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Abstract

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Investigation with Deuterium of the Mechanism of Acetylene Hydration by the Kucherov Reaction

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Despite the broad industrial application of the Kucherov reaction and the extensive literature devoted to its study ([1–3]), far from everything is yet clear in the mechanism of this process. In particular, until recently the question of the stage that determines the rate of hydration, and of the participation of water or acid molecules in the transition complex of the slow stage ([2,3]), has been discussed and experimentally studied. There is also no unified opinion on the composition and structure of the intermediate mercury compounds of acetylene, the hydrolysis of which leads to the formation of acetaldehyde ([1]).

While developing a method for the synthesis of deuteroacetaldehydes by the Kucherov reaction, we carried out the hydration of ordinary acetylene with solutions of D_2O and of deuteroacetylene with ordinary water. The results of these experiments shed light on the above-mentioned unclear features of the mechanism of acetylene hydration.

Experimental Part

We carried out the hydration of acetylene with solutions of the following composition: H_2O or D_2O 25.0 ml, HgSO 4.7 g, $Fe_2(SO_4)_3$ 3.8 g, H_2SO_4 ($d = 1.84$) 10.6 g. The hydrating solution was placed in a glass column ($l = 660$ mm, $d =$ 12 mm) filled with broken glass. Acetylene from a gasometer was passed through the column at 75-80°; the optimal rate was 10-12 liters of acetylene per hour. Under these conditions, the vapors of the acetaldehyde formed are carried away by the unreacted acetylene. The gaseous products from the column, after passing through a reflux condenser and a calcium chloride tube for removal of moisture, were condensed in two successive traps at −80 and −190°. In the first trap acetaldehyde collected with a small admixture of acetylene dissolved in it; in the second, almost pure acetylene, which was then again passed to hydration.

The acetaldehyde was purified by distillation, the vapors of the distillate being passed through calcium chloride and condensed at 0°. To obtain a product beginning to boil at 20.5° and distilling without residue within an interval of

one degree, two distillations were sufficient. The yield of acetaldehyde was 40% relative to the acetylene consumed.

Since we were interested not only in the total deuterium content in the molecules of the acetaldehyde formed, but also in its distribution between the methyl and aldehyde groups, we oxidized samples of the aldehyde obtained to acetic acid. For this purpose, a 30% aqueous solution of acetaldehyde cooled to 0° was added dropwise under the surface of a solution of potassium permanganate in 20% aqueous sulfuric acid at 60–70° with constant stirring. A drop of aldehyde, upon entering the oxidizing solution, reacts instantaneously, which makes it possible to minimize exchange between the aldehyde being oxidized and the medium. Control experiments on the oxidation of ordinary acetaldehyde in an oxidizing agent prepared with D_2O showed that in the pri-

under the conditions introduced, the isotopic exchange of the aldehyde with the medium is negligible, since in three parallel experiments the potassium acetate obtained contained less than 1% of the deuterium of the oxidizing solution.

The results of experiments on the hydration of ordinary acetylene with solutions containing D_2O are given in Table 1.

Table 1

Deuterium content in γ

No.	In the hydrating solution, before the experiment	In the hydrating solution, after the experiment	In the combustion water, CH_3CHO	In the combustion water, CH_3COOK, found	In the combustion water, CH_3COOK, calculated	Unreacted $CH{\equiv}CH$
1	27 860	–	9150	11 560	12 200	–
2	–	–	3520	4860	4680	–
3	–	–	1550	2040	2060	–
4	11 900	12 400	4000	–	5300	–
5	11 900	12 800	3900	–	5200	9
6	11 900	12 400	3900	–	5200	12

A comparison of the data on the isotopic composition of acetaldehyde and of the potassium acetate obtained from it (Table 1) shows that all the deuterium of acetaldehyde, when it is synthesized from $CH{\equiv}CH$ and D_2O, is concentrated in the methyl group. This follows from the fact that removal of the hydrogen of the carbonyl group by oxidation increases the deuterium content in the acetate, compared with the initial aldehyde, in the ratio 4 : 3, as also follows from the calculation. The absence of deuterium in the carbonyl group of acetaldehyde agrees with its absence in the acetylene isolated from the reaction medium, and

shows that the isotopic composition of the hydrogen of the aldehyde group is the same as that of the hydrogen in the initial acetylene.

If the hydration process were accompanied neither by an isotopic effect nor by exchange with the medium, the combustion water of the aldehyde, according to the equation

$$CH{\equiv}CH + D_2O = CHD_2CHO,$$

would be twice as light as the water distilled from the hydrating solution. In reality, the deuterium in the acetaldehyde is diluted not twofold but approximately threefold (see Table 1). Taking into account that, in the present case, isotopic exchange can only enrich the aldehyde molecules with deuterium, the data obtained testify to a considerable isotopic effect. The results of experiments on the hydration of acetylene labeled with deuterium by ordinary water are presented in Table 2. It is obvious that in these

Table 2

Hydration of labeled acetylene in H_2O
(Deuterium content in γ*)*

No.	In $CH{\equiv}CH$	In the combustion water, CH_3CHO, found	In the combustion water, CH_3CHO, calculated	In the combustion water, CH_3COOK, found	In the combustion water, CH_3COOK, calculated	Found/calculated	In the group $-CHO$
1	12 800	4200	5700	1800	3800	0,48	11 400
2	6 400	2200	2840	1040	1900	0,55	5680
3	6 400	2200	2990	960	1980	0,49	5980
4	11 800	4200	5600	1860	3700	0,50	11 200
5	22 100	8600	11 200	4000	7500	0,53	22 400

experiments, in contrast to the experiments of the first series, the influence of the isotopic effect is excluded, since upon hydration ordinary hydrogen passes to the acetylene molecules. The influence of exchange, on the contrary, can be directly detected by comparing the isotopic composition of the initial acetylene, acetaldehyde, and potassium acetate.

Table 2 gives the deuterium content in the water used to obtain acetylene from calcium carbide. The deuterium content in acetylene should be the same, since the reaction of calcium carbide with water proceeds quantitatively, and the water was taken in an amount corresponding to the stoichiometric amount. On the basis of the results of the experiments of the first series, the aldehyde obtained

from labeled acetylene should contain deuterium both in the methyl and in the aldehyde groups. We found the deuterium content in the aldehyde group by difference, determining the isotopic composition of the water from combustion of acetaldehyde and of the potassium acetate obtained by its oxidation from the equation $X = 4A - 3B$, where A and B are, respectively, the excess density of the water from combustion of acetaldehyde and potassium acetate (Table 2).

From an analysis of the quantities given in Table 2, it is seen that the aldehyde group of acetaldehyde contains as much deuterium as there was in the initial acetylene, in agreement with the results of the first series of experiments. The small loss of deuterium is apparently explained by the fact that we obtained acetylene from technical calcium carbide, which always contains an admixture of hydroxide. This is confirmed by the result of the last experiment, in which the initial acetylene was burned and analyzed.

Analysis of the data of Table 2 further shows that hydration is accompanied by considerable exchange. Indeed, if there were no exchange, acetaldehyde would contain half as much deuterium, and potassium acetate three times less deuterium, than in the aldehyde group (see columns 3 and 5). As is seen from Table 2, the ratio of the experimentally found values to those calculated on the assumption of absence of exchange for CH_3COOK is well reproduced and indicates that the hydrogen of acetylene which entered into the methyl group of the aldehyde was replaced during the hydration process by half with hydrogen of the medium.

Having determined the degree of exchange in the hydration process, it is possible, from the results of the experiments of the first series, to estimate approximately the magnitude of the kinetic isotope effect in the transfer of hydrogen from water (or acid) to acetylene molecules on the basis of the following considerations. If addition of both hydrogen atoms occurred without an isotope effect, then, with a hydrating solution in water of excess density 28 000 γ, the water from combustion of acetaldehyde, taking exchange into account, would have been $(28\,000 \cdot 2 + 28\,000 \cdot 0.5) : 4 = 17\,500$; while with a hydrating solution containing 12 000 γ of deuterium, the water from combustion of acetaldehyde would have been $(12\,000 \cdot 2 + 12\,000 \cdot 0.5) : 4 = 7500$ γ, i.e. 1.9–1.8 times greater than was found experimentally.

In the formation of acetaldehyde, two hydrogen atoms add to acetylene. According to existing ideas, they add in two different stages, of which only one can determine the rate of the process. In other words, the transfer of only one of the hydrogen atoms can be accompanied by an isotope effect. The decrease, by a factor of 1.8–1.9, in the content in the water from combustion of acetaldehyde of deuterium contained in the molecule in 4 hydrogen atoms corresponds, when recalculated per 1 hydrogen atom, to an isotope effect of the order of $1.9 \times 4 = 7.6$.

The presence of an isotope effect unambiguously proves that the rate of hydration is determined by the stage of transfer of one of the hydrogen atoms from

water molecules (or acid) to acetylene molecules and that, consequently, water molecules (or acid) enter into the composition of the transition complex of the slow stage. This conclusion contradicts the conclusion of Flid, Moiseev, and Kalmykova ([2]), who, having investigated the kinetics of liquid-phase hydration of acetylene, found that the influence of the oxidizing potential of the medium considerably exceeds the influence of pH on the reaction rate. On this basis the authors concluded that the slow stage of the process is the stage of activation of acetylene, not connected with the addition of protons. The presence of a kinetic isotope effect can apparently be reconciled with the results of the indicated authors by assuming that, in the rate-determining stage, water molecules add to acetylene molecules.

activated owing to the formation of a complex with the catalyst:

$$CH \equiv CH + HgX_2 \xrightarrow{\text{rapidly}} CH \equiv CH \cdot HgX_2,$$

$$CH \equiv CH \cdot HgX_2 + HOH \xrightarrow{\text{slowly}} CH_2 = CHOH \cdot HgX_2,$$

$$CH_2 = CHOH \cdot HgX_2 + H_3O^+ \xrightarrow{\text{rapidly}} CH_2 = CHOH \cdot H_3O^+ + HgX_2,$$

$$CH_2 = CHOH \cdot H_3O^+ \overset{\text{rapidly}}{\rightleftharpoons} CH_2 = CHOH_2^+ + H_2O,$$

$$CH_2 = CHOH_2^+ \rightarrow CH_3CHO + H^+.$$

The role of the acid in this case, in accordance with the kinetic data ([2]), is reduced to participation in the hydrolysis of the mercury complex in the stage following the rate-determining addition of water.

Our data unequivocally reject the isomerization of acetylene to isoacetylene as one of the stages of the Kucherov reaction ([1])

$$CH \equiv CH \rightarrow CH_2 = C <,$$

$$CH_2 = C < + HOH \rightarrow CH_2 = CHOH,$$

since in this case the hydrogen of the medium would have to enter the aldehyde group of acetaldehyde, which in fact is not observed. On the same grounds, mercarbides, i.e., fully substituted mercury-organic derivatives of acetylene, for example, of type A ([4])

$$\text{(A)}\ (XHg)_2C-CX_2$$
$$\backslash\ /$$
$$Hg$$

should be rejected as those intermediate compounds whose hydrolysis leads to the formation of acetaldehyde under the conditions of our experiments. As for the assumption of the formation of acetaldehyde by hydrolysis of initially formed compounds of type B ([4]) or V ([5])

$$\text{(B)}\ Hg=C-CHO$$
$$|$$
$$HgX$$

$$\text{(V)}\ CH=C-HgX,$$
$$\backslash$$
$$O-Hg$$

then, if hydration proceeded only through them, in the methyl group of acetaldehyde the hydrogen of the initial acetylene would have been completely replaced by the hydrogen of the medium. In experiments with labeled acetylene, however, we found that substitution occurs only by one half. On the other hand, in control experiments on the exchange of acetaldehyde under hydration conditions, only 25–30% of the hydrogen of the methyl group, instead of 50%, was replaced by the hydrogen of the medium. It may therefore be thought that acetaldehyde under our conditions is formed by hydrolysis both of Biginelli complexes $CH\equiv CH\cdot HgX_2$, and also, in part, through compounds of types B and V.

In conclusion it should be noted that carrying out the hydration of acetylene according to the recipe given above represents a convenient laboratory method for obtaining two isotopic varieties of acetaldehyde, namely CD_3CDO, if one starts from $CD\equiv CD$ and D_2O, and CD_2HCHO when hydrating $CH\equiv CH$ with solutions containing D_2O.

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