the two layers disappear and the liquid again becomes homogeneous, the trichloro-ether reacting with the water of the upper layer and forming dichloroacetaldehyde alcoholate :

$$\mathrm{CHCl_2{\cdot}CHCl{\cdot}OEt + H_2O \longrightarrow CHCl_2{\cdot}CH(OH){\cdot}OEt + HCl.}$$

The dichloroaldehyde alcoholate is then very slowly chlorinated to chloral alcoholate, which is the final product of the reaction, the hydrogen chloride escaping at the high temperature which is required during the last stage of the chlorination.

EXPERIMENTAL.

Action of Ethyl Hypochlorite upon Alcohol.—Ethyl hypochlorite (usually 12—13 grams, prepared from 10 grams of alcohol and 20 grams of sodium hydroxide in 100 c.c. of water by the method previously described [*J*., 1923, **123**, 3000]) was run as rapidly as possible through a tap-funnel into 20 c.c. of alcohol contained in a half-litre flask. This was cooled by ice and fitted with a double-walled condenser which was connected to a Volhard trap containing alcohol, similarly cooled, to retain any volatile products which might escape condensation. Within a minute a very vigorous reaction occurred accompanied by the evolution of heat and sometimes by a crackling sound. This action soon ceased and a colourless liquid containing much free hydrogen chloride remained in the flask. This and the contents of the Volhard trap were without delay poured into a flask containing an excess of precipitated calcium carbonate. It was found impracticable owing to the energetic action to bring more than these comparatively small quantities together at a time.

The operations were repeated until about 230 grams of ethyl hypochlorite had been added to 370 c.c. of alcohol. The whole was then filtered from the excess of calcium carbonate and distilled, when a considerable quantity of acetaldehyde came over; the bulk, however, was found in the residue, where it had been converted into paracetaldehyde and acetal.

Identification of Ethyl Hypochlorite as the First Product of the Chlorination of Alcohol.—Dry chlorine was passed through a fine tube, very slowly to avoid heating, into 5 c.c. of alcohol cooled to −18°. A yellow liquid was obtained which appeared identical with a freshly made, cold, dilute alcoholic solution of ethyl hypochlorite. Both had the same characteristic odour and both liberated iodine at once when added to a slightly acidified solution of potassium iodide. Both lost their yellow colour at the ordinary temperature, in a short time when light was excluded, and much more rapidly in bright light. In both cases hydrogen chloride was freely evolved during the decoloration and the presence of acetaldehyde in considerable quantity could be recognised in the acid colourless product. In view of the vigorous and immediate decomposition of ethyl hypochlorite in presence of alcohol, it was necessary, if it was to be identified, to chlorinate in an apparatus in which the bulk of the alcohol reacted almost immediately, and in which heating was avoided as far as possible. This was done by allowing small drops of alcohol distributed over a large, cooled surface to meet an excess of chlorine. Dry alcohol was allowed to drop slowly from a tap funnel drawn out to a fine capillary, down a narrow, cooled tube packed with glass beads up which a stream of chlorine was passed. Light was carefully excluded. The liquid product which condensed in the tube was collected in a well-cooled, blackened flask. Owing to the heat unavoidably produced locally, a small proportion of the products distilled over; this was condensed and collected in a similar cooled, blackened flask attached to the exit tube.

The stream of chlorine passing through the apparatus was so regulated that some of it issued unchanged from the exit tube. It was found that the alcohol could not be admitted faster than about 1 c.c. a minute, this rate allowing the heat produced to be dissipated. If the tube was not sufficiently cooled or if the alcohol was allowed to enter more rapidly, decomposition accompanied by a yellow flame occurred and carbon was deposited. Most of the reaction took place on the upper layer of beads, and the tube became slightly warm at that point. The product obtained was a heavy, yellow, fuming liquid with the irritating, characteristic odour of ethyl hypochlorite. It was poured on to crushed ice, when a yellow oil containing ethyl hypochlorite with some more highly chlorinated products separated as a lower layer. This was rapidly washed with iced water, separated, and dried over fused calcium chloride. To estimate the amount of ethyl hypochlorite present, a small, weighed portion was added to a solution of potassium iodide acidified with acetic acid, and the liberated iodine titrated. The amount was found to vary with the conditions and duration of the experiment. Collected as described above, in one experiment 8·2 per cent. of ethyl hypochlorite was found to be present. In a second experiment, in which the separation and drying were carried out more rapidly, 12·9 per cent. of ethyl hypochlorite was found to be present in the oil separating from the liquid condensed in the tube and 10·2 per cent. in the oil separating from the liquid which distilled over and condensed in the flask attached to the exit tube. It was found impracticable to obtain the ethyl hypochlorite in a pure condition by distillation. On heating the yellow oil rapidly, it boiled vigorously with obvious decomposition at about 40°, much hydrogen chloride was liberated, and a small quantity of a yellow liquid distilled over which contained only about 6 per cent. of ethyl hypochlorite.

Complete Chlorination of Alcohol without Cooling or External Heating.—A litre of 97 per cent. alcohol was allowed to drop through a capillary down the tube packed with beads previously described at the rate of about 1 c.c. in 5 minutes. Neither the tube nor the collecting flask was cooled, and a sufficient current of chlorine was maintained for it to escape freely from the exit. The alcohol was thus subjected to the action of excess of chlorine for a considerable period at a temperature not far removed from the ordinary. 998 Grams of a nearly colourless, fuming liquid, separated into two layers, collected in the receiver. The upper layer ($d_{4^\circ}^{16^\circ}$ 1·11), which consisted largely of water, weighed 582 grams and the lower layer ($d_{4^\circ}^{16^\circ}$ 2·22) weighed 416 grams. To the mixed layers a saturated solution of potassium carbonate was added until the free hydrochloric acid was neutralised. The liquid now separated into two layers, a lower layer consisting of a strong solution of potassium chloride and an upper, oily layer of a pale yellow colour giving off vapours which had a very irritating effect on the eyes. The pale yellow, oily liquid ($d_{4^\circ}^{16^\circ}$ 1·2) weighed 433 grams. It could not be separated into its constituents by fractionation. On heating, a considerable amount distilled over in the neighbourhood of 92°;

the temperature then rose rapidly to about 150°, when almost complete decomposition and charring of the remainder, a large part of the whole, occurred. The liquid distilling in the neighbourhood of 92°, which appeared to be a mixture of impure monochloroacetaldehyde alcoholate with some di- and tri-chloroether and a small quantity of monochloroacetaldehyde, could not itself be separated into its constituents, as on refractionation it decomposed with much frothing. As no pure product could be isolated by fractionally distilling the oily product, either under the ordinary or reduced pressure, a further quantity, prepared as above, was added to an equal weight of alcohol together with an excess of powdered chalk and the mixture heated to boiling for 8 hours. The product was then filtered and poured into water, when an oily liquid separated as a lower layer. This was washed with a little water, dried over calcium chloride, and fractionally distilled. It was thus separated into two main fractions boiling constantly at 155° and 182°, respectively, which analysis showed to be monochloroacetal (Found: Cl = 23·77. Calc., Cl = 23·24 per cent.), and dichloroacetal (Found: Cl = 38·11. Calc., Cl = 37·92 per cent.).

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