Oxidation of 2-Propanol by Peroxo Titanium Complexes: A Combined Experimental and Theoretical Study

Daniel H. Friese, Christof Hättig, Markus Rohe, Klaus Merz, André Rittermeier, and Martin Muhler

Lehrstuhl für Anorganische Chemie I, Ruhr-Universität Bochum, Universitätsstraße 150, D-44801 Bochum, Germany, Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, D-44801 Bochum, Germany, and Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, D-44801 Bochum, Germany

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The oxidation of 2-propanol by titanium peroxy complexes is investigated in a combined synthetic, spectroscopic, and computational study. We find in quantum chemical calculations for the thermal reaction in protic solvents that the temporary protonation of the peroxy group activates the latter as electrophile. This transient species is amenable to a concerted transfer of two electrons and a proton from the secondary C atom of 2-propanol. Simultaneously, the carbonyl group is formed and the alcoholic proton is transferred to the solvent. In line with the results of the calculations, we find experimentally that the activity of the titanium peroxy complexes as oxidant depends on the pH value of the reaction medium.

1. Introduction

The oxidation of organic substrates in the presence of titanium dioxide is currently an intensive research area.1–5 On a molecular basis, however, little is known about the processes that take place on the surface of solid titanium dioxide. In the case of the thermal and photochemical oxidation of 2-propanol, several products are reported.6–8 During both thermal and photochemical alcohol oxidation processes, active species are generated at the TiO2 surface. Molecular adsorbed oxygen and reduced oxygen species have been observed by using temperature-programmed desorption (TPD) and oxidation (TPO) methods.9,10 Once formed, these active species either react back to reforming alcohol, or dehydrate, or dehydrate to form products like propene, acetone, mesityl oxide, and carbon dioxide.11 In particular, the thermal process forms propene in remarkable amounts.6–10 To investigate the role of reduced oxygen in the thermal oxidation of 2-propanol, we transform the situation from the catalyst surface to a molecular level. By following a model catalyst approach, we synthesized well-defined titanium-oxo complexes modified by peroxy units and additional metal ions.

Peroxo-rich metal-oxo complexes are suitable substances to achieve deeper insight in the mechanism of the oxidation processes. Furia et al.12,13 investigated the thermal oxidation of secondary alcohols in the presence of vanadium and molybdenum peroxy complexes. On the basis of kinetic experiments, a radical pathway was postulated where the oxidation of the alcohol occurs coordinated to the metal center. We have previously reported that different metal-containing titanium peroxy complexes show high activity in the photo-oxidation of 2-propanol, whereas similar complexes without any peroxy units did not show any activity in the photochemical oxidation.14–16 In this work, we present a combined experimental and theoretical study on the thermal oxidation of 2-propanol by well-defined peroxy-rich molecular TiO complexes. The thermal oxidation of 2-propanol was monitored by in situ IR measurements, and the reaction mechanism was studied by quantum chemical calculations. As a suitable molecular model, we used water-soluble peroxy titanium complexes, which are accessible by hydrolysis of TiCl4 in the presence of H2O2, NH3, and citric acid or nitrilotriacetic acid. The incorporation of metal centers in these complexes can be achieved by treatment with appropriate metal salts.

2. Experimental Section

2.1. Preparation of K2[Ti(O2)N(CH2COO)3]2O × 5 H2O. Titanium(IV)chloride (2.2 mL, 20 mmol) was added dropwise to 30 mL of distilled water cooled in an ice bath. During hydrolysis, 20 mL (0.65 mol) of hydrogen peroxide (30%) and 3.8 g (20 mmol) nitritriacetic acid were added. Afterwards the pH value was adjusted to 2 by addition of 6 M aqueous solution of potassium hydroxide. The desired product crystallizes at 4 °C after several days from a water/THF mixture in the form of yellow-orange needles. The yield was 14.2 g (88.9%) for K2[Ti(O2)N(CH2COO)3]2O × 5 H2O.

Li2(NH3)4[Ti2(O2)2(cit)(Hcit)]2 × 5 H2O and (NH4)2[Ti(O2)2(N(CH2COO)3)]2O × 4 H2O were prepared using the literature procedures.14,17

2.2. IR Spectroscopy. ATR spectra were recorded using a heated HATR flow cell for ARK (Thermo) equipped with a ZnSe internal reflection element (IRE, 80 × 10 × 5 mm). The cell was mounted in a Nicolet Nexus FTIR spectrometer equipped with a mercury–cadmium–telluride (MCT-A) detector. Spectra were acquired at 4 cm−1 resolution accumulating 300 scans. The liquids were placed in a homemade glass reactor and were continuously circulated through the cell with a gear pump (ISMATEC Reglo-ZS). All flow rates used in the