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Abstract

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On the Synthesis of Esters and Other Derivatives of Carboxylic Acids under Conditions of Acid Catalysis from Carbon Monoxide, Olefins, and Acylatable Compounds

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Reactions for the formation of esters of carboxylic acids from carbon monoxide and olefins, or from carbon monoxide, olefins, and alcohols, have been studied very little. Until now these reactions, proceeding in the presence of acidic catalysts, have been carried out with all the starting components simultaneously present in the reaction mixture and under very severe conditions: at high pressures and elevated temperatures. Thus, from a mixture of carbon monoxide, ethyl alcohol vapors, and ethylene or propylene, ethyl esters of propionic or butyric acids were obtained[1] in low yields at temperatures above 300° and pressures up to 700 atm, in the presence of phosphoric acid on carbon. From a mixture of ethylene, propylene, and CO at 110° and 500 atm in the presence of boron fluoride hydrate, the ethyl ester of α,α-dimethylbutyric acid was obtained[2] in 14% yield. The ethyl ester of α-ethyl-α-methylbutyric acid was formed[3] from CO and C_2H_4 at 115° and 1000 atm, using boron fluoride hydrate as the catalyst.

In the present work, experimental data are presented on a new route for the synthesis of esters of carboxylic acids from CO, olefins, and alcohols, proceeding under conditions very mild for such reactions: temperatures of 0–50° and pressures from atmospheric to 80 atm. The possibility of synthesizing other derivatives of carboxylic acids under analogous conditions is also considered.

The synthesis of esters was carried out by us in two stages. At first, only the olefins and CO were present among the starting components in the reaction mixture; upon interaction with the catalyst (concentrated sulfuric acid), they formed an intermediate complex. After this, an alcohol was added, which reacted with the complex with formation of esters of carboxylic acids and regeneration of the sulfuric acid.

A theoretical consideration of the nature of the intermediate complex arising from CO, an olefin, and a mineral acid makes it possible to draw the following conclusions. First, the complex has the character of an acylating agent, as is evident from the formation of esters of carboxylic acids when it is treated with

an alcohol. Second, in its composition and structure the complex is very close to, and possibly identical with, the mixed anhydride of sulfuric acid and a carboxylic acid[4], as indicated by the participation of sulfuric acid in its formation and its liberation when an alcohol acts on the complex. Finally, formation of the complex proceeds with the intermediate formation of carbonium ions. This is shown by isomeric transformations, as a result of which, alongside esters of acids corresponding in structure to the starting olefin, there are also obtained esters of acids corresponding to its skeletal isomers.

All these conclusions, based on experimental facts, make it possible to represent the formation of the complex by the following reactions (5):

$$R_1R_2C{=}CR_3R_4 + H_2SO_4 \rightarrow R_1R_2HC{-}\overset{+}{C}R_3R_4 + \overline{O}SO_3H \xrightarrow{CO}$$

$$\rightarrow R_1R_2HC{-}R_3R_4C{-}\overset{+}{C}O + \overline{O}SO_3H \rightleftarrows R_1R_2HC{-}R_3R_4C{-}C(=O){-}OSO_3H \quad (1)$$

II III

The last stage—the interaction of the alcohol with the complex (in form II or III)—may be expressed by the reaction:

$$\text{II (or III)} + HX \rightarrow H_2SO_4 + R_1R_2HC{-}R_3R_4C{-}\underset{\underset{O}{\|}}{C}X \quad (2)$$

IV

where X is an alkoxyl group.

In isomeric transformations of carbonium ions I or II, esters isomeric with ester IV should be formed.

The acylating character of the complex, arising from the electrophilic nature of carbonium ion II or from the anhydride nature of form III, is general. It should therefore manifest itself in reactions with other compounds HX containing active hydrogen. Thus equation (2) expresses a series of reactions leading to the formation of carboxylic acid derivatives. For $X = H_2N{-}$, $HRN{-}$, $R_2N{-}$, $Cl{-}$, $Br{-}$, $RCOO{-}$, etc., equation (2) represents, respectively, reactions of formation of amides, acid halides, anhydrides, etc. In the particular case when $X = HO{-}$, this is the reaction for the synthesis of carboxylic acids, carried out by Koch (6) under conditions analogous to those described above.

In the present work we briefly set forth the results obtained in the study of the reaction for the formation of methyl esters of carboxylic acids (i.e., when $X = CH_3O-$) from isobutylene, and also from liquid olefins.

The reaction with isobutylene was carried out at a temperature of 0° and atmospheric pressure in a glass cylindrical vessel containing 0.5 l of 96% sulfuric acid. With vigorous stirring, 237 l of a gas mixture of composition 1 i-C_4H_8 : 1 CO was passed through the acid; 19.4 l (16.6%) CO and 118 l (100%) i-C_4H_8 were absorbed. To the lower acid layer, after separation from the oily isobutylene polymer, 0.7 l of methyl alcohol was added. The reaction mixture was then diluted with 2 l of water; 73 ml of methyl esters of carboxylic acids with a boiling range of 80.0–197.5° were isolated; the yield was 65.7 and 10.8% based on the CO that had entered into reaction and on isobutylene, respectively. Fractionation on a column of 40 theoretical plates gave methyl esters of monobasic carboxylic acids of the saturated series: C_5, 21%, and C_6, 3%.

For comparison, under analogous conditions, carboxylic acids were obtained from isobutylene and CO by Koch' s method (6), by treating the acid complex with water, with a yield of 47.8 and 14.9% based on the CO that had reacted and, respectively, on isobutylene. The acids were converted by reaction with diazomethane into methyl esters, which boiled in the range 88.5–220°. Fractionation on the same column gave esters of C_5 acids, 38%, and C_6, 4%.

As the liquid olefins there was used the fraction with b.p. 32–124° of the product of hydrocondensation of CO with propylene (7), which had d_4^{20} 0.6775, n_D^{20} 1.3902, bromine number 99.7, with an olefin content of 61.2%. The reaction was carried out in a stainless-steel autoclave, into which 0.5 l of 96% sulfuric acid and CO to 80 atm were charged. With intensive stirring, 215 ml of the above-mentioned fraction was added over the course of 6 hours. 16.5 l of CO was absorbed. The reaction mixture contained, in the upper layer, paraffinic hydrocarbons that were constituents of the starting fraction; in the lower layer –the acid complex (see equation (1)) and excess sulfuric acid. To the lower

0.7 l of methyl alcohol was added to the layer, and the reaction mixture was diluted with 2 l of water. A total of 101 ml of a mixture of methyl esters of carboxylic acids with a boiling range of 28-130° at 2 mm Hg was isolated; the yield was 63% based on the starting olefins and 78% based on the CO that had reacted. By fractionation on the aforementioned column, methyl esters of the following saturated carboxylic acids were isolated: C_5 12%, C_6 28%, C_7 27%, and C_8 6%.

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