

Ruthenium catalysed hydrogenation of dimethyl oxalate to ethylene glycol

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Dimethyl oxalate is efficiently hydrogenated to ethylene glycol under mild conditions [$p(\text{H}_2)$ 70 bar; 100 °C] using a ruthenium catalyst based on $\text{Ru}(\text{acac})_3$ and $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$.

The homogeneous hydrogenation of esters to alcohols is a difficult process and only a few papers dealing with this subject have appeared.^{1–3} Anionic ruthenium hydride catalysts have been described by Grey *et al.*¹ and neutral ruthenium catalysts were reported by Matteoli *et al.*^{2,3} In general, drastic conditions are required for the efficient conversion of an ester to the corresponding alcohol, unless the ester is activated by electron-withdrawing substituents. Thus, the hydrogenation of methyl glycolate (MGL) to ethylene glycol [EGL, eqn. (1)] requires drastic conditions [$p(\text{H}_2)$ 200 bar; 180 °C]² while dimethyl oxalate (DMO) is relatively easily reduced to MGL [eqn.(2)].



We report a ruthenium based homogeneous catalyst which is able to homogeneously catalyse the hydrogenation of DMO to EGL under substantially milder conditions.

Exploratory experiments were based on the $\text{Ru}(\text{acac})_3$ system, described by Hara and Wada for the hydrogenation of anhydrides to lactones.⁴ These experiments revealed that an active catalyst can be generated *in situ* from $\text{Ru}(\text{acac})_3$ and a donor ligand in MeOH in the presence of zinc. Zinc was added to initiate a fast reduction of the acetylacetonate complex. The influence of ligands on the catalytic activity of this system was explored in detail and is shown in Table 1.[†]

From Table 1 it is evident that ruthenium catalysts with phosphine ligands (except tricyclohexylphosphine, entry 7) show a higher activity than with the nitrogen or arsenic compounds (entries 3–6). The applied phosphine ligands induced remarkable differences in terms of catalytic activity as a function of their coordination properties. More specifically,

the activity of the ruthenium–phosphine catalysts in the hydrogenation of DMO (expressed as turnover frequency) increases in the order $\text{P}(\text{C}_6\text{H}_{11})_3 < \text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2 < \text{PPh}_3 < \text{PhP}(\text{C}_2\text{H}_4\text{PPh}_2)_2 \approx [\text{CH}_2\text{P}(\text{Ph})\text{C}_2\text{H}_4\text{PPh}_2]_2 \ll \text{MeC}(\text{CH}_2\text{PPh}_2)_3$. The extraordinary effect of the $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ligand⁵ on the catalytic activity is evident from the formation of EGL in high yield which was not observed in any previous experiment. (Note that the hydrogenation of MGL to EGL is not as activated by an electron-withdrawing substituent as the hydrogenation of DMO to MGL, *vide supra*.) Our catalytic system consisting of $\text{Ru}(\text{acac})_3$ and the tridentate ligand $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ (entry 11) is considerably better with respect to the selectivity of EGL formation and the turnover frequency when compared with the catalytic properties of the best known system so far, *i.e.* $\text{Ru}(\text{CO})_2(\text{AcO})_2(\text{PBu}_3)_2$.² Furthermore, our system displays catalytic activity under relatively mild conditions. The catalytic properties of the ruthenium catalyst derived from $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ indicate that a ruthenium complex with a *fac* coordinating ligand is essential for high catalytic activity. This conjecture is supported by the relatively low catalytic activity of the $\text{PhP}(\text{C}_2\text{H}_4\text{PPh}_2)_2$ and $[\text{CH}_2\text{P}(\text{Ph})\text{C}_2\text{H}_4\text{PPh}_2]_2$ derived systems, in which the ligands can coordinate either in a *fac* or *mer* fashion to ruthenium.

The $\text{Ru}(\text{acac})_3$ – $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ system was explored in more detail with respect to the influence of the hydrogen pressure, the substrate to catalyst ratio, and the role of zinc. From Table 2 it is clear that the turnover number increases from 160 (entry 1) to 642 (entry 3) when the Ru:DMO ratio decreases from 1.19 to 0.18%. As is seen from entries 8 and 9, decreasing the Ru:DMO ratio from 0.20 to 0.15 leads to significantly lower catalytic activity; the turnover frequency decreases from 53.5 to 15.5 h⁻¹.

As expected, the H₂ pressure has a significant influence on the turnover number and turnover frequencies. Decreasing the H₂ pressure from 70 to 20 bar (entries 3–5) leads to a decrease of the turnover frequency by a factor 3.6. Comparing the experiments in entries 3 and 6 (and 7 and 8), the influence of

Table 1 Influence of the ligand in the ruthenium catalysed hydrogenation of DMO to MGL and ethylene glycol (EGL)^a

Entry	DMO/ mmol	Ligand	Ru : DMO (%)	Ligand : Ru (%)	Zn : DMO (%)	Conver- sion DMO (%)	Yield MGL (%)	Select- ivity MGL (%)	Yield EGL (%)	Select- ivity EGL (%)	Turn- over number	Turn- over freq./ h ⁻¹
1	0.96	None ^b	1.64	0.00	0.27	18	2	10	0	0	1	0
2	0.99	PPh ₃	1.98	5.88	1.32	73	36	49	0	0	18.1	0.9
3	1.41	AsPh ₃	1.19	8.91	0.57	1	0	0	0	0	0	0
4	1.04	1,10-Phenanthroline	1.96	6.39	0.33	20	0	0	0	0	0	0
5	0.89	2,2' : 6',2''-Terpyridine	1.74	1.79	0.38	11	0	0	0	0	0	0
6	9.25	Pyrazolyl ligand ^c	0.21	2.32	0.06	14	1	4	0.22	0	2.9	0.2
7	0.89	$\text{P}(\text{C}_6\text{H}_{11})_3$	2.18	4.63	0.25	7	1	18	0	0	0.5	0
8	0.88	$\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$	1.82	2.94	0.42	18	11	60	0	0	5.9	0.4
9	1.14	$\text{PhP}(\text{C}_2\text{H}_4\text{PPh}_2)_2$	1.75	1.68	0.36	76	67	89	0	0	38.2	2.5
10	0.96	$[\text{CH}_2\text{P}(\text{Ph})\text{C}_2\text{H}_4\text{PPh}_2]_2$	2.38	1.02	0.33	91	85	93	0	0	35.7	2.2
11	1.77	$\text{MeC}(\text{CH}_2\text{PPh}_2)_3$	1.19	1.37	0.26	100	1	1	95	95	160	10
12	11.00	$\text{Ru}(\text{CO})_2(\text{OAc})_2(\text{PBu}_3)_2$ ^d	1.34	4.00	0.00	100	18	18	82	82	136	0.9

^a Conditions (unless otherwise indicated): $\text{Ru}(\text{acac})_3$, 100 °C, $p(\text{H}_2)$ = 70 bar, 16 h, MeOH (12 ml), used as received. ^b Reaction time 41 h. ^c Tris(3,5-dimethylpyrazol-1-yl)borohydride. ^d From ref. 2; reaction at 180 °C in MeOH, $p(\text{H}_2)$ = 200 bar, 144 h.

Table 2 Influence of zinc, $p(\text{H}_2)$ and MeOH quality on the catalytic properties of the $\text{Ru}(\text{acac})_3\text{-MeC}(\text{CH}_2\text{PPh}_2)_3$ system^a

Entry	DMO/ mmol	Ru : DMO (%)	Zn : DMO (%)	MeOH (12 ml)	Conversion DMO (%)	Yield MGL (%)	Selectivity MGL (%)	Yield EGL (%)	Selectivity EGL (%)	Turnover number	Turnover freq./h ⁻¹
1	1.77	1.19	0.26	comm. ^b	100	1	1	95	95	160	10
2	3.36	0.74	0.18	comm.	100	0	0	94	94	255	16
3	10.19	0.18	0.06	comm.	80	15	18	52	65	642	40.1
4	8.29	0.25	0.06	comm.	59 ^c	24	41	10	17	180	11.6
5	8.21	0.19	0.09	comm.	35 ^d	19	55	2	5	120	7.7
6	9.67	0.19	0.00	comm.	56	24	42	22	40	363	23.4
7	8.75	0.22	0.00	dry ^e	88	10	12	63	71	607	36.8
8	9.21	0.20	0.07	dry	100	0	0	84	84	857	53.5
9	14.32	0.15	0.05	dry	50	17	34	10	20	246	15.4

^a Conditions: 100 °C, $p(\text{H}_2) = 70$ bar, 16 h, ligand (1.1–1.6 equiv.). ^b Used as received (commercial quality). ^c $p(\text{H}_2) = 38$ bar. ^d $p(\text{H}_2) = 20$ bar. ^e Distilled from CaH_2 under nitrogen.

zinc in obtaining reasonable to good yields of EGL and high turnover numbers is demonstrated; the turnover number decreases by a factor 1.8 when zinc is omitted.† Finally, the methanol quality is important for the catalytic activity of our system (entries 7–9). Comparing the experiments of entries 3 and 8 on the one hand and the experiments of entries 6 and 7 on the other shows that the highest catalytic activity is observed in dry methanol, regardless of the presence of zinc. Altogether, a turnover frequency of 53.5 is reached with our catalytic system in the presence of zinc in dry MeOH.

In conclusion, we have demonstrated that a highly reactive catalyst for the hydrogenation of dimethyl oxalate to ethylene glycol can be generated *in situ* from $\text{Ru}(\text{acac})_3$ and $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ in methanol under H_2 pressure, which is the most efficient homogeneous catalyst for the hydrogenation of dimethyl oxalate to ethylene glycol.

We are grateful to the Innovation Oriented Research Programme (IOP-katalyse) for their financial support of this research. Dr J. G. de Vries (DSM) and Dr M. J. Doyle (SRTCA) are gratefully acknowledged for stimulating discussions.

Footnotes

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† General procedure: a home-built stainless steel autoclave was charged with the amount of ruthenium precursor, ligand, zinc and substrate

indicated. The autoclave was then flushed with nitrogen several times, after which the solvent was introduced *via* a cannula. Subsequently, the autoclave was pressurized with hydrogen and heated for a specific period (see Tables). The values of the H_2 pressure are given at room temperature. The reaction products were characterized by GC–MS while the yields were determined by GC with an internal standard.

‡ Employing zinc in the absence of $\text{Ru}(\text{acac})_3$ gave no hydrogenation of DMO whatsoever.

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Received in Cambridge, UK, 6th February 1997; Com. 7/00862G