

Continuous-Flow Homogeneous Catalysis using the Temperature-Controlled Solvent Properties of Supercritical Carbon Dioxide

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Electronic Supplementary Information

Experimental Section

General. NMR spectra were measured with a Bruker DPX-300 spectrometer. Determination of Rh, Ru and P contents was carried out by ICP-OES measurements (Thermo Elemental, IRIS Interprid DUO ER/S) at the University of Dortmund by the team of Prof. Dr A. Behr. The substrates 3-butene-2-ol and 1-octene-3-ol were purchased from Aldrich and purified by distillation under Ar atmosphere. 3-H²F⁶-TPP¹ and [Rh(cod)₂]BARF² were synthesised according to known procedures from literature. 4-H²F⁸-TPP and [RuCp(MeCN)₃]PF₆ were purchased from Fluka and Strem, respectively.

Procedure for the continuous isomerisation of 1-octene-3-ol

A solution of the phosphine ligand 4-H²F⁸-TPP (300 mg, 0.187 mmol) and of the Ru precursor [RuCp(MeCN)₃]PF₆ (40 mg, 0.092 mmol) in dry dichloromethane (20 mL) was charged into the reactor under an argon atmosphere. The solvent was removed under reduced pressure and the reactor filled with CO₂. 1-Octene-3-ol (2.0 g, 19.5 mmol) was added and the system equilibrated by setting the temperatures in the reaction and separation zone. After thermal equilibration the feed rates were set to 0.8 g h⁻¹ (2.8 mmol h⁻¹) for the substrate and 18.3 g h⁻¹ (0.42 mol h⁻¹) for CO₂. These feed rates were maintained over the full experiment time. In regular time intervals samples of the product stream were withdrawn from the cold trap, collected, and their composition determined by ¹H-NMR spectroscopy. The total mass balances as determined gravimetrically at the end of the reaction was about 50 %. Since the back pressure regulator assembly is based on a pneumatic valve with a significant degree of pulsation, parts of the product stream could not be condensed into the set of two cold traps. Independent experiments showed however that mixtures of substrate and product passing the reactor set-up were condensed into the cold traps without significant variations of the initial composition. Hence, selective loss of one component over the other can be excluded and the composition of the condensed stream reliably reflects the conversion in the reactor.

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2 B. Guzel, M. A. Omary, J. P. Fackler Jr., A. Akgerman, *Inorg. Chim. Acta* 2001, **325**, 45.