

# Effect of Organic Bases on the Hydroesterification of Propylene

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The hydroesterification of propylene with carbon monoxide and *n*-butanol (monohydric alcohols) at 160°C and in the presence of octacarbonyldicobalt functioning as a catalyst is activated mainly by  $\beta$ - and  $\gamma$ -picoline while  $\alpha$ -picoline, lutidines, and collidines are practically inactive. According to their activation effect, the bases investigated may be arranged in the sequence  $\beta$ -picoline  $\geq$  pyridine  $\geq$   $\gamma$ -picoline  $>$  quinoline  $>$   $\alpha$ -picoline, lutidines.

Mono-, di-, and triethanolamine as well as ammonia have only retardation effect.

On the other hand,  $\beta$ -picoline has a distinct retardation effect provided glycols have been used for the hydroesterification of propylene instead of monohydric alcohols.

It was found some time ago [1–4] that the bases present in small proportions have an activation effect on the hydroformylation of olefins. This effect is mainly due to speeding up the formation of cobalt carbonyls from cobalt(II) salts. But at higher concentrations, they retard or even stop hydroformylation since they form with cobalt carbonyls some catalytic inactive complexes. In the case of hydroesterification of olefins, the effect of organic bases is, however, different, especially from the quantitative point of view. Thus the use of considerable concentrations of pyridine results in stopping the hydroformylation [1, 5–7] while the hydroesterification is only partially suppressed [8]. But the presence of controlled quantities of pyridine in the reaction system where the hydroesterification of olefins takes place has an influence on the formation of isomers [9] and at the same time it raises the reaction rate considerably [9–13]. The presence of pyridine in reaction medium is even necessary for the hydroesterification to be successful [13, 14].

Among the bases investigated till now, pyridine has a quite exceptional position. It increases the rate of hydroesterification and hydrocarboxylation more than other bases which are either nearly ineffective under equal conditions ( $\alpha$ -picoline, quinoline, *N,N*-dimethylaniline, piperidine) [8, 14] or even inhibit hydroesterification (triethylamine, benzylamine) [8]. The inactivity of  $\alpha$ -picoline [8, 14] contrasting with pyridine, is explained [15] by the derangement of coplanar structure of the ion formed in the reaction of  $\alpha$ -picoline with intermediary acyl in the last but one step of the reaction mechanism of hydroesterification. Similar results have also been obtained with  $\alpha, \alpha'$ -lutidine and quinoline [15].

## Experimental

### *Substances*

Propylene — purity 99.5 weight %,  $1.5 \times 10^{-2}$  weight % of propane,  $2 \times 10^{-4}$  weight % of ethane,  $9 \times 10^{-5}$  weight % of water approximately.

Carbon monoxide — purity 98.6 weight %, 0.3 weight % of hydrogen, 0.3 weight % of carbon dioxide, 0.1 weight % of oxygen.

Mono-, di-, and triethanolamine were products of W. Pieck Chemical Works, Nováky.

Monoethanolamine — b.p. 170–172°C/757 Torr, purity 95.6 weight %, 4.4 weight % of water,  $n_D^{20}$  1.4438,  $d_4^{20}$  1.0349 g cm<sup>-3</sup>.

Diethanolamine — fraction with b.p. 150–153°C/12 Torr, purity 94 weight %, 1.35% of monoethanolamine, 3.3% of triethanolamine, 0.5 weight % of water,  $n_D^{20}$  1.4673,  $d_4^{20}$  1.0990 g cm<sup>-3</sup>.

Triethanolamine — fraction with b.p. 205–210°C/10 Torr, purity 85 weight %, 13.9% of diethanolamine, 0.4% of water,  $n_D^{20}$  1.4818,  $d_4^{20}$  1.1266 g cm<sup>-3</sup>.

Octacarbonyldicobalt — twice recrystallized from petroleum ether, spectral purity.

Pyridine — b.p. 115.4°C/754 Torr,  $n_D^{20}$  1.5028,  $d_4^{20}$  0.9868 g cm<sup>-3</sup>.

$\alpha$ -Picoline — b.p. 129.4°C/754 Torr,  $n_D^{20}$  1.5010,  $d_4^{20}$  0.9443 g cm<sup>-3</sup>.

$\beta$ -Picoline — b.p. 143.4–143.8°C/754 Torr,  $n_D^{20}$  1.4968,  $d_4^{20}$  0.9566 g cm<sup>-3</sup>.

$\gamma$ -Picoline — b.p. 144.8–144.9°C/754 Torr,  $n_D^{20}$  1.5057,  $d_4^{20}$  0.9548 g cm<sup>-3</sup>.

2,6-Lutidine — b.p. 156.4–156.6°C/757 Torr,  $d_4^{20}$  0.9381 g cm<sup>-3</sup>.

2,4,6-Collidine — b.p. 169.8–169.9°C/757 Torr,  $n_D^{20}$  1.4979,  $d_4^{20}$  0.9139 g cm<sup>-3</sup>.

1,8-Octanediol — b.p. 172°C/20 Torr, purity 99.8 weight %.

Quinoline — b.p. 108.8°C/10 Torr,  $n_D^{20}$  1.6267,  $d_4^{20}$  1.0931 g cm<sup>-3</sup>.

Ammonium hydroxide — concentration 25 weight %.

*n*-Butanol, toluene, ethylene glycol; anal. grade.

Diethylene glycol — purity 98.5 weight %, 0.1% of water, 0.4% of monoethylene glycol.

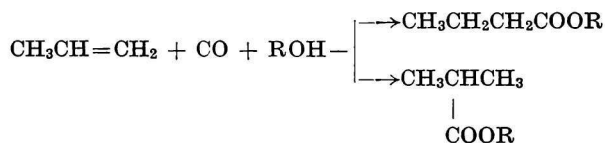
Triethylene glycol — purity 95.5 weight %, 0.6% of monoethylene glycol, 3.3% of diethylene glycol.

### Procedure

Alcohol, the quantity of which did not usually exceed 2 moles and the admixtures of bases were weighed and put into a half-liter autoclave together with a special ampoule containing 0.002 mole of octacarbonyldicobalt and *ca.* 10 ml of alcohol. On removing the air, the weighed amount of propylene (0.5 mole) was added and carbon monoxide was introduced until its pressure reached about 125 kp cm<sup>-2</sup>. Then the autoclave was heated to 160°C. After reaching this temperature, the solution of octacarbonyldicobalt was brought from the ampoule into reaction medium and the autoclave was set in rotation. The temperature was kept constant with the accuracy of  $\pm 2^\circ\text{C}$  and the drop of pressure (180–140 kp cm<sup>-2</sup>) was recorded in time intervals of 5–10 minutes. After 120 minutes the experiment was stopped by letting the content of autoclave go through an efficacious cooler. Then the mixture was weighed and analyzed. The conversion of propylene was calculated from the weight of the product obtained and checked by the measured drop of pressure.

### Results and Discussion

As evident from the results of the propylene hydroesterification



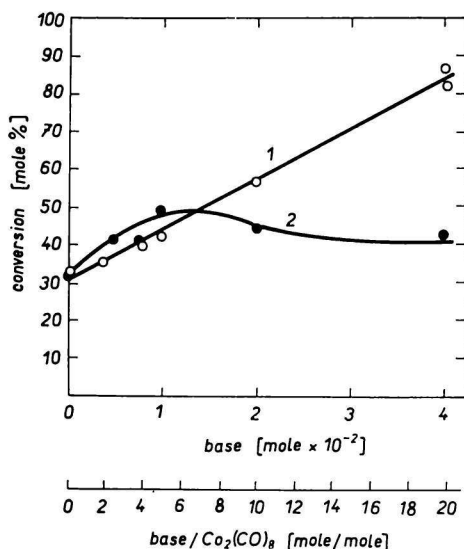


Fig. 1. Dependence of the conversion of propylene in the hydroesterification with carbon monoxide and *n*-butanol on the amount of  $\beta$ -picoline or quinoline.

1.  $\beta$ -picoline; 2. quinoline.

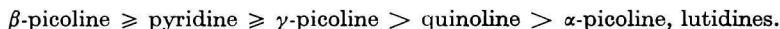
catalyzed by octacarbonyldicobalt in the presence of various bases or in the absence of them under equal reaction conditions, it is  $\beta$ -picoline and  $\gamma$ -picoline which besides pyridine raise the conversion of propylene into the products of hydroesterification. We have thus confirmed the rightness of some information [8–15] on the effect of pyridine,  $\alpha$ -picoline, and other bases on hydroesterification. Moreover we picked up some new pieces of knowledge on this problem. The positive effect of  $\beta$ -picoline is even higher than that of pyridine. On the other hand,  $\alpha$ -picoline, 2,6-lutidine, 2,4,6-collidine, and formamide do not practically influence the rate of hydroesterification whereas monoethanolamine, diethanolamine, triethanolamine, and ammonia have a marked retardation effect.

While the conversion of propylene in the presence of pyridine as well as  $\gamma$ -picoline was twofold in comparison with that in the absence of bases, the conversion in the presence of  $\beta$ -picoline was 2.6 times greater. A 1.35-fold conversion was also obtained with quinoline.

A smaller weight ratio of butyl butyrate to butyl isobutyrate in the product obtained in the presence of pyridine and picolines when compared with the results of reference experiments performed without addition of organic bases indicates to some extent that the pertinent complex compounds of pyridine and picolines with cobalt carbonyls are also catalytically active in the hydroesterification of olefins.

The other results concerning the effect of  $\beta$ -picoline and quinoline on the conversion of propylene in hydroesterification under conditions quoted in Table 1 are presented in Fig. 1.

In the order of their activation effect on the hydroesterification of propylene, the bases investigated may be arranged approximately in the sequence



The retardation effect of mono-, di-, and triethanolamine as well as of ammonia may be explained in a similar manner as in the case of hydroformylation [3, 4]. It can be supposed that they react nearly irreversibly with cobalt carbonyls, espe-

Table 1

Effect of different bases on the hydroesterification of propylene with *n*-butanol and carbon monoxide

Base	Quantity		Conversion of propylene into products of hydroesterification [%]	Weight ratio of butyl butyrate to butyl isobutyrate in the products of hydroesterification
	[g]	[moles]		
—	reference experiment		32.8	3.0
—	reference experiment		31.6	2.8
pyridine	3.16	0.04	65.7	2.2
$\alpha$ -picoline	3.72	0.04	34.4	2.0
$\beta$ -picoline	3.72	0.04	87.2	2.3
$\beta$ -picoline	3.72	0.04	82.5	2.3
$\gamma$ -picoline	3.72	0.04	63.0	2.1
2,6-lutidine	4.28	0.04	34.3	2.2
2,4,6-collidine	4.85	0.04	31.8	2.7
quinoline	5.16	0.04	43.3	2.4
formamide	2.00	0.04	30.5	2.4
monoethanolamine	2.44	0.04	7.1	—
diethanolamine	4.20	0.04	7.3	—
triethanolamine	5.95	0.04	12.8	—
ammonia	2.74 (25%)	0.04	15.7	—
ammonia	0.544 (25%)	0.008	30.1	2.6

Table 2

Yields obtained in the hydroesterification of propylene with alcohols and carbon monoxide in the presence of different admixtures

Content of admixtures						Conversion of propylene into products of hydroesteri- fication [%]
Alcohols and solvents			Bases			
Alcohol or solvent	Quantity		Kind of base	Quantity		
	[g]	[moles]		[g]	[moles]	
<i>n</i> -butanol	148.2	2	—	—	—	31.6
<i>n</i> -butanol	148.2	2	—	—	—	38.6
ethylene glycol	7.5	0.12	—	—	—	—
<i>n</i> -butanol	148.2	2	—	—	—	29.2
diethylene glycol	7.5	0.07	—	—	—	—
diethylene glycol	106.1	1	—	—	—	48.6
diethylene glycol	106.1	1	$\beta$ -picoline	3.72	0.04	0
diethylene glycol	106.1	1	$\beta$ -picoline	1.86	0.02	1.6
diethylene glycol	106.1	1	NH <sub>3</sub> (25%)	1.4	0.04	0
triethylene glycol	150.2	1	—	—	—	50.0
triethylene glycol	150.2	1	$\beta$ -picoline	3.72	0.04	23.8
triethylene glycol	150.1	1	$\beta$ -picoline	3.72	0.04	24.4
1,8-octandiol	73.5	0.50	$\beta$ -picoline	3.72	0.04	61.3
toluene	73.1	0.79	—	—	—	—
ethylene glycol	62	1	—	—	—	—
toluene	84	0.91	$\beta$ -picoline	3.72	0.04	20.0

cially with cobalt tetracarbonyl hydride under formation of some stable and catalytically inactive complexes. Thus the activation or retardation effect of bases depends on the fact whether they are able to form unstable or stable complex compounds with cobalt carbonyls.

An interesting phenomenon occurs when glycols are present instead of monohydric alcohols in the system. As evident from the results given in Table 2, the conversion of propylene in isochronous experiments performed at about 160°C was about 32% in the presence of *n*-butanol and nearly 50% in the presence of glycols. But in contrast to monohydric alcohols, the admixtures of  $\beta$ -picoline in the presence of glycols retard or even make the hydroesterification impossible.

However, it can be observed that the retardation effect of  $\beta$ -picoline decreases with increasing length of hydrocarbon chain of the molecules of diols.

These results indicate that also the complex compounds of cobalt carbonyls with  $\beta$ -picoline,  $\gamma$ -picoline, pyridine and eventually other bases may be effective as hydroesterification catalysts. The intermediary complex formed in the reaction of these complex compounds with olefin and carbon monoxide which reacts with monohydric alcohols may not be able to react with glycols under formation of the ester and regeneration of the catalyst because of steric relations (bulky molecules of bases and hydroxyl groups).

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