Formation of Formic Acid and its Esters under Conditions of Hydroformylation

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Hydroformylation of carbonyl groups in *n*- and isobutyraldehydes affords *n*- and isobutyl formiates, respectively. From the viewpoint of the formation of these esters isobutyraldehyde is more reactive. Formic acid found in the hydroformylation product arises from the hydrolysis of esters by water formed in the course of consecutive reactions of aldehydes.

Besides aldehydes [1] or alcohols also the products of consecutive and simultaneous reactions of starting olefins can be formed under the conditions of hydroformylation of olefins in the presence of dicobalt octacarbonyl as a catalyst. One group of these by-products is represented by formic acid and its esters.

Examination of the hydroformylation mechanism presumed the formation of formiates [2, 3], which were also found in the products of hydrogenation of oxoaldehydes [4, 5]. In spite of these statements the detailed analysis of the hydroformylation product fractions boiling at higher temperature [6] did not confirm the presence of formiates. At the same time, almost nothing is known about the formation of formic acid in the course of hydroformylation. From the point of view of corrosion of technological equipment the presence of formic acid in the reaction product should be considered as a potential hazard.

Experimental

Substances

Synthesis gas (equimolar mixture of carbon monoxide and hydrogen) contained max. 0.3% (v/v) of carbon dioxide and 0.05% (v/v) of oxygen.

Dicobalt octacarbonyl was prepared from cobalt oxides and recrystallized from light petroleum; b.p. 40–60°C.

n-Butyraldehyde was prepared by hydroformylation of propylene and distilled before use; b.p. 74.5°C/750 Torr, d_4^{20} 0.816 g cm^{-3}, chromatographically pure.

Isobutyraldehyde was prepared by hydroformylation of propylene and distilled before use; b.p. 63.5°C/745 Torr, d_4^{20} 0.793 g cm^{-3}, chromatographically pure.

Isobutyl formiate, b.p. 98.5°C/750 Torr, d_4^{20} 0.876 g cm^{-3}, n_D^{20} 1.3850, and *n*-butyl formiate, b.p. 105.5°C/740 Torr, d_4^{20} 0.880 g cm^{-3}, n_D^{20} 1.3894 were used as reference substances for gas chromatography. Both compounds prepared by esterification of formic acid (Lachema, Brno) with *n*- and isobutyl alcohol in the presence of $CaCl_2$, were chromatographically pure.

Analytical

n- And isobutyraldehydes were determined chromatographically (liquid—gas system) under following conditions: thermoconductometric detection, column temperature 130°C. The column (0.6 × 300 cm contained the material "Porovina" (Lachema, Brno) (grain size 0.25—0.4 mm) with 7% (w/w) of "Tridox" (alkyl polyglycol ether, W. Pieck Chemical Works, Nováky) as a stationary phase. Hydrogen (flow rate 50 ml min^{-1}) was used as a carrier gas.

Procedure

The measurements were carried out in a one-litre stainless steel rotating autoclave. After filling-up the autoclave with n- or isobutyraldehyde a small test tube containing the appropriate amount of dicobalt octacarbonyl dissolved in 5 ml of n-hexane was fastened to the thermometer tube. After closing the autoclave the air was replaced by carbon monoxide and the synthesis gas was introduced until its pressure reached 150 kp cm^{-2}. The autoclave was then heated to the reaction temperature in vertical position and after taking the first sample the pressure of the synthesis gas was increased to 240 kp cm^{-2}. The autoclave was then turned into horizontal position whereby the catalyst came into contact with the reaction mixture and the autoclave was set in rotation. In the appropriate time intervals the samples were withdrawn through an efficacious condenser and the formation of n- and isobutyl formiate was followed. In the study of the formation of n- and isobutyl formiate the amount of dicobalt octacarbonyl is expressed in % (w/w) of Co related to the quantity of propylene required for the formation of corresponding amounts of n- or isobutyraldehyde.

Results and Discussion

In the portion of propylene hydroformylation product boiling at higher temperature (the residue after separation of n- and isobutyraldehydes) we have found [7, 17] 6.79% (w/w) of n- and isobutyl formiates. Detailed study revealed that the conversion of n-butyraldehyde to n-butyl formiate under the conditions of hydroformylation increases with increasing temperature. Thus, from n-butyraldehyde 1.6% and 7% (w/w) of n-butyl formiate at 140 and 170°C, respectively, were formed during 100 minutes (Fig. 1). At higher temperatures and with larger amounts of cobalt carbonyls n-butyraldehyde reacts concurrently affording other, kinetically preferred products.

The formation of butyl formiates by homogeneous catalysis with $HCo(CO)_4$ proceeds under the conditions of oxo synthesis as hydroformylation of double (σ, π) bond of $C=\underline{\overline{O}}$ group [5]

$$RCHO + CO + H_2 \xrightarrow[HCo(CO)_4]{} HCOOCH_2R. \qquad (A)$$

In the presence of hydrogen and carbon monoxide in the hydroformylation medium the dicobalt octacarbonyl is transformed into cobalt tetracarbonyl hydride [8], which can exist in the equilibrium with cobalt tricarbonyl hydride [3, 9, 10]

$$HCo(CO)_4 \underset{+CO}{\overset{-CO}{\rightleftarrows}} HCo(CO)_3. \qquad (B)$$

Since the cobalt atom in the cobalt tricarbonyl hydride molecule is coordinately highly unsaturated [9, 10] its addition to the carbonyl group of aliphatic aldehydes can occur.

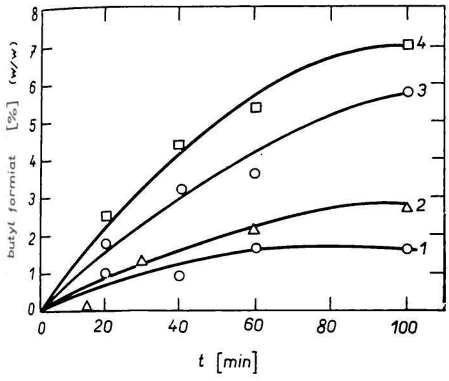


Fig. 1. Kinetics of n-butyl formiate formation from n-butyraldehyde under conditions of hydroformylation.
1. 140°C; *2.* 150°C; *3.* 160°C; *4.* 170°C. Conditions: 0.117% (w/w) of Co/n-butyraldehyde; Co in the form of $Co_2(CO)_8$; pressure of synthesis gas (equimolar mixture of CO and H_2) 240 kp cm^{-2}.

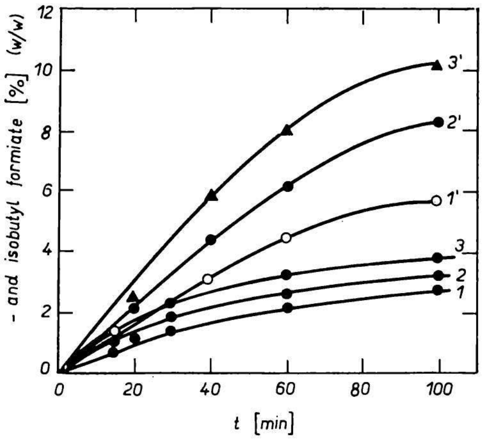


Fig. 2. Effect of the concentration of $Co_2(CO)_8$ on the kinetics of formation of n-butyl formiate (curves *1, 2, 3*) and isobutyl formiate (curves *1', 2', 3'*) from n- and isobutyraldehydes under conditions of hydroformylation.
Conditions: *1.,1'.* 0.117; *2.,2'* 0.234; *3.,3'* 0.351% (w/w) of Co/C_3H_7CHO respectively. Temperature 150°C, other conditions were the same as in Fig. 1.

One can assume that at high partial pressure of carbon monoxide (equation *B*) the equilibrium is shifted to the left side under the conditions of synthesis and that only after induction of π-electron shift by approaching cobalt tetracarbonyl hydride molecule the addition product is formed as follows

$$\mathrm{R{-}\overset{\curvearrowleft}{CH}{=}\underline{\overline{O}}} + \mathrm{HCo(CO)_4} \rightleftarrows \mathrm{CO} + \mathrm{RCH_2O{-}Co(CO)_3}, \tag{C}$$

$$\mathrm{RCH_2O{-}Co(CO)_3} \underset{-\,\mathrm{CO}}{\overset{+\,\mathrm{CO}}{\rightleftarrows}} \mathrm{RCH_2O{-}Co(CO)_4}. \tag{D}$$

In the first step (equation *C*) a σ bond cobalt—oxygen is formed. The resulting alkoxycobalt tricarbonyl can further equilibrate with alkoxycobalt tetracarbonyl (equation *D*). Alkoxycobalt tricarbonyl is due to the presence of alkoxyl group coordinately less unsaturated than $HCo(CO)_3$. From the point of view of hydroformylation mechanism [10] the formation of corresponding alkoxycobalt tricarbonyls through the transitory π-complex [3] should also be considered.

Alkoxycobalt tetracarbonyl further rearranges to carbalkoxycobalt tricarbonyl

$$\mathrm{RCH_2O{-}Co(CO)_4} \rightleftarrows \mathrm{RCH_2OCO{-}Co(CO)_3}. \tag{E}$$

The latter is then reduced by cobalt tetracarbonyl hydride to corresponding formiate

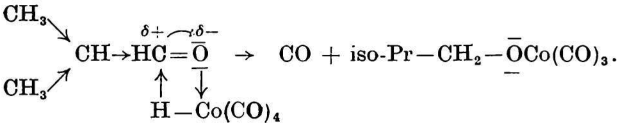
$$\mathrm{RCH_2OCO{-}Co(CO)_3} + \mathrm{HCo(CO)_4} \rightarrow \mathrm{RCH_2{-}O{-}CO{-}H} + \mathrm{Co_2(CO)_7}, \tag{F}$$

$$Co_2(CO)_7 + CO \rightleftarrows Co_2(CO)_8, \tag{G}$$

$$Co_2(CO)_8 + H_2 \rightleftarrows 2HCo(CO)_4. \tag{H}$$

Dicobalt hexacarbonyl and dicobalt heptacarbonyl are known [11] to exist as transitory carbonyls under the conditions of hydroformylation. Their reactions to carbonyl hydride (equations *G* and *H*) are of the same nature. The final formation of formiate is believed [3] to proceed also through an intermediate $RCH_2OCOCoH_2(CO)_3$ followed by its decomposition to $HCOOCH_2R$ and $HCo(CO)_3$. The existence of such an intermediate was, however, not confirmed.

For the formation of isobutyl formiate from isobutyraldehyde the same rules are valid as for the formation of *n*-butyl formiate from *n*-butyraldehyde. Nevertheless, a higher rate of formation of isobutyl formiate, when compared with that of *n*-butyl formiate, was observed. For example, with 0.6% of Co/C_3H_6 more than 10% of isobutyl formiate and merely about 4% of *n*-butyl formiate were obtained at 150°C (Fig. 2). Higher yields of isobutyl formiate can be explained by easier formation of isobutoxycobalt tricarbonyl from isobutyraldehyde (equation *D*) due to the greater induction effect of isopropyl group. In spite of the fact that two methyl groups in isobutyraldehyde molecule represent a considerable steric hindrance to the approaching $HCo(CO)_4$ molecule, in the case of relatively small hydrogen atom this circumstance does not play any role



$$(CH_3)_2CH \rightarrow H\overset{\delta+}{C}=\overset{\delta-}{\overline{O}} \; (H-Co(CO)_4) \rightarrow CO + \text{iso-Pr}-CH_2-\overline{\underline{O}}Co(CO)_3. \tag{I}$$

Further reaction course leading to the formation of isobutyl formiate is identical with the already described general reaction pattern for the formation of alkyl formiates. Increased reactivity of isobutyraldehyde in the formation of isobutyl formiate was confirmed also in experiments carried out at 160°C. Starting with equimolar mixture of *n*- and isobutyraldehydes (pressure of synthesis gas 240 kp cm^{-2}, 0.4% of Co) the ratio of product isomers, *n*-/iso-, was found to be 0.83.

According to [5], *n*-propyl formiate can be formed from *n*-propanol under the conditions of oxo synthesis (160°C, 5 hours, $CO : H_2 = 1$ 1, 300 kp cm^{-2}). The product contained 3.3% (w/w) of *n*-propionaldehyde and 3.2% (w/w) of *n*-propyl formiate which supposedly can be dehydrogenated to propionaldehyde and this further converted to formiate. The equilibrium constant calculated from the data given for the dehydrogenation of *n*-propanol [12] at 177°C ($\Delta G^0 = +13.20$ kcal mole^{-1}) is 3.72×10^{-7}. If we take into account also the high partial pressure of hydrogen, this route of formation of formiate seems to be less probable. In a similar reaction of *n*-butyraldehyde carried out even at temperatures of 180 and 200°C we were not able to detect any *n*-butyl formiates in the reaction product.

In the portion of hydroformylation product boiling at higher temperature we have identified [7] 0.27% (w/w) of formic acid. Its formation under the conditions of hydroformylation can be explained by the known [13] equation

$$H_2O + CO \rightleftarrows HCOOH \tag{J}$$

since the starting compounds (H_2O from dehydration of aldoles, CO in the synthesis gas) are present in the reaction medium. Our results (temperature 120—180°C, pressure of synthesis gas 240 kp cm^{-2}, $Co_2(CO)_8$ as catalyst), however, did not confirm this mechanism of the formation of formic acid even by using a hydrophilic solvent (dioxan). In this way we have confirmed the known fact [14] that relatively easily hydrolyzable lower alkyl formiates are being hydrolyzed by water present in the medium. The acidity of the medium necessary for the hydrolysis is secured by the presence of acidic cobalt tetracarbonyl hydride [15, 16].

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