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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

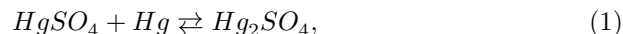
Hydration of  $C_2H_2$  to  $CH_3CHO$  in the presence of a mercury catalyst has a substantial drawback, consisting in the gradual deactivation of the catalyst and the need for its continuous regeneration. The cause of the decline in catalyst activity is considered to be reduction, by the reaction product—acetaldehyde, of mercury ions having a high ionization potential to the zero-valent state (<sup>1-7</sup>). It is known that in an alkaline medium  $CH_3CHO$  quantitatively reduces mercury ions (<sup>8</sup>). 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 (<sup>9</sup>). 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 (<sup>9, 10</sup>), 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 (<sup>9-11</sup>). 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



where the concentrations of the mercury ions  $Hg_2^{2+}$  and  $Hg^{2+}$  are related to one another as 116 : 1 (<sup>12</sup>). 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  $CH_3CHO$  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.

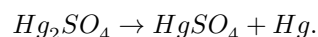
It is interesting to note that this ratio of the described forms of mercury is established 3-4 min after the start of passing the mixture of  $N_2$  with  $CH_3CHO$  and does not change until the end of an experiment lasting 120 min. The total concentration of dissolved mercury upon introduction of  $CH_3CHO$  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  $Hg_2^{2+}$  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:

$$C_{Hg_2SO_4}^I + C_{HgSO_4}^I = C_{Hg_2SO_4}^{II} + 2C_{HgSO_4}^{II}, \quad (II)$$

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



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  $\approx 0.85$ . 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**

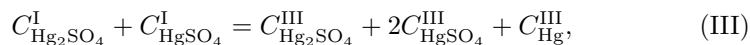
Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly solution	Composition of the cataly 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 conditions of the acetylene hydration reaction	Under conditions of the acetylene hydration reaction	Under conditions of the acetylene hydration reaction	Under conditions of the acetylene hydration reaction
$Hg_2^{2+}$ , mg-ion/l	$Hg^{2+}$ , mg-ion/l	$Hg_2^{2+}/Hg^{2+}$ , mg-ion/l	$Hg_2^{2+}/Hg^{2+}$ , mg-ion/l	$Hg^{2+}$ , mg-ion/l	$Hg_2^{2+}/Hg^{2+}$ , mg-ion/l	$Hg_2^{2+}/Hg^{2+}$ , mg-ion/l	$Hg_2^{2+}$ , mg-ion/l	$Hg^{2+}$ , mg-ion/l	$Hg_2^{2+}/Hg^{2+}$ , mg-ion/l	$Hg_2^{2+}/Hg^{2+}$ , mg-ion/l
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:



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.*

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