Studies of the rhodium iodide catalysed hydrocarboxylation of ethene

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Abstract

Consideration is given to the various parameters which affect the yield and selectivity of propanoic acid formation in the hydrocarboxylation of ethene using a rhodium/I^- catalyst. The source of rhodium, the solvent, the form of iodide promoter, the composition of the carbon monoxide/ethene mixture, and the effect of additives are all considered. Rhodium(III) chloride trihydrate rather than the iodide produces the highest reaction rate for the iodoethane promoted reaction. When dichloromethane is used as a diluent, the reaction rate and yield of acid are lowered by ca. 20–30% without affecting the nature of the products. However, diethylether and water are the major products when ethanol is the reaction solvent, but hydrocarboxylation continues, the reaction rate being enhanced 3-fold when ethene is present. Throughout, iodoethane is a better promoter than hydrogen iodide, but iodoethane alone is a poor solvent. CO:alkene mixtures in the range 1:2 to 2:1 are preferred and give similar yields and rates of acid production. In CH_2Cl_2 solvent, additives enhance the reaction in the order $H_2O > C_2H_5OH > C_2H_5COOH$, and when the solvent is glacial acetic acid, very small amounts of water have a dramatic promotional influence on the reaction rate. Iodine, hypophosphorous acid and lithium propanoate additives have an adverse effect on catalysis.

*Keywords:* Ethene hydrocarboxylation; Propanoic acid; Rhodium iodide

1. Introduction

Carbonylation of alkenes may lead to aldehydes, alcohols, acids, esters, amines, amides, and ketones, depending on the nature of the co-reagents, the metal catalyst and the reaction conditions [1]. Many of these reactions are undertaken on an industrial scale [2], and continue to be of great interest either as possible alternative routes to chemicals produced by older technology, or as routes to new materials. Hydrocarboxylation can be achieved using the same metals as those used in hydroformylation, and the active catalytic species are again metal hydrides [3]. Internal alkenes are converted to terminal esters in the presence of alcohols using cobalt, for example, under forcing conditions (i.e., 170°C, 200 atm) in basic solution [4]. Palladium catalysts, when used in an acidic medium, have a wide synthetic application for achieving hydroxy- and alkoxy-carbonylations, and are sometimes used with phosphines and tin(II)

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chloride for a wide variety of different alkene-containing molecules [5]. Interestingly, in very strong acidic media, e.g. H_2SO_4/SO_3, HF/SbF_5, metal catalysts are not required, and high yields of carboxylic acids are often obtained [6]. On an industrial scale, nickel carbonyl has been used as the catalyst for the production of propanoic acid from ethene, carbon monoxide and water [7], viz:

$$CH_2=CH_2 + CO + H_2O \rightarrow CH_3CH_2COOH \tag{1}$$
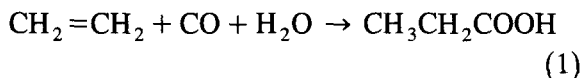
Poor catalyst stability, low reactivity, and low selectivity plague this BASF process which operates at 280°C and 240 atm total pressure. Multiple insertions lead to by-products. The reaction can also be adapted to produce unsaturated acids, such as acrylic acid, from ethyne [8]. For the corresponding cobalt carbonyl catalysed reaction, succinic acid is the main product [9], e.g.,

$$CH\equiv CH + 2CO + 2H_2O$$
$$\rightarrow HOOCCH_2CH_2COOH \tag{2}$$
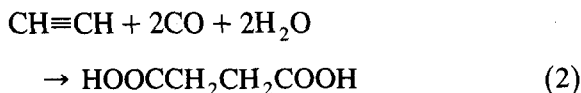
In 1969, Monsanto filed a patent on the hydrocarboxylation of primary alkenes using rhodium and iridium catalysts and iodide promoters [10]. Reaction in both the vapour and liquid state was claimed at temperatures 50–300°C and pressures 125–1000 atm, though the preferred conditions were 125–225°C and 2–65 atm. Iodide:rhodium molar ratios of 3:1 to 300:1 were preferred, though ratios 1:1 to 2500:1 achieve reaction. The reaction mechanism for this process was considered to be similar to that for the nickel carbonyl system [7], and for the rhodium system is shown in Fig. 1. An iodide:rhodium ratio of 3:1 is required according to the catalytic cycle. Oxidative addition of hydrogen iodide, followed by coordination of ethene allows for *cis* migration of hydrogen, then *cis* migration of the ethyl group so formed to carbon monoxide. The final stage of the cycle involves the reductive elimination of the acyl iodide. Hydrolysis regenerates hydrogen iodide
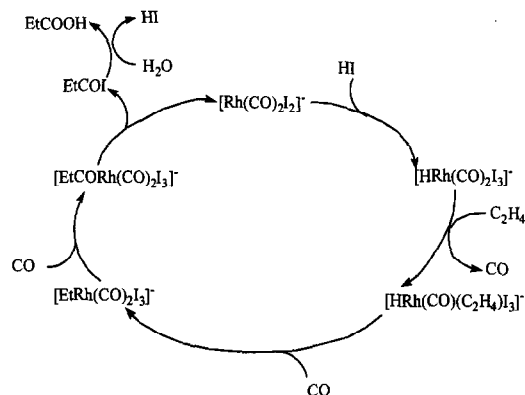

Fig. 1. A catalytic cycle for the hydrocarboxylation of ethene.

and produces propanoic acid. However, an investigation by Forster [11](a) showed that at 125°C and 35 atm pressure, iodoethane gave a reaction rate 80 times more rapid than when hydrogen iodide was the initiator. It was found also that addition of a small amount of hydrogen iodide to the iodoethane-promoted-reaction reduced the rate. Furthermore, the reaction (3) did not equilibrate within the reaction time. These results

$$HI + C_2H_4 \rightarrow C_2H_5I \tag{3}$$

suggest that the iodoethane mechanism operates for the reaction, and that it is the carbonylation of iodoethane which leads to propanoic acid. However, such an interpretation contradicts the accepted rates of oxidative addition, viz. $HI > CH_3I > CH_3CH_2I$. When sensitive radio-tracer techniques were applied [11](a), the results demonstrated conclusively that ethene hydrocarboxylation proceeds predominantly by HI addition. Further, it was shown that high levels of hydrogen iodide inhibited the rate by poisoning the catalyst, probably as follows:

$$[Rh(CO)_2I_2]^- + HI \rightarrow [HRh(CO)_2I_3]^- \tag{4}$$

$$[HRh(CO)_2I_3]^- + HI \rightarrow [Rh(CO)_2I_4]^- + H_2 \tag{5}$$
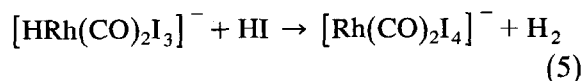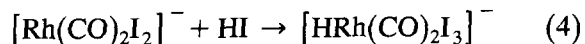
An implication of the faster rate when iodoethane is the initiator is the controlled formation of hydrogen iodide in concentrations insuf-

Table 1
Studies of hydrocarboxylation of ethene using different rhodium complexes as precursors

Reaction No./autoclave	Reactants/mol	Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)	Reaction time (min)	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h⁻¹	Rate (2) /mol kg⁻¹ h⁻¹	Turn-over (×10²)
1 [b]	$RhCl_3 \cdot 3H_2O$ 9.87×10^{-5} EtI_2 3.73×10^{-2} H_2O 1.67×10^{-1}	CH_3COOH (29 cm³)	192	CO 80 C_2H_4 40	12	0.23	0.142	85	415	18.1	14.4
2 [b]	RhI_3 1.04×10^{-4} EtI 3.73×10^{-2} H_2O 1.67×10^{-1}	CH_3COOH (29 cm³)	180	CO 80 C_2H_4 40	22	0.23	0.226	82	218	15.7	21.7

Key: a = autoclave 1, 500 cm³ (zirconium); b = autoclave 2, 105 cm³ (hastalloy 'C'); c = autoclave 3, 300 cm³ (hastalloy 'B').

Table 2
Studies of hydrocarboxylation using different solvents

Reaction No./autoclave	Reactants/mol	Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)		Reaction time	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h^{-1}	Rate (2) /mol kg^{-1} h^{-1}	Turn-over (×10^2)
3 [a]	RhI$_3$ 4.98×10^{-4} EtI 4.97×10^{-2} H$_2$O 5.00×10^{-1}	C$_2$H$_5$COOH ($187 \, cm^3$)	180	CO 30 C$_2$H$_4$ 30		78 min	1.23	0.55	>80	45.0	1.55	11.0
4 [a]	RhI$_3$ 5.01×10^{-4} EtI 4.97×10^{-2} H$_2$O 5.0×10^{-1}	C$_2$H$_5$COOH ($55 \, cm^3$) CH$_2$Cl$_2$ ($132 \, cm^3$)	180	CO 30 C$_2$H$_4$ 30		61 min	0.76	0.30	>80	35.4	1.24	6.0
5 [a]	RhCl$_3 \cdot$3H$_2$O 5.30×10^{-4} HI 2.11×10^{-3} EtI 2.48×10^{-2} H$_2$O 5.55×10^{-1}	EtOH ($180 \, cm^3$)	180	CO 50 C$_2$H$_4$ 30		10 h	0.84	0.27	34	4.0	0.15	5.1
6 [a]	RhCl$_3 \cdot$3H$_2$O 4.98×10^{-4} EtI 1.24×10^{-1}	EtOH (190 cm)	180	CO 50		5 h	0.36	0.055	6	3.2	0.32	1.1
7 [a]	RhCl$_3 \cdot$3H$_2$O 5.17×10^{-4} EtI 1.24×10^{-1}	EtOH ($190 \, cm^3$)	180	CO 50 C$_2$H$_4$ 30		6 h	1.32	0.64	47	10.5	0.99	12.4

Key as in Table 1.

Table 3
Studies of the effects of different promoters and degree of hydration on hydrocarboxylation

Reaction No./autoclave	Reactants/mol		Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)		Reaction time (h)	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h^{-1}	Rate (2) /mol kg^{-1} h^{-1}	Turn-over ($\times 10^2$)
8 [a]	RhCl$_3$·3H$_2$O	5.3×10^{-4}	EtOH	180	CO	50	8	0.61	0.25	47	3.4	0.13	4.7
	EtI	6.22×10^{-3}	(200 cm^3)		C$_2$H$_4$	30							
9 [a], 10 [a]	RhCl$_3$·3H$_2$O	5.28×10^{-4}	EtOH	180	CO	50	12	0.28	0.085	29	1.1	0.045	1.6
	HI	6.36×10^{-3}	(200 cm^3)		C$_2$H$_4$	30							
11 [a]	RhCl$_3$·3H$_2$O	5.30×10^{-4}	EtOH	180	CO	50	12	0.24	0.087	32	0.97	0.045	1.6
	HI	6.40×10^{-3}	(190 cm^3)		C$_2$H$_4$	30							
	H$_2$O	5.55×10^{-1}											

Key as in Table 1.

Table 4
Studies of the effects of using EtI as the solvent on hydrocarboxylation

Reaction No./ autoclave	Reactants/mol		Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)		Reaction time (h)	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h^{-1}	Rate (2) /mol kg^{-1} h^{-1}	Turn-over (×10^2)
12 [a]	$RhCl_3 \cdot 3H_2O$	4.89×10^{-4}	EtI	180	CO	80	11	0.65	0.059	> 90	2.8	0.013	1.2
	H_2O	5.55×10^{-1}	(190 cm^3)										
13 [a]	$RhCl_3 \cdot 3H_2O$	5.31×10^{-4}	EtI	180	CO	50	2	0.62	0.37	> 95	14.7	0.416	7.0
	HI	1.13×10^{-3}	(190 cm^3)		C_2H_4	30							
	H_2O	5.55×10^{-1}											

Key as in Table 1.

Table 5
Studies of the effects of carbon monoxide to ethene pressure on hydrocarboxylation

Reaction No./ autoclave	Reactants /mol		Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)		Reaction time	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h⁻¹	Rate (2) /mol kg⁻¹ h⁻¹	Turn-over (×10²)
14 [a]	RhI_3 EtI H_2O	5.04×10^{-4} 4.96×10^{-2} 5.00×10^{-1}	C_2H_5COOH (55 cm^3) CH_2Cl_2 (135 cm^3)	180	CO C_2H_4	48 12	2 h	0.63	0.24	> 80	15.0	0.99	4.8
15 [a]	RhI_3 EtI H_2O	4.95×10^{-4} 4.96×10^{-2} 5.00×10^{-1}	C_2H_5COOH (55 cm^3) CH_2Cl_2 (135 cm^3)	180	CO C_2H_4	40 20	2 h	1.85	0.27	> 80	44.0	1.46	5.5
16 [a]	RhI_3 EtI H_2O	5.12×10^{-4} 4.96×10^{-2} 5.00×10^{-1}	C_2H_5COOH (55 cm^3) CH_2Cl_2 (135 cm^3)	180	CO C_2H_4	30 30	80 min	0.99	0.30	> 80	35.4	1.24	5.9
17 [a]	RhI_3 EtI H_2O	4.98×10^{-4} 4.96×10^{-2} 5.00×10^{-1}	C_2H_5COOH (55 cm^3) CH_2Cl_2 (135 cm^3)	180	CO C_2H_4	20 40	2 h	1.26	0.30	> 80	30.0	1.45	6.0
18 [a]	RhI_3 EtI H_2O	5.04×10^{-4} 4.96×10^{-2} 5.00×10^{-2}	C_2H_5COOH (55 cm^3) CH_2Cl_2 (135 cm^3)	180	CO C_2H_4	12 48	20 h	0.65	0.085	> 80	1.54	0.04	1.7

Key as in Table 1.

Table 6
Studies of the effects of different oxygen nucleophiles on hydrocarboxylation

Reaction No./ autoclave	Reactants/mol		Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)		Reaction time (h)	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h^{-1}	Rate (2) /mol kg^{-1} h^{-1}	Turn-over ($\times 10^2$)
19 [a]	$RhCl_3 \cdot 3H_2O$ EtI H_2O	5.15×10^{-4} 6.20×10^{-2} 5.55×10^{-1}	CH_2Cl_2 (185 cm^3)	180	CO C_2H_4	40 30	1	0.88	0.44	93	42	1.17	8.5
20 [a]	$RhCl_3 \cdot 3H_2O$ EtI EtOH	5.20×10^{-4} 6.20×10^{-2} 4.26×10^{-1}	CH_2Cl_2 (170 cm^3)	180	CO C_2H_4	50 30	8	0.62	0.32	93	3.7	0.105	6.2
21 [a]	$RhCl_3 \cdot 3H_2O$ EtI C_2H_5COOH	5.13×10^{-4} 6.20×10^{-2} 5.02×10^{-1}	CH_2Cl_2 (165 cm^3)	180	CO C_2H_4	50 30	10	0.84	0.25	88	4.0	0.081	4.9

Key as in Table 1.

Table 7
Studies of the effect of water concentration on hydrocarboxylation

Reaction No./ autoclave	Reactants/mol		Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)		Reaction time	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h^{-1}	Rate (2) /mol kg^{-1} h^{-1}	Turn-over ($\times 10^2$)
22 [b]	RhI$_3$	1.05×10^{-4}	CH$_3$COOH	180	CO	40	3 h	0.051	0.071	72	6.0	0.603	6.8
	EtI	3.73×10^{-2}	(29 cm^3)		C$_2$H$_4$	40							
	H$_2$O	None											
23 [b]	RhI$_3$	1.08×10^{-4}	CH$_3$COOH	180	CO	40	20 min	0.048	0.0	60	51	6.86	8.3
	EtI	3.73×10^{-2}	(29 cm^3)		C$_2$H$_4$	40							
	H$_2$O	1.11×10^{-4}											
24 [b]	RhI$_3$	1.09×10^{-4}	CH$_3$COOH	180	CO	40	30 min	0.19	0.180	84	136	9.16	16.5
	EtI	3.73×10^{-2}	(29 cm^3)		C$_2$H$_4$	40							
	H$_2$O	1.11×10^{-3}											
25 [b]	RhI$_3$	1.04×10^{-4}	CH$_3$COOH	180	CO	40	25 min	0.22	0.245	80	185	15.0	23.6
	EtI	3.73×10^{-2}	(29 cm^3)		C$_2$H$_4$	40							
	H$_2$O	1.11×10^{-2}											

Key as in Table 1.

Table 8
Studies of the effects of HI and EtI as initiators for hydrocarboxylation

Reaction No./ autoclave	Reactants/mol		Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)		Reaction time	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h⁻¹	Rate (2) /mol kg⁻¹ h⁻¹	Turn-over (×10²)
26 [c]	RhI_3	2.89×10^{-4}	C_2H_5COOH (30 cm³)	180	CO	20	21 h	0.32	0.12	> 80	1.2	0.041	4.2
	H_2O	1.67×10^{-1}	CH_2Cl_2 (70 cm³)		C_2H_4	20							
27 [c]	RhI_3	2.89×10^{-4}	C_2H_5COOH (30 cm³)	180	CO	20	10 min	0.27	0.11	> 80	129	5.28	3.8
	H_2O	1.67×10^{-1}	CH_2Cl_2 (70 cm³)		C_2H_4	20							
	EtI	1.00×10^{-2}											
28 [c]	RhI_3	3.03×10^{-4}	C_2H_5COOH (30 cm³)	180	CO	'20	60 min	0.10	0.11	> 80	7.9	0.68	3.6
	H_2O	1.67×10^{-1}	CH_2Cl_2 (70 cm³)		C_2H_4	20							
	HI	1.00×10^{-2}											

Key as in Table 1.

Table 9
Studies of the effects of additives on hydrocarboxylation

Reaction No./ autoclave	Reactants/mol		Solvent (vol.)	Max. reaction temp. (°C)	Gas/pressure at 20°C (atm)		Reaction time	Mol of gas absorbed	Mol of propanoic acid produced	Selectivity (%)	Rate (1) /atm h^{-1}	Rate (2) /mol kg^{-1} h^{-1}	Turn-over ($\times 10^2$)
29 [b]	RhI$_3$	1.08×10^{-4}	CH$_3$COOH (29 cm^3)	192	CO	40	30 min	0.23	0.151	79	164	7.69	14.0
	EtI	2.48×10^{-2}			C$_2$H$_4$	40							
	H$_2$O	1.67×10^{-1}											
	HI	5.26×10^{-3}											
30 [b]	RhI$_3$	1.09×10^{-4}	CH$_3$COOH (29 cm^3)	191	CO	40	17 min	0.21	0.081	89	258	7.30	7.4
	EtI	3.73×10^{-2}			C$_2$H$_4$	40							
	H$_2$O	1.67×10^{-1}											
	I$_2$	1.01×10^{-3}											
31 [b]	RhI$_3$	1.06×10^{-4}	CH$_3$COOH (29 cm^3)	182	CO	40	2 h	0.25	0.183	89	45	2.34	17.3
	EtI	3.73×10^{-2}			C$_2$H$_4$	40							
	H$_2$O	1.67×10^{-1}											
	H$_3$PO$_2$	1.27×10^{-3}											
32 [b]	RhI$_3$	1.04×10^{-4}	CH$_3$COOH (29 cm^3)	182	CO	40	75 min	0.20	0.097	83	58	1.98	9.3
	EtI	3.73×10^{-2}			C$_2$H$_4$	40							
	H$_2$O	1.47×10^{-1}											
	C$_2$H$_5$COO$^-$ Li$^+$	1.39×10^{-3}											

Key as in Table 1.

ficient to de-activate the active catalyst. The most likely source is the hydrolysis of ethanoic iodide following carbonylation of iodoethene, viz.

$$C_2H_5I + [Rh(CO)_2I_2]^-$$

$$\rightarrow [C_2H_5Rh(CO)_2I_3]^-$$

$$\rightarrow [C_2H_5CORh(CO)I_3]^-$$

$$[C_2H_5CORh(CO)I_3]^-$$

$$+ CO \rightarrow [Rh(CO)_2I_2]^- + C_2H_5COI$$

$$C_2H_5COI + H_2O \rightarrow C_2H_5COOH + HI$$
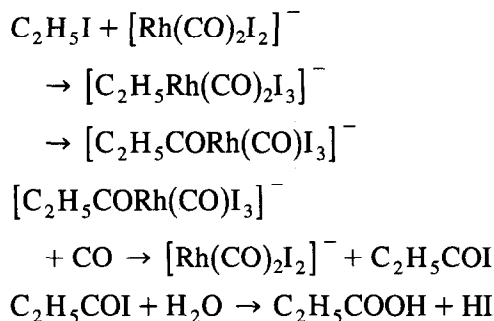
The iodoethene, therefore, acts as a reservoir source of the promoter, undergoing oxidative addition poorly compared with hydrogen iodide, but replenishing it when it is consumed by side reactions as outlined above.

A study of factors influencing the hydrocarboxylation of ethene is reported here supported by an infra-red spectral study of the same system under high temperature and high pressure conditions. Alternative sources of rhodium, and iodide are compared, alternative solvents and solvent mixtures assessed, different pressures and gas mixtures used, varying amounts of water added and various additional promoters tested.

2. Experimental

Details of the reactions studied and the results obtained are summarised in Tables 1–9. Rhodium(III) chloride trihydrate and rhodium(III) iodide were used as obtained from Johnson–Matthey Chemicals and Ventron. Iodoethane, iodine, ethanoic acid, propanoic acid, dichloromethane, hypophosphoric acid and lithium ethanoate dihydrate were obtained from Aldrich Chemical in the highest purity available (usually analytical grade) and used as supplied. Iodoethane was stored at low temperature in the dark. Hydrogen iodide was prepared from tetrahydronaphthalene and iodine by the method of

Hoffman [11](b) and passed directly into the solvent required. Collection yields for less-polar solvents such as dichloromethane were 20–40%, whereas for polar solvents such as water, yields were between 60–80%. The hydrogen iodide solutions were protected from the light until use. Commercial sources of hydriodic acid were not used as they contain the stabiliser, hypophosphoric acid, shown in this work to be detrimental to catalysis.

Three autoclaves were used for the reactions studied, as detailed below:

Autoclave 1: 500 cm³ zirconium autoclave,
Autoclave 2: 105 cm³ Hastalloy 'C' autoclave,
Autoclave 3: 300 cm³ Hastalloy 'B' autoclave with tipping facility.

Autoclaves 1 and 3 had MagneDrive stirring, whilst for autoclave 2 reaction mixtures were stirred using an internal magnetic follower at a pre-set speed. All autoclaves were heated by an external band heater controlled by a thermocouple placed in a well set in the reaction mixture, and connected to a Eurotherm controller. Reactants were loaded against a counter flow of nitrogen via inlet ports at the head of the autoclave as solids and mixtures of liquids. The tipping facility of Autoclave 3 was used to introduce reactants at the operating temperature of the reaction to minimise any side reactions which may occur during the heating period to 180°C. The catalyst was contained in a gelatin capsule and placed in a holder attached to the head of the autoclave, and supplied with its own gas inlet. The holder was separated from the main body of the autoclave by a sealed, hinged door, which opened when the pressure inside the holder was 2–5 atm higher than that in the main autoclave. Thus, catalyst and other components were added at the reaction temperature. For each reaction the autoclave was flushed with nitrogen, pressurised with carbon monoxide and the pressure released, before the reactant gases were introduced. Ethene was always introduced before carbon monoxide. The same stirrer speed was used for all reactions under-

taken in the same autoclave, though no attempt was made to standardise stirrer speeds in the three autoclaves. Consequently, since rates of reaction involving gaseous reactants are very dependent on the efficiency of mixing, i.e., stirring speed and design of stirrer, etc., rates given for reactions undertaken in different autoclaves should not be compared. The autoclave used for a series of comparative reactions is specified in the tables.

Infrared spectra were recorded for solutions under high pressures and at elevated temperatures using a Mattson Centauri FT spectrometer in conjunction with a Hastalloy IR cell [12] fitted with calcium fluoride windows. The region 2250–1800 cm^{-1} was monitored.

Gas up-take was recorded for each reaction by manual or computer monitoring of pressure gauges or transducers. The reaction time was considered as the period over which gas up-take could be detected, no change in pressure over a 10 min period being taken as completion of the

reaction, and the overall rates which are reported were calculated on this basis. Two rates have been calculated, Rate (1) referring to the rate of gas absorption per h and Rate (2) referring to the rate of propanoic acid produced. The unit used for propanoic acid formation is mol of the acid produced per kg of initial reaction solution per h of reaction.

Product mixtures were analysed by gas liquid chromatography, using a 1.3 m chromasorb 101 column in a Varian, model 3700, chromatograph. A temperature programme with a 10°C rise per min from 40–200°C, and a final resting time of 9 min was used. Integration was undertaken using a SpectroPhysics Chromojet integrator. Response factors for ethanoic acid, propanoic acid, and dichloromethane were determined using analytical grade materials, and other compounds were assumed to have a response factor of one. All volatile material was removed from metal residues by vacuum distillation and condensed in a trap at −196°C prior
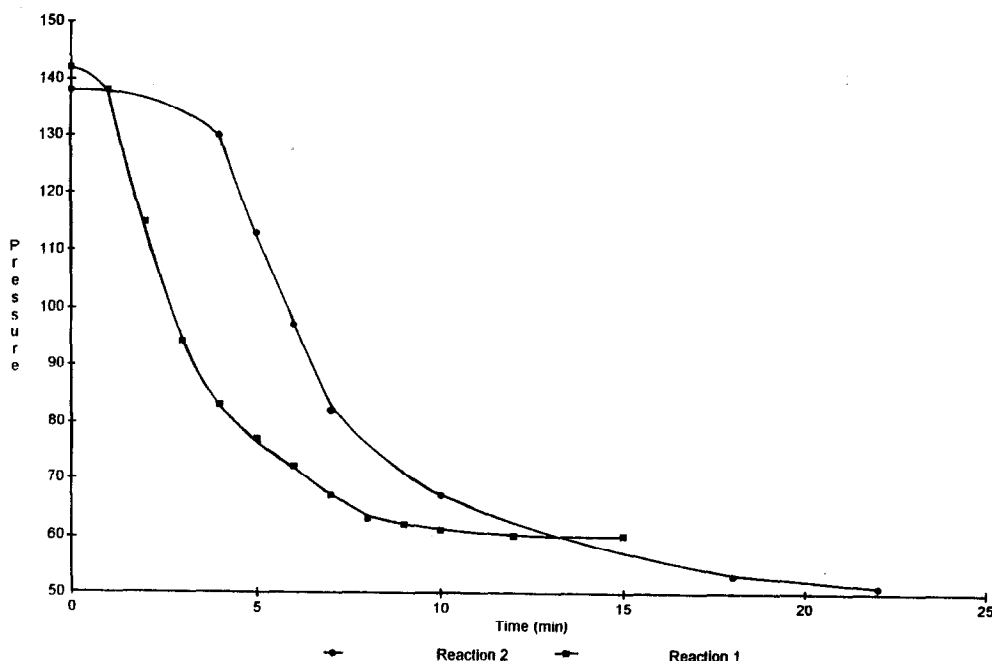
Fig. 2. Total CO/C_2H_4 pressure (atmospheres) plotted against time (min) for [$RhCl_3 \cdot 3H_2O$] (reaction (1)) and [RhI_3] (reaction (2)) catalysed hydrocarboxylation reactions of ethene.

to GLC analysis. Components detected or monitored included diethylether, ethanol, iodoethane, ethylpropanoate, propanoic acid and water.

3. Results and discussion

3.1. General aspects

The preferred components of the reaction mixture for the formation of propanoic acid from ethene and carbon monoxide are rhodium(III) chloride hydrate, the catalyst precursor, iodoethane as promoter, and a carboxylic acid as the solvent (see Table 1, reaction 1). Water is also a component. IR studies show that the rhodium chloride is rapidly converted to $Rh_2(CO)_4Cl_2$, $Rh(CO)_3Cl$, then $[Rh(CO)_2Cl_2]^-$, which in the presence of a source of iodide ions, leads quickly to $[Rh(CO)_2I_2]^-$ [13]. Rhodium chloride is preferred to the iodide on the grounds of the poor solubility of the latter, but data given in Table 1 (reactions 1 and 2), where results for the two systems are compared, show the rate for the rhodium chloride system to be only marginally greater than that for the iodide when taken over a 1 h reaction period (see Fig. 2). However, the RhI_3 reaction produces a greater amount of propanoic acid. Here, ethanoic acid is used as the solvent in preference to the commonly used propanoic acid, to permit better precision in the analysis of the product mixture. It is found that the $RhCl_3$ reaction has a much shorter initiation period and shows a small pressure drop before the temperature reaches 180°C, but that the RhI_3 reaction maintains a high rate for a longer period of time.

3.2. Choice of solvent

Both ethanoic and propanoic acids are suitable solvents for hydrocarboxylation, but when dichloromethane is used as a diluent (acid:CH_2Cl_2 = 1:2.4), the rate of reaction and amount of propanoic acid produced are lowered by ca. 20% (see Table 2, reactions 3 and 4), but the mixed solvent system appears not to change the course of the reaction. This result allows the use of CH_2Cl_2 as a diluent for the HPIR solution studies, and consequent improvements in spectral quality are obtained.

When ethanol is used as the reaction solvent, (see Table 2, reaction 5), the rate becomes about ten times slower, and diethylether and water become major products, dehydration of ethanol being the most likely source of these materials. Propanoic acid remains a product, two routes being possible for its formation, (i) hydrocarboxylation of ethene, and (ii) carbonylation of ethyl iodide generated from the solvent and iodide ions. Since the rates of oxidative addition are EtI < MeI < HI [14], route (ii) is expected to be slower than route (i) which involves oxidative addition of HI. To test the extent of propanoic acid formation from ethanol, reactions were undertaken with and without added ethene (see Table 2, reactions 6 and 7). Some propanoic acid is formed in its absence (reaction 6), but the yield is improved by the addition of ethene. Thus, formation of propanoic acid from ethene and ethanol appears to occur simultaneously. Despite the large amount of ethanol present compared with the amount of ethene, the data appears to show that ethene is the preferred route to propanoic acid.

Using ethanol as the solvent, two iodide promoters were studied, iodoethane and hydrogen iodide, (see Table 3, reactions 8 and 9) in identical molar quantities. Interestingly, the iodoethane reaction gives a rate of acid formation three times greater than for the HI promoted reaction. Under the reaction conditions used, the hydrogen iodide will react with the ethanol to form iodoethane, and an overall comparable reaction with the iodoethane reaction might be expected. However, differences are likely to arise from the rapid formation of $[HRh(CO)_2I_3]^-$ and $[Rh(CO)_2I_4]^-$ (see Eqs. (4) and (5)), which catalyse other non-hydrocarboxylation reactions such as ether formation and the water gas shift reaction [15]. Indeed, the

latter complex is observed in the IR spectrum of the reaction mixture under catalytic conditions, whereas when EtI is used as the promoter in ethanol, only $[Rh(CO)_2I_2]^-$ is detected.

When a comparison was made between hydrated and anhydrous reaction systems in ethanol as solvent (see Table 3, reactions 10 and 11), no difference in the rates of reaction was detected, though conversion to propanoic acid was low in both cases. Diethylether and water were the main products. Dehydration of ethanol to yield diethylether is usually achieved under acid conditions, so it is not surprising that this is a product if HI is present at elevated temperatures, albeit that ethanol will suppress its effects. However, ether in large quantities was also produced under non-acid conditions (see reactions 6 and 7 in Table 2), suggesting that the dehydration is catalysed by a rhodium complex. In ethanol, the main species detected by IR in the reaction solution under the forcing conditions is $[Rh(CO)_2I_2]^-$, and a possible cycle for ether formation is shown in Fig. 3. This cycle involves the generation of $[HRh(CO)_2I_3]^-$ either directly by the oxidative addition of HI to $[Rh(CO)_2I_2]^-$, or from $[EtRh(CO)_2I_3]^-$, the eventual product of oxidative addition of EtI to $[Rh(CO)_2I_2]^-$. The hydride is not detected by HPIR spectroscopy, which is not surprising since it is an active intermediate and is expected to have a short lifetime and low concentration.

The alternative cycle, given in Fig. 4, differs from the hydrocarbonylation cycle at stage A
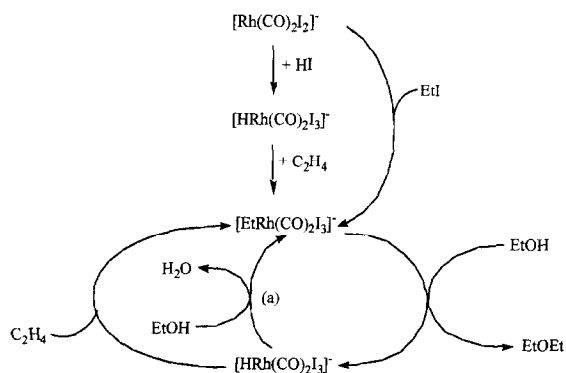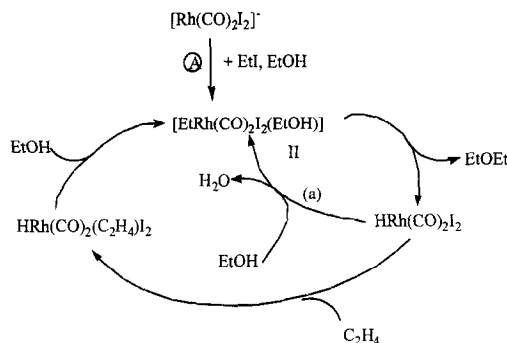
Fig. 4. An alternative catalytic cycle for the formation of diethylether.

following the attack at iodoethane by $[Rh(CO)_2I_2]^-$ to form $[EtRh(CO)_2I_2]$. The subsequent rapid *trans* addition of iodide ion will be in competition with addition of ethanol, and formation of $[EtRh(CO)_2I_2(EtOH)]$ appears a strong possibility under these conditions. Since hydrocarboxylation requires insertion of CO into the rhodium alkyl bond to form the acyl group, normally a rapid reaction, the preferential formation of an ether implies the occurrence of an even more facile reaction with ethanol.

The oxidative addition of HI to rhodium appears unlikely in alcohol at 180°C because of the rapid reaction of HI with alcohols to form iodoalkanes [16]. Hydrocarboxylation thus requires generation of a H–Rh species by an alternative route. Ethanol can provide a source of hydrogen, and the known [17] interaction between the N–H hydrogen in $R_3NH^+[Rh(CO)_2I_2]^-$, together with the observed [18] dependence of ν_{CO} for $[Rh(CO)_2I_2]^-$ on the nature of the solvent, suggests that rhodium(I) complexes form interactions of the type illustrated in (I, Scheme 1). Thus, $[HRh(CO)_2I_2]$, once formed either from the reaction of $[Rh(CO)_2I_2]^-$ or from $[EtRh(CO)_2I_2(EtOH)]$ (II, Scheme 1), could initiate the alternative cycle molecule in close proximity to the metal bound ethyl group, facilitating loss of diethylether and regeneration of the catalytic species, $[HRh(CO)_2I_2]$. Overall the reaction is:

$$CH_2{=}CH_2 + C_2H_5OH \rightarrow C_2H_5OC_2H_5$$

Fig. 3. A catalytic cycle for the formation of diethylether.

Scheme 1.

or

$$C_2H_5OH \xrightarrow{HI} C_2H_5I \xrightarrow{C_2H_5OH} C_2H_5OC_2H_5 + HI$$
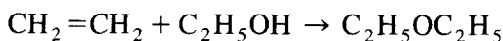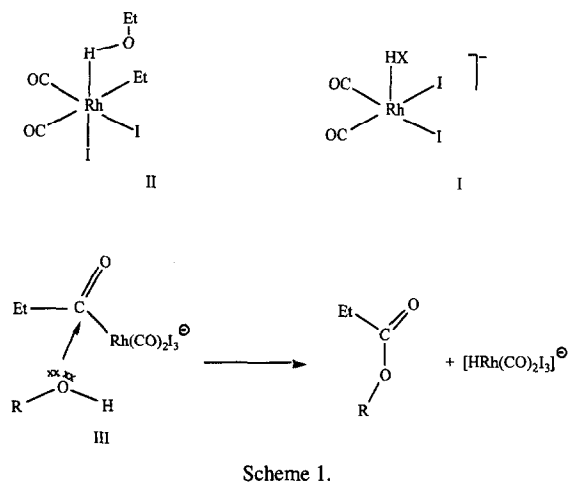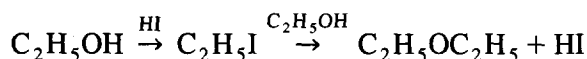
When iodoethane is used as the solvent (see Table 4, reactions 12 and 13), only small amounts of propanoic acid are produced in the absence of ethene. The rhodium is observed by HPIR spectroscopy to be predominantly present as $[Rh_2(CO)_2I_4]^{2-}$ and $[Rh(CO)_2I_4]^-$. Thus,

the route to propanoic acid via oxidative addition of iodoethane, gives at best low rates and yields of reaction. However, the addition of ethene improves both the parameters, although they still remain poor.

3.3. Effects of carbon monoxide to ethene pressures

Table 5 (see reactions 14–18) records the effects of changes in the relative pressures of carbon monoxide and ethene on hydrocarboxylation reactions in a mixed propanoic acid and dichloromethane solvent system, using a rhodium(III) iodide/iodoethane catalyst/promoter. The initial total pressure for all the five separate experiments was 60 atm. It is clear from the data that a four-fold excess of ethene or carbon monoxide is detrimental to catalysis, but that acid formation occurs to a similar extent and at a similar rate for ratios between 2:1 and 1:2 CO/ethene. Rates of acid formation are marginally better when carbon monoxide is in excess, and suggests that the step involving the
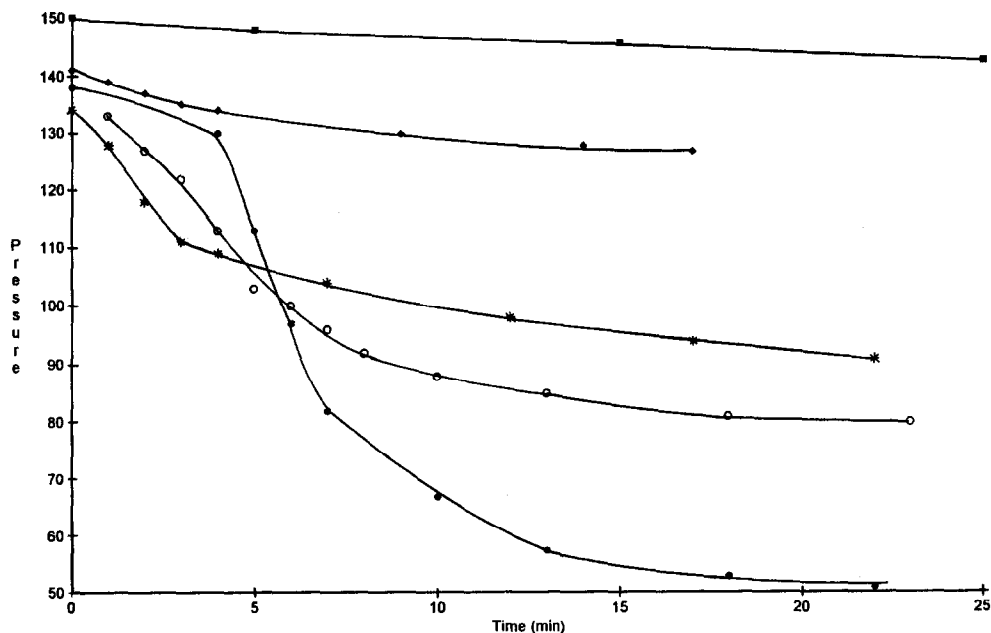
Fig. 5. Total CO/C_2H_4 pressure (atmospheres) plotted against time (min) for [RhI$_3$] catalysed hydrocarboxylation reactions of ethene containing different amounts of water. (Key; – • – reaction 2; – ■ – reaction 22; – ♦ – reaction 23; – * – reaction 24; – ○ – reaction 25).

addition of ethene to the metal centre is not the rate determining step. This conclusion is not surprising since the oxidative addition (here of hydrogen iodide) is expected to be rate determining, as found for the Monsanto process.

3.4. The effects of added water

In the proposed catalytic cycle (Fig. 1), the final reaction step to regenerate the hydrogen iodide and form propanoic acid may involve a variety of oxygen nucleophiles, including water, ethanol, and propanoic acid, which produce propanoic acid, ethyl propanoate, and propanoic anhydride respectively. To investigate the relative reactivity of these three ROH compounds, reactions were undertaken in dichloromethane (see Table 6, reactions 19–21), using an equal molar amount of each ROH compound separately. The amount of propanoic acid produced in the various forms (i.e. acid, ester, anhydride) shows a variation of less than a factor of two. However, the rate of production in the case of water is 10- to 15-fold greater than for the other two compounds. The action of water is therefore more significant than simply as a reagent for regenerating iodide ions, a step which is not part of the catalytic cycle and which should not affect the rate. Further studies were therefore undertaken to elucidate the role (see Table 1, reaction 2, Table 7, reactions 22–25, and Fig. 5).

Of note is the ten-fold increase in the rate of acid production achieved by the addition of a very small amount of water to the anhydrous, rhodium iodide catalysed reaction, though the amount of acid produced is only marginally greater (see Table 7, reactions 21 and 22) and remains small. This suggests a catalytic role for water in the reaction, though water does not feature in the normally-accepted catalytic cycle (Fig. 1). Consequently, alternative roles for water in the reaction require consideration. Two different possible roles are outlined below. Firstly, nucleophilic attack by water at the acyl group of $[EtCORh(CO)_2I_3]^-$, as shown in (III,

Scheme 1), would lead directly to formation of propanoic acid and generation of the catalytic species $[HRh(CO)_2I_3]^-$. Similar attack by alcohols and acids would achieve in principle a similar result. However, the dramatic effect of a small amount of water may be attributable also to acid catalysis. The reaction shown in (III, Scheme 1) is nucleophilic attack at the acyl carbonyl group, promoted by protonation of the acyl oxygen atom. Thus, the action of the water may be to increase the acidity of glacial acetic acid significantly for this to occur, but unfortunately, standard acidity functions are not available for the degree of hydration studied here.

Secondly, water may feature in the reduction of RhI_3 to $[Rh(CO)_2I_2]^-$, by reacting with EtI to generate EtOH (and HI), known to act as an effective reducing agent in rhodium(III) to rhodium(I) conversions. Thus, the amount of water present may determine the amount of RhI_3 converted into the active catalyst, thereby effecting the rate of acid formation, but not the selectivity (as is found).

The addition of increasing amounts of water to the anhydrous RhI_3 system (see Table 7, reactions 23–25) generally increases the rate of gas uptake and the rate of propanoic acid formed, though the selectivity of the reaction remains virtually unchanged at ca. 80%. Water appears to have a dramatic effect on the reaction rate at very low concentrations and continues to have a beneficial effect up to a concentration approximately similar to that of the iodoethane, when the effect levels out.

3.5. Comparison of iodoethane and hydrogen iodide as initiators

The effects of these two iodide sources as initiators are compared in Table 8 (see reactions 26–28) with the reaction having no initiator added except for the iodine in the catalyst precursor (RhI_3) itself. The last reaction is very slow indeed, and continues over a 21 h period. Thus, additional iodide (i.e. Rh:I$^-$ > 1:3) has a beneficial effect on the rate of reaction. In the

reactions 27 and 28 (see Table 8), the additional promoter was added at reaction temperature and pressure, using a tipping facility in the special autoclave. Separate additions of equal molar amounts of iodoethane and hydrogen iodide were found to produce different effects, the iodoethane having the greater influence on the rate of gas up-take and propanoic acid formation. Initial rates were the same despite the fact that HI oxidative addition is more rapid than that of iodoethane. The extremely rapid rate in the presence of EtI is attributed by Forster [11](a) to oxidative addition of HI generated as follows:

$$EtI + CO + H_2O \rightarrow EtCOOH + HI$$
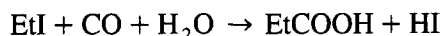
After this acceleration period, the amount of HI would not increase greatly as it becomes part of the catalytic cycle, and competes with the EtI in the oxidative addition reaction:

$$HI + C_2H_4 + CO \rightarrow CH_3CH_2COI$$
$$\rightarrow C_2H_5COOH + HI$$
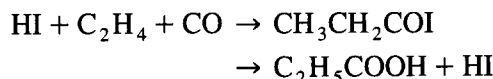
The surprisingly lower activity shown by added HI is probably the result of poisoning of the catalyst by the use of 30-fold excess of HI over the amount of rhodium. $[Rh(CO)_2I_2]^-$ is converted first to $[HRh(CO)_2I_3]^-$, and then to $[Rh(CO)_2I_4]^-$ or $[Rh(CO)I_5]^{2-}$, the effect being to remove the rhodium from the hydrocarboxylation catalytic cycle.

HPIR spectral studies show that when EtI is used as the promoter $[Rh_2(CO)_4I_2]$, $[Rh(CO)_2I_2]^-$, $[Rh(CO)_2I_4]^-$ and $[Rh_2(CO)_2I_4]^{2-}$ are all observed during the heating process under a pressure of CO up to 180°C, and that the addition of ethene had little effect on the mixture. When HI was used, the same complexes were detected, with the additional complex $[Rh(CO)I_5]^{2-}$. Thus, rhodium is found to be in forms which effectively remove the metal from the hydrocarboxylation cycle.

## 3.6. The effect of further additives

A series of reactions was undertaken in which various further additives, detailed in Table 9

(reactions 29–32), are included in the reactions. The main component concentrations (RhI_3, EtI, H_2O, CH_3COOH, CO, C_2H_4) are kept constant and the same molar amount of each additional component (HI, I_2, H_3PO_2, CH_3COOLi) added. Again when hydrogen iodide is added, the rate of reaction decreases and selectivity falls slightly. The effect of HI is again considered to produce $[Rh(CO)_2I_4]^-$ (identified by HPIR spectroscopy), thereby removing rhodium from the hydrocarboxylation cycle. A similar decrease in the rate of reaction is observed when iodine is added, though iodine does not have such a detrimental effect as HI. De-activation of the catalyst by oxidative addition of iodine to form $[Rh(CO)_2I_4]^-$, $[Rh(CO)I_5]^{2-}$ and RhI_3 has been shown to occur.

Commercial hydriodic acid is stabilised by the presence of hypophosphorous acid which reduces free iodine as follows:

$$H_3PO_2 + H_2O + I_2 \rightarrow H_3PO_3 + 2HI$$
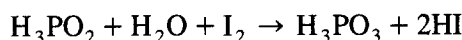
In order to check the effect of the stabiliser, hypophosphorous acid was added in the absence of HI, and in a molar quantity greater than that in the commercial hydriodic acid. A marked decrease in rate occurs, even in comparison with the effects of iodine and HI. It had been expected that hypophosphorous acid would reduce Rh(III) species to Rh(I) by removing iodide from the complex, viz

$$[Rh(CO)_2I_4]^- + H_3PO_2 + H_2O$$
$$\rightarrow [Rh(CO)_2I_2]^- + 2HI + H_3PO_3$$
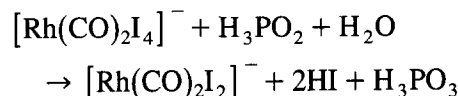
and thus promote hydrocarboxylation. However, the decreased rate indicates that the reagent acts in a way different to that expected.

The promotional effects of alkali metal ions on carbonylation reactions are well documented [19]. Also, our own work shows that propanoate ions promote the formation of rhodium(I) complexes. Thus the addition of lithium propanoate to the reaction mixture was expected to result in enhanced catalysis. In practice the salt has a marked detrimental effect on the reaction rate, very little propanoic acid being formed. Thus,

though propanoate maintains the presence of rhodium(I) in solution, it is not conducive to efficient catalysis. Coordination of the carboxylate group to the rhodium is a distinct possibility, though why such an effect should not occur also when ethanoic and propanoic acids are used as solvents, can not be readily understood.

4. Conclusions

Hydrocarboxylation of ethene in ethanoic acid is best achieved using $RhCl_3 \cdot 3H_2O$ as the catalyst and iodoethane as the promoter. RhI_3 gives marginally lower rates, and HI leads to the formation of rhodium(III) carbonyl iodides, thereby reducing the catalyst concentration. Diethylether and water are the major products when ethanol is used as the solvent, both ethanol and ethene contributing to the diethylether formation. Reaction is stopped by high concentrations of iodoethane and hydrogen iodide. When the reaction solvent is glacial ethanoic acid, very small amounts of water in the RhI_3/EtI system produce a dramatic increase in the reaction rate.

Acknowledgements

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