Journal of Organometallic Chemistry, 240 (1982) 169–177
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

USE OF ALCOHOLS AS SOURCES OF HYDROGEN IN THE TRANSFORMATION OF CO-OLEFIN MIXTURES

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(Received June 15th, 1982)

Summary

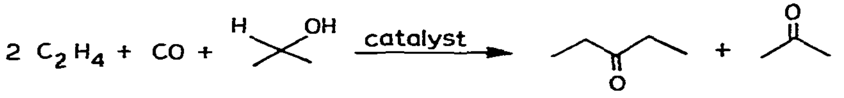
A study has been made of the catalytic activities of various ruthenium complexes in the synthesis of ketones from olefin-carbon monoxide mixtures and an alcohol as source of hydrogen: major side products were shown to be the alkyl propionates and ethane. The effects of base, concentration of catalyst (for $RuCl_3$- and $Ru_3(CO)_{12}$-based systems), pressure, temperature, CO/olefin ratio and the water content of the alcohol have been examined.

Introduction

Much of the world's hydrogen is derived indirectly from petroleum products by processes (steam-cracking and the water-gas-shift (WGS) reaction) wherein the carbon is ultimately lost, as CO_2, eq. 1 [1].

$$CH_4 \xrightarrow{H_2O/O_2} CO + 3\,H_2 \xrightarrow{H_2O} 4\,H_2 + CO_2 \qquad (1)$$

However, hydrogen is currently a by-product of certain industrial processes, hydrocarbon cracking to alkenes, dehydrogenation of alcohols to ketones, electrochemical regeneration of chlorine, etc. [2]. There is thus a certain economic interest in using this hydrogen in the conversion of the oxides of carbon to compounds of value, especially in direct hydrogen transfer reactions which permit the dehydrogenation of substrate and the transformation of CO to operate concurrently, as for example, in the synthesis of ketones from an olefin and CO, with an alcohol as source of hydrogen, eq. 2.



(2)

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The latter reaction is well documented, especially in the patent literature, and soluble transition metal complexes of Rh, Ir and particularly cobalt have been used as catalysts [3–5]. However, both ruthenium and rhodium are excellent catalysts for the transfer of hydrogen from secondary alcohols to unsaturated substrates [e.g. 6–10]. We therefore undertook the present studies of the reactions of alcohols, carbon monoxide and olefins in the presence of soluble ruthenium compounds and of $Rh_6(CO)_{16}$ as reference. The text describes the products formed and discusses some key reaction parameters.

Results and discussion

Products

Preliminary experiments indicated that under our relatively mild reaction conditions (see Experimental and Table 1) ruthenium compounds, like the cobalt derivatives [3], lead to a complex mixture of products. Thus for the system ethylene/CO/2-propanol/160°C/15 bar, we observed, along with the expected formation of acetone (DMK) and diethyl ketone (DEK), production of isopropyl propionate (IPP) and ethane and smaller quantities of hydrogen, CO_2, C_1 to C_4 hydrocarbons [11], propionaldehyde, n-propanol and isopropyl formate [12]. These by-products indicate the occurrence of several parallel reactions involving either the reagents CO, C_2H_4, 2-C_3H_7OH or the various organic additives (NEt_3 etc., see Table 1).

Isopropyl propionate is probably formed by the alkoxycarbonylation of ethylene, though the precise catalyst remains undefined. The C_2 to C_4 hydrocarbons originate in secondary transformations (hydrogenation, dimerisation, dehydration, etc.) of the ethylene, the alcohol or the organic addenda [14]. The methane could be formed in part by the hydrogenation of CO catalysed by traces of metallic Ru. The carbon dioxide could stem from the water-gas-shift reaction with the water formed in the methanation of CO or dehydration of the alcohol.

TABLE 1

NATURE OF CATALYST SYSTEM IN THE REACTION OF C_2H_4 (5 bar), CO (10 bar), and 2-PrOH (40 ml). Autoclave (300 ml); 160°C; 24 h

Exp. No.	Complex [a] (mmol metal)		Addenda (mmol)	$CH_3CH_2COCH_2CH_3$ [b]	
				(mmol)	(mmol/mmol metal)
1	$Rh_6(CO)_{16}$	0.34	–	10	29
2	$Rh_6(CO)_{16}$	0.22	NEt_3 7.2	11	50
3	RuH_2L_4	0.11	–	0	0
4	RuH_2L_4	0.17	NEt_3 7.2	0.02	0.1
5	$RuH(OCOC_2H_5)L_3$	0.19	–	0	0
6	$Ru_3(CO)_{12}$	0.29	–	[c]	[c]
7	$Ru_3(CO)_{12}$	0.24	NEt_3 7.2	0.5	2
8	$RuCl_2L_3$	0.19	–	0	0
9	$RuCl_3$	0.19	–	7	37
10	$RuCl_3$	0.19	NEt_3 7.2	1	6

[a] $L = PPh_3$. [b] Product present in total distillate. [c] Traces.

Propionaldehyde and propanol are always accompanied by gaseous hydrogen, and we conclude that they are probably formed by the conventional oxo-process (CO/H_2) and not by direct hydrogen transfer processes involving the secondary alcohol.

Catalyst systems

Amongst the numerous products identified only two, diethyl ketone (DEK) and isopropyl propionate (IPP) are formed from ethylene, CO and isopropanol, as in eq. 2 and 3.

(3)

The results, summarized in Table 1, indicate, however, that the yields of DEK are profoundly influenced both by the nature of the ruthenium complex and by the presence of a base. Thus the carbonyl (run 6), and the propionate (run 5) are virtually inactive as, surprisingly, are the dihydro- and dichloro-ruthenium compounds (runs 3 and 8) which are active in the transfer of hydrogen from alcohols to unsaturated substrates [8,10]. Ruthenium trichloride on the other hand gives an active system (run 9), with turnover numbers similar to those observed for $Rh_6(CO)_{16}$ (run 1). The addition of a base enhances considerably the effectiveness (in DEK) of both the ruthenium and rhodium carbonyl systems [15] (runs 7 and 2) and to a lesser extent of the hydride (run 4). Base, however, decreases the activity of the trichloride (run 10). The results illustrated in Table 2 (runs 1 to 4) indicate that in the case of triruthenium dodecacarbonyl similar but smaller promoting effects may be obtained with other bases. Table 2 reveals, however, that these modifications in activities for the ruthenium carbonyl and chloride systems are accompanied by an increase in the production of propionate (IPP).

A further distinguishing feature between the chloride and the carbonyl systems is the influence of the catalyst concentration (Fig. 1). Thus with $RuCl_3$ the production of DEK increases with increasing catalyst concentration whilst for $Ru_3(CO)_{12}$ it decreases. This implies that in the case of the carbonyl the active entity is not the aggregate $Ru_3(CO)_{12}$ but rather a breakdown product thereof (possibly $Ru(CO)_5$) [16]. The base-promoted carbonyl gives, at high dilutions (1×10^{-3} mol l^{-1}) the more active catalyst system (DEK turnover Nos: $Ru_3(CO)_{12}$, 70; $RuCl_3$, 12) under our conditions. However, the productivities are low. High productivities may be obtained with the carbonyl system by increasing the total CO pressure, as is illustrated in the synthesis of dipropyl ketones (from propylene), experiments 2 and 3, Table 3. These results are also in accord with a dissociation of the aggregate promoted by carbon monoxide pressure. The results listed in Table 3, experiments 1 and 2, indicate that a base also enhances the activity of the carbonyl system in the synthesis of dipropyl ketones from propylene, CO and a secondary alcohol.

Reaction parameters

With the aim of optimising the catalyst performance we studied the influence of various reaction parameters on the course of the reaction with the carbonyl and chloride catalysts. Preliminary experiments with NEt_3, NEt_2H, 2-PrOH, 2-BuOH and ethanol established that the amines were ineffective as sources of hydrogen, whilst 2-butanol was somewhat superior to 2-propanol (Table 2, run 1 and Table 4,

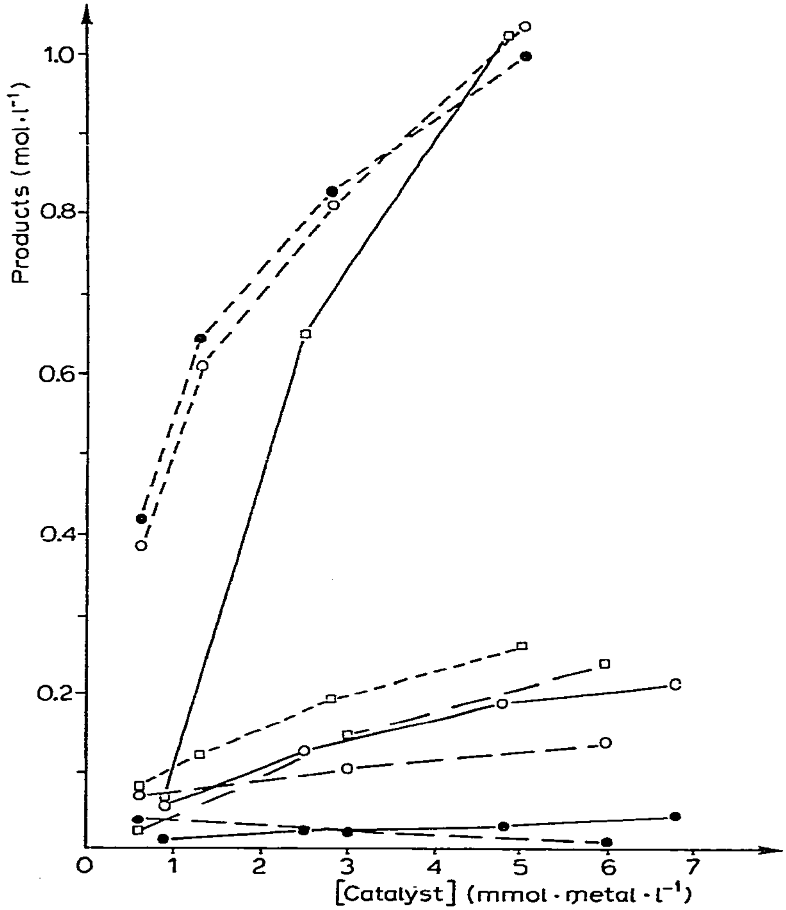

Fig. 1. Influence of catalyst concentration: autoclave (300 ml). — — — $Ru_3(CO)_{12}$, 2-PrOH (40 ml), NEt_3 (1 ml), C_2H_4 (5 bar), CO (10 bar), 160°C, 24 h. ——— $RuCl_3$, 2-PrOH (40 ml), NEt_3 (1 ml), C_2H_4 (5 bar), CO (10 bar), 160°C, 24 h. ------ $RuCl_3$, 2-BuOH (60 ml), C_2H_4 (20 bar), CO (10 bar), 170°C, 18 h. ● diethylketone, ○ acetone or methyl ethyl ketone, □ 2-propyl- or 2-butyl-propionate.

TABLE 2

INFLUENCE OF BASE IN REACTION OF C_2H_4 (5 bar), CO (10 bar), and 2-PrOH (40 ml). AUTOCLAVE (300 ml); 160°C; 24 h

Exp. No.	Catalyst (mmol metal)	Addenda (mmol)	Products (mmol)		
			DMK [a]	DEK	IPP
1	$Ru_3(CO)_{12}$ (0.024)	NEt_3 (7.2)	2.4	1.7	1.0
2	$Ru_3(CO)_{12}$ (0.024)	NMe_3 (7.2)	0.9	0.9	1.5
3	$Ru_3(CO)_{12}$ (0.024)	NBu^n_3 (7.2)	0.5	0.5	0.8
4	$Ru_3(CO)_{12}$ (0.024)	KOH (7.2)	0.4	0.5	0.3
5	$Ru_3(CO)_{12}$ (0.29)		0.7	0	0
6	$Ru_3(CO)_{12}$ (0.24)	NEt_3 (7.2)	5.5	0.5	9.5
7	$RuCl_3$ (0.19)		7.2	7.2	7
8	$RuCl_3$ (0.19)	NEt_3 (0.6)	19	2.7	21
9	$RuCl_3$ (0.19)	NEt_3 (7.2)	7.5	1.2	41

[a] DMK = acetone; DEK = diethyl ketone; IPP = isopropyl propionate.

TABLE 3

INFLUENCE OF BASE AND CO PRESSURE IN CARBONYL-CATALYSED SYNTHESIS OF DIPROPYL KETONES. AUTOCLAVE (300 ml); 2-BUTANOL (80 ml); 200°C; 8 h

Exp. No.	Catalyst system (mmol catal, mmol)	CO (bar)	C_3H_6 (mmol)	DPK[a] (mmol)	MEK[b] (mmol)
1	$Ru_3(CO)_{12}$, 0.46	165	830	30	39
2	$Ru_3(CO)_{12}$, 0.47 NEt_3, 7.4	160	830	123	122
3	$Ru_3(CO)_{12}$, 0.82 NEt_3, 7.4	98 N_2, 25[c]	1400	103	119
4	$RuCl_3$, 0.38	150	790	33	41

[a] DPK = isomeric mixture of dipropyl ketones. [b] MEK = methyl ethyl ketone. [c] N_2 introduced to give same final pressure.

run 1). Ethanol favoured ester formation (25 mmol ethyl propionate and 23 mmol DEK), and acetaldehyde diethyl acetal was formed as a by-product (see Experimental).

The pressure and the $CO:C_2H_4$ ratio profoundly influence the yields of DEK. Thus as is summarized in Table 4 (runs 1, 2) with a 2 : 1 $CO:C_2H_4$ ratio an increase in pressure increases the yield of DEK and to a lesser extent that of the ester (SBP). At the same pressure a change to a 1 : 2 $CO:C_2H_4$ ratio (run 3) further increases the yields of ketone (DEK) and ester (SBP). These observations are in accord with the stoichiometries of eq. 2 and 3, and the curves (Fig. 1) indicate that with $RuCl_3$ under these conditions, MEK production (by dehydrogenation of 2-butanol) follows closely that of DEK formation. The actual formation of DEK is a relatively slow process (initial turnover rate 170 h^{-1}) (runs 4 and 5), and is probably limited by the final partial pressure of ethylene [17] and not by catalyst modification.

The reaction temperature also has a profound influence upon the final yields of ketone and ester. Thus, in the case of the chloride system, as is illustrated in Fig. 2, these (at 30 bar) pass through a maximum situated around 190–200°C. At this

TABLE 4

INFLUENCE OF PRESSURE AND CO/C_2H_4 RATIO. AUTOCLAVE (300 ml); 2-BUTANOL (40 ml)

Exp. No.	Catalyst system (mmol metal, mmol)	CO (bar)	C_2H_4 (bar)	Time (h)	DEK (mmol)	SBP[a] (mmol)
1[b]	$Ru_3(CO)_{12}$, 0.025 NEt_3, 7.2	10	5	24	3.4	0.4
2[b]	$Ru_3(CO)_{12}$, 0.025 NEt_3, 7.2	20	10	24	6	0.6
3[b]	$Ru_3(CO)_{12}$, 0.025 NEt_3, 7.2	10	20	24	16	5
4[c]	$RuCl_3$, 0.038	10	20	8	28	11
5[c]	$RuCl_3$, 0.038	10	20	18	45	29

[a] SBP = sec-butyl propionate. [b] At 160°C. [c] At 200°C.

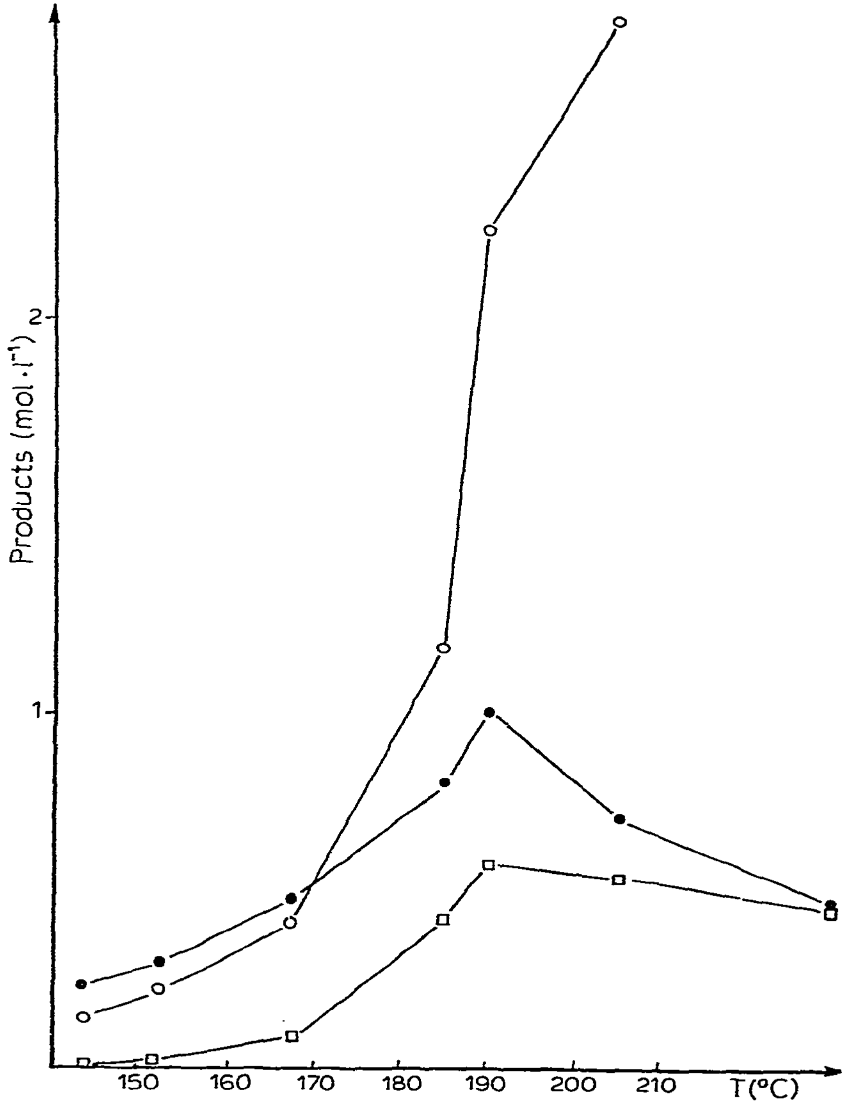

Fig. 2. Influence of temperature: autoclave (300 ml); 2-BuOH (60 ml); $RuCl_3$ (10 mg); C_2H_4 (20 bar); CO (10 bar). ● diethyl ketone, ○ methyl ethyl ketone, □ 2-butyl propionate.

temperature there is also a marked increase in methyl ethyl ketone (MEK) production concurrent with a substantial increase in ethane formation. These observations are consistent with an evolution of the catalyst system from one favouring the ketone (DEK) synthesis to one promoting the direct hydrogenation of ethylene to ethane. Marko and Speier [10] have suggested that in the ruthenium-catalyzed transfer of hydrogen from benzyl alcohol to benzylidene acetone the catalyst system changes with the reaction temperature as outlined in eq. 4, L = PPh_3. Our initial attempts to isolate discrete crystalline products from our reaction mixtures have been unsuccessful.

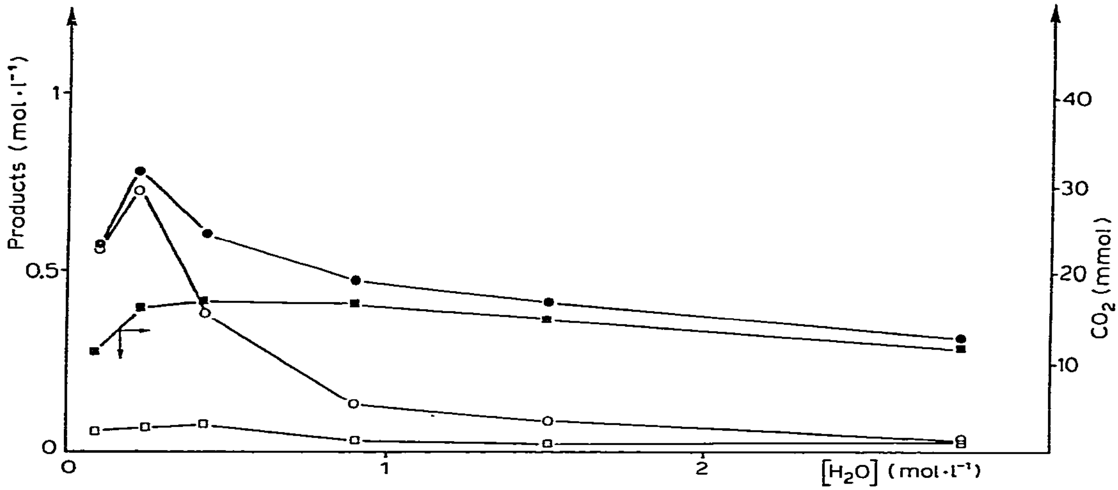

Fig. 3. Influence of water: autoclave (300 ml); 2-butanol (40 ml); $RuCl_3$ (10 mg); C_2H_4 (20 bar); CO (10 bar); 160°C; 18 h. ● diethylketone, ■ CO_2, ○ methyl ethyl ketone, □ 2-butylpropionate.

$$\begin{tikzcd}
RuCl_2L_3 \arrow[r, "RCH_2OH/60^\circ C"] \arrow[dr, "RCHO/200^\circ C"'] & RuClHL_3 \arrow[r, "RCH_2OH/120^\circ C"] & RuH_2L_3 \arrow[d, "190^\circ C"', "RCHO"] \\
 & RuCl_2(CO)_2L_2 & RuH_2(CO)L_3
\end{tikzcd} \qquad (4)$$

The water content of the alcohol also influences the course of the reaction and may become the preferred source of hydrogen. Thus, as is illustrated in Fig. 3 ($RuCl_3$), at low concentrations (up to 0.3 mol l^{-1}) water has a beneficial influence. Thereafter it has an inhibitory effect particularly on MEK-production, i.e. on the dehydrogenation of the secondary alcohol. Diethyl ketone (DEK) formation does not drop off so sharply, the difference between DEK and MEK formation reaching a maximum at about 1 mol l^{-1}. This, together with the fact that CO_2-production parallels that of DEK formation, leads us to conclude that water can become the preferred source of hydrogen in the synthesis of DEK even in the presence of a secondary alcohol.

Experimental *

All the reactions were carried out in glass-lined 300 ml Autoclave Engineers autoclaves equipped with Magnedrive units. The alcohols were dried over molecular sieves and degassed (argon). The organometallic compounds $Rh_6(CO)_{16}$ [18];

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[*] With the collaboration of Mr. B. Béguin (CNRS) and Mr. M. Renaud (PCUK).

RuH_2L_4 [19]; $RuH(OCOC_2H_5)L_3$ [20], $Ru_3(CO)_{12}$ [21] and $RuCl_2L_3$ [22] were prepared by literature methods.

The products were analyzed either directly (gas-phase) or after distillation (liquid phase) by vapour phase chromatography (VPC) or by VPC-mass spectrometry (VPC-MS) [13]. Gaseous products CO, CO_2, H_2O on Carbosieve B, Porapak Q columns with thermal conductivity detectors. Gaseous and liquid (distillate) products on Porapak Q, Porapak R columns and capillary (Silicone CP.Sil. 8) columns with flame ionization detectors.

In a typical run, the catalyst (e.g. $Ru_3(CO)_{12}$, 5.2 mg) was dissolved in degassed 2-butanol (40 ml) containing Et_3N (1 ml). The solution was transferred under argon into the autoclave, which was then purged with ethylene and pressurized with ethylene (5 b) then CO (10 b) prior to stirring and heating (160°C). After 24 h the gaseous phase was analyzed by VPC; Carbosieve B; H_2 (traces), CO (too great to measure), CO_2 (0.6 mmol); Porapak Q: CH_4 (0.008 mmol), C_2H_4 (too great to measure), C_2H_6 (0.09), C_3- (traces), C_4-hydrocarbons (0.002 mmol). After venting the autoclave the liquid was distilled under atmospheric pressure and the distillate analyzed by VPC; Porapak Q (180–210°C): EtCHO (0.3 mmol), 2-BuOH, MEK and 2-butyl formate (not adequately resolved), DEK (3.4 mmol), SBP (0.4 mmol); a Porapak R column (180°C) was used to quantify MEK (3 mmol) and 2-butyl formate (1.3 mmol).

Similarly the catalyst ($RuCl_3$, 10 mg) was dissolved in degassed ethanol (80 ml) and the solution transferred under argon to the autoclave, which was then purged with ethylene and pressurized with ethylene (20 bar) and CO (10 bar). After heating at 170°C for 18 h, the gaseous products were analyzed by VPC; Carbosieve B: H_2 (none), CO (too great to measure), CO_2 (13 mmol); Porapak Q: CH_4 (0.01mmol), C_2H_4 (too great to measure), C_2H_6 (0.03 mmol), C_3 (traces), C_4-hydrocarbons (0.13 mmol). The liquid distillate analyzed by VPC; CPSil 8-capillary (30–180°C), CH_3CHO (traces), EtOH (too great to measure), DEK (23 mmol), ethylpropionate (25 mmol), $CH_3CH(OEt)_2$ (16 mmol).

Conclusions

$RuCl_3$ and base-promoted $Ru_3(CO)_{12}$ constitute efficient catalyst systems, under relatively mild conditions, for the synthesis of diethyl ketone (DEK) from ethylene and CO in the presence of 2-propanol and 2-butanol as source of hydrogen. The corresponding alkoxycarbonylation product (alkyl propionate) together with ethane are major secondary products.

The chloride and carbonyl systems differ in that for the former DEK production is proportional to catalyst concentration whilst for the latter it is inversely proportional. The nature of the active species remain to be defined, but the evidence indicates that they are probably mono- (or bi-) nuclear entities. The reactant ratios, pressure and temperature of reaction are key parameters. Thus a CO : ethylene ratio in accord with the reaction stoechiometry and elevated pressures increase the selectivity and productivity for DEK formation. The temperature can modify the overall reaction course; thus at 20–40 bar temperatures up to 190–200°C favour DEK, but above that the hydrogenation of ethylene becomes the dominant process.

Trace amounts of water have little influence, while higher concentrations inhibit the dehydrogenation of the alcohol, and at concentrations greater than 1 mol l^{-1} water may become the preferred source of hydrogen in the synthesis of DEK.

Acknowledgements

We thank la Société des Produits Chimiques Ugine Kuhlmann for generous support of this research, and in particular for a stipendium to one of us (P. Isnard).

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12 In certain experiments the use of mass-spectrometry coupled with gas chromatography [13] not only confirmed the above findings but also enabled us to identify minor quantities of higher molecular weight products [ketone self-condensation products and polycarbonyl products (octane-3,6-dione)]. However, these are formed by secondary transformations of the initial products and are not discussed further at present.
13 We thank Mr D. Page of PCUK for the GC-MS measurements.
14 Control experiments under N_2, with 2-butanol and with tributylamine confirmed these origins for the C_2, C_3, C_4 and in part the C_1 hydrocarbons.
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