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## Abstract

## Full Text

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# ON THE CATALYTIC HYDROGENATION OF ESTERS

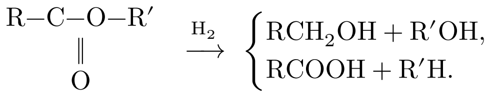
The carbalkoxy group has a reduced capacity for catalytic hydrogenation in comparison with olefinic and carbonyl bonds. As a rule, esters of unsaturated acids are converted by catalytic hydrogenation into the corresponding esters of saturated acids. Thus, for example, esters of acrylic acid are hydrogenated to esters of propionic acid in the gas phase on a nickel catalyst at 180° ([1]). Hydrogenation of amyl oleate in the gas phase on platinized asbestos leads to analogous results. Here too only the olefinic bond is hydrogenated, and the amyl ester of stearic acid is formed ([2]).

Recently we obtained experimental data showing that, under conditions of vapor-phase hydrogenation on platinum, hydrogenolysis of the ester bond of the furan ring proceeds more readily than hydrogenation of the carbalkoxy group ([3]). All these results indicate the high stability of the carbalkoxy group with respect to the reaction of catalytic hydrogenation. Indeed, successful hydrogenation of an ester group proved possible only under conditions of elevated hydrogen pressure ([4]). It was found that esters are reduced to two alcohols according to the reaction

$$\mathrm{RCOOR'} \xrightarrow{\mathrm{H_2}} \mathrm{RCH_2OH} + \mathrm{R'OH}.$$

This reaction proceeds most smoothly on copper chromite. For example, ethyl valerate on a copper-chromium catalyst at 250° and 220 atm pressure forms amyl alcohol in a yield of 94% ([4]).

The search for conditions for the catalytic reduction of esters was only a partial solution of the more general problem of the catalytic hydrogenation of the carbalkoxy group. In more general form, the question may be posed as follows: what transformations is the carbalkoxy group capable of under conditions of catalytic hydrogenation? To this end, we first undertook a study of the action of various catalysts on the carbalkoxy group during hydrogenation in the vapor phase at atmospheric pressure; then, in some cases, the influence of hydrogen pressure and temperature was studied. The results we obtained can be explained by relating them, on the one hand, to the specificity of the action of the catalysts and, on the other, to the influence of hydrogen pressure. Depending on these two conditions, the carbalkoxy group under hydrogenation is capable of transformations in two directions: it may be reduced so that two alcohols are formed from the ester, or it may undergo hydrogenolysis, forming a carboxyl group and a hydrocarbon:



$$\underset{\displaystyle\overset{\|}{O}}{R{-}C{-}O{-}R'} \xrightarrow{H_2} \begin{cases} RCH_2OH + R'OH, \\ RCOOH + R'H. \end{cases}$$

Hydrogenolysis of the ester group proceeds most smoothly on platinum and palladium catalysts when hydrogenation is carried out at atmospheric pressure. Of these two catalysts, platinum proved more active than palladium. At 300°, hydrogenolysis of esters on Pt—C proceeds practically to completion, whereas on Pd—C the conversion of the ester under the same conditions is about 65%.

$$CH_3COO \cdots R \xrightarrow[300^\circ]{H_2;\ Pt{-}C} CH_3COOH + RH,$$

$$R = n\text{-}C_5H_{11},\ n\text{-}C_6H_{13},\ n\text{-}C_7H_{15};$$

$$CH_3CH_2CH_2COO \cdots \text{iso-}C_5H_{11} \rightarrow CH_3CH_2CH_2COOH + \text{iso-}C_5H_{12}.$$

Temperature has a substantial influence on the hydrogenolysis reaction of esters. Thus, at 250° only a very slight conversion of the ester into acid and hydrocarbon is observed.

As is known from the work of Sabatier and Mailhe ($^6$), esters can undergo decomposition into an acid and an ethylenic hydrocarbon. It could be assumed that this reaction also takes place during the hydrogenation of esters under the conditions of our experiments and that, consequently, the formation of the paraffinic hydrocarbon occurs as a result of hydrogenation of the ethylenic hydrocarbon. However, investigation of the behavior of isoamyl butyrate on Pt—C at 300° in the absence of hydrogen showed that isopentene is formed under these conditions in an amount of not more than 3-4%. Consequently, the formation of paraffinic hydrocarbons occurs as a result of direct hydrogenolysis of the C—O bond in the carbalkoxy group. In addition to the catalyst, the direction of ester transformations is substantially affected by the hydrogen pressure at which hydrogenation is carried out. Thus, hexyl acetate on Pt—C at a pressure of 50 atm and 350°, along with the hydrogenolysis reaction, undergoes reduction of the carbalkoxy group, which is proved by the presence in the catalyzate of acetic acid, hexane, and pentane. The formation of pentane is possible as a consequence of successive reactions of dehydrogenation of hexyl alcohol to the corresponding aldehyde and decarboxylation of the latter to pentane. Thus, hydrogenation of esters on a platinum catalyst at elevated hydrogen pressure does not proceed selectively, as it does at atmospheric pressure.

On a skeletal Cu—Al catalyst, the opposite relationship is observed between hydrogen pressure and the selectivity of transformations of the carbalkoxy group, which only at elevated hydrogen pressure is smoothly reduced with formation of hydroxyl groups, whereas at normal pressure it also undergoes other transformations leading to the formation of a complex mixture of paraffinic and olefinic hydrocarbons.

$$CH_3COOR \xrightarrow[300^\circ,\ 50\ \text{atm.}]{H_2;\ \text{Cu—Al}} ROH + C_2H_5OH.$$

$$R = C_5H_{11},\ C_6H_{13}$$

The properties of the skeletal Ni—Al catalyst were studied by us in the hydrogenation of amyl acetate and hexyl acetate at atmospheric pressure and temperatures of 250 and 300°. The degree of conversion of hexyl acetate at 250 and 300° was, respectively, 30 and 80%. At 250°, hexane is formed predominantly from hexyl acetate, with an admixture of hexenes. At 300°, the catalyzate from hexyl acetate also contains small amounts of pentane and pentenes. These data show that the skeletal Ni—Al catalyst at atmospheric pressure carries out hydrogenolysis of the carbalkoxy group, although less smoothly than platinum and palladium. The results of our investigation allow the following conclusions to be drawn.

Catalytic hydrogenation of esters in the vapor phase can lead either to their reduction to two alcohols or to hydrogenolysis with the formation of an acid and a paraffinic hydrocarbon. The first of these reactions is favored by elevated hydrogen pressure. The most effective catalyst for the reduction of esters proved to be skeletal copper. Conversely, hydrogenolysis of esters proceeds smoothly over platinized and palladized carbon at normal pressure. Hydrogenation of esters was carried out in a flow-type apparatus at normal and elevated hydrogen pressure with a space velocity of 0.15 $h^{-1}$.

Alkyl acetates were obtained by the interaction of alcohols with an excess of acetic anhydride in the presence of freshly fused sodium acetate on heating.

The catalysts—platinized carbon, palladized carbon, skeletal nickel-aluminum, and skeletal copper-aluminum catalyst—were prepared by the procedure described by us earlier [6]. The catalysts were decomposed on a column; the reaction products were identified by determination of physical constants and by gas-liquid chromatography.

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

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