

Reductive Carbonylation of Ethanol (Homologation of Ethanol) Using Homogeneous Cobalt-Ruthenium Catalysts

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The homologation of ethanol has been achieved in the presence of cobalt-ruthenium catalysts. Conditions can be selected such that propanol and its derivatives are the main products. A systematic study of the influence of various parameters has been undertaken. Determining parameters are the nature of the promoter and the pressure. The homologation process is believed to proceed (at least partially) via an olefinic intermediate which is subsequently hydroformylated. The exact role of the mixed catalyst (which introduces a synergism in the production of propanol) is still unclear. © 1987 Academic Press, Inc.

INTRODUCTION

The homologation of methanol to ethanol has been and continues to be the subject of numerous patents and papers (1-3). The major problem is the selectivity to C₂H₅OH, since usually high selectivities are reached only at low or moderate conversions. In recent times, however, selectivities as high as 80-90% were claimed with appreciable rates (4, 5). Ethanol is a valuable industrial product which may become the preferred material for the synthesis of ethylene, as well as being an excellent precursor for the synthesis of saturated long chain alcohols, if produced economically in large quantities. The synthesis of higher alcohols is an extremely interesting extension of the homologation reaction, because these alcohols can be used as additives to gasoline and, in addition, be dehydrated to produce α -olefins.

The hydrocarbonylation of alcohols other than methanol, however, has hardly been explored, except in the case of benzyl alcohol (6). They were shown to undergo homologation like methanol though at a considerably lower rate (7). An obvious dis-

advantage is that the reaction requires high pressure (80-100 MPa) (8). This is also the case when the direct synthesis of alcohols (C₁ to C₉) from syngas is performed in various media as the minimum pressure required is 300 MPa in the presence of soluble ruthenium catalysts (9). In this case, the concentration of the alcohols produced follows approximately a Schulz-Flory distribution (except, oddly enough, for ethanol and propanol), indicative of a polymerization reaction.

The best recognized homologation catalytic systems are combinations of cobalt compounds and iodine or iodide promoters via the intermediate HCo(CO)₄ which is formed *in situ*. Elemental iodine is often preferred, since it seems to exhibit a greater promoting effect than either alkali iodides (which is probably due to a cation effect) or covalent iodides (4, 10). The effect of promoters in the homologation of methanol and higher alcohols has recently been reviewed (11).

In recent years, ruthenium complexes have been increasingly used in conjunction with cobalt compounds to achieve homologation of various compounds (12-14). In the specific case of the hydrocarbonylation of methanol, the catalytic mixture (Co-Ru)

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shows enhanced activity and sometimes improved selectivity to ethanol (15–17). It was assumed that ruthenium does not combine with cobalt to form a new active species, but readily hydrogenates the acetaldehyde intermediate formed (17).

These results prompted us to look into the reductive carbonylation of ethanol, the next higher alcohol, in the presence of cobalt and ruthenium catalysts or their mixtures.

EXPERIMENTAL

Reagent grade ethanol was dried over molecular sieves and distilled before use. The catalysts used were cobalt acetate, tetrahydrate (Prolabo), and ruthenium acetylacetonate (Johnson Matthey). A typical batch run was conducted as follows. The 15-ml high pressure autoclave was flushed by means of an argon stream and filled with catalyst (0.9 mmol of metal), promoter (1.5 mmol), and ethanol (90 mmol). The autoclave was then closed, connected to the pressure line and charged with the appropriate CO:H₂ mixture up to the desired pressure. After disconnection from the line, the vessel was heated and shaken for a constant reaction time. The pressure drop was followed continuously. After cooling to ambient temperature, the pressure was released very slowly; a gas sample was taken for analysis and the autoclave opened. After addition of 200 μ l of diglyme (internal standard), the liquid phase was collected and analyzed by GC.

(a) Analysis of gases: Intersmat IGC 12 M (catharometer), injection (200°C), detection (170°C), column (6 m, ϕ 3.2 mm, Porapak Q 80–100 mesh).

(b) Analysis of liquids: Intersmat IGC 120 M (catharometer), injection (200°C), detection (250°C), columns (Porapak R, 3 m, ϕ $\frac{1}{8}$ in., 65–230°C, 2°C/min, with the combination of IGEPAI – CO 880 10% on Chromosorb W80/100, 4 m, ϕ $\frac{1}{8}$ in. and DEGS 10% on Chromosorb WHDS 80–100, 8 m, ϕ $\frac{1}{8}$ in., 35–120°C, 2°C/min).

The following symbolism and definitions

will be used: Et₂O—diethyl ether, EtOPr—ethylpropyl ether, Pr₂O—di-*n*-propyl ether, PrOH—*n*-propanol, BuOH—*n*-butanol, EtOAc—ethyl acetate, EtPr—ethyl propionate, PrPr—propyl propionate, EtCHO—*n*-propanal, EtCO₂—propionic acid.

The selectivity to a product X is the ratio (percent ethanol converted into X: percentage ethanol converted into products). τ is the ratio [Co]/([Co] + [Ru]).

RESULTS

The effect of various parameters on the homologation process was extensively investigated. The major detectable organic reaction products were ethers (diethyl ether ethylpropyl ether, di-*n*-propyl ether), alcohols (*n*-propanol, *n*-butanol, but neither isopropanol nor isobutanol), an acid (propionic acid, but with a very low yield), esters (ethyl acetate, ethyl propionate, propyl propionate), and propionaldehyde (under special conditions, *vide infra*). Formates were almost absent in the reaction mixture: under GC FID conditions, very small amounts of ethyl formate (the only formate) were sometimes detected. All these products are normally expected on the basis of the corresponding methanol reaction.

In each run, the typical gas composition was as follows: unreacted syngas, carbon dioxide, alkanes (ethane 95%, propane 4.8%, *n*-butane 0.2%). The composition hardly changed from one run to another, except at temperatures above 200°C or at high ruthenium concentrations favoring hydrocarbon formation. Only relatively small amounts of gases are produced (2–8% based on transformed ethanol) for optimal catalytic ratios (*vide infra*) and when using moderate temperatures (180°C and less).

1. Effect of Catalyst Composition on Product Formation and Ethanol Conversion

Table I lists the data recorded for various catalytic molar ratios [Co]/([Co] + [Ru]).

TABLE I
Influence of the Catalyst Composition on the Product Distribution^a

Run	τ^b	Ethanol conversion (%)	Liquid products (mmol)									Σ^c (%)
			Et ₂ O	EtOAc	PrOH	BuOH	EtOPr	Pr ₂ O	EtPr	PrPr	EtCO ₂ H	
1130	0 ^d	81	16.8	0.3	1.4	0	0.8	0	2.5	0.1	0.3	2.0
1161	0.33	76	14.9	0.3	2.5	0	3.1	0	1.7	0.1	0.6	3.8
1158	0.50	70	14.5	0.4	3.8	0.1	3.6	0	3.4	1.2	0.3	6.2
1160	0.67	61	9.1	0.9	6.3	0.2	5.4	0.3	2.0	0.5	0.4	11.9
1164	0.80	53	7.0	0.2	7.1	0.3	6.4	0.7	2.2	0.4	0.4	15.4
1106	0.83	58	9.4	0.2	9.6	0.4	4.8	0.4	1.5	0.7	0.2	18.4
1165	0.87	70	16.4	1.6	4.1	0.2	4.6	0.2	2.7	0.5	0.6	8.0
1084	1	67	16.4	1.4	2.3	0.2	1.4	0.1	1.7	0.5	0.7	3.9

^a Reaction conditions. Ethanol (89 mmol), catalyst (0.9 mmol), iodine (1.5 mmol), $T(200^\circ\text{C})$, $P(30\text{ MPa})$, $\text{CO}:\text{H}_2$ (1:2), time (3 h).

^b Molar ratio $[\text{Co}]/([\text{Co}] + [\text{Ru}])$.

^c Selectivity to free propanol in the liquid phase.

^d Ruthenium acetylacetonate as only catalyst.

As can be seen from the table, a marked effect is observed both in the conversion of ethanol and the selectivity to higher alcohols (propanol + butanol) when both catalysts are used together. With the cobalt or the ruthenium catalyst used alone, a high conversion of ethanol is achieved, but the major liquid product (by far) is diethyl ether. This result demonstrates the difficulty of homologating ethanol with cobalt catalysts, as described earlier in the literature (17), in sharp contrast with the corresponding methanol reaction.

The fact remains that cobalt acetate used together with the ruthenium catalyst promotes the production of propanol (particularly free propanol). Optimum conditions would appear to be τ -values around 0.80–0.83 under the conditions of Table 1. For these ratios, the yield of free or total propanol is highest. When both catalysts are used together, the conversion decreases slowly with a minimum marked at about $\tau = 0.80$. The lowering of the conversion is due to a dramatic catalyst effect on the etherification reaction: the dehydration of ethanol is reduced by a factor of 2, probably due to the increase of the propanol concentration since di-*n*-propyl and ethylpropyl

ether are formed in relatively high amounts, thus excluding a weakening of the acidity of the medium.

The formation of the higher alcohol, *n*-butanol, is also enhanced by the mixed catalytic system. The concentration of the C₄ alcohol, however, remains low, which shows how difficult it is to perform the homologation of higher alcohols.

On the other hand, propionates are not really favored by the combination of the two catalysts. This may result from a lowering of the carbonylation power of the cobalt catalyst, due to the presence of the hydrogenation ruthenium catalyst.

Ethyl acetate is a minor product as long as $\tau < 0.83$. Only in runs 1165 and 1084 where the cobalt concentration is highest, the carbonylation of ethanol yields higher amounts of acetate. Interestingly propyl formate is either not formed or barely formed in the homologation reaction.

As a first conclusion, the association of a ruthenium and a cobalt catalyst promotes the homologation of ethanol.

2. Effect of Pressure

The role of pressure in homologation processes is somewhat puzzling and not cor-

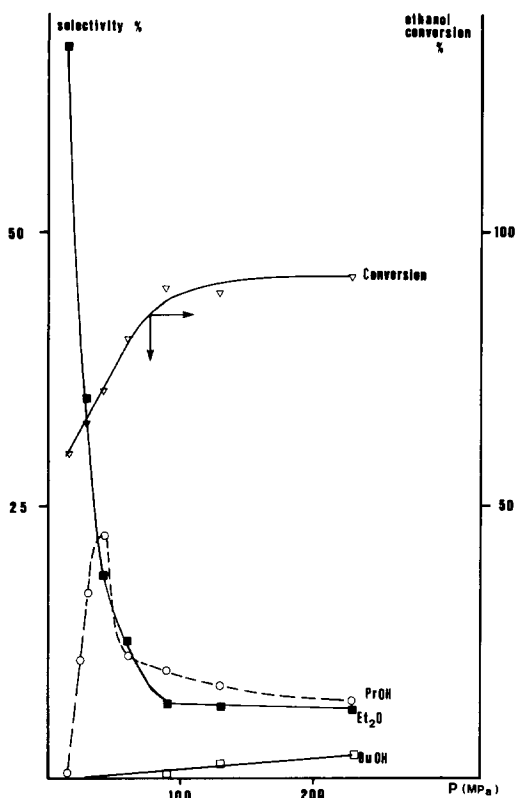


FIG. 1. Homologation of ethanol. Pressure effect (conditions as in Table 1, $\tau = 0.83$). (For sake of clarity, the selectivity to EtOPr is not shown in the figure, the values being close to the PrOH values).

rectly understood (5, 14), but it is not negligible as was clearly shown in the hydrocarbonylation of methanol to acetaldehyde (5). The ethanol reaction was therefore examined up to 230 MPa using the best catalytic Ru-Co system as mentioned in the previous section. Figure 1 shows the pressure effect.

At 200°C, the partial CO pressure must be at least 10 MPa to stabilize the active species derived from the cobalt catalyst. Indeed, for pressures below this value, very little propanol is formed and the etherification of ethanol is the major reaction. This result may be suggestive of an independent functionality of the bimetallic catalytic system (the ruthenium compound does not improve the stability of the cobalt catalyst).

An increase in pressure promotes the homologation reaction by reducing considerably the formation of diethyl ether (at 100 MPa, its concentration is 10 times lower than at 15 MPa). The conversion of ethanol is apparently a linear function of the pressure up to 100 MPa and is little modified above this pressure (compare with our previous methanol result (5)). The optimum pressure regarding the selectivity to free propanol lies in the range 40–45 MPa. At higher pressures the propanol concentration decreases as well as that of the derived ethers (EtOPr, Pr₂O) (not shown in Fig. 1). Higher boiling unidentified products are formed as evidenced by GC. Interestingly, the butanol concentration increases with pressure, in accordance with the fact that the pressure is an essential parameter for the homologation of higher alcohols, due to its beneficial effect on CO insertion (9).

3. Effect of Temperature

Although there is probably an interdependence between the pressure and the temperature, the temperature effect was investigated by operating at a constant pressure (42 MPa) and taking a catalytic ratio $\tau = 0.83$. The results are shown in Table 2.

When plotted against the temperature, the conversion of ethanol is an almost linear function. In the temperature range (160–180°C), there is little effect on the formation of propanol and its derivatives (ethers and esters). The best selectivity to free propanol amounts to 34.5% at 170°C (by way of comparison, this selectivity falls to 7.5% at 220°C).

An increase in temperature results in higher diethyl ether concentrations (increase of acidity of the medium?). Temperatures higher than 180°C are detrimental to the homologation products. Also larger quantities of ethane are produced.

At low temperatures, some propionaldehyde is formed. This is a possible parallel to acetaldehyde formation in the hydrocarbonylation of methanol (5). The case, however, is not strong.

TABLE 2
Influence of Temperature on the Homologation of Ethanol^a

Run	T (°C)	Ethanol conversion (%)	Liquid products (mmol)								Σ ^c (%)
			Et ₂ O	EtOAc	PrOH	BuOH	EtOPr	Pr ₂ O	EtCHO	Other ^b	
1178	150	49	3.0	1.4	14.6	0.2	6.2	1.2	1.5	3.2	36.5
1175	160	52	3.2	1.2	17.3	0.6	5.9	0.9	1.0	3.4	40.6
1177	165	54	3.1	1.2	15.4	0.5	7.1	1.2	1.0	3.9	33.4
1171	170	56	3.0	1.2	18.0	0.5	6.4	0.9	0.4	2.0	34.5
1168	180	58	3.1	1.3	17.9	0.8	6.4	0.8	0.2	2.7	35.5
1170	190	62	5.4	1.5	11.7	0.4	7.4	0.8	0	3.5	20.4
1162	200	66	5.9	1.5	12.6	0.4	5.8	0.7	0	2.4	20.4
1169	220	85	7.1	1.3	5.5	0.7	5.2	0.5	0	4.4	7.4

^a Conditions: as in run 1106, but with pressure = 42 MPa. [Co]/([Co] + [Ru]) = 0.83.

^b Ethyl propionate + propyl propionate + propionic acid.

^c Selectivity to free propanol.

4. Effect of Reaction Time

The residence time may be expected to affect the product distribution as obviously some reaction products are produced sequentially. Product selectivity and ethanol conversion are plotted in Fig. 2 against the residence time.

Ethanol conversion increases with reaction time as normally expected. Diethyl ether is the dominant product in the early stages of the reaction. Ethyl acetate is present from the very start of the reaction and its concentration is fairly constant throughout the reaction, thus denoting that the carbonylation of ethanol occurs from the beginning. This result should be compared with that obtained in the synthesis of acetaldehyde from methanol, in which methyl acetate is immediately produced, and its concentration does not change until completion of the reaction (5).

Propanol is formed rapidly and becomes the major product after 30 min. For $t = 2$ h, the maximum is reached. For longer reaction times, its concentration decreases dramatically while higher boiling products are formed. This also holds true for the formation of butanol which appears after one hour, with a maximum at $t = 3$ h. The concentration of the remaining products (pro-

pyl ethers and esters) do not change significantly over the investigated time range. Finally it should be mentioned that propanaldehyde is formed only for short resi-

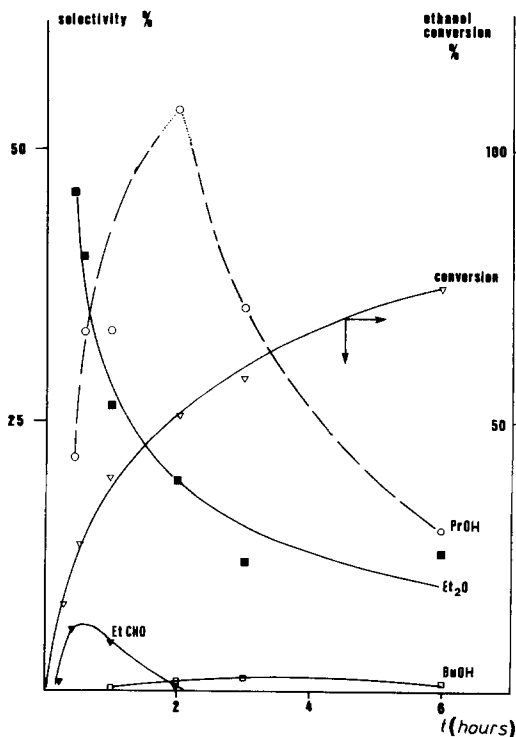


FIG. 2. Homologation of ethanol. Influence of reaction time (conditions as in Table 2, $T = 180^{\circ}\text{C}$).

dence times; ultimately all EtCHO is hydrogenated to propanol.

5. Effect of Syngas Composition

Modification of the CO:H₂ ratio leads to the results shown in Fig. 3.

The optimal syngas composition CO:H₂ lies in the range 1:1 to 1:2, e.g., in the hydrocarbonylation of methanol. The best conversion yields and selectivity to propanol are obtained for these compositions. A mixture enriched in carbon monoxide is detrimental to the production of propanol. High concentrations of hydrogen in the starting syngas lead to a slight lowering of the propanol yield, but more diethyl ether is produced.

6. Effect of Catalyst and Iodine Concentration

The effect of the catalyst concentration and of the ratio (catalyst:iodine) were investigated, while keeping constant the [Co]:[Ru] ratio (Table 3).

Increasing catalyst concentrations leads to an increase of overall conversion and propanol concentration. The best homologation results as regards selectivity to propanol were obtained with run 1171.

The catalyst:iodine ratio is an important parameter, not so much for ethanol conversion but rather with respect to propanol selectivity. Lower iodine concentrations result in improved selectivity to PrOH while more diethyl ether is formed at higher iodine concentrations (run 1187, for example).

7. Promoting Effect of Iodine and Iodides

The addition of iodine or iodides is undoubtedly essential for the success of the hydrocarbonylation. There is little reaction in the absence of a promoter. Various sources of iodine were used and their effect on the homologation of ethanol was investigated (Table 4).

Elemental iodine and alkyl iodides give the best conversion results, but alkyl iodides lead to extensive dehydration of etha-

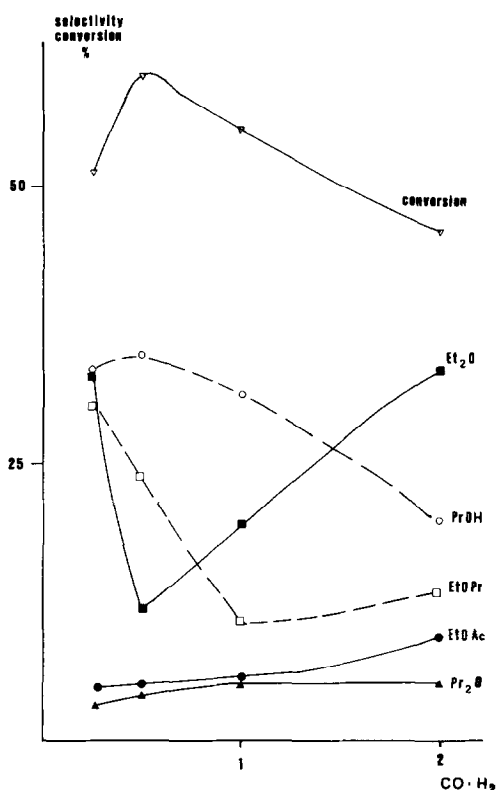


FIG. 3. Homologation of ethanol. Influence of syngas composition (conditions as in Fig. 2, reaction time: 3 h).

no, thus decreasing the propanol yield. Although ionic iodides are less active than covalent iodides, in the presence of KI, diethyl ether is produced only in very low amount, thus leading to a good selectivity to propanol, as in run 1189. Keeping in mind the synergism previously observed in the corresponding methanol reaction (4), we associated a covalent iodide with an ionic one (runs 1193, 1194). While the above-mentioned synergism does not occur, the selectivities to propanol are somewhat improved.

The addition of a phosphine has a negative effect regarding both conversion and propanol selectivity. This result stands in sharp contrast with the improved ethanol selectivity in the homologation of methanol (19).

The hydrocarbonylation reaction carried

TABLE 3
Influence of Catalyst and Iodine Concentration on the Homologation of Ethanol^a

Run	[Co + Ru] (mmol)	[Catalyst] ^b [iodine]	Ethanol conversion (%)	Liquid products (mmol)							Σ ^c (%)
				Et ₂ O	EtOAc	PrOH	BuOH	EtOPr	Pr ₂ O	EtPr + PrPr	
1181	0.22	0.6	33	6.3	0.3	5.9	0	2.9	0.1	0.5	20.6
1179	0.45	0.6	48	5.6	0.6	12.8	0.2	5.0	0.8	1.4	30.7
1171	0.9	0.6	56	3.0	1.2	18.0	0.5	6.4	0.9	2.0	34.5
1185	0.9	1.2	35	1.9	0.9	13.4	0.2	2.1	0.3	0.8	44.0
1171	0.9	0.6	56	3.0	1.2	18.0	0.5	6.4	0.9	2.0	34.5
1187	0.9	0.3	70	11.0	1.1	11.0	0.2	6.1	0.5	2.2	18.1

^a See footnote (a) in Table 1, except *P* (42 MPa), *T* (170°C), [Co]/([Co] + [Ru]) = 0.83.

^b Molar ratio.

^c Selectivity to free propanol.

out in a chelating solvent (run 1197) seemingly does not yield the result expected on the basis of the methanol data (20). This is true insofar as propanol is concerned. The substantial formation of butanol (representing a 51% molar percentage), however, seems at first sight rather surprising. Nevertheless, a blank run carried out in the presence of THF alone also leads to *n*-buta-

anol, thus denoting a C—O cleavage of the tetrahydrofuran ring under conditions used in this study.

DISCUSSION

The widely accepted mechanism for the methanol homologation involves the protonation of the alcohol to activate methyl groups; this is best achieved with HCo

TABLE 4
Effect of Iodides, Additives, and Solvents in the Homologation of Ethanol^a

Run	Promoter	Ethanol conversion (%)	Products (mmol)							Σ ^b (%)
			Et ₂ O	EtOAc	PrOH	BuOH	EtOPr	Pr ₂ O	Propionates	
1234	None	4	0.6	1.9	1.5	0	0.4	0	0	43.1
1189	I ₂	56	3.0	1.2	18.1	0.5	6.4	0.9	2.1	34.5
1192	CH ₃ I	72	15.6	1.6	10.8	0	6.4	0.5	2.0	18.3
1238	C ₂ H ₅ I	85	16.1	1.9	11.3	1.1	8.7	0.9	3.0	17.3
1235	HI	80	15.0	1.5	16.4	1.4	8.3	0.1	3.0	27.3
1191	KI	31	0.5	1.4	9.7	0.3	4.4	0.3	1.5	36.0
1193	KI + CH ₃ I ^c	41	1.3	1.4	17.2	0.5	4.4	0.5	1.7	52.1
1194	KI + CH ₃ I ^c	47	4.0	1.0	11.0	0.3	3.7	0.5	2.1	24.3
1189	I ₂	56	3.0	1.2	18.0	0.5	6.4	0.9	2.0	34.5
1198	KI + I ₂ + P(C ₄ H ₉) ₃ ^d	15	0.1	1.7	1.2	0	0.6	0.2	0.2	8.1
1197	I ₂ ^e	50	0.6	0	1.6	2.5	0.2	0	0	12.3

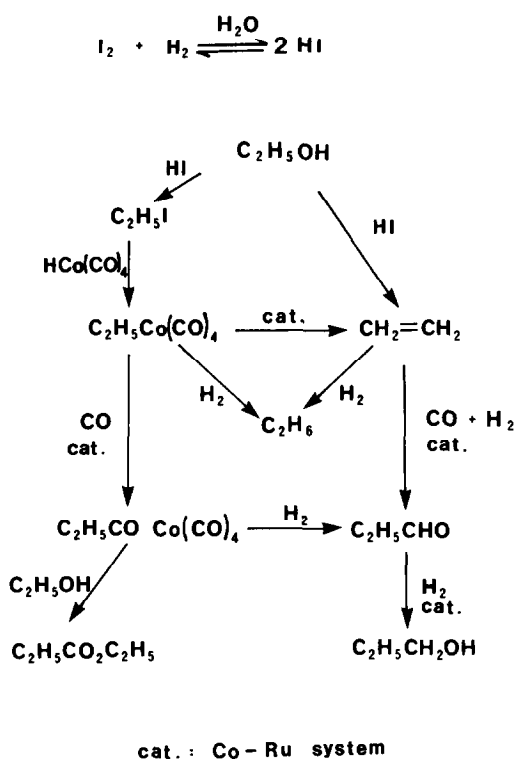
^a Conditions as in run 1171 in Table 3.

^b Selectivity to free propanol.

^c Run 1193: KI (0.9 mmol), CH₃I (0.16 mmol). Run 1194: KI (0.23 mmol), CH₃I (0.82 mmol).

^d P(C₄H₉)₃ (1.6 mmol), KI (0.9 mmol), I₂ (0.16 mmol).

^e C₂H₅OH (1.5 ml), solvent THF (4.5 ml).



SCHEME 1.

(CO)₄, due to its unusually high acidity. Thus, it is quite possible that with cobalt alone, propanol is formed according to a mechanism largely similar to that operating in the methanol homologation.

Ruthenium alone exhibits a lower homologation activity, but the combination of both catalysts leads to a synergistic effect. The fact that both ruthenium and cobalt (in the presence of iodine) promote the dehydration of ethanol makes it possible to imagine that ethylene can also form in addition to diethyl ether. It is known that the formation of the ether or the olefin from the corresponding alcohol is:

—greatly encouraged by the presence of a strong acid;

—difficult to orient to one or the other products.

According to our results, the combination of both catalysts under certain conditions may provide a means for controlling olefin formation. Once the olefin is formed,

hydroformylation can take place, leading to propionaldehyde and catalyzed by a ruthenium hydride formed *in situ* (21). In the last step, propionaldehyde is readily hydrogenated into propanol. The scheme shown below summarizes roughly the two mechanistic possibilities evoked here.

No further mechanistic speculations will be made at the present time. As this work is part of a wider study encompassing a number of higher alcohols, mechanistic proposals will be included in a forthcoming paper, although the validity of a common mechanism is yet to be demonstrated.

To sum up, the homologation of ethanol is a great deal more difficult than the hydrocarbonylation of methanol. Indeed, the results found for the C₁ alcohol cannot be extrapolated for ethanol, due to the tendency of the latter to undergo dehydration with relative ease. A possible way to reduce its transformation into diethyl ether is to combine a cobalt catalyst with a ruthenium catalyst in the appropriate ratio under adequate reaction conditions. In this reaction, the source of iodine and pressures are among the most important factors. The major product is the homologation product (*n*-propanol) which can be produced under certain conditions up to 52% selectivity for an ethanol conversion of 40%. It is apparent from the experimental results that the combined activity of the two metallic species is nonadditive.

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