

An Intense Green Propylene Oxide Process that Operates Under Mild Conditions

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Introduction

The epoxidation of propylene to propylene oxide (PO) on the industrial scale is among the most challenging chemical processes. Propylene oxide is mainly used for the production of propylene glycol and polyester, and is the starting material for polyurethane, unsaturated resins, and other products. Industrially, over 4.5 million tons of propylene oxide are produced each year using either the chlorohydrin¹ or the hydroperoxide process¹. The chlorohydrin process used today consumes large amounts of chlorine and lime which are finally converted to useless and environmentally polluting waste. The hydroperoxide process provides the second major industrial method for large scale synthesis of PO. The economic viability of this process depends on the market value of co-products because 3-4 times more co-product is produced than the weight of propylene oxide produced. To solve these problems, direct oxidation of propylene to propylene oxide with O₂ would be highly desirable, but the presence of propylene's highly reactive allylic hydrogens renders this approach quite difficult.

MTO, methyl trioxorhenium, is a well-established catalyst^{2,3} for reactions of H₂O₂, including the epoxidation of alkenes. In this report, we apply MTO and 50 wt% H₂O₂/H₂O in a mixed aqueous/methanol solvent, with an added base, to epoxidize light alkenes (ethylene, propylene) in a liquid phase reaction. The effects of pressure, temperature and concentrations were examined for the solvent and the base. The effects of increased pressure due to two gases CO₂ and N₂, were explored.

Materials and Methods

A view-cell reactor, made of titanium and equipped with two sapphire windows, a gas inlet valve and an outlet valve is used. The view cell is interfaced with a pressure transducer, a thermocouple, and a pressure relief valve. The pressure and temperature are computer-monitored during the reaction. H₂O₂/H₂O (0.6 ml of 50 wt%, 10.41 mmoles) and 0.20ml of pyridine (2.47 mmoles), or another base, were dissolved in 5 ml of acetonitrile or methanol, and the solution added to the reactor. Dense CO₂ or N₂ was charged after 100mg of propylene (2.38 mmoles) had been added to the reactor. The reactor was heated with a band heater. Batch experiments with 3, 6, 12, and 24 h durations were performed at temperatures ranging from 40 – 70°C. Products were analyzed by GC and GC/MS.

Results and Discussion

Effect of CO₂ Pressure: The reactor was charged with MTO, base and H₂O₂ (50 wt% in H₂O) in methanol (or light alcohols) or acetonitrile. Liquid CO₂ was then added to the cell by bubbling through the liquid at a predetermined pressure (48 bars). The reaction mixture compositions, including CO₂ pressure, were chosen to produce a single liquid phase in the

reactor. The reaction was monitored for 3 hr at 40°C. As shown in Table 1, the highest yield of PO was produced with methanol/H₂O as the solvent and pyridine N-oxide as the base. The higher solubility of propylene in methanol produces higher yields of PO than those obtained with acetonitrile. The selectivity of propylene oxide is over 96% in all cases. Trace amounts of propylene glycol (PG) in CO₂/CH₃CN or 1-methoxy-2-propanol (1M2P) in CO₂/MeOH are produced during the reactions.

Table 1. Propylene oxidation with CO₂-Expanded CO₂ (CXL) system

Yield of PO (%)	Selectivity (%)	Base	Organic solvent
14.7	N/A	No	Acetonitrile
18.2	N/A	Pyridine	Acetonitrile
60.3	98	Pyridine	MeOH
72.7	96	Pyridine N-oxide	MeOH

The relative effects of N₂ and CO₂ pressure on the oxidation of propylene were evaluated, using the preferred solvent, MeOH, and base, pyNO. The reactor was charged with MTO, base and H₂O₂ (50 wt% in H₂O) in methanol. The propylene was charged into the reactor which was then pressurized with N₂ to give a pressure equivalent to that in previous reactions using CO₂ based CXLs (48 bars). Various N₂ pressures were examined as shown in Table 2.

Table 2. N₂ pressure effect on propylene oxidation at 40°C, Reaction time: 3 hr (error ±5%)

Pressure (bars)	% Yield of PO	Selectivity	byproducts	Condition
~ 48	72.7	>95	1.9% (1M2P), 0.6% (PG)	With CO ₂
~ 48	>99	>95	2.3% (1M2P)	With N ₂
~ 15.8	>98	>95	1.0% (1M2P)	With N ₂
~2.4	82.6	>95	0.6% (1M2P)	With propylene alone

CO₂ readily dissolves in the methanol-dominated solution at tens of bars while N₂ dissolves only slightly but increases the pressure acting on the system. The dilution by CO₂ dissolution results in lower PO yields compared to pressurization with either N₂ or propylene alone. Increased N₂ pressures (at fixed propylene partial pressures) enhances the propylene concentrations in the liquid phase resulting in 95+% propylene conversion as well as PO selectivity. The byproducts in this system are 1-methoxy-2-propanol or PG depending upon the pH of the reaction medium and reaction time. The TON corresponding to the 95+% PO yields in N₂-based systems surpasses those reported in the literature with other catalysts.⁴

The separation of products is a major issue in current industrial practice. In the proposed process, propylene and PO separation are favorable, involving a simple distillation at atmospheric pressure and moderately low temperature (below 50°C). Solvent and catalyst recycle are also straightforward.

References

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