Synthesis of acetaldehyde based on acetylene in liquid phase

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Annotation. New mixed polyfunctional catalysts for the hydration of acetylene to acetaldehyde and acetone have been developed, their properties have been developed, and various ways of formation of acetylene by the reaction of hydration condensation have been proposed.

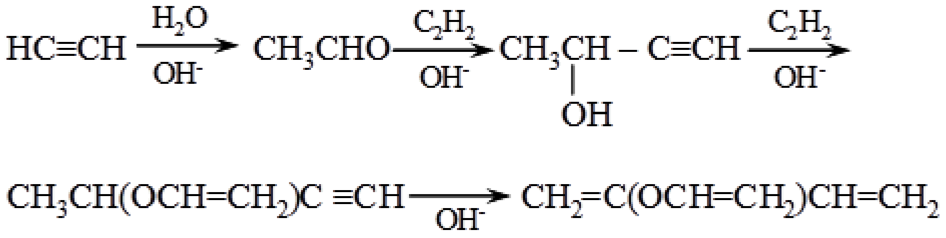
Key words: acetic acid, acetic anhydride, ethyl alcohol, pentaerythritol, aldol, glyoxal, lactic acid, acrolein, acetone

Acetaldehyde is used in large quantities as an intermediate in numerous industrial syntheses. Acetal, acetic acid, acetic anhydride, ethyl alcohol, pentaerythritol, aldol, glyoxal, lactic acid, acrolein, cellulose acetate, etc. can be obtained directly from acetaldehyde.

A special case of nucleophilic addition of water to a triple bond is discovered by B.A. Trofimov et al. a group of reactions called hydration oligomerization [1]. In superbasic media (DMCO - KOH – H_2O) at a temperature of 80-120°C and P = 1.0-1.4 MPa, 2-vinyloxybutadiene-1,3 is formed from acetylene.

$$3C_2H_2 + H_2O \longrightarrow CH_2=C(OCH=CH_2)CH=CH_2$$

It has been experimentally established that in this case, acetaldehyde and its ethynyl derivatives are first formed, the addition of the next acetylene molecule leads to the formation of 2-vinyloxybutadiene-1,3 according to the scheme:



$$HC\equiv CH \xrightarrow[OH^-]{H_2O} CH_3CHO \xrightarrow[OH^-]{C_2H_2} CH_3\underset{\substack{|\\ OH}}{C}H - C\equiv CH \xrightarrow[OH^-]{C_2H_2}$$

$$CH_3CH(OCH=CH_2)C\equiv CH \xrightarrow[OH^-]{} CH_2=C(OCH=CH_2)CH=CH_2$$

In all cases of acid-base catalysis, the water molecule is added to the triple bond according to Markovnikov's rule.

The main disadvantage of an industrial mercury catalyst (composition in % wt: - $HgSO_4$ - 0.2; $Fe_2(SO_4)_3$ - 20; H_2SO_4 - 8-10; $FeSO_4$ - 1-2) is its relatively rapid deactivation due to the reduction of Hg(II) (3-4 hours under standard conditions) [1] and high toxicity of wastewater and gas emissions due to the entrainment of mercury vapor and volatile organomercury compounds.

Subsequently, other authors determined the activity of catalytic systems based on complexes of copper (I), silver (II), palladium (II), rhodium (III), ruthenium (III), manganese (II-IV), platinum in the reaction of hydration of acetylene compounds. The highest reaction rate was found in solutions of Cu(I) complexes.

Carrying out the process in an electrochemical system or under conditions of continuous solution exchange makes it possible to maintain the optimal ratio [Cu(II)]/[Cu(I)] ≈ 0.1 and carry out hydration under stationary conditions [6; c.320]. At a temperature of 110°C and $[H_2SO_4]$=5.3 mol/l, the selectivity of the reaction is 94-98% at a degree of acetylene conversion of 25% and a feed rate of 20-30 h-1.

The direction of the hydration reaction of monosubstituted alkylacetylenes in Hg(II) solutions obeys the Markovnikov rule. In the case of electron-withdrawing substituents (CF_3-PhCO, etc.), aldehydes and ketones are formed as a result of the reaction. The direction of hydration of disubstituted acetylene compounds was studied in detail in the works of B.S. Kupin, D.V. Sokolsky, G.Kh. Shestakova and others [1].

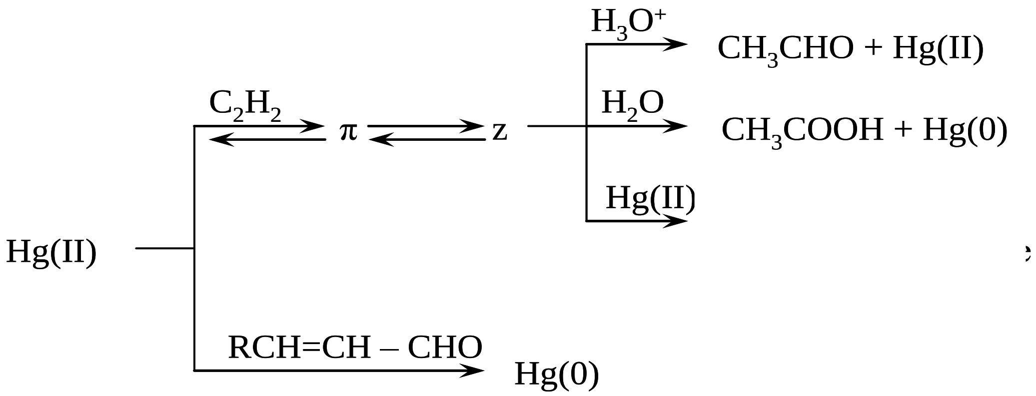
O.H. Temkin and his co-workers discovered an anomalous addition of water. In the copper-chloride system, water can be added to methylacetylene according to the Markovnikov's rule and against the Markovnikov's rule (MRP) [2]:

$$2CH_3 - C \equiv CH + 2H_2O \xrightarrow{Cu(I)} CH_3 - CO - CH_3(98\%) + CH_3CH_2 - CHO(2\%)$$

Propyne Acetone Propionic aldehyde The use of catalytic amounts of soluble mercaptans as additives makes it possible to increase the propionaldehyde selectivity to 70% [3].

The catalysts for the hydration of vinylacetylene to methylvinylketone are $HgSO_4$ and Cu_2SO_4. The hydration reaction of acetylenic compounds played an important role in the development of the theory of metal complex catalysis. In this area, particular attention should be paid to works [1], which were the first to use the potentiometric method to measure the activity of mercury (II, I) in Kucherov's catalyst and to study the state of Hg(II) in sulfuric acid solutions.

In solutions of mercury sulfate, for the first time, the relationship between the observed rate constant of hydration and the activity of mercury (lnK=A+BE, where E is the potential of a mercury or platinum electrode) was shown. The coefficient α in the equation $Kn=Ka\alpha Hg_2+$ in the $HgSO_4$ - H_2SO_4 system is close to unity [4]. Reduction of Hg(II) with acetaldehyde according to D.V. Sokolsky does not occur. Therefore, we can present the following simplified scheme of reactions in the mercury system



The hydration reaction of acetylene and its derivatives in the presence of Cu(I) complex compounds has been studied in detail. It has been established that the main reason for the deactivation of copper sulfate catalysts is the formation of ethynyl compounds Cu(I) and the occurrence of oxidative dehydropolycondensation of acetylene as a result of their oxidation of Cu(II) [2].

The hydration of acetylene in aqueous solutions in the presence of iron, cobalt, nickel, copper, zinc ($SO_3nL2n+6$; n=0.1,2,3…) polyphthalocyan sulfonates at temperatures of 40–100°C was studied [1]. It has been established that copper and zinc polyphthallocyan sulfonates exhibit the highest activity in the reaction. The maximum yield of acetaldehyde is observed at a temperature of 80°C and is 21.4% with a selectivity of 100%.

In [5], the reaction of hydration of acetylene to acetaldehyde in Amberlist 15 ion-exchange resin containing H^+, Hg^{2+}, and Fe^{3+} ions was studied. It has been shown that for a series of catalysts containing H^+ and Hg^{2+} ions, the reaction rate increases linearly with an increase in the Hg^{2+} content, which confirms the catalytic role of Hg^{2+}. Samples containing Fe^{3+} are more active than catalysts with the same Hg^{2+} content.

The kinetics of acid-catalytic hydration RC≡CR, where R and R’ = H, CH3, C2H5, C4H9, etc., in aqueous solutions of sulfuric acid was studied [73; pp.71-77]. Based on the data on the kinetic isotope effects KH/KD > 1 and the relationship between the rate constants and the acidity function of the medium, a mechanism of hydration is proposed, the rate-limiting step of which is the protonization of the substrate.

In [6], a theoretical study of the process of acetylene hydration catalyzed by acids in an excited state was carried out.

A method was proposed for concentrating mercury-containing waste solutions of catalytic hydration of acetylene to acetaldehyde containing mercury sulfate, ferrous and ferric iron in dilute sulfuric acid [6].

ISSN NO: 2770-4491
Date of Publication:17-02-2023

There is a method for producing acetaldehyde by hydration of acetylene in the presence of a mercury catalyst and a redox system [$FeSO_4$ and $Fe_2(SO_4)_3$] at a temperature from 90°C to the boiling point of the mixture [1].

In [1-5], the kinetics of liquid-phase hydration of acetylene, partially catalyzed by resin, was studied. In the environment of dimethylformamide (DMF) and propanol on a catalyst obtained by mechanical mixing of mercury oxide and Amberlite R-200 ion-exchange resin in hydrogen form (Kt-1) and processing of the ion-exchange resin.

$$C2H2 + H2O \rightarrow CH3CHO \rightarrow CH3COOH \text{ (reaction 1)}$$

Kt-1 and Kt-2 were deactivated during reaction (1), but no products of side reactions were found. It has been established that Kt-2 has a high activity in reaction (1) at room temperature and significantly exceeds Kt-1.

Patented is a method for regenerating the contact fluid in the production of acetaldehyde [7] by hydration of acetylene in the presence of a mercury-containing catalyst, by treating the contact fluid with a 40–70% solution of nitric acid at a temperature of 90–150°C.

References:

1. Tangyarikov N.S., Musulmanov N.Kh., Turobzhonov S.M., Ikramov A., Prokofiev V.Yu. Catalytic hydration of acetylene and its derivatives. - Moscow, Lenand, 2014. P. 150.
2. 2.Temkin O.N. Chemistry of acetylene. Properties, structure and reactivity of alkynes.// Soros obrazov zhurn. 12. (1988) S. 52-57.
3. Yusupov D., Fayzullaev I. I., Egamberdiev R. Vapor phase catalytic hydration of acetylene and its derivatives // Uzb. chem. magazine 1. (2001) pp. 34-37.
4. Temkin O. II., Flid R. M. Catalytic transformations of acetylenic compounds in solutions of metal complexes. M. Science. (1968) 212 p.
5. Yusupov B.D. Development of new catalysts for the vapor-phase hydration of acetylene and the study of their properties / / dissertation of the candidate of sciences Tashkent -2009 p.106
6. Turobzhonov S.M., Yusupov D., Ikramov A., Yusupov B.D. Development and study of the properties of new catalysts for the synthesis of acetaldehyde. // XVIII Mendeleev Congress on General and Applied Chemistry. Theses.reports M., September 23-28, 2007 T-3, p.29
7. Yusupov D., Shirinov Kh.Sh., Korotoev A.V., Ivanov V.E. A catalyst for the production of acetone. //Problems of development of chemistry and technology of organic compounds in Uzbekistan. // Collection of scientific works, T., 1998, p.50.