# Ruthenium catalysed hydrogenation of dimethyl oxalate to ethylene glycol

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**Dimethyl oxalate is efficiently hydrogenated to ethylene glycol under mild conditions [$p(H_2)$ 70 bar; 100 °C] using a ruthenium catalyst based on $Ru(acac)_3$ and $MeC(CH_2PPh_2)_3$.**

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 [$p(H_2)$ 200 bar; 180 °C][2] while dimethyl oxalate (DMO) is relatively easily reduced to MGL [eqn.(2)].

$$MeO_2CCH_2OH + 2\ H_2 \rightarrow HOCH_2CH_2OH + MeOH \quad (1)$$

$$MeO_2CCO_2Me + 2\ H_2 \rightarrow MeO_2CCH_2OH + MeOH \quad (2)$$

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 $Ru(acac)_3$ 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 $Ru(acac)_3$ 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 $P(C_6H_{11})_3 < Ph_2PC_2H_4PPh_2 < PPh_3 < PhP(C_2H_4PPh_2)_2 \approx [CH_2P(Ph)C_2H_4PPh_2]_2 \ll MeC(CH_2PPh_2)_3$. The extraordinary effect of the $MeC(CH_2PPh_2)_3$ ligand[5] 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 $Ru(acac)_3$ and the tridentate ligand $MeC(CH_2PPh_2)_3$ (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.* $Ru(CO)_2(AcO)_2(PBu_3)_2$.[2] Furthermore, our system displays catalytic activity under relatively mild conditions. The catalytic properties of the ruthenium catalyst derived from $MeC(CH_2PPh_2)_3$ 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 $PhP(C_2H_4PPh_2)_2$ and $[CH_2P(Ph)C_2H_4PPh_2]_2$ derived systems, in which the ligands can coordinate either in a *fac* or *mer* fashion to ruthenium.

The $Ru(acac)_3$–$MeC(CH_2PPh_2)_3$ 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 $H_2$ pressure has a significant influence on the turnover number and turnover frequencies. Decreasing the $H_2$ 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 (%) | Conversion DMO (%) | Yield MGL (%) | Selectivity MGL (%) | Yield EGL (%) | Selectivity EGL (%) | Turnover number | Turnover 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 | 0 | 2.9 | 0.2 |
| 7 | 0.89 | $P(C_6H_{11})_3$ | 2.18 | 4.63 | 0.25 | 7 | 1 | 18 | 0 | 0 | 0.5 | 0 |
| 8 | 0.88 | $Ph_2PC_2H_4PPh_2$ | 1.82 | 2.94 | 0.42 | 18 | 11 | 60 | 0 | 0 | 5.9 | 0.4 |
| 9 | 1.14 | $PhP(C_2H_4PPh_2)_2$ | 1.75 | 1.68 | 0.36 | 76 | 67 | 89 | 0 | 0 | 38.2 | 2.5 |
| 10 | 0.96 | $[CH_2P(Ph)C_2H_4PPh_2]_2$ | 2.38 | 1.02 | 0.33 | 91 | 85 | 93 | 0 | 0 | 35.7 | 2.2 |
| 11 | 1.77 | $MeC(CH_2PPh_2)_3$ | 1.19 | 1.37 | 0.26 | 100 | 1 | 1 | 95 | 95 | 160 | 10 |
| 12 | 11.00 | $Ru(CO)_2(OAc)_2(PBu_3)_2$[d] | 1.34 | 4.00 | 0.00 | 100 | 18 | 18 | 82 | 82 | 136 | 0.9 |

[a] Conditions (unless otherwise indicated): $Ru(acac)_3$, 100 °C, $p(H_2)$ = 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, $p(H_2)$ = 200 bar, 144 h.

**Table 2** Influence of zinc, $p(H_2)$ and MeOH quality on the catalytic properties of the $Ru(acac)_3$–$MeC(CH_2PPh_2)_3$ 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, $p(H_2)$ = 70 bar, 16 h, ligand (1.1–1.6 equiv.). [b] Used as received (commercial quality). [c] $p(H_2)$ = 38 bar. [d] $p(H_2)$ = 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 $Ru(acac)_3$ and $MeC(CH_2PPh_2)_3$ in methanol under $H_2$ pressure, which is the most efficient homogeneous catalyst for the hydrogenation of dimethyl oxalate to ethylene glycol.

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## 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 $Ru(acac)_3$ gave no hydrogenation of DMO whatsoever.

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