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Abstract

Full Text

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ON THE MECHANISM OF INTERACTION OF THE COMPONENTS OF THE KUCHEROV REACTION WITH THE CATALYST

Hydration of C_2H_2 to CH_3CHO in the presence of a mercury catalyst has a substantial drawback, consisting in the gradual deactivation of the catalyst and the need for its continuous regeneration. The cause of the decline in catalyst activity is considered to be reduction, by the reaction product—acetaldehyde, of mercury ions having a high ionization potential to the zero-valent state ([1–7]). It is known that in an alkaline medium CH_3CHO quantitatively reduces mercury ions ([8]). If CH_3CHO exhibited analogous chemical properties in an acidic medium, the hydration reaction of C_2H_2 would rapidly cease. However, the hydration process on a single charge of HgO (1% of the weight of the contact acid) continues for about two hours ([9]). In this connection, in the present work we investigated the interaction of CH_3CHO and C_2H_2 with mercury ions in a sulfuric-acid medium. For successful study of this question it is necessary that a definite concentration of mercury in the solution remain constant for a long time. Therefore, in this work we used a method of stabilizing the mercury catalyst that makes it possible to maintain a specified amount of mercury salt in the contact acid for an unlimited time. The investigation was carried out, unlike other works ([9], [10]), in the absence of ferric oxide sulfates in the catalytic solution, since the presence of a strong oxidizing agent distorts the true picture of the process.

The interaction of C_2H_2 and CH_3CHO with the catalyst was studied in a flow apparatus. The temperature of the contact acid was maintained within the limits of 92° and was regulated by a contact thermometer. For the experiments, 2.5 M sulfuric acid was used, the volume and concentration of which were kept constant; C_2H_2 and N_2 were fed into the column through a porous glass filter; the aldehyde was trapped in absorbers cooled with ice water.

The mechanism of interaction of the reaction components with the catalyst was judged from the change in the quantitative ratio of the different forms of mercury (Hg^{2+}, Hg^{+}, and Hg^{0}) depending on whether the latter were in an atmosphere of N_2 or C_2H_2 and CH_3CHO. The content of the different forms of mercury in the contact acid was determined by the method described in a number of works ([9–11]). However, in contrast to previous works, the analyzed contact acid contained no iron sulfates, which contributed to greater accuracy of the analyses. All experiments were carried out with solutions of mercuric sulfate containing an excess of metallic mercury.

When mercury is oxidized by our method in an N_2 atmosphere, the solution contains mainly Hg_2^{2+} ions. This is explained by the fact that, in the presence of an excess of metallic mercury, an equilibrium is established in the H_2SO_4 solution according to the scheme

$$HgSO_4 + Hg \rightleftarrows Hg_2SO_4, \tag{1}$$

where the concentrations of the mercury ions Hg_2^{2+} and Hg^{2+} are related to one another as 116 : 1 (^{12}). In our case, according to the data of Table 1, this ratio is somewhat smaller and is equal to 80, which is associated with the difficulty of determining small amounts of Hg^{2+}. We then investigated the influence of the presence of CH_3CHO in the solution on the ratio of Hg_2^{2+} and Hg^{2+}. To maintain a constant concentration of CH_3CHO in the contact acid, N_2 containing 30–35 vol.% CH_3CHO was passed through the reactor. The conditions for activation of mercury when passing N_2 and N_2 with CH_3HCO were identical. Analyzing the values

table 1, characterizing the composition of the catalytic solution in an atmosphere of N_2 and CH_3CHO, it may be noted that in the presence of the latter, the solution of H_2SO_4 contains mainly Hg^{2+} ions. The appearance of CH_3CHO in the contact acid leads to a decrease in the amount of Hg_2^{2+} by approximately a factor of 20, from 3.9 to 0.2 mg-ion/l. At the same time, the concentration of Hg^{2+}, on the contrary, increases by approximately a factor of 40, from 0.05 to 1.9 mg-ion/l.

It is interesting to note that this ratio of the described forms of mercury is established 3–4 min after the start of passing the mixture of N_2 with CH_3CHO and does not change until the end of an experiment lasting 120 min. The total concentration of dissolved mercury upon introduction of CH_3CHO into a sulfuric-acid solution of mercurous oxide falls by approximately a factor of 2 (K_1). This indicates that the presence of CH_3CHO in the Hg_2SO_4 solution causes disproportionation of the latter according to scheme (I), and in this case the equilibrium is shifted almost completely to the left. If pure N_2 is passed through an $HgSO_4$ solution containing dissolved CH_3CHO, then, gradually, as the aldehyde is swept out, the concentration of Hg_2^{2+} ions increases, while the amount of Hg^{2+} falls owing to the reduction of Hg^{2+} during oxidation of the metal according to scheme (I).

The sums of both forms of mercury detected in the solution when N_2 and a nitrogen-aldehyde mixture are passed through the reactor obey the equation:

$$C^{I}_{Hg_2SO_4} + C^{I}_{HgSO_4} = C^{II}_{Hg_2SO_4} + 2C^{II}_{HgSO_4}, \tag{II}$$

where C^{I} and C^{II} are the concentrations of the corresponding forms of mercury in an atmosphere of N_2 and a mixture of N_2 with CH_3CHO. On the right-hand side of equation (II) the amount of Hg^{2+} ions is doubled, since they were formed as a result of the reaction

$$Hg_2SO_4 \rightarrow HgSO_4 + Hg.$$

It should be added that the amount of Hg^{2+} in sulfuric acid does not change even after prolonged contact with CH_3CHO in the absence of mercury activation by the method we propose.

Thus, summarizing the results of studies of the interaction of mercury ions with aldehyde, one may conclude that Hg^{2+} ions in a sulfuric-acid medium form a complex compound with CH_3CHO and are not reduced by the latter. However, this complex is rapidly destroyed when the concentration of CH_3CHO in the solution is decreased.

In this connection, the opinion established in the literature that the cause of deactivation of the mercury catalyst is the reduction of mercury ions by aldehyde is not substantiated.

Comparing the experimental data of table 1, which characterize the composition of the contact acid in an atmosphere of N_2 and under conditions of hydration of C_2H_2, it may be noted that the entry of C_2H_2 into the catalytic solution is accompanied by an increase in the concentration of Hg^{2+} by a factor of approximately 17, from 0.05 to 0.85 mg-ion/l. Simultaneously, the amount of Hg_2^{2+} decreases from 3.8 to 0.7 mg-ion/l. From these data it is evident that in the catalytic solution under the conditions of the hydration reaction both forms of mercury (Hg_2^{2+} and Hg^{2+}) are present at nearly equal concentrations. The ratio of Hg_2^{2+} to Hg^{2+} is ≈ 0.85. This quantitative ratio of Hg_2^{2+} and Hg^{2+} is established after C_2H_2 is admitted to the reactor within 3-4 min and remains constant until the end of an experiment lasting 180 min.

Taking into account that CH_3CHO promotes the appearance of Hg^{2+} ions in a sulfuric-acid medium, the reason for the increase in the concentration of Hg^{2+} upon introduction of acetylene into the solution under study becomes clear, for C_2H_2 was converted by 30-35 vol.% into CH_3CHO. At this concentration of CH_3CHO in the gas, Hg^{2+} ions should mainly be present in the liquid phase. However, as noted above, during hydration of C_2H_2 Hg_2^{2+} and Hg^{2+} ions are present at similar concentrations. This indicates that C_2H_2 prevents the disappearance of Hg_2^{2+}, forming a complex compound with them.

In view of the fact that the presence of CH_3CHO in the contact acid causes decomposition of part of the Hg_2SO_4 and the appearance of Hg^{2+} ions, then, proceeding from

quantities presented in Table 1, this should reduce the total concentration of ions in the solution by approximately a factor of 1.3.

Table 1

Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution	Composition of the catalyst solution
In an atmosphere of nitrogen	In an atmosphere of nitrogen	In an atmosphere of nitrogen	In an atmosphere of a mixture of nitrogen and aldehyde	In an atmosphere of a mixture of nitrogen and aldehyde	In an atmosphere of a mixture of nitrogen and aldehyde	In an atmosphere of a mixture of nitrogen and aldehyde	Under the conditions of the acetylene hydration reaction	Under the conditions of the acetylene hydration reaction	Under the conditions of the acetylene hydration reaction	Under the conditions of the acetylene hydration reaction
Hg_2^{2+}, mg-ion/l	Hg^{2+}, mg-ion/l	Hg_2^{2+}/Hg^{2+}	Hg_2^{2+}, mg-ion/l	Hg^{2+}, mg-ion/l	Hg_2^{2+}/Hg^{2+}	K_1	Hg_2^{2+}, mg-ion/l	Hg^{2+}, mg-ion/l	Hg_2^{2+}/Hg^{2+}	K_2
3.8	0.05	76	0.2	1.9	0.105	1.83	0.7	0.85	0.82	2.48
3.9	0.05	78	0.2	2.0	0.1	1.8	0.8	0.85	0.94	2.4
4.0	0.05	80	0.3	2.0	0.15	1.76	0.7	0.85	0.82	2.6
4.0	0.05	80	0.2	1.9	0.105	1.93	0.65	0.75	0.87	2.9
4.1	0.05	82	0.3	2.0	0.15	1.82	0.8	0.85	0.94	2.5

Note. K_1 is the ratio of the total concentration of mercury ions in the solution in an N_2 atmosphere to the concentration of ions in the presence of CH_3CHO. K_2 is the ratio of the total concentration of mercury ions in the solution in an N_2 atmosphere to the concentration of ions during hydration of C_2H_2.

However, if one compares the sums of the concentrations of dissolved mercury found when passing N_2 and C_2H_2, it may be noted that when C_2H_2 is introduced into the system the amount of salt decreases on average by a factor of 2.6 (K_2), despite the fact that the conditions for activation of mercury did not change.

This means that during hydration of C_2H_2 not only does disproportionation of Hg_2SO_4 occur, but also reduction of a certain fraction of the mercury ions to the zerovalent state. In this connection, equation (II) is valid when N_2 and a mixture of N_2 and CH_3CHO are present in the gas phase, whereas under the conditions of the C_2H_2 hydration reaction it takes the following form:

$$C^{\mathrm{I}}_{\mathrm{Hg_2SO_4}} + C^{\mathrm{I}}_{\mathrm{HgSO_4}} = C^{\mathrm{III}}_{\mathrm{Hg_2SO_4}} + 2C^{\mathrm{III}}_{\mathrm{HgSO_4}} + C^{\mathrm{III}}_{\mathrm{Hg}}, \qquad \text{(III)}$$

where C^{I} and C^{III} are the concentrations of the corresponding forms of mercury when nitrogen and acetylene are passed through the catalyst solution.

The reduction of part of the dissolved mercury to the metal is the result of the interaction of C_2H_2 and Hg ions. This follows unambiguously from the fact that the total amount of mercury ions drops by a factor of 2.6 immediately after C_2H_2 is introduced into the Hg_2SO_4 solution. The established concentration then does not rise, but remains constant until the end of the experiment, although the conditions for activation of mercury were maintained the same as before the introduction of C_2H_2.

In the absence of continuous activation of mercury, the hydration reaction of C_2H_2 rapidly dies out, owing to continuous reduction of the catalytically active mercury ions to the metal.

Thus, the reduction of mercury salts and deactivation of the mercury catalyst are the result of interaction of acetylene, not aldehyde—as is accepted in the literature—with mercury ions.

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