

# Low temperature rhodium-catalyzed dehydration of primary alcohols promoted by tetralkylammonium and imidazolium halides

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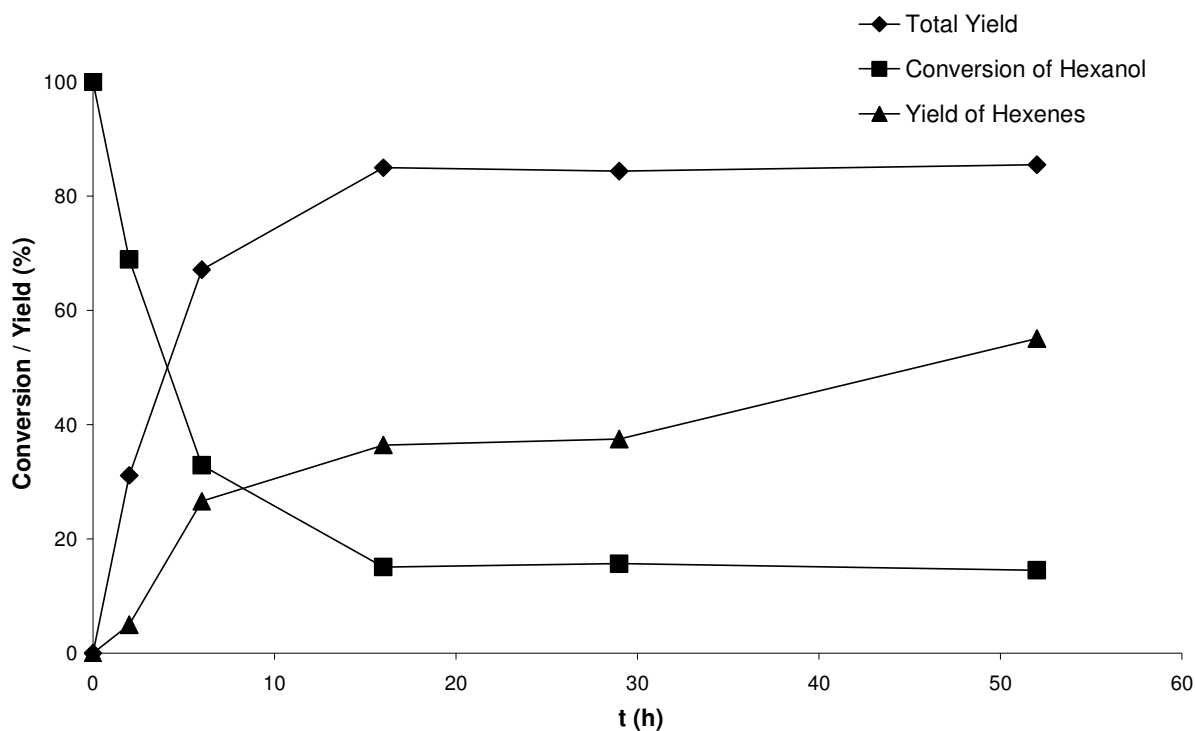
## Experimental details

**General:** All procedures were carried out under an inert ( $N_2$ ) atmosphere using standard Schlenk line techniques or in an inert atmosphere (Ar) glovebox. Ethanol (96%), *n*-propanol (99%), *n*-butanol (99%), *n*-hexanol (98%) and 57% (wt.) aqueous hydriodic acid were degassed prior to use. All chemicals were obtained commercially and used without further purification. Infra-red spectra were recorded on a Perkin-Elmer 1600 series FTIR Spectrometer in dichloromethane or the catalytic run solution. NMR spectra were recorded on a JEOL ECP 300 spectrometer at 300 MHz ( $^1H$ ) and are referenced chemical shifts relative to high frequency of residual solvent. Yields and conversion for catalytic runs were determined by GC, calibrated against authentic samples.

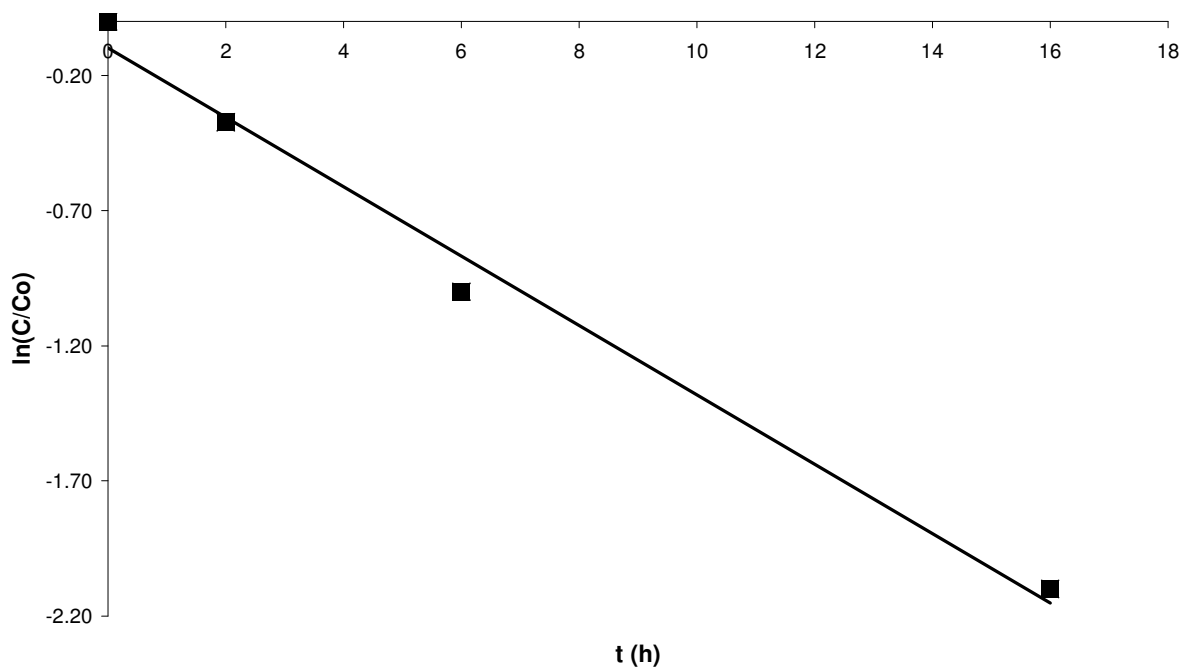
**Dehydration catalytic runs:** Hexanol dehydrations were carried out under nitrogen atmosphere in Schlenk-type vessels using a 12-cell Radley's carousel stirred reactor. Dehydrations of ethanol, *n*-propanol and *n*-butanol were carried out in a stainless steel autoclave (Parr, 320 ml). The gaseous products were allowed to react with bromine and the formed dibromoalkanes were analyzed by GC. Calibration of this method with olefin solutions of known concentration demonstrated good agreement. For ethanol, the yield of ethylene can be determined by the pressure increase after completion of the reaction according to equation of state  $\Delta PV = \Delta nRT$ . This was found to be in a good agreement with the yield determined by the bromination method. Hexadecane was used as a standard in all cases.

In a typical run, a Schlenk vessel was charged with  $PMes_3$  (14.4 mg, 0.13 mol. %),  $Rh_2(CO)_4Cl_2$  (6 mg, 0.065 mol. %) and  $Bu_4NBr$  (1.66 g, 21.6 mol. %). The vessel was filled with nitrogen, and degassed *n*-hexanol (3 ml, 23.9 mmol) was added *via* a syringe followed by addition of 57% aq. HI (0.2 ml, 6 mol. %). The reaction temperature was raised to 110 °C within ca. 30-40 min. The solution was stirred at this temperature for the reaction time, cooled to room temperature and analysed by GC.

**Kinetic run:** This was performed as described above, with aliquots for GC analysis being taken from the ongoing reaction as indicated. Results are presented in Figure 1.<sup>1</sup> A plot of  $\ln(C/C_0)$  showing approximate first order kinetic over the first 18 h of the reaction is shown in figure 2.



**Figure 1.** Plot of conversion and yield with time



**Figure 2.** Plot of  $\ln(C/C_0)$  with time

**Synthesis of  $[Bu_4N][Rh(CO)_2Br_2]$  and  $[Bu_4N][Rh(CO)_2I_2]$ :**

These were synthesised by the same method, described here for  $[Bu_4N][Rh(CO)_2I_2]$ . Degassed ethanol (5ml) was added to a mixture of  $[Rh_2(CO)_4Cl_2]$  (50 mg, 0.13 mmol) and  $Bu_4NI$  (240mg, 0.65 mmol) in a Schlenk tube. This was heated to 70 °C and stirred for 2 hours. After this time, the solution was concentrated to 1 ml and cooled to -20 °C. Yellow needle-like crystals slowly precipitated, which were isolated by filtration, washed (2 x 2 ml) with cold (-20 °C) ethanol and dried *in vacuo*. Yield 113mg (66%).

Elemental Analysis: Calcd for  $C_{18}H_{36}RhNO_2I_2$  (%): C 33.90, H 5.69, N 2.53, found: C 33.57, H 5.63, N 2.36.

***NMR spectroscopy of ethanol dehydration run:***

Reactions to be followed by NMR spectroscopy were run in either Youngs-tap NMR tubes, to prevent ethene escape. Pre-formed catalyst  $[\text{Bu}_4\text{N}][\text{Rh}(\text{CO})_2\text{X}_2]$  (where X = Br or I) was added to the NMR tube with the required amount of the tetraalkylammonium salt. Methanol- $\text{d}_4$  (0.7mL) was then added, followed by ethyl iodide reactant and a standard (mesitylene).

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<sup>1</sup> Note: The concentration of hexyl iodide is low (ca. 5% of total substrate/reagent) and constant, and has been omitted for clarity.