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HOMOGENEOUS CATALYTIC HYDROGENATION OF DICARBOXYLIC ACID ESTERS. II *

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Summary

Hydrogenation of dimethyl oxalate in the presence of $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ gives methyl glycolate and subsequently ethylene glycol. The formation of the glycol is favoured by hydroxylated solvents.

Introduction

Mono- and bi-carboxylic acids [2] and the esters of the latter [1] may be reduced in the homogeneous phase using $H_4Ru_4(CO)_8(PBu_3)_4$ as catalyst precursor. Other catalysts for hydrogenating such diesters [3] and carboxylic acids [4] are ruthenium carbonyl carboxylates, such as $Ru_4(CO)_8(CH_3COO)_4(PBu_3)_2$, $Ru_2(CO)_4(CH_3COO)_2(PBu_3)_2$ or $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$.

From both mono- and bi-carboxylic acids [2,4], esters are usually the main products. Hydroxy esters are formed from diesters [1]. In the exceptional case of glutaric acid, 60% of the product is the glycol either free or incorporated in 1,7-dioxacyclododecane-2,6-dione [2].

Recently we observed hydrogenation of dimethyl oxalate to give ethylene glycol with $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ as catalyst precursor [3]. We want to present the results of an investigation on the influence of the nature of the phosphine ligand in the catalyst, of the solvent and of the alkyl group of the carboalkoxy moiety on the course of the reaction. We also describe results obtained by monitoring the reaction in order to observe the rates of formation of the glycolate and the glycol.

* For part I see ref. 1.

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Results

The influence of the phosphine ligand was examined using dimethyl oxalate as substrate, benzene as solvent and $H_4Ru_4(CO)_8P_4$ or $Ru_2(CO)_4(CH_3COO)_2P_2$ as catalytic precursor; the phosphines (P) used were PBu_3, PPh_3, and PCy_3 (tricyclohexylphosphine) (Table 1). We were not, however, able to synthesize the PCy_3 derivative of the ruthenium hydride.

The reduction of the diester to give the hydroxy ester and methanol proceeds with 100% selectivity with PBu_3- or PPh_3-substituted catalyst precursors. Only in the case of the PCy_3 derivative was significant decomposition of the diester (about 50%), with formation of carbon dioxide, observed. All the PPh_3-substituted derivatives are far less active than the PBu_3-species. The $Ru_2(CO)_4(CH_3COO)_2P_2$ complexes in all cases gave more of the hydroxy ester than the corresponding ruthenium hydride

TABLE 1

REDUCTION OF DIMETHYL OXALATE TO METHYL GLYCOLATE IN THE PRESENCE OF RUTHENIUM COMPLEXES CONTAINING VARIOUS PHOSPHINE LIGANDS (Substrate 11 mmol; catalyst precursor 0.073 mg-atom Ru; benzene 15 ml; $p(H_2)$ 130 atm at 20°C; T 180°C; reaction time 144 h)

Catalyst precursor	Yield (%)
$H_4Ru_4(CO)_8(PPh_3)_4$	0
$H_4Ru_4(CO)_8(PBu_3)_4$	49.5
$Ru_2(CO)_4(CH_3COO)_2(PCy_3)_2 \cdot C_6H_5CH_3$	41.3 [a]
$Ru_2(CO)_4(CH_3COO)_2(PPh_3)_2$	6.2
$Ru_2(CO)_4(CH_3COO)_2(PBu_3)_2$	79.2
$Os_2(CO)_4(CH_3COO)_2(PBu_3)_2$	16.7
$Ru(CO)_2(CH_3COO)_2(PBu_3)_2$	87.1 [b]

[a] Carbon dioxide, from the decomposition of dimethyl oxalate (48%), was present in the residual gas. [b] Reaction time 22 h.

TABLE 2

REDUCTION OF DIMETHYL OXALATE IN THE PRESENCE OF $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$: CONVERSION AT DIFFERENT TIMES (Substrate 11 mmol; catalyst precursor 0.073 mg-atom Ru; benzene 15 ml; $p(H_2)$ 130 atm at 20°C; temperature 180°C)

Reaction time (h)	Conversion (%)	Product composition (mol%)	
		Methyl glycolate	Ethylene glycol
2	6.0	100	–
4	30.1	100	–
8	54.5	100	–
16	77.0	100	–
22	87.1	100	–
29	91.8	100	–
50	100	100	–
144	100	93.2	6.8

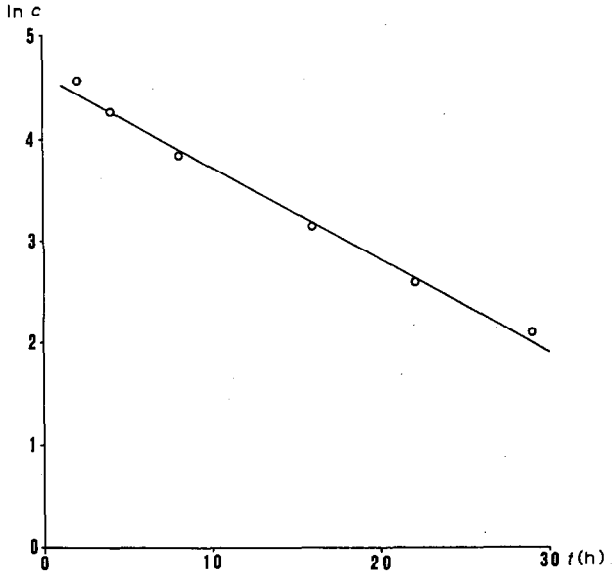

Fig. 1. Hydrogenation of dimethyl oxalate to methyl glycolate (data from Table 2). Plot of ln of the concentration of dimethyl oxalate against time.

derivatives. The osmium carbonyl carboxylate, $Os_2(CO)_4(CH_3COO)_2(PBu_3)_2$, showed no appreciable catalytic activity.

As previously noted [3] the mononuclear complex $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ appears to be the most active of the catalysts examined. The course of the reaction has been investigated with this complex as catalyst precursor.

As is evident from Table 2, the conversion of the dimethyl oxalate to the corresponding hydroxy ester preceeds the reduction of the latter to glycol. A good first order plot was observed for conversion of the oxalate to the hydroxy ester (Fig. 1).

The solvent can have a significant influence (Table 3). Ethers seem not to affect the activity of the catalyst, but an aromatic solvent such as benzene or a hydroxylic solvent such as methanol enhance the activity of the catalytic intermediates.

TABLE 3

REDUCTION OF DIMETHYL OXALATE IN THE PRESENCE OF $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$: INFLUENCE OF THE SOLVENT (Substrate 11 mmol; catalyst precursor 0.073 mg-atom Ru; solvent 15 ml; $p(H_2)$ 130 atm at 20°C; temperature 180°C; reaction time 144 h)

Solvent	Conversion (%)	Product composition (mol%)	
		Methyl glycolate	Ethylene glycol
Dioxane	95.4	100	–
Tetrahydrofuran	97.2	100	–
Benzene [a]	100	93.2	6.8
Methanol	100	73.3	26.7

a Benzene was hydrogenated to cyclohexane (25%).

TABLE 4

REDUCTION OF DIALKYL OXALATES IN THE PRESENCE OF $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$: INFLUENCE OF THE ALKYL GROUP (Substrate 11 mmol; catalyst precursor 0.073 mg-atom Ru; benzene 15 ml; $p(H_2)$ 130 atm at 20°C; temperature 180°C; reaction time 144 h)

Substrate	Conversion (%)	Product composition (mol%)	
		Alkyl glycolate	Ethylene glycol
Dimethyl oxalate	100	93.2	6.8
Di-iso-propyl oxalate	100	100	–
Di-n-propyl oxalate	93.7	100	–
Di-n-hexyl oxalate	69.7	100	–

In Table 4 are shown data for the hydrogenation in benzene of the methyl, iso-propyl, n-propyl and n-hexyl oxalates in the presence of $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$. Esters of heavier alcohols are evidently less reactive. Only in the case of the methyl ester is the glycol formed.

Discussion

Reduction of dimethyl oxalate to the corresponding hydroxy ester takes place with 100% selectivity in the presence of all the PBu_3 and PPh_3 ruthenium catalysts tested.

In an appropriate solvent the hydroxy ester may be reduced to glycol in a subsequent reaction step. Methyl alcohol favours the second reaction to such an extent as to suggest that it participates in the catalytic cycle.

In order to obtain evidence about the favourable influence of hydroxylated compounds on the course of the reaction the reduction of the diester was performed in the presence of small amounts of the hydroxy ester or the glycol. From the results (Table 5) it is clear that the hydroxylated reagent is definitely involved in the catalytic intermediate.

The ruthenium complexes recovered at the end of the reaction are different from those initially taken as catalyst precursors.

TABLE 5

REDUCTION OF DIMETHYL OXALATE TO METHYL GLYCOLATE IN THE PRESENCE OF $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$: INFLUENCE OF HYDROXYLATED REAGENTS (Substrate 11 mmol; catalyst precursor 0.073 mg-atom Ru; hydroxylated reagent 2.4 mmol; benzene 15 ml; $p(H_2)$ 130 atm at 20°C; temperature 180°C; reaction time 4 h)

Added hydroxylated reagent	Yield (%)
None	30.1
Methyl glycolate	48.7
Ethylene glycol	77.6

Experimental

GLC analyses were performed on a Perkin–Elmer Sigma 1 System; IR spectra were recorded using a Perkin–Elmer 580B Data System; GLC mass spectra were recorded with a HP 5970A spectrometer.

Materials

Dimethyl oxalate and ethylene glycol were commercial products.

Di-iso-propyl oxalate, di-n-propyl oxalate and di-n-hexyl oxalate were made from oxalic acid and the corresponding alcohol by standard procedures.

Methyl glycolate was prepared by reduction of dimethyl oxalate (30.0 g, 0.254 mol) with $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ (100 mg) in benzene (40 ml) in the presence of hydrogen (200 atm at 20°C) in a 180 ml stainless steel rocking autoclave which was kept at 180°C for 100 h. Distillation gave methyl glycolate, b.p. 147–149°C [5] (20.0 g, 0.222 mol, 87.4% yield).

Catalyst precursor

$H_4Ru_4(CO)_8(PBu_3)_4$ [6], $H_4Ru_4(CO)_8(PPh_3)_4$ [6], $Ru(CO)_2(CH_3COO)_2$-$(PBu_3)_2$ [7], $Ru_2(CO)_4(CH_3COO)_2(PBu_3)_2$ [7], $Ru_2(CO)_4(CH_3COO)_2(PCy_3)_2 \cdot C_6H_5CH_3$ [7], $Ru_2(CO)_4(CH_3COO)_2(PPh_3)_2$ [8] and $Os_2(CO)_6(CH_3COO)_2$ [8] were prepared as previously described.

The osmium complex $Os_2(CO)_4(CH_3COO)_2(PBu_3)_2$ was prepared by the method used for the analogous complex, $Os_2(CO)_4(CH_3COO)_2(PPh_3)_2$ [8]. Thus PBu_3 (0.186 g, 0.92 mmol) was added to a suspension of $Os_2(CO)_6(CH_3COO)_2$ (0.186 g, 0.56 mg-atom Os) in n-heptane (5 ml) and the mixture was refluxed for 5 h under nitrogen. When the resulting pale-yellow solution was kept at −20°C a pale-yellow solid separated, and this after three recrystallizations gave 0.170 g (0.33 mg-atom Os, 59.0% yield) of the title compound; the IR spectrum (KBr pellet) showed bands at 1998s, 1951m, 1920s, 1890w, 1870vw, 1580s, 1440s and 1420sh cm^{-1}. Elemental analysis. Found: C, 37.93; H, 5.98. $C_{32}H_{60}O_8P_2Os_2$ calcd.: C, 37.86; H, 5.96%.

Hydrogenation and analytical procedures

The hydrogenation of dialkyl oxalates was carried out as described previously [2]; the amounts of reactants and the reaction conditions are indicated in the tables.

For the experiments reported in Table 5, the catalyst and the additive were placed in a small ampoule inside the autoclave containing the substrate, the solvent and a stainless steel ball. The autoclave was kept at the desired temperature for 1 h and then rocked to bring the contents of the ampoule in contact with the substrate. In the case of ethylene glycol as additive, 0.5 ml of benzene were also present in the ampoule.

The composition of the products (residual dialkyl oxalate, alkyl glycolate and ethylene glycol) in the crude was determined by GLC (2 m column packed with FFAP 5% on Chromosorb G AW-DMCS) using calibration curves.

Identification of products

The residual gas from each experiment was monitored by IR spectroscopy. Carbon monoxide and methane were absent in all cases; carbon dioxide (bands at 2349 and 667 cm^{-1} [9]) was detected in the residual gas from the experiment carried out in the the presence of $Ru_2(CO)_4(CH_3COO)_2(PCy_3)_2 \cdot C_6H_5CH_3$.

Methyl glycolate, ethylene glycol, methanol, n-propanol, iso-propanol and n-hexanol were identified from their GLC-mass spectra [10].

iso-Propyl glycolate was identified by its GLC-mass spectrum, which showed peaks at *m/e*: 75 $[M - CH(CH_3)_2]^+$, 59 $[M - OCH(CH_3)_2]^+ = [HOCH_2CO]^+$, 45 $[CH_3CHOH]^+$, 43 $[CH(CH_3)_2]^+$, 41 $[CH_2{=}CHCH_2]^+ = [O{=}C{=}CH]^+$, 39 $[C_3H_3]^+$, 31 $[CH_2OH]^+$.

n-Propyl glycolate was identified by its GLC-mass spectrum, which showed peaks at *m/e*: 77 $[HOCH_2C(OH)_2]^+$, 61 $[C_2H_5O_2]^+$, 59 $[M - OCH_2CH_2CH_3]^+$, 43 $[CH_2CH_2CH_3]^+$, 42 $[CH_2{=}CHCH_3]^+$, 41 $[O{=}C{=}CH]^+ = [CH_2{=}CHCH_2]^+$, 39 $[C_3H_3]^+$, 31 $[CH_2OH]^+$, 29 $[CH_3CH_2]^+$, 27 $[C_2H_3]^+$.

n-Hexyl glycolate was identified by its GLC-mass spectrum, which showed peaks at *m/e*: 129 $[M - CH_2OH]^+$, 85 $[CH_2CH_2CH_2CH_2CH_2CH_3]^+$, 84 $[CH_2{=}CH\text{-}CH_2CH_2CH_2CH_3]^+$, 77 $[HOCH_2C(OH)_2]^+$, 69 $[C_5H_9]^+$, 61 $[C_2H_5O_2]^+$, 57 $[CH_2CH_2CH_2CH_3]^+$, 56 $[CH_2{=}CHCH_2CH_3]^+$, 55 $[CH_2 = CHCH_2CH_2]^+$, 43 $[CH_2CH_2CH_3]^+$, 42 $[CH_2{=}CHCH_3]^+$, 41 $[CH_2{=}CHCH_2]^+$, 31 $[CH_2OH]^+$, 29 $[CH_3CH_2]^+$.

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