MECHANISM OF HYDRATION AND DEHYDRATION REACTIONS
IN PRESENCE OF ZINC HALIDES

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Processes of hydration and dehydration are extensively used in the industry of organic synthesis and preparative chemistry for the preparation of substances of great practical importance, particularly alcohols and unsaturated hydrocarbons. These reactions proceed successfully only in presence of catalysts. The catalysts most frequently used are sulfuric and phosphoric acids, alumina, thoria, and various salts [1]. It is to be noted that, in spite of the great practical importance of hydration and dehydration reactions, their mechanisms have not been adequately elucidated. There are various schemes in the literature for the course of these reactions in presence of certain protonic acids [2], but there are substantially no soundly based data on the mechanisms of these reactions in presence of aprotic acids. We must point out also that metal halides have long been used as hydrating and dehydrating agents; and among these the most extensively used is zinc chloride.

Dehydration of Alcohols

Many investigators [3-5] have studied the dehydration of various alcohols with the aid of zinc chloride, and, on the basis of their experimental results, they have explained the mechanism of the reaction of alcohols with zinc chloride in various ways. Kondakov [6] considers that zinc chloride acts exclusively as a water-eliminating agent and does not admit the possibility of the formation of intermediate compounds. Liebmann [7] also regards zinc chloride as a water-eliminating agent. According to these views, the reaction of zinc chloride with alcohols is expressed in the following scheme:

\[
\begin{align*}
\text{ZnCl}_2 + \text{C}_n\text{H}_{2n+1}\text{OH} &\rightarrow \text{C}_n\text{H}_{2n} + \text{H}_2\text{O}; \\
2\text{ZnCl}_2 + 2\text{C}_n\text{H}_{2n+1}\text{OH} &\rightarrow (\text{C}_n\text{H}_{2n+1})_2\text{O} + \text{H}_2\text{O}.
\end{align*}
\]

Other authors, however, hold a different view of the mechanism of reactions of zinc chloride with alcohols. Thus, going back to Williamson [8], we find that in his theory of the formation of ethers he considered that zinc chloride reacts like sulfuric acid with alcohols, forming intermediate zinc alkoxides, which then give ethers:

\[
\begin{align*}
2\text{C}_2\text{H}_5\text{OH} + \text{ZnCl}_2 &\rightarrow (\text{C}_2\text{H}_5\text{O})_2\text{Zn} + 2\text{HCl}; \\
2\text{C}_2\text{H}_5\text{OH} + 2\text{HCl} &\rightarrow 2\text{C}_2\text{H}_5\text{Cl} + 2\text{H}_2\text{O}; \\
(\text{C}_2\text{H}_5\text{O})_2\text{Zn} + 2\text{C}_2\text{H}_5\text{Cl} &\rightarrow 2\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5 + \text{ZnCl}_2.
\end{align*}
\]

The same view was developed later by Walter [9], who observed the formation of mixed zinc alkoxides in the reaction of zinc chloride with alcohols:
\[ \text{i-C}_3\text{H}_7\text{OH} + \text{ZnCl}_2 \rightarrow \text{i-C}_3\text{H}_7\text{OZnCl} + \text{HCl}. \]

At high temperature the mixed zinc alkoxide decomposed into various new substances:

\[
\begin{align*}
\text{RCH} & \rightarrow \text{CH}_2 + \text{Zn} \quad \text{OH} \\
\text{RCH}_2\text{CH}_2\text{O} \cdot \text{ZnCl} & \rightarrow \text{H}_2\text{ZnCl} + \text{RCH} \rightarrow \text{CH}_2 + \text{RCH}_2\text{C}=\text{CH} \\
\end{align*}
\]

From the products of this reaction Walter succeeded in isolating an oily compound, to which he ascribed the formula \( \text{C}_9\text{H}_{11}\text{OZnCl} \), although there was a great discrepancy between the found and calculated values for the zinc, carbon, and hydrogen contents. After an investigation of the decomposition products of aluminum and zinc alkoxides, Tishchenko [10] concluded that reaction between alcohols and zinc chloride proceeds as follows:

\[
\begin{align*}
\text{ZnCl}_2 + 2\text{ROH} & \rightarrow \text{Zn} (\text{OR})_2 + 2\text{HCl}; \\
2\text{ROH} + 2\text{HCl} & \rightarrow 2\text{RCI} + 2\text{H}_2\text{O}. \\
\end{align*}
\]

The author considered that the alkyl chloride reacts with the zinc alkoxide with formation of an ether,

\[
\text{Zn} (\text{OR})_2 + 2\text{RCI} \rightarrow \text{ZnCl}_2 + 2\text{R}_3\text{O}. 
\]

and olefins are formed by decomposition of the zinc alkoxide. Favority [11] pointed out the resemblance between the mechanisms of the reactions of sulfuric acid and zinc chloride with \( \alpha \)-glycols and assumed the formation of mixed zinc alkoxides as intermediate products.

There is, therefore, a divergence of opinion on the mechanism of the dehydration of alcohols in presence of zinc chloride, and it is difficult to judge which of the suggested schemes is the correct one. The views of authors of the first group, which assume that zinc chloride is merely a water-removing agent, are not in accord with the experimental facts and, in our opinion, must be regarded as doubtful. The various schemes proposed by authors of the other group, which assume the formation of intermediate compounds in the course of the dehydration of alcohols under the action of zinc chloride, have the drawback of being based on indirect experimental facts. For example, when reaction between zinc chloride and alcohols was carried out at high temperatures (350-400\(^\circ\)) in iron vessels [3, 4], there were by-products in the formation of which iron and its oxide probably played a major part. However, in the establishment of the mechanism of the action of zinc chloride on alcohols the effect of these factors was not taken into consideration by earlier investigators.

With the object of elucidating the nature of the catalytic effect of zinc halides in the course of hydration and dehydration, we undertook an investigation of the reactions of alcohols and olefins with zinc chloride and bromide [12]. Taking into account the importance of studying intermediate products for the establishment of reaction mechanisms, we first tried to determine the conditions for the formation of the products which, as we showed, are formed in the reaction between zinc halides and alcohols. We studied the action of anhydrous zinc