CHEMISTRY

K. V. PUZITSKII, Ya. T. EIDUS, and K. G. RYABOVA

1961

SovietRxiv

Abstract

Full Text

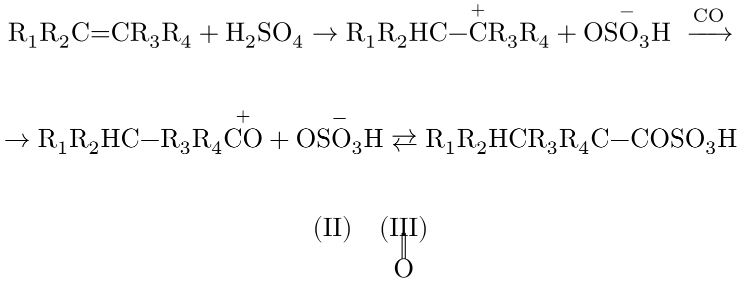
CHEMISTRY

K. V. PUZITSKII, Ya. T. EIDUS, and K. G. RYABOVA

ON THE SYNTHESIS OF CARBOXYLIC ACIDS AND THEIR ESTERS UNDER CONDITIONS OF ACID CATALYSIS FROM CARBON MONOXIDE AND ALCOHOLS

(Presented by Academician B. A. Kazanskii, 26 VI 1961)

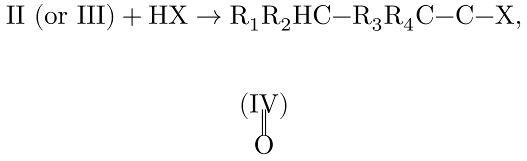
Carboxylic acids of branched structure and their esters can be synthesized under comparatively mild conditions and in good yields by carboxylation (^{1}), and correspondingly by carbalkoxylation (^{2}), of olefins with the aid of carbon monoxide. The synthesis is carried out in two stages. First, from the olefin and carbon monoxide, with the participation of the catalyst—concentrated sulfuric acid—at elevated pressure (up to 90 atm), intermediate compounds are formed which have the character of acylsulfuric acids and are in equilibrium with acylcarbonium and hydrosulfate ions



$$R_1R_2C{=}CR_3R_4 + H_2SO_4 \rightarrow R_1R_2HC{-}\overset{+}{C}R_3R_4 + \overset{-}{OSO_3}H \xrightarrow{CO}$$

$$\rightarrow \underset{(II)}{R_1R_2HC{-}R_3R_4\overset{+}{C}O + \overset{-}{OSO_3}H} \rightleftarrows \underset{(III)}{R_1R_2HCR_3R_4C{-}\underset{\|}{\underset{O}{C}}OSO_3H} \qquad (1)$$

Then, on interaction with water or an alcohol, carboxylic acids or their esters are formed:



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

where X = OH or OR.

In view of the fact that the process is accompanied by skeletal isomerization, the principal reaction products are forms isomeric with IV.

From reaction (1) it is seen that, in essence, the starting reagent is the carbonium ions (I). Consequently, it could be supposed that, in addition to olefins, other compounds forming similar carbonium ions with sulfuric acid should also be prone to reaction (1), in particular alcohols:

$$\mathrm{RCH_2CH_2OH + H_2SO_4 \rightarrow RCH_2\overset{+}{C}H_2 + OS\overset{-}{O}_3H + H_2O.} \tag{3}$$

It was therefore of interest to determine whether, in the process described above, the initial olefins could be replaced by alcohols. Such a possibility seemed quite realistic in light of the results of Koch and Haaf ([3]), who showed that, similarly to olefins, alcohols are converted at atmospheric pressure into carboxylic acids on interaction with formic acid in the presence of a large excess of sulfuric acid. It should be noted that, according to literature data ([4]), up to now a one-stage synthesis of carboxylic acids from alcohols and carbon monoxide has been used at high temperatures and very high pressures (up to 1000 atm).

In the present work it was shown that, at elevated pressure and room temperature, alcohols and carbon monoxide in the presence of sulfuric acid as catalyst form intermediate compounds, which are subsequently converted, on interaction with water or alcohols,

into branched carboxylic acids or, respectively, their esters. In this synthesis, as in the case of the starting olefins, the acids formed are predominantly those having in the molecule one carbon atom more than in the starting alcohol, and a quaternary (more rarely tertiary) carbon atom in the α-position to the carboxyl group. Formally, this synthesis may be regarded as the addition of carbon monoxide to an alcohol with simultaneous isomerization of the hydrocarbon radical of the latter

$$\mathrm{ROH + CO \rightarrow R_1COOH,} \tag{4}$$

where R_1 is a more highly branched radical than R, with the same number of carbon atoms. However, the chemistry of this process at the first stage may be represented either by dehydration of the alcohol to an olefin:

$$\mathrm{RCH_2CH_2OH \rightarrow RCH{=}CH_2 + H_2O,} \tag{5}$$

which then reacts according to equations (1) and (2), or by direct conversion of the alcohol into a carbonium ion according to reaction (3). The second pathway is more probable. This, in particular, agrees with the data of Koch and Haaf ([4]), according to which carboxylic acids are obtained in good yields by reaction at atmospheric pressure with formic acid in the presence of an excess of sulfuric acid of such alcohols as, for example, neopentyl alcohol, which cannot be directly dehydrated to an olefin by reaction (5).

The synthesis of the acids and their esters was carried out in such a way that, in the first stage, the alcohol, carbon monoxide, and sulfuric acid (*d* 1.84) reacted at a pressure of 60-90 atm, and in the second stage an excess of water or methyl alcohol was added to the reaction mixture. In the first case carboxylic acids were obtained; in the second, their methyl esters with an admixture of the carboxylic acids themselves. Thus, from *n*-butyl and isobutyl alcohols, when water was added in the second stage to the reaction mass, a mixture of acids was obtained in 70-80% yield; when methyl alcohol was added, a mixture of esters and acids (in a weight ratio of 5:1) was obtained with an overall yield of about 60%. The main reaction products were: with *n*-butyl alcohol—α-methylbutyric acid or, respectively, its ester; with isobutyl alcohol—trimethylacetic acid or its ester. The content of these compounds in the mixture of reaction products was 85-90%.

Thus, under comparatively mild conditions, a reaction of alcohols with carbon monoxide has been carried out, as a result of which carboxylic acids of branched structure, or their esters, are formed*.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
21 V 1961

CITED LITERATURE

1. H. Koch, *Brennst.-Chem.*, **36**, 321 (1955).
2. Ya. T. Eidus, K. V. Puzitskii, K. G. Ryabova, DAN, **120**, 323 (1958); K. V. Puzitskii, Ya. T. Eidus, K. G. Ryabova, I. V. Guseva, ZhOKh, **29**, 3019, 4014 (1959); DAN, **128**, 555 (1959); Ya. T. Eidus, K. V. Puzitskii, O. D. Sterligov, ZhOKh, **30**, 3799 (1960).
3. H. Koch, W. Haaf, *Lieb. Ann.*, **618**, No. 1-3, 251 (1958).
4. Ya. T. Eidus, *Usp. khim.*, **16**, 599 (1947).
5. H. Koch, W. Haaf, *Angew. Chem.*, **70**, No. 10, 311 (1958).
6. A. De Benedictis, K. E. Furman, U.S. Patent 2913489 (1959); RZhKhim., 1961, 7 6; *Chem. Zbl.*, 1730 (1961).

* After completion of this work, the authors became aware of data from an American patent (^{6}), in which the synthesis of carboxylic acids from alcohols

and carbon monoxide under analogous conditions is described.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.