

# Studies on the Activation of N<sub>2</sub>O by Homogeneous Catalysts



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The controlled oxygenation of alkenes is one of the most important transformations to convert crude oil and natural gas to valuable commodity chemicals. Although catalysis can be used to promote both the rate of reaction and the selectivity with respect to the oxidation products, many of these traditional processes are not environmentally benign. The considerable pressure to replace these older technologies with ones that use inexpensive and environmentally friendly oxidants has spurred our interest in developing new catalysts to achieve this goal.

N<sub>2</sub>O is a potent greenhouse gas that has potential as a mild and selective oxidant. The molecule is difficult to activate, as it is kinetically inert. However, early work by the Groves group suggested that N<sub>2</sub>O could epoxidize olefins at room temperature. The reasons that all subsequent work using this oxidant has required high temperatures and pressures to facilitate effective oxidation are not clear.

In this study, the kinetics of the oxidation of cholesteryl acetate with N<sub>2</sub>O were examined using a high-valent Ru oxo complex supported by a sterically bulky porphyrin ligand. The data indicate several features that lead to improved catalysts.

- increased steric bulk to prohibit competitive binding of the olefin over N<sub>2</sub>O, including controlling the “top” vs. “side” access of the reagents to the metal center
- homo- and heterobimetallic catalysts that promote N<sub>2</sub>O activation by binding the molecule in a bridging mode
- homotrimetallic catalysts that bind N<sub>2</sub>O in a bridging fashion, as well as facilitate disproportionation of Ru(IV)(por)(O) to Ru(VI)(por)O<sub>2</sub> and Ru(II)(por)

