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Syngas Reactions

V. Ethylene from Synthesis Gas[1]

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A new two-step process scheme for the production of ethylene from synthesis gas is proposed, wherein ethyl esters of aliphatic carboxylic acids are first generated directly from synthesis gas and the appropriate acid, through the use of homogeneous ruthenium catalysts coupled with quaternary phosphonium salt promoters. Pyrolysis of the isolated, intermediate ethyl ester yields ethylene and recyclable acid.

INTRODUCTION

Numerous routes have been proposed for the manufacture of ethylene from synthesis gas, including:

(1) variations in Fischer–Tropsch chemistry (*1–8*);

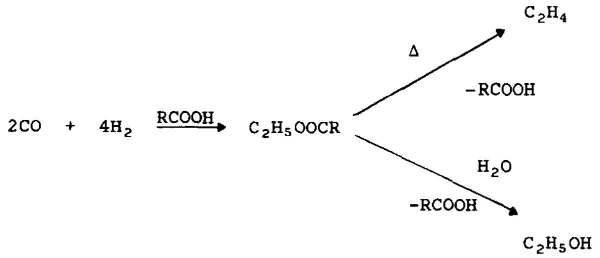
(2) methanol homologation to ethanol, followed by dehydration (*7–13*);

(3) catalytic cracking of methanol over specific zeolite catalysts (*14–18*);

(4) direct synthesis from CO/H_2 (*1, 3, 6, 8, 19, 20*).

While not all these processes are at the same stage of development, it is predicted that syngas-based ethylene will likely become commercial by 1990, possibly earlier (*21*). Economic considerations dictate that ≥50% carbon selectivities to ethylene will be needed for this technology to be competitive with traditional pyrolysis of paraffinic cuts (*9*).

As part of our continuing research program into the generation of large-volume chemicals from synthesis gas via homogeneous catalysis (*22–27*), here we propose an alternative process scheme for making ethylene-rich olefins, ethanol, and ethyl esters of aliphatic carboxylic acids (*28*). The first stage is CO hydrogenation in the presence of an aliphatic carboxylic acid coreactant; this yields the corresponding ethyl ester as a major product fraction (Eq. (1)). Soluble ruthenium species, modified with certain quaternary Group 5B salts, are the novel catalysts effective for this reaction. Pyrolysis of the intermediate ethyl ester would yield ethylene (Eq. (1)). Alternatively, where ethanol is the desired product, CO hydrogenation is followed by hydrolysis.



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[1] For previous paper in this series see: Knifton, J. F., *J. Catal.* **76**, 101 (1982).

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Although the direct conversion of synthesis gas to a variety of C_2-oxygenates—particularly ethanol, acetaldehyde, acetic acid, and ethylene glycol—has been demonstrated by a number of researchers (*26, 27, 29–38*), the selective synthesis of ethyl esters from CO/H_2 and the corresponding aliphatic carboxylic acid (Eq. (1)) is believed to be novel (*28*). The thermodynamics of ethyl ester production, e.g., ethyl propionate synthesis (Eq. (2)), are attractive and, in contrast to related data for other C_2-oxygenate preparations (*26, 38*), at 500°K the equilibrium of Eq. (2) lies far to the right. Furthermore, the equilibrium constant *Kp* shows a marked sensitivity to reaction temperature (*39*):

$$2CO + 4H_2 + C_2H_5COOH \rightarrow \quad \Delta G_{500} = -9.1 \text{ kcal/mole}$$
$$C_2H_5COOC_2H_5 + 2H_2O. \quad (2)$$
$$\log Kp = 9.20$$

RESULTS AND DISCUSSION

Synthesis of Carboxylic Acid Esters

The preparation of aliphatic carboxylic acid esters from synthesis gas and the corresponding acid is illustrated by the experimental data summarized in Table 1. Here propionic acid is the coreactant (Eq. (2)) and CO hydrogenation yields substantial quantities of C_1–C_4 alkyl propionates. Some 14 catalyst combinations of soluble ruthenium species coupled with various

TABLE 1

Propionate Esters from Synthesis Gas[a]

Expt.	Ruthenium catalyst precursor	Propionic acid conversion (%)	Propionate ester yield (g)[b]				C_1–C_4 alkyl propionate selectivity (wt%)[c]
			Methyl	Ethyl	Propyl	Butyl	
1	$RuO_2 \cdot xH_2O$–$HpPh_3PBr$	69	9.1	21.2	4.7	0.4	89
2	$RuO_2 \cdot xH_2O$–Bu_4PBr	98	19.0	20.2	2.2	1.3	68[d]
3	$RuO_2 \cdot xH_2O$–Bu_4PBr[e]	76	28.1	16.0	3.1	0.8	87
4	$RuO_2 \cdot xH_2O$–$MePh_3PBr$	82	18.1	18.7	4.0	0.4	88
5	$RuO_2 \cdot xH_2O$–$BzPh_3PBr$	39	5.2	2.6	11.2[f]	0.9	95
6	$RuO_2 \cdot xH_2O$–Ph_4PBr	51	7.4	7.4	8.5	0.7	94
7	$RuO_2 \cdot xH_2O$–Ph_4PCl	67	20.9	1.0	7.8	0.3	94
8	$RuO_2 \cdot xH_2O$–Bu_4PCl	85	26.6	3.0	8.3	0.7	74[g]
9	$RuO_2 \cdot xH_2O$–Bu_4PI	20	1.3	1.8	2.5	0.6	78
10	$Ru_3(CO)_{12}$–$BuPh_3PBr$	87	20.8	21.5	3.6	1.2	89
11	$Ru(acac)_3$–$HpPh_3PBr$	86	18.1	18.9	5.9	0.4	88
12	$RuO_2 \cdot xH_2O$–Me_4NBr	84	26.4	5.3	5.0	1.3	92
13	$RuO_2 \cdot xH_2O$–Bu_4NBr	70	5.3	1.7	5.6	9.9	86
14	$RuO_2 \cdot xH_2O$–$CsBr$	<10	3.8	0.2	0.7		
15	$RuO_2 \cdot xH_2O$	22	9.8	0.1	0.3	0.5	54

[a] Reaction charge: Ru, 4.0 mmole; Ru/P: 1/10; C_2H_5COOH, 50 g. Run conditions: 220°C; 430 atm constant pressure; CO/H_2 (1 : 1), 18 h.

[b] Analysis of crude liquid product by GLC using modified porous polymer column, programmed from 140–280°C at 30 cm^3/min He flow; smaller quantities of water, methanol, ethanol, 1-propanol, dimethyl ether, diethyl ether, and glycol propionates also detected; carbon dioxide and methane were present in product gas samples along with unreacted CO/H_2.

[c] Estimated on the basis of the quantity of propionic acid converted.

[d] Product also contains 4.8 g MeOH; 9.1 g EtOH.

[e] Run time, 6 h.

[f] Also includes some isopropyl propionate.

[g] Product also contains 4.5 g MeOH; 1.0 g EtOH.

quaternary Group 5B and alkali-metal promoters are considered. The important features of the catalysis are as follows:

1. Ethyl propionate is the major product fraction (Expts. 1, 2, 4, 10, and 11) and total C_1–C_4 alkyl propionate selectivities may reach 94% in some cases (e.g., Expts. 5, 6, and 7). Synthesis has been demonstrated over a broad range of conditions (*28*).
2. The catalysts are highly productive, and turnover frequencies may exceed 5.7×10^{-3} s^{-1} at 220°C (Expt. 3).
3. All alkyl propionate esters can be readily isolated from the crude liquid product by fractional distillation and the residual ruthenium catalyst recycled (*28*).

Ethyl propionate is in fact the dominant product fraction for a variety of ruthenium(IV) oxide–quaternary tetraalkyl- and alkylarylphosphonium halide combinations (Table 1), with methyl and propyl propionates the major by-products in nearly all cases. Where propionic acid conversions exceed 80%, significant amounts of C_1–C_3 alcohols may also be detected (e.g., Expts. 2 and 8). The balance of products includes butyl and ethylene glycol propionates, as well as CO_2 and methane, plus smaller quantities of water (see Experimental Section). The carbon dioxide is believed to originate primarily from ruthenium-catalyzed water-gas shift (*25*) (Eq. (3)) of the aqueous by-product, formed as a result of the stoichiometry of Eq. (2). This conclusion would be consistent with the much smaller molar yields of H_2O found in typical liquid-phase products as compared to the total production of C_1–C_4 alkyl propionates (viz. Table 1).

$$CO + H_2O \rightarrow CO_2 + H_2. \qquad (3)$$

Ruthenium(IV) oxide-*n*-heptyltriphenylphosphonium bromide combinations (Expt. 1) display the highest selectivity to ethyl propionate achieved so far in this work (60% of the total C_1–C_4 alkyl propionate fraction) under our preferred operating conditions (*28*). Fastest reaction rates are realized with ruthenium(IV) oxide tetra-*n*-butylphosphonium bromide (Expt. 3); here the ethyl product fraction appears both as ethyl propionate and, in the presence of insufficient acid, as unesterified ethanol (Expt. 2).

Table 2 summarizes the relationships linking ruthenium catalyst structure with ethyl propionate + ethanol productivity. As in the preparation of vicinal glycol esters from syngas (*27*), the choice of quaternary Group 5B salt is critical to achieving good yields of desired products. The structure of the aryl and alkyl radicals, the selection of ammonium or phosphonium salts, and the nature of the counterion are all important (Table 2). Large, thermally stable, phosphonium salts of moderately polarizable anions are generally preferred. The corresponding ammonium salts oftentimes undergo Hofmann degradation (illustrated in Table 1, Expt. 13, where Bu_4NBr leads to

TABLE 2

Ethyl Propionate/Ethanol Syntheses—Effect of Catalyst Composition

Catalyst composition	Ethyl propionate + ethanol productivity (mole)[a]
RuO_2–$10R_4EBr$:	$Ph_4P(73) < Ph_3MeP(183) < Ph_3HpP(207) < Bu_4P(395)$
RuO_2–$10Bu_4PX$:	$Cl(51) < Br(395) > I(18)$
RuO_2–$10Ph_4PX$:	$Cl(10) < Br(73)$
RuO_2–$10Bu_4EBr$:	$N(17) < P(395)$

[a] Productivity data based upon yields given in Table 1.

the formation of significantly increased quantities of butyl propionate). Other combinations with arylphosphonium salts (e.g., $BzPh_3PBr$, Ph_4PX, Expts. 5–7) ensure the formation of up to 56% propyl propionate. In these examples the competing reactions are reduction of the propionic acid coreactant to *n*-propanol, followed by esterification (Eq. (4)). The presence of chloride ion favors methyl ester formation (Expts. 7 and 8), but inhibits further homologation to C_2 products. Ruthenium(IV) oxide alone, in the absence of quaternary salt, yields very little desired ethyl ester (Expt. 15).

$$C_2H_5COOH + 2H_2 \rightarrow C_3H_7OH \xrightarrow{C_2H_5COOH} C_2H_5COOC_3H_7. \quad (4)$$

The essential features of this catalysis have been probed further through spectroscopic and kinetic measurements. The syntheses are generally believed to be homogeneous; since hydrocarbons higher than methane are rarely detected (*40*), there is no evidence of ruthenium plating (*41*), and the catalyst remains active upon multiple cycling (*28*).

Following CO hydrogenation (Table 1, Expt. 1) the typical deep-red liquid products exhibit infrared spectra (ν_{CO} = 2054m, 2032s, 1988s, 1967m cm^{-1}) characteristic (*42*) of the ruthenium carbonyl anion $[Ru(CO)_3(C_2H_5COO)_3]^-$. Other product solutions (e.g., Expt. 3) also, however, exhibited additional bands in this region at 2016s, 1989s, 1954m cm^{-1}, as well as ^1H NMR spectra consistent with a second ruthenium carbonyl anionic species $[HRu_3(CO)_{11}]^-$ (*26, 44*). This cluster has been reported previously to be a predominant species in related ruthenium-catalyzed syngas conversions to C_2-oxygenates (*26, 45*). Residual catalyst samples (*46*) (after recovery of the ethyl propionate ester), as well as recycled product solutions, displayed similar spectral patterns.

Selective ethyl ester production (Eq. (1)) is achieved only in the presence of greater than stoichiometric quantities of bulky cation, such as the heptyltriphenylphosphonium cation (see Fig. 1). The optimum P : Ru ratios (ca. 10 : 1), as in related ruthenium catalysis (*26, 27*), are contrary to any known charge ratio, either for ruthenium hydrocarbonyl monomeric or cluster species (e.g., $[Ru(CO)_3(C_2H_5COO)_3]^-$ and $[HRu_3(CO)_{11}]^-$, vide supra). They likely reflect changes in solvent media properties brought about by the addition of high concentrations of phosphonium salts. Alterations in ionic strength and dielectric constant, the degree of ion pairing (e.g., $[HpPh_3P]^+[Ru(CO)_3(C_2H_5COO)_3]^-$), as well as changes in syngas and ruthenium solubility, may each radically affect the ethyl ester productivity (*47*).

A typical reaction profile for the RuO_2–$HpPh_3PBr$ catalyst (depicted in Fig. 2) shows rapid initial formation of methyl propionate, but ethyl propionate concentrations subsequently increase so it becomes the predominant product. During this second stage there is an accompanying decline in methyl propionate concentration, consistent with the methyl ester being an intermediate in the sequential formation of its ethyl congener (Eq. (5)).

$$C_2H_5COOH + CO + 2H_2 \rightarrow C_2H_5COOCH_3 \xrightarrow{CO/H_2} C_2H_5COOCH_2CH_3. \quad (5)$$

Iodide-promoted, ruthenium-catalyzed methyl ester homologations have already been researched by Braca and *et al.* (*48, 49*). In the case of ethyl acetate formation from MeOAc, where iodocarbonylruthenium species are essential for ester homologation, Braca *et al.* demonstrated (*49*) that the ethyl fraction originates both from homologation (Eq. (6)) and through hydrogenation of the acetic acid coreactant (Eq. (7)).

$$CH_3COOCH_3 + CO + 2H_2 \rightarrow CH_3COOC_2H_5 + H_2O. \quad (6)$$

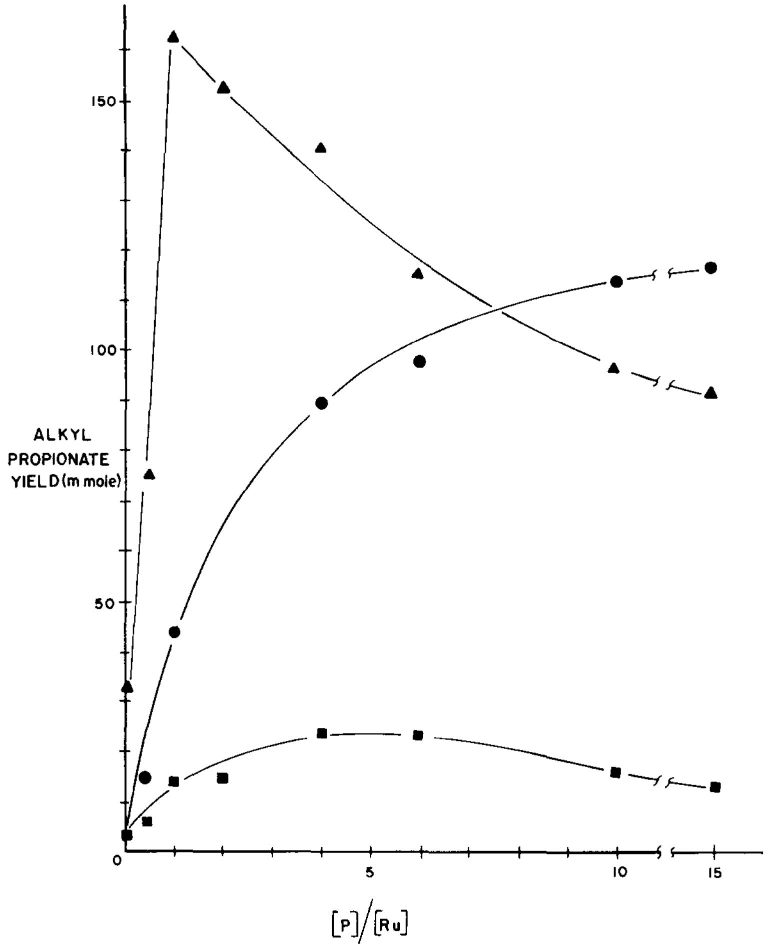

FIG. 1. Alkyl propionates from synthesis gas—effect of ruthenium catalyst composition (HpPh$_3$PBr : RuO$_2$): Ethyl propionate, ●; methyl propionate, ▲; *n*-propyl propionate, ■. Operating conditions: RuO$_2$ · xH$_2$O, 2.0 mmole; C$_2$H$_5$COOH, 25.0 g; CO/H$_2$, 1 : 1; 220°C; 18 h; 430 atm constant pressure.

$$CH_3COOH + 2H_2 \rightarrow C_2H_5OH \xrightarrow{CH_3COOH} CH_3COOC_2H_5. \quad (7)$$

This complication (Eqs. (6) and (7)) is resolved in our iodide-free system by the use of substituted (*28*) and higher-MW aliphatic carboxylic acids, such as propionic acid (Table 1), because now the acid-reduction pathway no longer yields the desired ethyl ester (e.g., see Eq. (4)). Furthermore, for the ruthenium(IV) oxide–heptyltriphenylphosphonium bromide catalyst couple, ^{13}C-enriched acetic acid coreactant has been used to unambiguously identify the carbon source for the ethyl ester. Ethyl acetate product exhibits ^{13}C enrichment only at the carbonyl carbon, consistent with the stoichiometry of Eq. (8).

$$2CO + 4H_2 + CH_3\overset{*}{C}OOH \rightarrow CH_3CH_2OO\overset{*}{C}CH_3 + 2H_2O. \quad (8)$$

Nevertheless there remain several possible routes to the formation of ethyl esters from CO/H$_2$ (see Scheme 1). The direct production of ethanol (path (c)) can be discounted in our systems since both methanol and ethanol are generated in significant concentrations at high propionic acid conversions (see Table 1, Expts. 2 and 8). Path

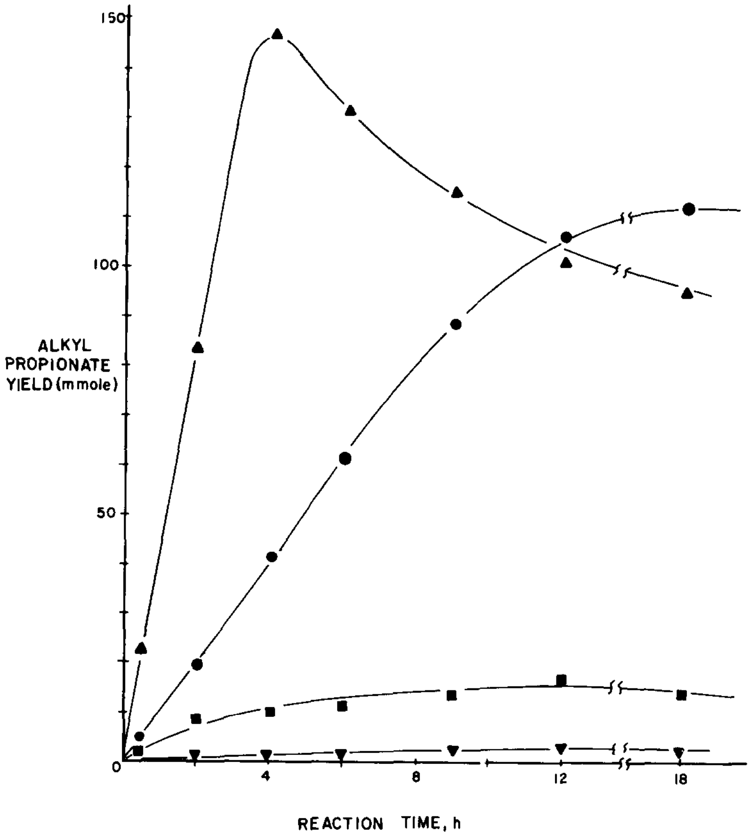

FIG. 2. Alkyl propionates from synthesis gas—reaction profile: Ethyl propionate, ●; methyl propionate, ▲' propyl propionates, ■; butyl propionates, ▼. Operating conditions: $RuO_2 \cdot xH_2O$, 2.0 mmole; $HpPh_3PBr$, 20 mmole; C_2H_5COOH, 25.0 g; CO/H_2, 1 : 1; 220°C; 430 atm constant pressure.

(d) appears less likely in view of the relatively slow rates of I-free, ruthenium-catalyzed, methanol homologation (*54*), relative to esterification. Paths (a), also Eq. (5), and (b), however, could represent parallel reaction paths where at high acid levels (and therefore low acid conversions) the ester route (a) might be expected to predominate (we see little or no evidence for methanol under those conditions). Preliminary

$$CO/H_2 \xrightarrow{RCOOH} CH_3OOCR \xrightarrow{CO/H_2} CH_3CH_2OOCR \qquad (a)$$

$$CO/H_2 \longrightarrow CH_3OH \xrightarrow{RCOOH} CH_3OOCR \xrightarrow{CO/H_2} CH_3CH_2OOCR \qquad (b)$$

$$CO/H_2 \longrightarrow CH_3CH_2OH \xrightarrow{RCOOH} CH_3CH_2OOCR \qquad (c)$$

$$CO/H_2 \longrightarrow CH_3OH \xrightarrow{CO/H_2} CH_3CH_2OH \xrightarrow{RCOOH} CH_3CH_2OOCR \qquad (d)$$

SCHEME 1. Routes to ethyl ester formation from synthesis gas.

results with stronger aliphatic acid coreactants, such as trifluoroacetic acid, are also in accord with these conclusions.

Pyrolysis of Carboxylic Acid Esters

The second stage of our proposed ethylene synthesis (Eq. (1)) has been demonstrated also for typical intermediate ethyl esters. Pyrolysis of acyclic, aliphatic carboxylic acid esters to alkenes and the parent acid is well documented (*50–53*) and in our work C_1–C_3 alkyl propionates, prepared by the synthesis techniques of Table 1 (Expts. 1 and 11) and isolated by fractional distillation, were pyrolyzed to ethylene, propylene, and propionic acid by the homogeneous gas-phase method (see Table 3). In the initial experimental series, 98+% ethyl propionate is passed over Pyrex helices at 460°C (Expt. 16). Ethyl propionate conversion averages ca. 30% per pass; selectivity to propionic acid is 95–97%; ethylene comprises 92% of the light gas fractions.

Pyrolysis of the crude C_1–C_3 alkyl propionate distillate fraction from Expt. 1 yields ethylene, propylene, and propionic acid as the principal products (see Table 3, Expt. 17). Ethyl and propyl propionate conversions are estimated to be 53 and 41%, respectively; the methyl propionate fraction passes through the thermolysis unit relatively unchanged. Where the feed liquid is richer in propyl propionate, additional propylene is concentrated in the light gas fraction (Expt. 18). Overall carbon selectivity to ethylene in a combination of Expts. 1 and 17 is ca. 40%. Ethylene plus propylene selectivity is ca. 50%. These figures would be higher if the methyl propionate by-product were recycled and homologized to additional ethyl ester (Fig. 2). The full scope and utility of this new ethylene process remains under study (*54*).

EXPERIMENTAL

Synthesis gas was purchased from Big Three Industries in various proportions of carbon monoxide and hydrogen. All ruthenium derivatives, alkali metal salts, as well as quaternary ammonium and phosphonium salts, were purchased from outside suppliers. All high-pressure experiments were conducted in 450-ml- and 845-ml-capacity Aminco pressure reactors constructed of 316 stainless steel, fitted with

TABLE 3

Pyrolysis of Alkyl Propionates[a,b]

		Composition of liquid fraction (wt%)[c]				Composition of gas fraction (%)[d]		
Expt.		$EtCOOC_2H_5$	$EtCOOH$	$EtCOOCH_3$	$EtCOOC_3H_7$	C_2H_4	C_2H_6	C_3H_6
16[e]	Charge	100						
	Product	72	27	0.1		92	4	
17	Charge	58	1.8	23	11			
	Product	27	34	25	6.2	55	6	34
18	Charge	36	24	19	14			
	Product	28	33	24	10	33	1.1	54

[a] Pyrolysis was conducted in a vertically mounted, externally heated, 49-cm Vycor glass tube containing a 30-cm bed of ⅛-in. Pyrex helices.

[b] Operating conditions: 460°C; He flow, 20 cm³/min; liquid feed rate, 3 ml/min.

[c] Collected in two traps cooled with air and dry ice/acetone; analyses as per Table 1.

[d] Collected in trap cooled with 1-propanol/liquid nitrogen slush bath; analyses by GLC.

[e] Operating conditions: He flow, 60 cm³/min; liquid feed rate, 6 ml/min.

heating and agitation means, and hooked to large, high-pressure, synthesis gas reservoirs. Each reactor was fitted with interchangeable Pyrex glass liners.

The extent of reaction and distribution of products were determined by gas–liquid chromatography using a modified porous polymer column programmed from 140 to 280°C with 30 cm^3/min He flow. The ester products, particularly ethyl esters like ethyl propionate, were isolated by fractional distillation *in vacuo,* and by GLC trapping, and identified by NMR, FTIR, mass spectroscopy, and elemental analyses.

Synthesis of Ethyl Esters

In a typical synthesis, the glass-lined reactor is charged, under a nitrogen atmosphere, with a mixture of 0.764 g of ruthenium(IV) oxide, hydrate (4.0 mmole), 17.64 g of heptyl(triphenyl)phosphonium bromide (40 mmole), and propionic acid (50 g). Upon stirring under the nitrogen atmosphere most of the solids dissolve to give a deep-red solution. The reactor is then sealed, flushed with CO/H_2, pressured to 2000 psi with synthesis gas (a 1 : 1 mixture of hydrogen and carbon monoxide), and heated to 220°C with agitation. At temperature, the pressure within the reactor is raised to 6300 psi with CO/H_2 mix, and the pressure held constant throughout the 18-h run by automatic addition of more synthesis gas from the large surge tank. Upon cooling, the excess gases are sampled and vented, and the deep-yellow liquid product (73.8 g) removed for analysis. There is no solid product fraction.

Analysis of the liquid fraction by gas–liquid chromatography (GLC) shows the presence of:

38.2 wt% ethyl propionate
16.5 wt% methyl propionate
8.4 wt% propyl propionate
0.8 wt% butyl propionate
0.9 wt% glycol dipropionate
2.7 wt% water
27.8 wt% unreacted propionic acid.

Analysis of a typical gas fraction by GLC shows the presence of:

27% hydrogen
22% carbon monoxide
32% carbon dioxide
17% methane.

The ethyl propionate, together with the corresponding methyl, propyl, and butyl propionates, was isolated from a portion of the crude liquid product (58.8 g) by stripping under reduced pressure (0.8 g Hg). The residual liquid "bottoms" (32.1 g) contained the solubilized ruthenium catalyst; the clear distillate fraction (26.1 g) contained:

58.3 wt% ethyl propionate
22.9 wt% methyl propionate
10.5 wt% propyl propionate
0.4 wt% butyl propionate.

This distillate liquid was further purified by fractional distillation.

Pyrolysis of Ethyl Esters

A 3.5-cm-diameter quartz tube, 43 cm in length, is packed with glass helices, set in a vertical plane, and heated to 450–460°C. Helium is passed through the tube at a rate of 60 ml/min, and the clear, distillate liquid product from above is added dropwise to the top of the helix bed of the pyrolysis reactor at a rate of 1–2 ml/min. The bed temperature is 450–460°C. The effluent gases are passed first through an air trap and then through two further traps cooled in dry ice–acetone (trap 2) and a liquid nitrogen-*n*-propanol slush bath (trap 3). After 30 min of operation, an analysis of the water-white liquid (15.5 g) in trap 1 showed the presence of:

33.9 wt% propionic acid
24.9 wt% methyl propionate
27.2 wt% ethyl propionate
6.2 wt% propyl propionate.

The liquid collected in trap 3 showed the presence of:

55% ethylene
6% ethane
34% propylene.

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