The Hydroesterification of Propylene with Carbon Monoxide and Methanol in the Presence of Dicobalt Octacarbonyl

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The syntheses of esters from olefins, alcohols, and carbon monoxide in the presence of dicobalt octacarbonyl, that is, the hydroesterification of olefins,[1] have been investigated by Natta and his co-workers.[2,3] This reaction is of a considerable interest from the industrial point of view, however, its application to industry has not yet been realized. This may have been due to the fact that this reaction proceeds at a rate much slower than the hydroformylation reaction. Starting with propylene and methanol, the authors of this paper have succeeded in increasing the reaction rate of hydroesterification to such a high level as to be comparable with that of hydroformylation. The details of the rate and the yields of products will be reported in this paper.

Experimental

The hydroesterification reactions were carried out by using the same 300-cc. stainless-steel autoclave as was used in the hydroformylation reaction of propylene.[4] The procedure was essentially the same as the one previously used except that in most of the runs a small amount of hydrogen was added to the autoclave from a 30-cc. hydrogen-pressure storage before carbon monoxide was introduced from another 500-cc. carbon monoxide pressure storage. The amount of hydrogen introduced was calculated from the pressure drop in the former pressure storage. After the temperature and pressure had been adjusted to definite levels, the stirrer was started. The dicobalt octacarbonyl in a stainless saucer held on a wing of the stirrer was allowed to drop into the liquid phase, and the reaction began. During the reaction period, carbon monoxide was continuously introduced from the pressure storage through a needle valve in order to maintain the autoclave pressure at a constant level of 190 kg./cm^2. The pressure in the pressure storage tended to drop as the reaction proceeded, but a simple recording of the pressure drops with time could not always serve as a measurement of the initial rate of hydroesterification, because the hydroesterification and the hydroformylation occurred simultaneously. As it was, the initial rate of the two reactions was determined independently by analyses of the product; samples of a small portion of the liquid product were withdrawn from the autoclave at time intervals during the reaction and were analyzed for methyl butyrate and butyraldehyde dimethylacetal. The former is the product of the hydroesterification of propylene, while the latter is the product formed by the combination of the butyraldehyde formed by the hydroformylation and methanol. The samples were analyzed by means of gas chromatography using a 4 m. column of triethanolamine on cellite at 80°C.[5] Ethylbenzene was used as an internal reference. The gaseous product was analyzed in the same way as has been described previously.[4]

Commercially-available propylene, methanol, and pyridine were used. Propylene was 93% pure and contained 6.5% propane and 0.5% ethane. Methanol and pyridine were distilled before use. The procedure for the preparation of dicobalt octacarbonyl, $Co_2(CO)_8$, was quite the same as has been mentioned previously.[4] Carbon monoxide was prepared by decomposing commercial formic acid with sulfuric acid and was more than 97% pure, containing less than 0.5% hydrogen.

Results and Discussion

The hydroesterification of propylene using carbon monoxide of a high purity usually proceeds at a much slower rate than the hydroformylation with the $1H_2$-$1CO$ synthesis gas. It has now been found that the addition of even a small amount of hydrogen into the autoclave results in a considerable increase in the rate of propylene conversion, and that some amounts of butyraldehyde dimethylacetal are also produced as a result of the hydroformylation of propylene.

In this connection, attention should be called to the finding of Wender et al.,[6] who stated that the rate of the hydroformylation of cyclohexane is increased by the addition of very small amounts of organic bases and decreased when larger amounts of these bases are present.

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[1] I. Wender and H. W. Sternberg, "Advances in Catalysis," VII, Academic Press, N. Y. (1955), p. 604.

[2] G. Natta, *Brennstoff-Chem.*, 36, 176 (1955).

[3] R. Ercoli, M. Avanzi and G. Moretti, *La Chimica e L'industria*, 37, 865 (1955).

[4] H. Uchida and A. Matsuda, This Bulletin, 37, 375 (1964).

[5] Such standard samples for the gas chromatographic analyses as methylesters of *n*- and isobutyric acids and dimethylacetals of *n*- and isobutyraldehydes were prepared by a reaction of the respective acids and aldehydes with methanol in the presence of *p*-toluenesulfonic acid; they were distilled before use by the aid of a rectifying column of the spinning-band type.

[6] I. Wender, H. Greenfield, S. Martin and M. Orchin, "Catalysis," V. Reinhold Publishing, N. Y. (1957), p. 110.

Table I. Preliminary experiments

Expt. No.[a]	Hydrogen mol.	Pyridine mol.	Propylene conversion mol.%	Products yields per mol. C_3H_6 after 1 hr.'s reaction, mol.			
				n-Ester	*i*-Ester	*n*-Acetal	*i*-Acetal[b]
1	None	None	45	0.32	0.09	0.01	0.004
2	0.1	None	69	0.46	0.12	0.07	0.03
3	0.1	0.03	93	0.64	0.19	0.07	0.03

a) Every run was conducted at the total pressure of 190 kg./cm² at 180°C by use of 0.5±0.01 mol. C_3H_6, 2 mol. CH_3OH, and 4 mmol. $Co_2(CO)_8$ with or without hydrogen and pyridine.

b) Abbreviations *n*-, *i*-esters and *n*-, *i*-acetals stand for methyl esters of *n*- and isobutyric acids, and dimethylacetals of *n*- and isobutyraldehydes respectively.

Table II. Effects of organic bases on the yields of products

Expt. No.	Base	Amount of base mol.	Propylene conversion mol. %	Products yields per mol. C_3H_6 after 1 hr.'s reaction, mol.			
				n-Ester	*i*-Ester	*n*-Acetal	*i*-Acetal
4	None	0	41	0.26	0.08	0.02	0.01
5	Pyridine	0.02	73	0.51	0.14	0.02	0.01
6	Pyridine	0.04	85	0.62	0.17	0.03	0.01
7	Pyridine	0.06	92	0.67	0.19	0.02	0.01
8	*N*, *N*-Dimethylaniline	0.04	42	0.28	0.08	0.02	0.01
9	Quinoline	0.04	54	0.39	0.11	0.02	0.01
10	α-Picoline	0.04	45	0.32	0.09	0.02	0.01
11	Triethylamine	0.004	40	—	—	—	—
12	Triethylamine	0.02	0	0.26	0.08	0.02	0.01
13	Piperidine	0.004	37	—	—	—	—
14	Piperidine	0.02	0	—	—	—	—
15	Benzylamine	0.02	0	—	—	—	—
(16	Zinc acetate	0.008	0	—	—	—	—)

The raw material consisted of 0.5±0.01 mol. C_3H_6, 2 mol. CH_3OH, and was added with 4 mmol. $Co_2(CO)_8$. A small amount of hydrogen (0.02 mol.) was introduced before the autoclave was pressured with CO. Every run was conducted at the total pressure of 190 kg./cm² at 160°C.

This finding suggests that the addition of an appropriate amount of organic bases might serve to improve the selectivity for hydroesterification, even though it might retard the rate of propylene conversion to some extent. A few preliminary experiments made along this line have surprisingly proved that the addition of such a large amount of pyridine as 0.03/0.004 in terms of moles of pyridine/moles of $Co_2(CO)_8$ ratio not only improves the selectivity for hydroesterification, but also increases the rate of propylene conversion (cf. Table I). Accordingly, the effect of a variety of organic bases on the yield of the hydroesterification product will have to be examined more closely.

The Effect of Bases on the Yield of Hydroesterification Product. — Table II summarizes data obtained on the hydroesterifications in the presence of different amounts of various organic bases. Among the bases studied, pyridine has been found to be most effective in the production of methylbutyrate, and the yield increases with the amount of pyridine in the range under investigation; by the use of 0.06 mol. pyridine, the yield of the reaction for 1 hr. attains as high a level as 0.86 mol. from 1 mol. propylene. In contrast to this base, such strong bases as triethylamine, piperidine, and benzylamine inhibit the hydroesterification completely, even in the relatively small amount of 0.02 mol. The effects of *N*, *N*-dimethylaniline, quinoline, and α-picoline on the yield are very small.[7] Further investigation, therefore, will be directed to the problem of the presence of pyridine.

Figures 1, 2 and 3 illustrate plots of the amounts of methyl butyrate and of butyraldehyde dimethylacetal produced vs. the reaction time at the reaction temperatures of 160, 170 and 180°C respectively. The runs were conducted by using the same amounts of raw materials, of hydrogen, and of $Co_2(CO)_8$, as in the runs of Table II, but pyridine was varied

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[7] The hydroesterification does not take place at all in the presence of a very small amount of zinc acetate, which reacts readily with $Co_2(CO)_8$ to form the mixed metal carbonyl.

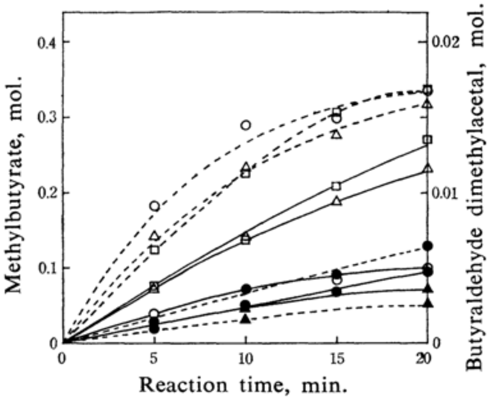

Fig. 1. Products yields from hydroesterification and hydroformylation in the presence of varying amounts of pyridine as function of reaction time.
Full line; methyl butyrate
Dotted line; butyraldehyde dimethylacetal
React. temp., 160°C

Expt. No.	17	18	19	20	21
Pyridine, mol.	0	0.03	0.06	0.09	0.12
Mark	○	△	□	●	▲

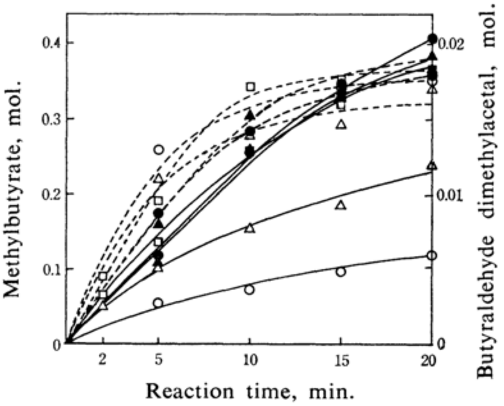

Fig. 2. Products yields from hydroesterification and hydroformylation in the presence of varying amounts of pyridine as function of reaction time.
Full line; methyl butyrate
Dotted line; butyraldehyde dimethylacetal
React. temp., 170°C

Expt. No.	22	23	24	25	26
Pyridine, mol.	0	0.03	0.06	0.09	0.12
Mark	○	△	□	●	▲

in amount at 0.03 mol. intervals between 0 and 0.12 mol. The figures show that, throughout every series of runs at the different reaction temperatures, the amount of methyl butyrate produced after a 20 min. reaction increases with the amount of pyridine, reaches a maximum, and then decreases. The optimum amount of pyridine is increased as the reaction temperature is raised.

As is evident from the formula of $C_3H_6+CO+H_2 \rightarrow C_3H_7CHO$ for the hydroformylation, the

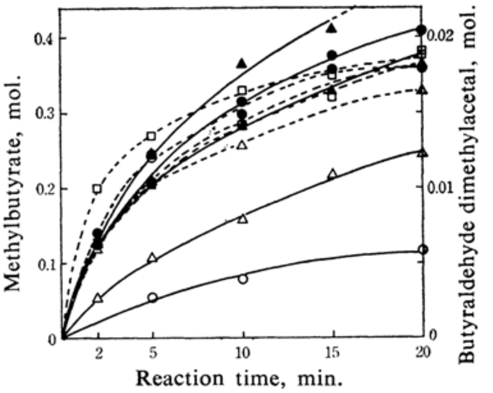

Fig. 3. Products yields from hydroesterification and hydroformylation in the presence of varying amounts of pyridine as function of reaction time.
Full line; methyl butyrate
Dotted line; butyraldehyde dimethylacetal
React. temp., 180°C

Expt. No.	27	28	29	30	31
Pyridine, mol.	0	0.03	0.06	0.09	0.12
Mark	○	△	□	●	▲

hydrogen in an autoclave tends to diminish as the hydroformylation proceeds, and the amount of butyraldehyde or its dimethylacetal in the products can not exceed 0.02 mol., which is equivalent to the initial hydrogen content in the autoclave. In fact, the acetal remains about 0.018 mol. at the most. These facts make it difficult to estimate the selectivity for hydroesterification from a simple comparison of the experimental rate of hydroesterification with that of hydroformylation, unless a certain attention is paid to the amount of hydrogen existing in the autoclave. In connection with this, a more reasonable measure of the selectivity may be given by means of the ratio of the initial rate at the zero-conversion of propylene for hydroesterification (hereafter denoted by r_{oe}) to the corresponding rate for hydroformylation (hereafter denoted by r_{of}); at this stage, the amount of hydrogen is 0.02 mol. The values of r_{oe} and r_{of} are obtained from slopes of the tangents drawn along the plots at the origin.

The Effect of Pyridine on the Initial Rates of Hydroesterification and Hydroformylation at Zero-conversion.—Figure 4 illustrates the plots of r_{oe} vs. the amount of pyridine for series of runs at 160, 170, and 180°C. Every plot first rises with the amount of pyridine, and in each the rise at the higher temperature is more rapid than that at the lower temperature. At 160 and 170°C, the maximum of the curve appears at the pyridine amount of 0.06 mol., whereas at 180°C the r_{oe} is maintained essentially constant over the range from 0.06 to 0.12 mol. of pyridine.

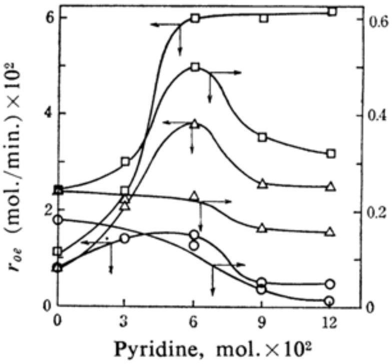

Fig. 4. Initial rates at zero-conversion of propylene for hydroesterification (r_{oe}) and hydroformylation (r_{of}) as function of pyridine amount.
React. temp.: ○ 160°C, △ 170°C, □ 180°C

Figure 4 includes the same plots with respect to r_{of}. The situation is different from that of r_{oe}; the plots of r_{of} at 160 and 170°C continue to be lowered slowly with the amount of pyridine, but the plot at 180°C shows a slight maximum at 0.06 mol. The retarding effect of pyridine on the initial hydroformylation rate becomes so remarkable at lower reaction temperatures that the reaction at 160°C is almost completely inhibited by the addition of 0.12 mol. of pyridine.

Figure 5A presents selectivity data for hydroesterification at 160, 170, and 180°C. The curve at 180°C shows an approximately linear increase over the whole range of pyridine amount studied, whereas the curves at 160 and 170°C show the increase only in the range below 0.06 mol. Beyond that amount of pyridine, the ratios stay on the same level, about 12. It should be noted that the molar ratio, $C_3H_7CHO/C_3H_7CH(OCH_3)_2$, after the reaction of 1 hr. is much higher than the r_{oe}/r_{of} ratio; e. g., the former ratio from run No. 7 in Table II is twice as large as the latter ratio of run No. 29. The ratio of r_{oe}/r_{of} thus can not directly relate the yield ratio after a prolonged duration of a batchwise reaction, where the initial hydrogen is allowed to diminish as the reaction proceeds.

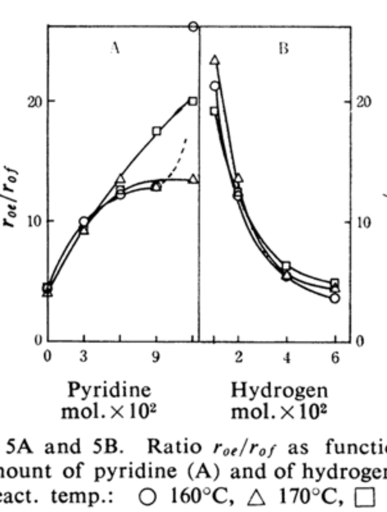

Fig. 5A and 5B. Ratio r_{oe}/r_{of} as function of amount of pyridine (A) and of hydrogen (B).
React. temp.: ○ 160°C, △ 170°C, □ 180°C

The Effect of Hydrogen on the Initial Rates of Hydroesterification and Hydroformylation at Zero-conversion.—The r_{oe} and r_{of} values in the presence of various amounts of hydrogen in an initial charge of autoclave were determined by the above-described method. The runs for this purpose were always conducted with the same amounts of raw materials, while the pyridine amount was fixed at 0.06 mol. The hydrogen amount was varied at intervals from 0 to 0.06 mol. Figure 6 illustrates plots of r_{oe} vs. the initial hydrogen amount in the autoclave at 160, 170, and 180°C. Every curve first rises with the amount of hydrogen, reaches a maximum, and then decreases slowly. The rise of the curve at the high temperature is more rapid than that at the lower temperature; at 180°C, the r_{oe} in the presence of 0.02 mol. hydrogen can be five times as fast as the r_{oe} in its absence. It is natural that the r_{of} should increase with the hydrogen amount, as is shown in Fig. 6.[8]

As is shown in Fig. 5B, three plots at 160, 170, and 180°C of r_{oe}/r_{of} vs. the initial amount of hydrogen similarly decrease with the amount of hydrogen. The initial hydrogen amount in an autoclave should be less than 0.01 mol. in order to have such a high selectivity for the hydroesterification as 15 in terms of the r_{oe}/r_{of} ratio. This initial hydrogen content in the

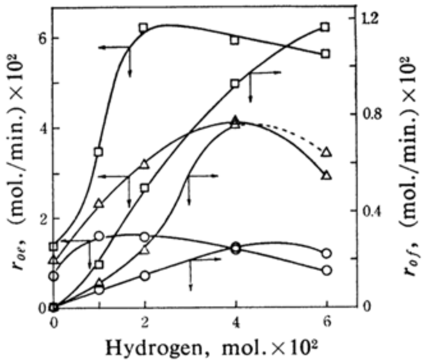

Fig. 6. Dependency of r_{oe} and r_{of} on hydrogen amount.

	Expt. No.	React. temp.
-○-	32—35	160°C
-△-	36—39	170°C
-□-	40—43	180°C

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[8] Figure 6 indicates falls in both the r_{oe} and r_{of} by the addition of 0.06 mol. hydrogen at the lower reaction temperatures. There is, as yet, no probable explanation of this finding.

autoclave at the reaction conditions is equivalent to 0.013 in terms of the H_2/CO molar ratio.

The Initial Rate of Hydroesterification as a Function of the Propylene Concentration.—Although Ercoli et al.[3] have pointed out the zero-order reaction of the hydroesterification of olefins, such as 1-hexene, cyclohexene, and 2-ethyl-1-hexene, with respect to the olefin concentration, the data presented here on this reaction of propylene, as shown in Figs. 1—3, are rather suggestive of another order, presumably of the first order. However, the experimental runs in the figures were conducted in such a manner that the hydrogen in an initial charge of the autoclave was allowed to decrease with the progress of a simultaneous side-reaction, hydroformylation; hence, the data are not sufficient for us to draw a conclusion from them. An alternative run, therefore, was attempted, in which the hydrogen content was kept at a constant level during the run. The autoclave was charged with the raw material consisting of 0.51 mol. of C_3H_6, 2 mol. of CH_3OH, 0.06 mol. of pyridine, and 1 mmol. of $Co_2(CO)_8$ placed in a stainless steel saucer; then carbon monoxide containing 2.7% hydrogen was introduced. The initial hydrogen in the gas phase under the reaction conditions amounted to 1.9 mol.%. During the run, the synthesis gas (composed of 91.9% CO, 6.3% H_2, and 1.8% N_2) was continuously introduced from the pressure storage in order to maintain the total pressure at 190 kg./cm^2 at 180°C, and pressure drops in the storage with the reaction time were recorded, from which values the amounts of the gas supplied, V_s (mol.), could be calculated.

When the run was finished, after 1 hr., V_s amounted to 0.526 mol., and propylene was reduced to 0.05 mol. from 0.51 mol., corresponding to a 90% conversion of propylene. The hydrogen was found to be 1.7 mol. %, almost the same as the initial content. The products were 0.32, 0.09, 0.02, and 0.01 mol. for methyl esters of *n*- and isobutyric acids and for dimethylacetals of *n*- and isobutyraldehydes respectively. The sum of products was 0.44 mol. No products other than ethyl acetate[9] (less than 0.005 mol.) were detected. On the basis of these data, the percentage conversion of propylene was calculated to be 86%; this rate is close to, but not identical with, the value obtained from the data of propylene consumption.[11]

In a previous paper[4] dealing with the hydroformylation of propylene, it was described how the amount of synthesis gas supplied stands for the sum of two portions, one consumed by the hydroformylation itself and the other, that necessary to compensate for the fall in partial propylene pressure as the reaction proceed, and that the amount of gas supplied for a hydroformylation run, V_{sf} (mol.), is expressed by:

$$\left.\begin{aligned} & V_{sf}=2(c_0-c)+ap_0(c_0-c)/c_0 \\ \text{or}\quad & V_{sf}=(2+ap_0/c_0)(c_0-c) \end{aligned}\right\} \quad (1)$$

where c_0 (mol.) is the initial propylene concentration; c (mol.) is the concentration at the reaction time t, p_0 is the initial partial propylene pressure, and a is a coefficient whose value is dependent on the reaction temperature. Similarly, the amount of gas supplied for a run of hydroesterification, V_{se} (mol.), is expressed by:

$$V_{se}=(1+ap_0/c_0)(c_0-c) \quad (2)$$

In the present run, in which both of the reactions occur, the amount of gas supplied, V_s (mol.), is, hence, given by Eq. 3, if it may be assumed that the (moles of gas consumed by hydroestrification)/(moles of gas consumed by hydroformylation) ratio remains invariable during the run.

$$V_s=\alpha(c_0-c) \quad (3)$$

where α is a coefficient whose value lies in a range between $(2+ap_0/c_0)$ and $(1+ap_0/c_0)$.

The substitution of the experimental data of V_s at $t=60$ min. (0.526 mol.), c_0 (0.51 mol.), and c at $t=60$ min. (0.05 mol.) into Eq. 3 results in the evaluation of α as 1.14.[12] Once α is evaluated, c at any t can, in turn, be calculated by the aid of Eq. 3.

As is shown in Fig. 7, a plot of (c_0-c) vs. t is not linear, whereas a plot of $\ln(c_0/c)$ is linear. This finding leads to the following expression of the over-all initial rate of propylene consumption, r (mol./min.):

$$r=-\mathrm{d}c/\mathrm{d}t=kc \quad (4)$$

In the present run, the over-all initial rate is the sum of two initial rates, the initial rate of propylene consumption by hydroesterification, r_e, and the initial rate by hydroformylation, r_f:

$$r=r_e+r_f=kc \quad (5)$$

On the other hand, it has already been shown that the r_f is of the first-order with respect to propylene concentration, namely, $r_f=k'c'$, hence,

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[9] Ethylacetate can be a product of acetaldehyde, which is produced from methanol under the reaction conditions of oxo synthesis (cf. Ref. 10).

[10] G. Natta and R. Ercoli, "Catalysis," II, Reinhold Publishing, N. Y. (1957), p. 171.

[11] The disagreement may perhaps be due to an inaccuracy in the determinations of propylene and its products.

[12] This value of α is applicable only to the data of the present run.

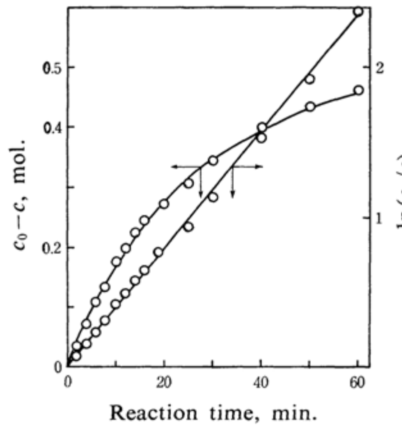

Fig. 7. Amount of propylene consumed under high pressure of carbon monoxide containing hydrogen at 180°C plotted against reaction time (Expt. No. 44).

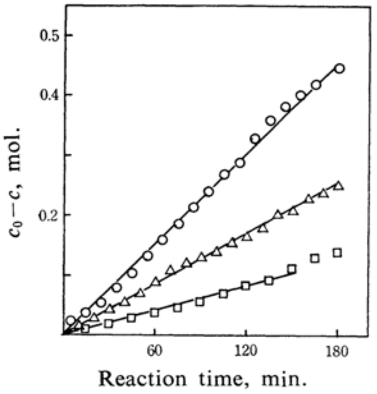

Fig. 8. Amount of propylene consumed under high pressure of pure carbon monoxide at 180°C plotted against reaction time.

	Expt. No.	$Co_2(CO)_8$, mmol.
-□-	45	1
-△-	46	2
-○-	47	4

$$r_e+k'c=kc \quad \text{or} \quad r=(k-k')c \qquad (6)$$

Equation 6 plainly indicates that the initial rate of hydroesterification is first-order with respect to propylene concentration, provided that the run is conducted in the presence of excess pyridine and with carbon monoxide containing a small amount of hydrogen.

Runs (No. 45—47) were conducted with pure carbon monoxide[13] in order to compare them with run No. 44. In these runs, the same amounts of propylene and methanol as in run No. 44 were used with no pyridine, while $Co_2(CO)_8$ was varied in amount over a range from 1 to 4 mmol. The data are presented as plots of (c_0-c) vs. t. The plots are linear, showing that the hydroesterification is zero-order with respect to propylene concentration, in accordance with the result of Ercoli et al.[3] Moreover, an approximately linear relationship is found between the initial rate and the amount of $Co_2(CO)_8$. It should also be noted that the initial rate, as conventionally expressed by $(c_0-c)/t$ (mol./min.), where $(c_0-c)=0.1$ mol., of run No. 44 in Fig. 7 is about 30 times as high as the rate of run No. 45 in Fig. 8 with the same amount of $Co_2(CO)_8$ (1 mmol.).

Ercoli et al.[3] stated that cobalt hydrocarbonyl can be the real catalyst for the hydroesterification of olefins. Therefore, it is likely that the addition of hydrogen results in an increase in the initial rate, for the addition considerably facilitates the formation of the hydrocarbonyl. However, in the presence of excess pyridine and methanol, other salts, which contain $[Co(CO)_4]^-$ as an anionic constituent, can be formed. These salts may be, for instance, $[Co(CH_3OH)_6][Co(CO)_4]_2$, $[Co(Pyr)_6][Co(CO)_4]_2$, and $[PyrH][Co(CO)_4]$, and they presumably participate in the reaction as catalysts, either positive or negative. However, no satisfactory interpretation of the effects of hydrogen and pyridine on the initial rate of this reaction can be expected until sufficient knowledge of the catalyst materials and their catalytic behaviors are available.

Summary

Propylene can be hydroesterified to methyl butyrate in a good yield and with an initial rate as high as the initial rate of the hydroformylation of propylene, provided a small amount of hydrogen and excess pyridine are present. Detailed data on the initial rates at the zero-conversion of propylene for both the hydroesterification and hydroformylation and the ratio between the two initial rates have been presented as a function of the amount of pyridine and hydrogen, together with data on the products obtained from the respective reactions.

The initial rate of hydroesterification in this study has proved to be first-order with respect to the propylene concentration. This result is different from that of Ercoli et al., who carried out hydroesterification runs of olefins with pure carbon monoxide.

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[13] The carbon monoxide contained 0.3% hydrogen.