CONDUCTIVITY OF ACID CATALYSTS AND ITS VARIATION
DURING ALKYLATION AND POLYMERIZATION REACTIONS

Ya. M. Paushkin and M. V. Kurashev

One of the fundamental properties of acid catalysts is the electrical conductivity associated with the ionic character of acids. According to modern views, acid catalysis is to be explained by the ability of acids to dissociate into ions, which take part in the intermediate stages of the reaction. The mechanism of alkylation (I) and polymerization (II) with the participation of protons may be represented by the following scheme [1]:

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{C}=\text{CH}_2 + \text{H}^+ & \rightarrow \text{(CH}_3\text{)}_2\text{C}^+ \text{O} \text{C}_8\text{H}_{16} + \text{H}^+ \\
\text{C}_4\text{H}_{10} & \text{O} \text{C}_8\text{H}_{16} + \text{H}^+ \\
\text{C}_4\text{H}_{10} & \text{O} \text{C}_8\text{H}_{16} + \text{H}^+
\end{align*}
\]

Reaction is initiated by addition of a proton at a double bond, which leads to the formation of a tert-butyl carbonium ion. This carbonium ion then adds to 2-methylpropene with formation of a \( \text{C}_4\text{H}_{10} \) carbonium ion, which, depending on the reaction conditions, may be converted in presence of isobutane into an octane isomer and a carbonium ion (alkylation), or may be converted into an octene isomer (polymerization) with elimination of a proton.

In connection with the participation of ions in the reaction, it is of interest to investigate the conductivity of acid catalysts as a supplementary physicochemical parameter that gives an indication of the variation of the properties of the catalyst, particularly its ionic character, in the course of the reaction. Volkenshtein [2] points out that catalytic activity, like conductivity, must be assigned to the category of "structure-sensitive" properties of heterogeneous catalysts. There is a relationship between the catalytic activity of a semiconductor and its conductivity, i.e., between the rate constant for the reaction and the conductivity of the catalyst \( k \) at a given temperature, and it may be represented by the function:

\[
k_T = k_0(c^\infty T).
\]

The conductivity can serve as a characteristic of the activity only insofar as we are concerned with various samples of the same catalyst differing in the content of an additive that does not affect the general nature of the catalyst. The specific conductivity of liquid electrolytes is determined by the concentration of ions and their mobility:

\[
\kappa = c(u + v),
\]

in which \( \kappa \) is the specific conductivity, \( c \) is the ionic concentration, and \( u \) and \( v \) are the ionic mobilities, i.e., the product of charge and velocity. The mobility of the hydrogen ion is 313 coulomb-cm/sec, and those of the ions \( \text{F}^- \), \( \text{SO}_4^2^- \), and \( \text{H}_2\text{SO}_4^+ \) vary over the range 46.6-67 coulomb-cm/sec.

For heterogeneous catalysts a direct relationship has been established purely theoretically between catalytic activity and the conductivity of the catalyst. If acid catalysis were due directly to free protons, it would be possible to find a relationship between conductivity and catalytic activity.

As will be seen below, however, no general relationship is to be observed between the conductivity and activity of acid catalysts. This may be explained by the fact that protons are not met in the free state in anhydrous acids, but are combined in the form of complex ions of the type \( [\text{H}_2\text{X}]^+ \). The formation of a carbonium ion may, therefore, be associated with two successive stages: elimination of a proton from complex ion, \( [\text{H}_2\text{F}]^+ \), \( [\text{H}_2\text{SO}_4]^{1+} \), or \( [\text{H}_2\text{PO}_4]^+ \), and its addition to a double bond. The tendency for protons to be eliminated is not identical for different ions and may not be related to the conductivity.

The catalytic activity is most fully expressed by Hammett's function [3], which is determined with the aid of indicators and characterizes the tendency for an acid catalyst to lose a proton when a proton acceptor appears. Since this method is associated with the use of colored indicators, it is suitable only for uncolored media.
In the present investigation we have studied the conductivity of a number of acid catalysts in relation to their catalytic activities, and we have studied also the variation of conductivity in the course of alkylation and polymerization reactions. Apart from the usual alkylation and polymerization catalysts, the compounds of boron trifluoride, which comprise a large group of catalysts, are of great interest. The most interesting of these are the strong complex acids, such as BF₃·H₂O; BF₃·2H₂O; HF·H₂O·BF₃; H₃PO₄·BF₃.

A number of papers has appeared recently on the electrochemistry of boron trifluoride compounds. The material published on this question is, however, very limited in scope, and is concerned with only a few compounds. Thus, up to 1950 the conductivity was known for only five boron trifluoride compounds [4]:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conductivity at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₂H₅O)·BF₃</td>
<td>κ = 2.97·10⁻⁴ ohm⁻¹·cm⁻¹</td>
</tr>
<tr>
<td>BF₃·H₂O</td>
<td>κ = 4.20·10⁻⁵ ohm⁻¹·cm⁻¹</td>
</tr>
<tr>
<td>BF₃·2H₂O</td>
<td>κ = 1050·10⁻⁶ ohm⁻¹·cm⁻¹</td>
</tr>
<tr>
<td>BF₃·2C₂H₅OH</td>
<td>κ = 22·10⁻⁸ ohm⁻¹·cm⁻¹</td>
</tr>
<tr>
<td>BF₃·2C₂H₅OH·BF₃</td>
<td>κ = 5·10⁻⁹ ohm⁻¹·cm⁻¹</td>
</tr>
<tr>
<td>BF₃ liquid at -120°C</td>
<td></td>
</tr>
</tbody>
</table>

The conductivity of the etherate of boron trifluoride has been investigated over the range -9.4°C to +44.7°C [4], its extreme values being 1.344·10⁻⁴ and 4.58·10⁻⁴ ohm⁻¹·cm⁻¹ respectively. The conductivity of boron trifluoride dihydride BF₂·2H₂O varies from 4.87·10⁻² to 10.52·10⁻² ohm⁻¹·cm⁻¹ over the range +2.6°C to -45.5°C [8]. Conductivity varies linearly with temperature.

A paper has been published recently by Sklyarenko [9] on the determination of the conductivity and other physicochemical properties of orthophosphoric acid at various concentrations at 25°C.

<table>
<thead>
<tr>
<th>Concentration of H₃PO₄ (%)</th>
<th>Density (g/cc)</th>
<th>Specific conductivity (ohm⁻¹·cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>81.39</td>
<td>2.6401</td>
<td>0.09916</td>
</tr>
<tr>
<td>88.22</td>
<td>1.7242</td>
<td>0.07466</td>
</tr>
<tr>
<td>93.10</td>
<td>1.7886</td>
<td>0.06150</td>
</tr>
<tr>
<td>97.35</td>
<td>1.8443</td>
<td>0.05633</td>
</tr>
</tbody>
</table>

For sulfuric acid at concentrations of 80, 90, and 100% at 18°C, conductivity values of 0.110, 0.107, and 0.0157 ohm⁻¹·cm⁻¹ respectively are cited.

The investigation of the conductivity of a few BF₃ compounds has made it possible to elucidate the structure of boron trifluoride compounds [10]. Thus, the high conductivity of boron trifluoride hydrates shows that they are strong acids of the type of trifluoroxyboric acid H⁺[HO:BF₃] and the hydrate of this acid H₂O⁺[HO:BF₃]. The ethyl-etherate of boron trifluoride has a considerably greater conductivity (2.97·10⁻⁴ ohm⁻¹·cm⁻¹) than those of the original ether (3·10⁻⁵ ohm⁻¹·cm⁻¹) and liquid BF₃ (5·10⁻⁸ ohm⁻¹·cm⁻¹), thus indicating the appreciable ionization of the etherate molecule. Electrolysis of the ethyl-etherate is accompanied by evolution of hydrogen and ethane. On this basis we can regard the etherate of boron trifluoride as an ethyl derivative of trifluoroethoxyboric acid C₂H₅⁺[C₂H₅O·BF₃], the ionization of which is less marked than that of the acid itself [4].

**EXPERIMENTAL**

The conductivity of the acid catalysts was determined by the usual method with an apparatus consisting of an alternating-current sound generator GZ-1, a resistance box R-14, a drum slide wire, and a vessel containing platinum electrodes. In determining the conductivity, the catalyst (5-6 ml) was placed in a beaker, which was kept in a thermostat to acquire the required temperature. The platinum electrodes were then lowered into the electrolyte, and the conductivity was measured. Several determinations of the conductance were made, and on the basis of these the specific conductivity was calculated by the formula \( \kappa = c \cdot k \), in which \( c \) is the cell constant and \( k \) is the conductance. Below we give the conductivities of a number of acid catalysts, according to the authors' determinations, and also information on the catalytic activity of the catalysts in alkylation and polymerization reactions.

Although acid catalysts are not completely chemically pure substances, since they cannot be distilled or purified by known methods, different samples of the same catalyst prepared at different times were found to have conductivities of the same order. In Table 1 a systematic scheme is given showing the activities and conductivities of a number of catalysts.