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TRANSITION METAL CATALYSED INTERACTION OF ETHYLENE AND ALKYL FORMATES

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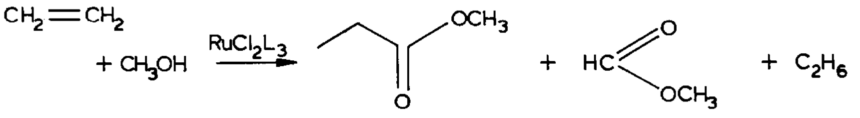
Summary

Methyl propionate may be obtained by the homogeneous ruthenium catalysed interaction of ethylene and methyl formate. Product formation probably involves an initial fragmentation of the formate to free or ligand CO.

Introduction

Our studies [1,2] concerning the use of alcohols as a source of hydrogen in the synthesis of diethyl ketone (from ethylene and CO) revealed the unique behaviour of methanol. In effect, in the absence of CO, methanol acted not only as a source of hydrogen, but also as a source of carbon [3] in the formation of methyl propionate (I) eq. 1, L = PPh_3. Methyl formate is always a major side product of this reaction [5]. This, together with the reports [6] that alkyl formates will undergo "oxidative addition" to certain Pt and Ru complexes (to give alkoxycarbonyl entities MCOOR) prompted us to investigate whether the propionate could originate from the transition-metal catalysed interaction of an alkyl formate and an olefin.



(1)

(I) (II)

Results and discussion

The results (Table 1, run 1) indicate that the reaction of methyl formate and ethylene does indeed lead to propionate (I). The results with other formates,

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TABLE 1

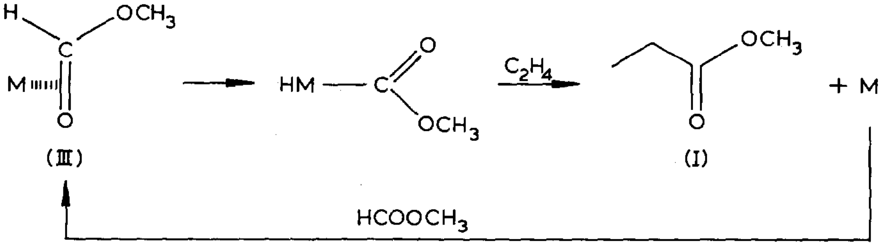
INTERACTION OF ETHYLENE AND ALKYL FORMATES ($RuCl_2L_3$ (0.14 mmol), Autoclave 300 ml, C_2H_4 (10 bar), N_2 (10 bar), 190–200°C, 18 h)

Run	Alkyl formate (ml)	Solvent (ml)	Propionate (mmol)	CO (mmol)
1	Methyl (80)	none	40	55
2	Ethyl (60)	none	0	14
3 [a]	Benzyl (60)	Acetone (20)	0	26
4 [b]	Allyl (10)	Toluene (50)	0	0.3
5 [c]	Methyl (20)	Toluene (60)	–	11
6 [c]	Ethyl (20)	Toluene (60)	–	1.1
7	Methyl (20)	Toluene (60)	0	1.3
8	Methyl (20)	Chlorobenzene (60)	0	2.5
9	Methyl (20)	Cyclohexanone (60)	1.5	14
10 [d]	Methyl (20)	DMF (60)	0	445

[a] Products contain CO_2 (32 mmol), toluene, benzylalcohol, benzaldehyde. [b] Products contain CO_2 (105 mmol), propylene (80 mmol), [c] Reaction carried out in the absence of ethylene. [d] Reaction stopped after 2 h.

however, are less encouraging (Table 1, runs 2–4). Thus, contrary to a literature report [6], virtually no reaction was observed with ethyl formate. Allyl and benzyl formates underwent extensive decomposition, possibly by retro-ene type processes, to give carbon dioxide together with propylene and toluene, respectively.

Propionate formation may be rationalised in terms of the "oxidative addition" of II to a ruthenium centre followed by the well documented [7,8] transfer of the alkoxycarbonyl group to the olefin eq. 2, M = Ru and associated ligands.



(2)

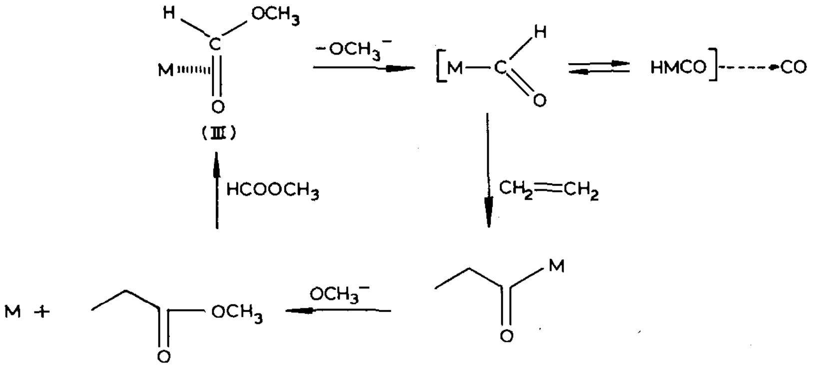
However such a scheme cannot account for the differences observed between methyl and ethyl formates. An alternative pathway to I involves degradation of the alkyl formate, by alkoxide extrusion in III, leading to free or ligand CO, (and alcohol). A conventional hydroalkoxycarbonylation [8] would then lead to the propionate, e.g. eq. 3, M = Ru and associated ligands.

The differences in reactivities between methyl and ethyl formates would then be associated with differences in the nucleophilicities of the methoxide and ethoxide ions. Support for such a scheme comes from the observations that carbon monoxide is always a side product and that in the absence of ethylene (Table 1, runs 5,6) the quantity of CO obtained from HCOOMe is superior to that obtained from HCOOEt. Furthermore there is a pronounced solvent effect (Table 1, runs 7–10); HCOOMe decomposes rapidly in DMF in the presence of $RuCl_2L_3$. Ionizing solvents should

TABLE 2

INTERACTION OF ETHYLENE AND ALKYL FORMATES ($RuCl_3 \cdot 3H_2O$ (0.103 mmol), Autoclave 300 ml C_2H_4 (10 bar), N_2 (10 bar), 190–200°C, 18 h)

Run	Alkyl formate (ml)	Solvent (ml)	Propionate (mmol)	CO (mmol)
1	Methyl (10)	DMF (70)	5.6	225
2	Methyl (10)	DMF (30, Toluene (40)	6.7	215
3	Methyl (10)	DMF (10), Toluene (60)	9.2	19
4	Methyl (10)	DMF (2), Toluene (68)	5.0	9
5	Methyl (10)	Toluene (70)	0	5
6	Methyl (10)	NMP (10), Toluene (60)	17	2.8
7	Methyl (10)	NEt_3 (10), Toluene (60)	0	7.6
8	Ethyl (10)	NMP (10), Toluene (60)	1.2	2.9



(3)

favour alkoxide extrusion in III and thus promote the formation of CO and propionate, the quantity of CO formed from HCOOMe increases according to the sequence toluene < chlorobenzene < cyclohexanone ≪ DMF [9].

There does not appear to be any clear correlation between the quantities of carbon monoxide and propionate produced. Thus with catalyst systems bases on $RuCl_3$, and toluene/DMF mixtures, the CO produced increases with increasing DMF content whilst the production of propionate is at an optimum at 10–20% DMF (Table 2, runs 1–5). With *N*-methylpyrrolidone (NMP)/toluene mixtures, good selectivities in methyl propionate may be obtained at 10% conversions (turnover number; 170 mol propionate/mol catalyst) (Table 2, run 6). Trace amounts of ethyl propionate may be obtained by the interaction of ethylene and ethyl formate in this same solvent mixture (Table 2, run 8).

Preliminary experiments indicate that propylene also reacts with methyl formate in the presence of $RuCl_2L_3$, giving approximately equal proportions of linear and branched methyl butyrates (see Experimental).

Experimental (in collaboration with Mr B. Béguin (CNRS) and Mr M. Renaud (PCUK))

All the reactions were carried out in glass-lined 300 ml Autoclave Engineers autoclaves equipped with magnedrive units. $RuCl_2L_3$ was prepared by literature methods [10].

The reaction products were analysed either directly (gas-phase) or after distillation (liquid phase) by vapour phase chromatography (VPC) or by VPC-mass spectrometry (VPC-MS) [11]: gaseous products, CO, CO_2, H_2O on Carbosieve B, Porapak Q (TC-detector). Gaseous and liquid (distillate) organic products on Porapak Q, Porapak R and capillary (Silicone CP.Sil 8) columns (FID).

In a typical run $RuCl_2L_3$ (100 mg, 0.104 mmol) was dissolved in oxygen-free methyl formate (80 ml). The solution was transferred under argon into the autoclave, which had been purged with nitrogen and pressurised with ethylene (10 b) then nitrogen (10 b), prior to stirring and heating (190°C). After 18 h the gaseous phase was analyzed by VPC; Carbosieve B; H_2 (10 mmol), CO (55 mmol), CO_2 (2.1 mmol); Porapak Q; CH_4 (0.015 mmol), C_2H_4 (too great to measure), C_2H_6 (0.4 mmol), C_3-hydrocarbons (0.035 mmol), C_4-hydrocarbons (traces). After venting the autoclave the liquid was distilled under atmospheric pressure and analyzed by VPC; capillary CP Sil 8 (30–220°C); CH_3OH (50 mmol), $HCOOCH_3$ (too great to measure), $CH_3CH_2COOCH_3$ (40 mmol). The methyl propionate was identified by VPC-MS as well as by aqueous alkaline-hydrolysis of an aliquot of the distillate and subsequent characterization (IR, NMR) of the sodium propionate.

Similarly $RuCl_2L_3$ (500 mg, 0.52 mmol) dissolved in acetone (22 ml) and methyl formate (63 ml) was pressurised with propylene (174 mmol) and nitrogen (106 bar). After 8 h, the distilled reaction product was shown to contain (VPC-MS-analysis): methanol (93 mmol), isopropyl formate (16 mmol), methyl n-butyrate (3 mmol) and methyl isobutyrate (2.5 mmol).

Conclusions

Methyl propionate may be obtained by the ruthenium-catalysed interaction of methyl formate and ethylene, preferably in polar solvents. The bulk of the evidence indicates that the reaction probably proceeds by an initial fragmentation of the C_1-molecule, rather than by the transfer of an alkoxycarbonyl entity. Further studies in this area are in progress [12].

Acknowledgments

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References

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2 R.P.A. Sneeden, J. Mol. Catal., 17 (1982) 349.

3 The production of mixtures of linear methyl alkanoates, which contain methyl propionate (I), from ethylene, methanol and $Ru(CO)_3L_2$ as catalyst has been described [4].

4 Shell Oil., USP 3,646,116 (1972).

5 We have observed that Cu/Zn contact masses will also catalyse the formation of I and II from ethylene and methanol (autoclave, 200°C).

6 M.E. Vol'pin and I.S. Kolomnikov, in E.I. Becker and M. Tsutsui (Ed.) Organometallic Reactions, Vol. 5, 1975, p. 357, and ref. cited therein.

7 R.F. Heck, J. Am. Chem. Soc., 90 (1968) 5518.

8 G.W. Parshall, Homogeneous Catalysis, Wiley, New York, 1980, p. 85.

9 The dielectric constants of these solvents (25°C) follow the same sequence: toluene (2.38), chlorobenzene (5.62), $HCOOCH_3$ (8.25), cyclohexanone (18.3), DMF (36.71), NMP (32.2).

10 P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., XII (1970) 237.

11 We thank Mr D. Page of PCUK for the VPC-MS measurements.

12 Very modest yields of methyl propionate may also be obtained by the interaction of ethylene and methyl formate on Cu/Zn contact masses (autoclave 200°C): carbon monoxide, together with CO_2, dimethyl ether and C_1, C_3, C_4-hydrocarbons are the major products.