ACTION OF WATER AND ALCOHOLS ON ACID CHLORIDES IN THE GASEOUS STATE

V. V. Ponomarev, K. A. Andrianov,
A. P. Dushechkin, and S. A. Golubtsov*

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It is known that water and alcohols easily, and in the absence of catalysts, react with the acid chlorides (AC) of organic and inorganic acids to give the corresponding acids or their esters. At the same time, the esters of these acids practically fail to hydrolyze in the absence of either acid or alkaline catalysts. In the case of the esters of inorganic acids, for example the alkoxysilanes, the catalyst of the reaction is the liberated HCl.

The effect of HCl as the catalyst can be excluded if the process is run in the gas phase, since HCl fails to dissociate in the gaseous state. At the same time, a determination of the composition of the products obtained in the gas phase is quite complicated, since during condensation their reaction proceeds at high speed and it is not clear which part of the process actually went in the gas phase.

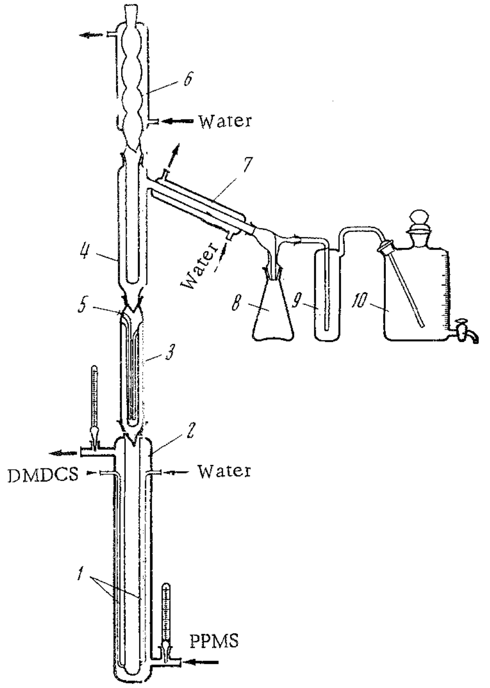

Fig. 1. Reactor: 1) vaporizer; 2) tube; 3) trap containing hexachlorosiloxane; 4) fractionating column; 5) thermocouple; 6) reflux condenser; 7) condenser; 8) receiver; 9) trap; 10) gas meter.

It is known that the HCl formed during esterification easily reacts with the starting alcohol to give the alkyl chloride and water. CH_3Cl was obtained in high yield when a mixture of methanol and HCl vapors was passed through an empty tube at 200°C. Methyl chloride was not obtained when a mixture of methanol and $(CH_3)_2SiCl_2$ vapor was passed through under analogous conditions. This can be associated with the fact that HCl was absent in the tube, i.e., at 200° (the same was also observed at 250°) methanol vapors do not react with dimethyldichlorosilane (DMDCS) vapors. If the tube is filled with an acid catalyst ($ZnCl_2$ deposited on pumice), then the vapor-phase reaction proceeds under the same conditions with the formation of CH_3Cl in quantitative yield.

For a more rigorous proof that a catalyst has to be present when either the hydrolysis or the esterification of an AC is run in the gas phase we passed a mixture of DMDCS with either an excess of water or methanol through a special reactor, after which the reaction products were trapped at 100-120° by either hexachlorosiloxane or bis(trichlorosilyl)benzene. These compounds in the liquid phase reacted with either the water or the alcohol, whereas the DMDCS was isolated for the most part unreacted. The obtained results suggest that methanol and water do not react with DMDCS in the gas phase.

The outer AC behave in a similar manner. Thus, when a mixture of $SiCl_4$ and water vapors, or of acetyl chloride

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*Deceased.

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and water, was passed through the described reactor at 200°, the water was quantitatively trapped from the mixture by bis(trichlorosilyl)benzene, while the AC was obtained in the unchanged form.

The absence of AC esterification and hydrolysis is, in general, apparently characteristic when the reaction with water or with alcohols is run at temperatures that exceed the boiling point, and proves the catalytic character of these reactions.

EXPERIMENTAL METHOD*

Reaction of HCl and Dimethyldichlorosilane with Methanol. Into a tube with a diameter of 32 × 1200 mm, heated to 200-220°, were passed HCl from a cylinder and CH_3OH vapors that had been preheated to 120-150°. The amount passed through in 12 min was 32 g of CH_3OH and 36 g of HCl. The reaction products were trapped by cooling in a Dry Ice–acetone mixture. Distillation of the condensate gave 27.5 g of CH_3Cl (bp – 22 to – 24°, identified by GLC). The reaction of CH_3OH (32 g) and DMDCS (26 g) vapors, heated to 200°, was run under analogous conditions. CH_3Cl was not detected in the reaction products.

The tube was filled with pieces of pumice that had been impregnated with $ZnCl_2$ solution. The catalyst was dried for 12 h at 185° in a nitrogen stream. Under the conditions of the preceding experiment, a mixture of 106 g of DMDCS and 82.5 g of CH_3OH was passed through in 40 min.

Reaction of Dimethyldichlorosilane with Methanol and Water. Into the special reactor (Fig. 1), through vaporizer 1, at 120-125°, were fed DMDCS and CH_3OH at respective flow rates of 2.7 and 3.3 g /min (mole ratio = 1 : 4.8). The mixture entered the 1200 × 32 mm tube 2, heated to 300°, and then into trap 3 which was equipped with a bubbling device, heated by the vapors and filled with 70 g of hexachlorodisiloxane. The CH_3OH-free gas mixture entered the fractionating column 4 with refluxing benzene in order to recover the entrained hexachlorodisiloxane. The unreacted DMDCS, contaminated with hexachlorodisiloxane, was condensed in condenser 7 and collected in receiver 8. The amount passed through in 9 min was 24.3 g of DMDCS and 29.7 g of CH_3OH. In the receiver 8 we collected 25.1 g (86%) of a mixture that contained 21.1 g of DMDCS (GLC). In the experiment, run in a similar manner in the absence of CH_3OH, the DMDCS recovery was 87%.

In a similar manner, the passage of 49.4 g of DMDCS and 13.4 g of water (mole ratio = 1 :2) led to the isolation of 35 g of DMDCS. In addition, 5.2% of DMDCS was found in the escaping gases.

Reaction of $SiCl_4$ and Acetyl Chloride with Water. Instead of hexachlorodisiloxane, trap 3 of the reactor was filled with 70 g of bis(trichlorosilyl)benzene. Under the conditions of the preceding experiment, the passage of 85 g of $SiCl_4$ and 18 g of water gave 76 g of unreacted $SiCl_4$.

In a similar manner, the passage of a mixture of 11 g of CH_3COCl and 2 g of water gave 10.8 g of CH_3COCl.

CONCLUSIONS

The esterification and hydrolysis of a number of acid chlorides (dimethyldichlorosilane, $SiCl_4$, acetyl chloride) fail to go when they are treated with water or with alcohols in the gas phase.

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