ON THE VAPOUR-PHASE HYDROLYSIS.

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There have been a great many investigations on the reactions of organic compounds with water, particularly in connection with the hydrolysis of esters in aqueous solutions. All these results have brought about a number of theories regarding the mechanism of the reaction: the theory generally accepted states that the hydrolytic reaction occurs in two stages, the first being a rapid formation of a substrate-water complex and the second the subsequent reaction of the complex with hydrogen-ion to give final products of the hydrolysis.(1) For example, the hydrolysis of esters in aqueous solutions can be represented by the following scheme:

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(1) Cf., for example, F.O. Rice, " The mechanism of homogeneous organic reactions," Chemical Catalog Co., 1928, 104.

$$\text{ester}+\text{water} \rightleftarrows \text{ester}\cdot\text{water},$$

$$\text{ester}\cdot\text{water}+H^+ \rightarrow \text{acid}+\text{alcohol}+H^+.$$

If the above-mentioned mechanism be correct, then the hydrolytic reaction should be very difficult to occur in the vapour phase, where the formation of the substrate-water complex will be greatly retarded and at the same time ions are not known to exist at least in the stable form. As there have been very few works on the reactions of organic compounds with water vapour, it occurred to the present authors that an inquiry into the nature of this type of reactions in the vapour phase would be interesting. Although Berthelot and Péan de St. Gilles(2) already noticed in their memorial work on the ester equilibrium that not only the formation but also the hydrolytic decomposition of ethyl acetate was greatly retarded in the vapour phase, and G. Harker(3) has recently pointed out that benzyl chloride is slowly attacked by liquid water but not by steam.

The present paper is concerned with the non-reactivity of water vapour on benzyl chloride, the reaction of which with liquid water was already studied by one of the authors a few years ago,(4) and on ethyl acetate, which is one of the typical substances for the study of the hydrolytic reaction.

The reaction vessel shown in Fig. 1 is made of glass and has half a liter capacity. It was well cleaned with chromic mixture and steamed before every use. Weighed quantities of the ester and water were separately sealed in small thin-walled glass bottles of about 0.1 c.c. capacity. The ester-bottle was placed on the bottom of the center tube B and the water-bottle on the bottom of the tube C. A glass rod a few centimeters long was placed over each bottle, and both tubes B and C were connected by fusing at points D with respective side tubes in the lower part of the reaction vessel. The reaction vessel was then well pumped out through tube A and was sealed off at point A. After the small bottles containing substances were

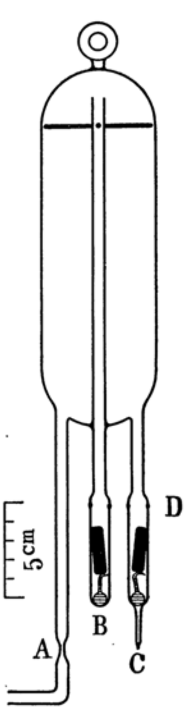

Fig. 1.
Reaction Vessel

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(2) Berthelot and Péan de St. Gilles, *Ann. chim. phys.*, **65** (1865), 385; *Chem. Z.*, **7** (1862), 908.

(3) G. Harker, *J. Chem. Soc.*, **1924**, 500.

(4) T. Titani and K. Kurano, *Bull. Chem. Soc. Japan*, **6** (1931), 152.

broken by hammering them with the glass rods (caused by shaking), the reaction vessel was placed in an electrically heated air thermostat. The temperature was gradually raised up to the desired point, where it was able to be maintained constant automatically within ±1° for a long period. The quantities of the substances taken are shown in Table 1, where the total pressure exerted by the vaporized substances in the reaction vessel was calculated.

Table 1. Average amounts of the substances taken.

Substance	Temp. C.	Ester in mol	Water in mol	Total pressure calc. in atm.
Benzyl chloride	130°	0.0005	0.0004	0.06
	200°	0.001	0.005	0.30
Ethyl acetate	130°	0.001	0.001	0.13
	200°	0.002	0.008	0.78

After the reaction vessel was heated for a measured time, it was taken out of the thermostat and was quickly cooled down. As soon as it attained room temperature, a measured quantity of water (about 30 c.c. twice) was forced into the vessel through the right side tube C by breaking its capillary end in the water. The reaction vessel was rinsed in this way and whole water thus employed was carefully collected to be titrated against 0.02 N baryta, the titration being carried out as soon as possible. A few drops of the baryta were found enough, in most cases, to give an end point. A slight correction due to the carbonic acid from air had to be taken into consideration. The acidity thus determined was divided by the total mols of the ester employed, and then multiplied by 100. This value, which may be regarded as a percentage decomposition of the ester, is plotted against the duration of each run in hours (small circles in Fig. 2 and 3). Small triangles in these figures represent the results of the comparative experiments where the vapour of ester only was heated without an addition of water vapour. It will be seen from the figures that the degree of decomposition is very small in every case, on the whole 0.5% for benzyl chloride at 130°C. and 200°C. and 0.05% for ethyl acetate at 200°C. No trace of decomposition was found for ethyl acetate at 130°C. even after 150 hours' heating. This slight tendency to decompose is, moreover, always the same irrespective of whether the esters are heated with or without an addition of water vapour. This slight decomposition is by no means caused by the hydrolytic reaction in vapour phase, but either by the hydrolysis in the liquid phase during the washing and titration or by the thermal decomposition in the vapour phase. It was tried to avoid as far as possible the thermal decomposition at the temperatures employed by keeping the inner surface of the vessel clean and by gradually raising the temperature of the thermostat, so as not to superheat the esters in the liquid state. Nevertheless, the thermal effect became too remarkable at 300°C. to obtain a reproducible result above this temperature.

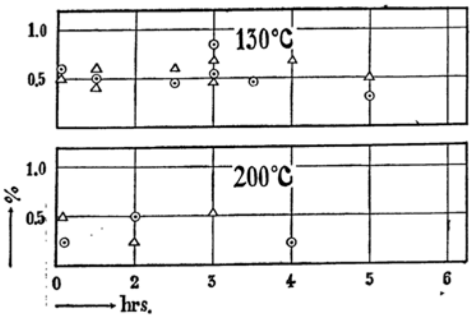

Fig. 2. Benzyl chloride

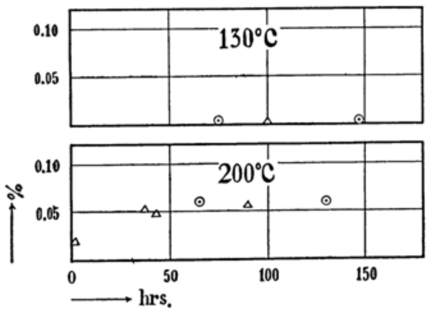

Fig. 3. Ethyl acetate

We may draw a following conclusion from the result so far obtained: (1) the hydrolysis is not a merely molecular reaction between ester and water molecules; (2) the heat of activation for the hydrolytic reaction in the vapour phase will be much larger than that of the thermal decomposition or polymerization.

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