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Condensation And Polymerization Of Some Lower Aldehydes And The Influence Of Acid And Basic Groups Of The Catalyst On The Reaction Rate

Shavkat Shayimovich Oblokulov

Bukhara State Medical Institute named after Abu Ali ibn Sino, Uzbekistan

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Abstract: Acidic or basic catalytic systems, as well as zeolite-type catalysts are used for condensation and polymerization reactions of ethyl and unsaturated carbonyl compounds. Reactions involving lower aldehydes, as a rule, are carried out in the gas-phase variant and have rather low selectivity and conversion of reagents. This problem is partially solved by recirculation of unreacted reagents. The most promising way to solve the problem of selectivity and activity is selective carrying out of the reaction under conditions of homogeneous catalysis with varying acid-base properties of the catalyst and reaction medium.

Keywords: Crotonic aldehyde, acetaldehyde, homo-condensation, polymerization, propionic aldehyde, polycrotonic aldehyde, oligomers, IR spectrometer.

Introduction:

The present approach would allow such transformations to be carried out selectively.

Therefore, the objectives of the present work are as follows:

1. Development of new homogeneous-catalytic systems to realize the condensation of lower aldehydes.
2. Study of the influence of acid-base properties of catalytic systems on the selectivity of croton aldehyde polymerization and aldol condensation of lower aldehydes. Study of the influence of acid and basic components on the selectivity of aldol condensation in the presence of bifunctional systems.
3. Establishment of optimal conditions for the realization of selective method of liquid-phase preparation of polycrotonic aldehyde.
4. Study of liquid-phase homo-condensation of acetaldehyde for selective production of croton aldehyde.
5. Study of sequential homo-condensation of lower aldehydes using acetaldehyde as an example. Development of a method for obtaining a certain set of products. Verification of the possibility of realization of the above systems in reactions involving crotonic aldehyde.
6. Croton aldehyde (2-butenal) is a reactive compound. To obtain polycrotonic aldehyde use NaOH and study the rate of polymerization.

Unsaturated aldehydes are reactive compounds. Polymers obtained on their basis retain double bonds and aldehyde groups, on which various chemical transformations are possible in order to obtain new polymers.

Species from such unsaturated aldehydes as acrolein are widely used in industry. Crotonic aldehyde, on the other hand, is a poorly studied aldehyde. Croton aldehyde is an irritant, is included in the list of particularly dangerous substances. Widespread in nature. It is found in some foods, such as soybean oil. Croton aldehyde belongs to unstable compounds, gradually oxidizes in air. This substance is a strong lacrimator.

Obtaining polymers from croton aldehyde is of practical interest due to its availability as a waste product of acetic aldehyde production. In the literature there are some studies in the field of polymerization of this monomer. However, few studies have been carried out. This is due to the fact that in crotonic aldehyde the double bond is symmetrically substituted, which leads to difficulties in its polymerization.

Experimental part

A given amount of freshly distilled croton aldehyde at 100 0C was placed in a three-neck flask equipped with a thermometer, a reflux condenser and a dropping funnel with a magnetic stirrer. Then an aqueous solution of NaOH was introduced into the flask using a drop funnel. Polymerization was carried out at 30-80 0C.

Polymerization of croton aldehyde

Crotonic aldehyde (CA) -140 grams, initiator NaOH, polymerization time -3 h.

Experience №	NaOH moles	NaOH:CA moles	H_2O ml	t ^{0}C	Output %
1	0,25	1:8	200	30	5
2	0,25	1:8	200	50	4
3	0,25	1:8	200	80	3
4	0,1	1:20	40	30	60
5	0,05	1:40	40	30	74
6	0,025	1:80	40	30	82
7	0,005	1:400	40	40	70

The table shows the results of croton aldehyde polymerization depending on the initiator concentration at a constant amount of monomer. In experiments 1-3, the reaction mixture at the end of the process was stratified into aqueous and organic phases. The polymer was precipitated from the aqueous phase with acetone and from the organic phase with water. The separated powders were washed and dried to constant weight. In other experiments, the reaction mass at the end of the process contained no liquid phase.

Carbonyl groups in the obtained products were determined according to the method [6], carboxylate hydroxyl and double bonds - according to the methods [7]. The spectra of the obtained compounds were taken on SHIMADZU (IR), Tesla BS-567 A (NMR) spectrometers.

Found C-65.16-65.73% H-8,06-8,08%

C-68.6% H-8.5% (69:9) was calculated for (C4H6O)n

The products isolated in Experiments 4-6 and from the organic phase 1-3 are, in contrast to those previously described, light orange powders. They are soluble in organic solvents (acetone, pyridine, etc.) but insoluble in water. The softening point of this powder is 120-130 0C. Molecular mass determined by measuring the thermal effects of condensation is 580-600. The obtained compounds are oligomers with coefficient of polymerization 8-9. The IR spectra of the oligomers show absorption bands of aldehyde groups (1950 cm-1), C-C double bonds (1500, 1100 cm-1) and hydroxyl groups (1100, 650 cm-1).

The presence of aldehyde groups in the oligomers of polycrotonic aldehyde is conditioned by polymerization of the monomer along the double bond to form links

-C(CH3) -CH(CHO) - (A)

Double bonds in oligomers are the result of polymerization over the aldehyde group to form the links

-CH(CH=CH-CH3)-O- (B)

Hydroxyl groups should be attributed to the hydrate form of the aldehyde groups in the links (A)

-C(CH3) -CH(CH(OH)2) - (C)

Quantification of aldehyde and hydroxyl groups and double bonds showed that the structures A,B,C are in the ratio of 3:2:1.

Studies of the aqueous phase showed that it contains the products of croton aldehyde transformation, which differ from the oligomers isolated from the organic phase both in physicochemical properties and composition. They are white powders with a decomposition temperature of 130-140 0C, which are soluble in water but insoluble in organic solvents. IR spectra of water-soluble compounds contain additionally absorption bands of carboxylate groups and do not contain absorption bands of aldehyde groups.

Comparative studies of acetaldehyde homo-condensation in the presence of a number of catalytic systems used in the study of cross-condensation were carried out to identify general regularities and differences in the condensation reactions.

The main purpose of studying acetaldehyde homo-condensation was to determine the influence of the basic properties of the catalyst on the conversion, composition and yield of homo-condensation products. Studies of acetaldehyde homo-condensation were carried out in the presence of amines in various solvents.

The yield of crotonic aldehyde increases with decreasing amine basicity, and the conversion increases with increasing solvent basicity. Studies of acetaldehyde homo-condensation in the presence of amine salts were also carried out.

With increasing basicity of amine salts in a polar solvent, the conversion of reagents increases with a simultaneous decrease in selectivity for 2-butenal. At the same time, the yield of polycondensation products with higher molecular weight increases. The structure of amine salts and the size of substituents also significantly affect the process. For monosubstituted amine salts, the selectivity for 2-butenal increases, but the conversion of acetaldehyde is lower than for salts with two substituents. Increasing the size of the substituent promoted the formation of 2-butenal while maintaining sufficiently close values for the conversion of acetaldehyde.

The homo-condensation of acetaldehyde in the presence of various amino acids has been studied.

In the presence of amino acids, regardless of the nature of the solvent, the reaction proceeds with high yields and selectivity in the whole range investigated.

The influence of solvents on the reaction has also been studied. In basic solvents a significant amount of products of sequential condensation of acetaldehyde is formed. The same tendency is observed with increasing basicity of the catalyst. In nonpolar solvents (toluene) crotonic aldehyde is selectively formed (except for salts of secondary amines).

In the reactions of homo-aldol condensation of acetaldehyde in the presence of amino acids, the ratio of homo-interaction products corresponds to the experiments performed in the presence of formaldehyde.

For reactions in the presence of amine salts, the same patterns are observed, but in the presence of formaldehyde, the main route of interaction is cross-condensation.

It should be noted that at high conversion of acetaldehyde, over 95%, the amount of polyenal increases compared to the yield of 2-butenal, this fact indicates the series-parallel character of the reaction of acetaldehyde homo-condensation. On the basis of this fact, we can conclude that in the realization of cross-condensation of acetaldehyde and formaldehyde it is necessary to control the formation of reaction products and exclude the possibility of complete consumption of formaldehyde. At homo-condensation the formation of the dimerization product of propionic aldehyde 2-methyl-2-pentenal (69.3 %), as well as the oligomerization product of propenal - tributylacetylcitrate and polyenals of different structure was observed.

In the reaction of propionic aldehyde and formaldehyde, 2-methyl-2-propanal (29.4%) and the by-product of the side homo-condensation of propionic aldehyde 2-methyl-2-pentenal (17.3%) were formed. Mainly the formation of polyenals of different structures, over 50 %, was observed.

In the aldol condensation of propionic aldehyde and acetaldehyde a significant number of reactions occur, approximately in equal proportions formed products of cross-condensation - 2-pentenal (19.7%), homo-condensation of propionic aldehyde - 2-methyl-2-pentenal (1.5%), and homo-condensation of acetaldehyde - 2-butenal (19.6%). In all cases of cross-condensation of propionic aldehyde, the formation of cyclic ketones, enones and lactones was observed. This reaction is of exceptional interest for further development of a method for the selective preparation of aldehydes and alcohols of branched structure.

The obtained data on yields and selectivity of reactions in the presence of acid-base systems can be explained within the framework of mechanisms of substrate activation by different types of catalysts.

With an acid catalyst, the initial step is the acidcatalyzed conversion of acetaldehyde to enol. The acid activates the substrate by protonating it, increasing the electrophilicity of the carbonyl carbon atom.

In the presence of both acid and basic catalysts, acetaldehyde homo-condensation reaction leading to the formation of 2-butenal is possible.

The reaction rate is determined by the electron density on the a- carbon atom. The activation of the substrate also depends on the electron density on the a-carbon atom. Since in 2-butenal methyl fragment and the presence of a double bond significantly increase the electron density, it will be the most active substrate in this reaction, but at the initial stage, when its concentration is low, occurs mainly the reaction of homo interactions, which is reflected in the yield of reaction products.

At high values of acetaldehyde conversion the amount of 2-butenal decreases, and the amount of heavier products of sequential condensation increases, so at acetaldehyde conversion approaching 100 % the yield of 2-butenal and heavier product 2,4,6-octatrienal is 4 % and 81.3 %, respectively.

In the case of sequential interaction, in addition to condensation of the initial substrates, interaction of reaction products with the reactant is possible, since 2-ethyl-2-butenal conjugated aldehyde of branched structure. In the presence of acetaldehyde in the system with formaldehyde, a more preferable mechanism of activation of the latter occurs. The homo-condensation product of formaldehyde in such a system is practically not formed, which was confirmed by analyzing the composition of reaction products by derivative chromatography. The cross-condensation reaction of acetaldehyde with formaldehyde leads to the formation of acrolein, a valuable monomer for the chemical, pharmaceutical, and polymer industries. The currently developed approaches to the reaction in the gas phase using basic heterogeneous catalysts are certainly available and technologically attractive in terms of catalyst cheapness, ease of apparatus design, but have a number of significant disadvantages: the inability to fully regenerate the catalyst and control the selectivity of the process. The formation of reaction by-products requires significant energy consumption for their separation, which overrides the benefit from the use of cheap catalysts.

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