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Abstract

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THE ROLE OF COMPLEX COMPOUNDS AND OF CATIONS OF COMPLEX-FORMING COMPONENTS IN THE POLYMERIZATION REACTION OF ACETYLENE

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The mechanism of the polymerization reaction of acetylene cannot be considered definitively established ([1,2]). Investigation of the conditions for the formation of complex compounds of acetylenic hydrocarbons with CuCl—MCl solutions and of the role of the individual components of the solutions in the process of acetylene polymerization made it possible to establish the significance of complex compounds in catalytic reactions and to confirm the ionic mechanism of the acetylene polymerization reaction ([3]).

In connection with the mobility of the π-electrons, acetylenic compounds are readily polarized by the central copper atom, entering into complex compounds and thereby displacing chlorine atoms from the coordination sphere of copper and taking their place. The formation of complex compounds of acetylenic hydrocarbons in CuCl—MCl solutions is confirmed by a considerable increase in the solubility of acetylene and vinylacetylene, with a simultaneous increase in the solubility of CuCl, and also by the subsequent precipitation from the solution of crystalline deposits containing complex-bound hydrocarbons.

Fig. 1. Change in the pH of a CuCl—MCl solution upon absorption of acetylenic hydrocarbons (A) and change in the concentration of hydrogen ions in a CuCl —MCl solution upon absorption of acetylenic hydrocarbons as a function of the concentration of the components in the solution (B):
1 —C_4H_4; 2 —C_2H_2; 3—5 M CuCl, 5 M NH_4Cl; 4—2.5 M CuCl, 5 M NH_4Cl; 5—5.0 M CuCl, 5 M NH_4Cl; 6—2.5 M CuCl, 5 M NH_4Cl.

Investigation of the composition of the precipitates showed that they vary depending on the nature of the MCl cation, on the ratio CuCl : MCl in the solution, and on the nature of the acetylenic hydrocarbon. Thus, for the complex compounds of acetylene obtained in CuCl—KCl solution, Shavastlon ([4]), and also Zhurikh and Ginzburg ([3a]), proposed the following composition:

$$C_2H_2 \cdot 4CuCl \cdot KCl$$

Figure 2

Figure 1: Figure 2

$$C_2H_2 \cdot 4CuCl \cdot 2KCl$$

$$2C_2H_2 \cdot 4CuCl \cdot KCl$$

The latter authors, on the basis of data from analysis of the mother liquor and the raw precipitate, proposed the following composition for the complex compounds formed by acetylene and vinylacetylene in a CuCl—NH_4Cl solution:

$$2C_2H_4 \cdot 6CuCl \cdot 3NH_4Cl \quad \text{and} \quad C_4H_4 \cdot 2CuCl \cdot NH_4Cl$$

These complex compounds were obtained by us in the individual state, and the composition proposed by Tsorikh and Ginzburg was confirmed. In addition, the complex compound of acetylene was isolated from a CuCl—CH_3NH_2HCl solution, as were complex compounds formed by divinylacetylene and the tetramer of acetylene. In composition, these complex compounds correspond to the following empirical formulas:

$$2C_2H_2 \cdot 4CuCl \cdot CH_3NH_2HCl$$

$$C_6H_6 \cdot 2CuCl; \quad C_8H_8 \cdot 2CuCl$$

Fig. 2. Effect of the acidity of the CuCl—MCl solution on the degree of ionization and the rate of polymerization of acetylene: 1 —degree of ionization of C_2H_2, 2 —rate of polymerization of C_2H_2.

Study of the properties of all the above-mentioned complex compounds in the crystalline state showed that, in terms of thermal stability and rate of formation, they can be arranged (depending on the nature of the hydrocarbon) in the following sequence:

$$C_2H_2 > C_4H_4 > C_6H_6 > C_8H_8,$$

i.e., the acetylene complex compounds are the most stable.

It was established that in CuCl—MCl solutions, when acetylene or vinylacetylene is dissolved in them, the concentration of hydrogen ions increases (Fig. 1A), which is connected with ionization of the acetylenic hydrocarbons.

In the limiting case, ionization of acetylene occurs with dissociation of the two hydrogen atoms of acetylene, and for vinylacetylene, of one hydrogen atom. During formation of the complex compounds of divinylacetylene and of the tetramer of acetylene, no change occurs in the concentration of hydrogen ions of the CuCl—MCl solutions. It was noted that during polymerization of vinylacetylene the concentration of hydrogen ions decreases, and by the end of polymerization the pH of the solution corresponds to the pH of the initial CuCl—MCl solution. The degree of ionization of acetylenic hydrocarbons is determined not only by their nature, but also by the composition of the initial CuCl—MCl solution, as well as by the concentration of the components in the solution (Fig. 1B).

With an increase in the concentration of MCl, i.e., of chloride ions, which displace acetylene from the complex, the degree of ionization decreases. The degree of ionization also depends on the acidity of the medium: with an increase in the concentration of HCl in the initial solution, the degree of ionization decreases.

All these phenomena can be explained on the basis of the concept of the existence of a dynamic equilibrium between the cation, chloride ions, and hydrogen ions. An increase in the concentration of chloride ions in the solution entails displacement of acetylene from the coordination sphere of copper, thereby decreasing its concentration in the solution; correspondingly, the degree of ionization of the dissolved acetylene decreases.

An increase in the concentration of HCl in the solution has a considerably greater effect, since, along with the influence of chloride ions, complex compounds of a different composition, containing HCl, are formed.

A close relationship was established between the ionization capacity of the complex compounds and the catalytic activity of their solutions. The catalytic activity increases with an increase in the degree of ionization of hydrogen in the hydrocarbon. In accordance with the change in the degree of ionization under the influence of various factors, the rate of polymerization of acetylene changes. The degree of ionization of acetylene, as indicated above, depends on the pH of the medium.

The influence of the acidity of the CuCl—MCl solution on the degree of ionization and the rate of polymerization of acetylene is shown in Fig. 2.

It should be noted that water plays a role consisting in the hydration of ions formed by the complex compounds, as a result of which the catalytic activity of CuCl—MCl solutions increases. In the absence of water, ionization of the complex compounds and, correspondingly, polymerization of acetylene do not occur. Thus, for example, from an anhydrous acetylene complex stored for 960 hours at 20°, the acetylene was completely regenerated, whereas in the presence of even traces of moisture (air-dry complex), 5% of the acetylene polymerizes in two days.

All the foregoing confirms the ionic mechanism of the processes of acetylene polymerization.

Figure 3: Influence of the field strength of the cation (MCl) on the degree of ionization of acetylene and vinylacetylene in a CuCl—MCl solution. Degree of ionization of C_2H_2 (1) and C_4H_4 (2). The vertical axis is "Concentration of H^+ per 1 mole of $C\ H_2\ {}_2$, g-eq" ; the horizontal axis is "Field strength of the cation."

Figure 2: Figure 3: Influence of the field strength of the cation (MCl) on the degree of ionization of acetylene and vinylacetylene in a CuCl—MCl solution. Degree of ionization of C_2H_2 (1) and C_4H_4 (2). The vertical axis is "Concentration of H^+ per 1 mole of $C\ H_2\ {}_2$, g-eq" ; the horizontal axis is "Field strength of the cation."

Fig. 3. Influence of the field strength of the cation (MCl) on the degree of ionization of acetylene and vinylacetylene in a CuCl—MCl solution. Degree of ionization of C_2H_2 (1) and C_4H_4 (2)

The composition and properties of the complex compounds formed by acetylene and vinylacetylene with ($CuCl \cdot MCl$), and their catalytic activity, depend, in addition to the factors cited, also on the nature of the cation M^+ of the complex-forming component (MCl). The following regularities were established for the influence of the cation M^+: the greater the field strength of the cation, the more strongly it affects the properties of the complex compounds (the solubility of CuCl and hydrocarbons, the capacity for polymerization, and the activity in the process of acetylene polymerization).

These properties decrease with increasing field strength of the cations in the following sequence (the field strength is given in parentheses):

$$NH_4^+ > K^+ > Mg^{++} > Al^{+++}$$

$$(0.48) \qquad (0.60) \qquad (3.3) \qquad (9.2)$$

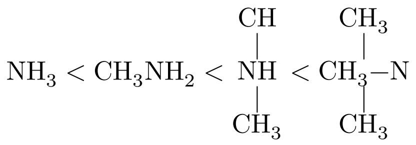
The dependence of the degree of ionization of the complex compounds of acetylene and vinylacetylene on the field strength of the cation is presented in Fig. 3.

Salts of amines can also be used as complex-forming components (MCl). It is known that the polarity of amines increases with increasing substitution. Correspondingly, a change in their

influence on the composition and properties of complex compounds and on the catalytic activity of their solutions. According to the degree of polarity, characterized by the dissociation constant, the amines may be arranged in the following series (the dissociation constants are given in parentheses):

Fig. 4. Activity of the catalytic solution CuCl—MCl as a function of the nature of the cation (MCl)

Figure 3: Fig. 4. Activity of the catalytic solution CuCl—MCl as a function of the nature of the cation (MCl)



$$NH_3 < CH_3NH_2 < \underset{CH_3}{\underset{|}{\overset{CH}{\overset{|}{NH}}}} < \underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{CH_3}}}}\!-\!N$$

$(1.79 \cdot 10^{-5})$ $(4.38 \cdot 10^{-4})$ $(5.2 \cdot 10^{-4})$ $(5.45 \cdot 10^{-4})$

The dependence of the catalyst activity on the nature of the amine is presented in Fig. 4, from which it is evident that the conversion of vinylacetylene into the tetramer of acetylene increases as the molecular weight of the cation decreases, which in the indicated series can characterize the polarity of the cations of the amine salts; moreover, the activity of the catalysts decreases with increasing polarity.

Fig. 4. Activity of the catalytic solution CuCl—MCl as a function of the nature of the cation (MCl)

The influence of the nature of the cation is explained by their polarizing action on acetylenic hydrocarbons, directed oppositely to the influence of the charge of the central copper atom. The counter-polarizing effect of the cations M^+ in MCl is the greater, the greater the field strength of the cation, or its positive polarity for amine salts.

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Note: Figure translations are in progress. See original paper for figures.