

# Hydroesterification of Olefins under Conditions of Hydroformylation

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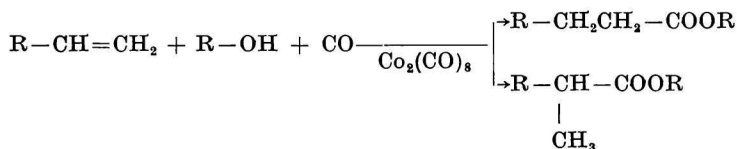
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Conversion of propylene in the course of its hydroesterification with carbon monoxide and alcohol depends on the kind of alcohol used. Reactivity of alcohols decreased in the following order: primary > secondary > tertiary alcohols. Addition of organic bases increased the reaction rate and changed the reaction order. The increased temperature (130–140°C) enhanced the conversion of propylene while the molar ratio of product isomers (*n*-butyl *n*-butyrate/*n*-butyl isobutyrate) remained constant:  $3.6 \pm 0.1$ .

Under the conditions of hydroformylation of olefins esters can be formed from alcohols arising in homogeneous hydrogenation of forming aldehydes or from alcohols intentionally used as solvents for olefins [1]



This reaction, so far not realized on industrial scale, is also interesting [14] from the technical point of view. The known results of hydroesterification of olefins were obtained mainly in the presence of methanol [2–7]. There is, however, lack of detailed information about the formation of isomers and especially about the possibilities to hydroesterificate the olefins with different kinds of alcohols.

## Experimental

### *Substances*

Propylene of 99.4% (w/w) purity was prepared by contact dehydration of isopropyl alcohol on alumina and purified by freezing out.

Carbon monoxide — 98.8% (w/w), contained 0.4% (w/w) of hydrogen, 0.3% (w/w) of carbon dioxide and 0.1% (w/w) of oxygen.

Dicobalt octacarbonyl was prepared from cobalt oxides at total pressure of the synthesis gas (CO : H<sub>2</sub> = 2 : 1) of about 200 kPa cm<sup>-2</sup> at 150°C in light petroleum and recrystallized from light petroleum to spectral purity.

Pyridine (Lachema, Brno) was distilled before use; b.p. 115.4°C/754 Torr,  $n_D^{20}$  1.5028,  $d_4^{20}$  0.9868 g cm<sup>-3</sup>.

Triethylamine (Lachema, Brno) was distilled before use; b.p.  $89^{\circ}\text{C}/745$  Torr,  $d_4^{20}$   $0.726$  g  $\text{cm}^{-3}$ .

Methanol (Lachema, Brno) — anal. grade.

Ethanol was dried before use, chromatographically pure.

*n*-Propyl, isopropyl, *n*-butyl, isobutyl, *tert*-butyl, *n*-pentyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-undecyl, and *n*-dodecyl alcohols (Lachema, Brno) were distilled before use, chromatographically pure.

### Analytical

Saponification number was determined titrimetrically [28]. *n*-Butyl *n*-butyrate and *n*-butyl isobutyrate were determined chromatographically as described previously [29].

### Procedure

Alcohol (2 moles) was placed in a half-litre stainless steel rotating autoclave and a small test tube containing 3.56 millimoles of dicobalt octacarbonyl dissolved in a small part of alcohol used was fastened to the thermometer tube. The autoclave was then closed, three times flushed with carbon monoxide in order to remove the air and propylene (0.5 mole) and carbon monoxide were introduced until its pressure reached 100 kp  $\text{cm}^{-2}$ . The autoclave was then heated in the vertical position and after attaining the reaction temperature it was tilted to horizontal position whereby the catalyst came into contact with the reaction mixture. This moment was considered as the zero time of the reaction. Temperature and pressure of the reaction mixture were recorded in 5–10-minute intervals. After termination of reaction, but not later than after 3 hours, the product was discharged through a condenser, weighed and analyzed.

## Results and Discussion

In the course of hydroesterification the conversion of propylene with carbon monoxide and alcohols to alkyl esters of *n*- and isobutyric acids at  $160^{\circ}\text{C}$  decreases with the length of hydrocarbon chain of the corresponding alcohol (Fig. 1). While with methanol and ethanol the conversion goes up to 80%, with higher alcohols and with dodecyl alcohol the conversion is only about 22% (w/w).

Primary alcohols react under the conditions of hydroesterification unambiguously to form the corresponding esters. In the presence of secondary alcohols, in addition to their esters, also the hydroformylation products and dialkyl ketones are formed [8].

Table 1

Alkoxy radical	$\Delta H^{\circ}$ [kcal mole $^{-1}$ ]
$\text{CH}_3\text{O}\cdot$	2
$\text{C}_2\text{H}_5\text{O}\cdot$	– 6.6
<i>n</i> - $\text{C}_3\text{H}_7\text{O}\cdot$	– 11.0
<i>i</i> - $\text{C}_3\text{H}_7\text{O}\cdot$	– 15.0
<i>n</i> - $\text{C}_4\text{H}_9\text{O}\cdot$	– 17.0
<i>i</i> - $\text{C}_4\text{H}_9\text{O}\cdot$	– 18.0
<i>tert</i> - $\text{C}_4\text{H}_9\text{O}\cdot$	– 24.0

Increased affinity to the formation of ketones can be observed mainly when lower the molar ratio alcohol/olefin. Decrease in the conversion of propylene can be observed in the sequence: *n*-butyl alcohol (42.5%), isobutyl alcohol (36.0%) and *tert*-butyl alcohol (15.0%).

The low yield of *tert*-butyl esters observed in the case of *tert*-butyl alcohol can be explained, in addition to existing steric hindrance, also by a shift of  $\sigma$  electrons of the C→O bond caused by the induction effect (+I) of *tert*-butyl residues and thus by changing the character of the O—H bond.

The values of enthalpies of formation ( $\Delta H^\circ$  at 298 K) for the corresponding alkoxy radicals as the products of homolytic dissociation of the RO—H bond [9] vary in a rather wide range (Table 1). The alkoxy radicals possessing negative  $\Delta H^\circ$  values are more stable. Binding energy,  $D$ , of *tert*-butyl alcohol (*tert*-C<sub>4</sub>H<sub>9</sub>OH) is 103 kcal mole<sup>-1</sup> or 110 kcal mole<sup>-1</sup> [10] which is 1 or 8 kcal mole<sup>-1</sup> more than that of *n*-butyl alcohol (*n*-C<sub>4</sub>H<sub>9</sub>OH).

The ratio of isomeric *n*-butyl *n*-butyrate and isobutyrate in the reaction product does not vary with temperature and is about 3.6 (Fig. 2). Similarly as with other alcohols also in hydroesterification of propylene with butanol the ratio of *n*-butyrate/isobutyrate is essentially constant and reaches the value of  $3.5 \pm 0.1$  (Fig. 1). Conversion of propylene to its C<sub>8</sub>-esters increases with increasing temperature. At 170°C the conversion is 60% (w/w) whereas at 180°C 63% (w/w).

Kinetic measurements of hydroesterification of cyclohexene and methanol [11] show that the reaction is of the zero order with regard to olefin and of the first order with regard to methanol. Linear time function of  $\log(p_0 - p_K)/(p_t - p_K)$  is a criterion of the first order reaction [12] supposing that the change of olefin concentration in the course of hydroesterification is proportional to the decrease of CO pressure

$$\ln \frac{p_0 - p_K}{p_t - p_K} = k t,$$

where  $p_0$  is the pressure of carbon monoxide at zero time,

$p_t$  is the pressure of carbon monoxide at the time  $t$ ,

$p_K$  is the terminal pressure of CO at assumed 100% conversion.

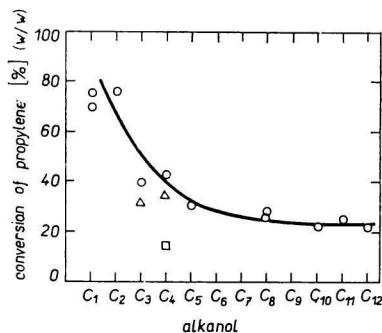


Fig. 1. Effect of the kind of alkanol on the conversion of propylene in the course of hydroesterification.

○ primary *n*-alcohols; △ isopropyl alcohol and isobutyl alcohol; □ *tert*-butyl alcohol.

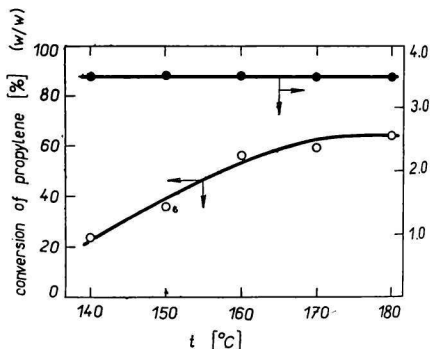


Fig. 2. Effect of temperature on the conversion of propylene and on the mass-ratio of C<sub>8</sub>-esters found in hydroesterification product.

As can be seen from Fig. 3, the initial velocity of hydroesterification of propylene with *n*-butyl alcohol corresponds to the kinetics of the first order reaction. We suppose that after addition of pyridine to the reaction mixture (curve 5, Fig. 3) the properties of the catalyst are, due to the partial substitution of CO ligands in  $\text{Co}_2(\text{CO})_8$  molecule by pyridine or as a consequence of homomolecular disproportion of cobalt carbonyls [26], modified

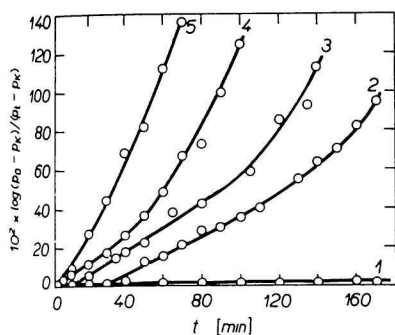


Fig. 3. Effect of pyridine and triethylamine on the kinetics of hydroesterification of propylene at 170°C.

1. triethylamine (0.1 mole); 2. no addition (standard experiment); 3. pyridine (0.1 mole); 4. pyridine (0.14 mole); 5. pyridine (0.3 mole).

so that by addition of 0.3 mole of pyridine per 1 mole of propylene the reaction order becomes visibly fractional. After addition of stronger base, for example triethylamine (Fig. 3), the hydroesterification is slowed down and practically stops. In our previous work we have found that some substituted derivatives of pyridine, for example  $\beta$ -picoline, increase the rate of hydroesterification [13].

In spite of the fact that the mechanism of hydroesterification was not investigated in detail we suppose, on the basis of several indications [21] that it is similar to the mechanism of hydroformylation [15–17]. Cobalt carbonyls [ $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_2(\text{CO})_7$ ] can react with alcohols to form alkoxy cobalt tricarbonyls and corresponding cobalt carbonyl hydride. The latter forms in the presence of an olefin *n*- and isoalkylcobalt tetracarbonyls which exist in the equilibrium [18, 19] and can rearrange by shifting the CO molecule to the corresponding acylcobalt carbonyls. The reaction of acylcobalt carbonyl with alkoxy cobalt carbonyl leads finally to the formation of an alkyl ester of aliphatic acid.

The addition of pyridine promotes the total conversion of olefins in the course of hydroesterification. If the conversion of propylene in control experiments is 56%, addition of 0.2 mole of pyridine per mole of propylene would raise it up to 93% under the same conditions. The increase of pyridine concentration in hydroesterification media causes the decrease of *n*-butyl *n*-butyrate/*n*-butyl isobutyrate ratio (Fig. 4). If triethylamine

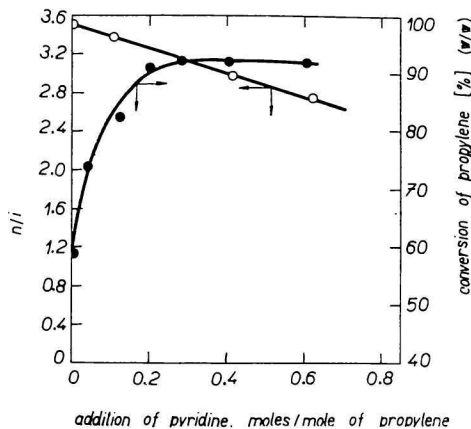


Fig. 4. Effect of pyridine on the conversion of propylene and on the mass-ratio of formed  $\text{C}_3$ -esters.

is added to the reaction mixture the hydroesterification does not practically proceed (Fig. 3). Triethylamine probably forms a stable, catalytically ineffective complex with cobalt carbonyls, similarly as it was observed in the experiments with ammonia [20]. On the other hand [23], it is known that even stronger bases (diethylamine,  $K_B = 1.26 \times 10^{-3}$ , pyridine,  $K_B = 1.4 \times 10^{-9}$  and triethylamine,  $K_B = 5.65 \times 10^{-4}$ ) do not retard the hydroformylation of methacrylate [22]. This observation can be explained by the fact that these amines are able to bind free acids formed in hydrolysis of esters by the effect of water present in used raw materials. The binding of free acids also eliminates their negative effect [21] on cobalt carbonyls. Finally, it should be mentioned that mainly at higher temperatures, the amines can play the role of hydrogen donors in the reaction of olefins with carbon monoxide catalyzed by dicobalt octacarbonyl. This reaction can lead to corresponding acid amides [24], similarly as the reaction of primary and secondary amines leads to alkylacyl amines and dialkylacyl amines, respectively. Strong bases which do not possess nitrogen-bonded hydrogen (for example tertiary aliphatic amines) have similar negative effect on hydroesterification forming the stable complexes with cobalt carbonyls.

From the results of hydroesterification of propylene with alcohols and carbon monoxide it follows that, mainly at temperatures higher than 140°C, the hydroesterification of olefins can, due to the increased concentration of alcohols formed by homogeneous hydrogenation of aldehydes [8, 21, 25] in the reaction medium, proceed as a simultaneous reaction. The same is true when alcohols are used as solvents [1, 21, 24].

## References

1. Macho V., Mistrík E. J., Střešinka J., *Chem. Prům.* **13**, 343 (1963).
2. Matsuda A., Uchida H., *Bull. Chem. Soc. Jap.* **38**, 710 (1965).
3. Natta G., *Brennst.-Chem.* **36**, 176 (1955).
4. Gankin V. J., Gordina N. J., Kacnelson M. G., Rudkovskij D. M., *Ž. Prikl. Chim.* **4**, 1862 (1967).
5. Pino P., Piacenti F., Bianchi M., Lazzaroni R., *Chim. Ind. (Milan)* **50**, 106 (1968).
6. Piacenti F., Bianchi H., Lazzaroni R., *Chim. Ind. (Milan)* **50**, 318 (1968).
7. Ercoli R., Signorini G., Santambrogio E., *Chim. Ind. (Milan)* **42**, 587 (1960).
8. Polievka M., *Thesis*. Slovak Technical University, Bratislava, 1968.
9. Kerr J. A., *Chem. Rev.* **66**, 494 (1966).
10. *Organikum, Organisch-chemisches Grundpraktikum*, p. 148. VEB Deutscher Verlag der Wissenschaften, Berlin, 1963.
11. Ercoli R., Avanzi H., Moretti G., *Chim. Ind. (Milan)* **37**, 864 (1955).
12. Natta G., Ercoli R., *Chim. Ind. (Milan)* **34**, 503 (1952).
13. Macho V., Polievka M., Gregor F., *Chem. Zvesti* **25**, 44 (1971).
14. Macho V., Polievka M., *Czechoslov. Patent* 137 187 (1970).
15. Heck R. F., Breslow D. S., *Chem. Ind.* **1960**, 467.
16. Heck R. F., Breslow D. S., *J. Amer. Chem. Soc.* **83**, 4023 (1961).
17. Heck R. F., Breslow D. S., *Actes du 2<sup>eme</sup> Congrès International de Catalyse*, p. 67. Paris, 1960.
18. Takegami Y., Yokokawa C., Watanabe Y., Okuda Y., *Bull. Chem. Soc. Jap.* **4**, 181 (1964).
19. Heck R. F., Breslow D. S., *J. Amer. Chem. Soc.* **85**, 2779 (1963).
20. Macho V., *Thesis*. Slovak Technical University, Bratislava, 1961.

21. Macho V., *Thesis*, pp. 4, 30—33, 83—90. Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague — Suchdol, 1968.
22. Lange N. A., *Handbook of Chemistry*. McGraw-Hill, New York, 1967.
23. Iwanaga R., *Bull. Chem. Soc. Jap.* **35**, 865 (1962).
24. Striegler A., Weber J., *J. Prakt. Chem.* **29**, 4. Reihe, 281 (1965).
25. Markó L., *Proc. Chem. Soc.* **1962**, 67.
26. Rudkovskij D. H., Trifel A. G., Aleksejeva R. A., *Chim. Prom.* **1959**, 652.
27. Wender I., Sternberg H. W., Orchin H., *J. Amer. Chem. Soc.* **74**, 1216 (1952).
28. Jureček M., *Organická analýsa*, Vol. 2. (*Organic Analysis*.) P. 328. Nakladatelství ČSAV. (Publishing House of the Czechoslovak Academy of Sciences.) Prague, 1957.
29. Polievka M., Mistrík E. J., *Chem. Zvesti* **26**, 149 (1972).

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