

Transition Metal-Catalyzed Deoxydehydration: Missing Pieces of the Puzzle

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Supporting Information

Calculation of turnover frequencies from information in the literature –
to complement Table 10

Cook and Andrews,¹ Glycerol DODH with PPh₃

From the text: “The prototype carbohydrate, glycerol, is also cleanly deoxydehydrated by PPh₃ to the corresponding alkene, allyl alcohol (67 turnovers in 23 h), in a biphasic, saturated solution in chlorobenzene at 125 °C”

$$TOF = \frac{67}{23 \text{ h}} = 2.9 \text{ h}^{-1}$$

Yi et al.,² Glycerol DODH with glycerol

Initial rate of formation of allyl alcohol read from Figure 1: about 0.75 mmol in 20 min

From Experimental Section: catalyst charge (methyltrioxidorhenium): 1.1 mmol

$$TOF = \frac{0.75 \text{ mmol} * 60 \text{ min}}{20 \text{ min} * \text{h} * 1.1 \text{ mmol}} = 2.0 \text{ h}^{-1}$$

Raju et al.,³ 1,2-Octanediol DODH with PPh₃

Initial rate of formation of 1-octene read from Figure 2: about 25% yield in 1 h

From text, the amount of catalyst is 2 mol%: “Initial catalytic reactions were performed with 2 mol% catalyst 2 at 180 °C in chlorobenzene with 1.1 equiv. triphenylphosphine as the reductant under an inert nitrogen atmosphere, that is, under similar conditions to those previously reported by Cook and Andrews for Cp*ReO₃ in this reaction.[7] A profile of the reaction over time showed that it proceeded to completion within 15 h, and exclusively yielded octenes (1-octene/2-octene=1:0.05; Figure 2).”

$$TOF = \frac{0.25}{0.02 * 1 \text{ h}} = 12.5 \text{ h}^{-1}$$

Liu et al.,⁴ Hydrobenzoin DODH with 3-octanol

Rate of hydrobenzoin concentration change from slope of linear fit in Figure 2b: 0.0007 M/s

Hydrobenzoin starting concentration from intercept of linear fit in Figure 2b: 0.54 M

From Figure 2 caption: 2.5 mmol hydrobenzoin and 0.05 mmol methyltrioxidorhenium

$$TOF = \frac{0.0007 \text{ M} * 2.5 \text{ mmol} * 3600 \text{ s}}{0.54 \text{ M} * \text{s} * 0.05 \text{ mmol} * \text{h}} = 233 \text{ h}^{-1}$$

Zhang et al.,⁵ Mucic acid DODH with 3-pentanol

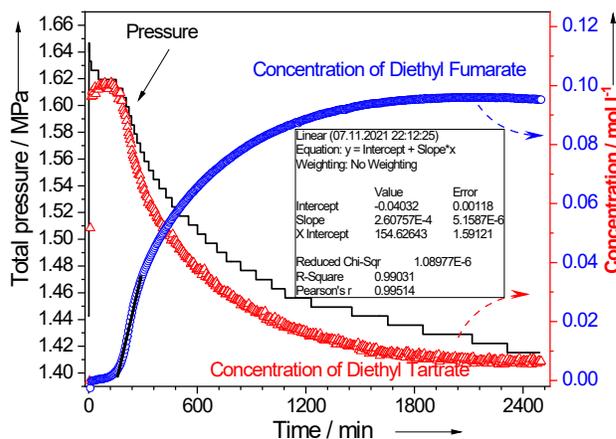
Initial rate of formation of muconic acid read from Figure 2 and from associated text: 65% converted with 98% selectivity within 4 h

From Experimental Section, Homogeneous DODH reactions, the amount of mucic acid is 1.0 mmol and the amount of rhenium catalyst is 0.05 mmol.

$$TOF = \frac{0.65 * 0.98 * 1 \text{ mmol}}{0.05 \text{ mmol} * 4 \text{ h}} = 3.2 \text{ h}^{-1}$$

Denning et al.,⁶ Diethyltartrate DODH with H₂

Data from Figure 3, linear portion of diethylfumarate concentration increase starting at about 3.5 h. Since the measurement is from our own laboratory, we fit the original data:



Initial rate of change in diethylfumarate concentration from slope of linear fit: $2.6 * 10^{-4}$ M/min

From SI, the reaction volume is approximately 120 ml (assumed to be equal to amount solvent)

From the SI, the amount of ReO_x-C catalyst is 1.4 g.

From the Experimental Section, the rhenium content of the ReO_x-C catalyst is about 4 %.

The atomic weight of rhenium, 186.2 g/mol

$$TOF = \frac{2.6 * 10^{-4} \text{ M} * 0.12 \text{ L} * 60 \text{ min}}{\text{min} * \text{h}} \frac{186.2 \text{ g}}{1.4 \text{ g} * 0.04 * \text{mol}} = 6.2 \text{ h}^{-1}$$

References

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