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Spin Surface Crossing in Chromium-Mediated Olefin Epoxidation with O_2

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The development of catalytic oxidation processes using readily available dioxygen (O_2) as the terminal oxidant is one of the goals of "green chemistry". An atom-efficient approach to this problem is the metal-mediated activation of dioxygen without the need for a co-reductant, such that both oxygen atoms are utilized to transform organic substrates.[1] We are attempting to combine laboratory experiments and high-level computations into a synergistic strategy for identifying catalysts for a variety of processes.[2] Herein we report initial results of our search for O_2-driven catalytic oxidations.

One of the requirements for this task is a catalyst that reacts with O_2 to generate two equivalents of a strong oxidant. Mindful of the long history of high-valent chromium compounds in stoichiometric oxidations,[3] we chose to examine the known Cp*Cr(O)X_2 system.[4] Exposure of a CH_2Cl_2 solution of [Cp*Cr(μ-Cl)Cl]$_2$ (Cp* = η^5-C_5Me_5) to O_2 gas at ambient pressure and temperature yielded the Cr(V) oxo complex Cp*Cr(O)Cl_2 (**1**) in essentially quantitative yield. **1** has been fully characterized by spectroscopy and X-ray crystallography (see Figure 1).[5] It was stable in the solid state, but in solution it slowly decomposed, producing mostly [Cp*Cr(μ-Cl)Cl]$_2$ and other unidentified products.

1 rapidly and stoichiometrically transferred oxygen atoms to certain substrates, and it catalyzed some oxidations with O_2. For example, reaction of **1** with PPh_3 or $AsPh_3$ yielded Cp*Cr($OPPh_3$)Cl_2 (**2a**) and Cp*Cr($OAsPh_3$)Cl_2 (**2b**), respectively. In the presence of O_2, the chromium complex catalyzed the oxidation of triphenylphosphine to triphenylphosphine oxide, and the dehydrogenation of 1,4-cyclohexadiene to benzene and water.

To gauge the oxidizing power of **1**, it is informative to note that [Cp*Cr(μ-Cl)Cl]$_2$ accepted an oxygen atom from trimethylamine-*N*-oxide ($ONMe_3$), to generate **1** and NMe_3 via the spectroscopically (^1H NMR) observable intermediate Cp*Cr($ONMe_3$)Cl_2 (**2d**). However, reaction of the Cr(III) chloride with pyridine-*N*-oxide (Opy) stopped at the stage of stable Cp*Cr(Opy)Cl_2 (**2c**), although **1** did not react with pyridine to form **2c**. The latter observation is consistent with the assumption that the oxygen atom transfer from **1** to pyridine (and its reverse) is close to thermoneutral.[6] If that is so, then **1** should be oxidizing enough to epoxidize olefins, which have a considerably higher oxygen affinity than pyridine.

To our consternation, mixtures of **1** and olefins produced at best traces of oxidation products. It was not readily apparent from these experiments alone why **1** failed to transfer oxygen to olefins to form an epoxide, or more likely its adduct Cp*Cr(L)Cl_2 (L = epoxide). A ^1H NMR spectrum of a mixture of [Cp*Cr(μ-Cl)Cl]$_2$ and excess cyclohexene oxide in CD_2Cl_2 exhibited a set of resonances tentatively assigned to Cp*Cr(OC_6H_{10})Cl_2. This observation is consistent with the expectation that the epoxide adduct is thermodynamically stable with respect to separated cyclohexene and **1**, but it gives no insight into the nature of the rate-limiting step that prevents the reaction of **1** with cyclohexene from readily occurring at room temperature.

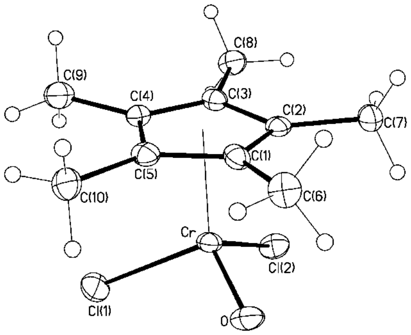

Figure 1. The molecular structure of **1**. Selected interatomic distances [Å] and angles [deg]: Cr−O, 1.578(4); Cr−Cl(1), 2.231(2); Cr−Cl(2), 2.246(2); Cr−C_{avg}, 2.29; O−Cr−Cl(1), 105.7(2); O−Cr−Cl(2), 104.6(2); Cl(1)−Cr−Cl(2), 96.4(1).

To understand the mechanism of epoxidation by **1**, with an eye toward rational modifications that may lower the activation barrier, we turned to first-principles theory. This is a subtle calculation since two electronic states are involved: the reactant Cr(V) oxo complex (**1**) has doublet spin-multiplicity, so with a singlet alkene the reactant system is overall a spin doublet; the epoxide adduct is formally a Cr(III) complex and has quartet spin-multiplicity. In principle, the reaction rate can be limited by a transition state on the potential surface for either electronic state, or by the rate to cross between surfaces.[7] Consequently, we have calculated the activation barriers on both potential surfaces, and the lowest-energy point at which crossing can occur between the two spin-states.

Calculated geometries and energies were obtained with the B3LYP hybrid density functional[8] as implemented in the Gaussian 98 suite of programs.[9] An effective core basis set was used, with a triple-ζ valence basis and polarization functions.[10] All coordinates were optimized in searches for the minimum energy crossing point (MECP) between the two potential-energy surfaces (PES), using a method based upon that of Bearpark et al.[11] in which DFT energies and gradients were calculated for the individual spin adiabats.

Initial calculations were carried out on a prototype reaction of ethylene with CpCr(O)Cl_2 (**3**). Formation of the epoxide adduct, CpCr(OC_2H_4)Cl_2 (**4**), was found to be exothermic by 16.3 kcal/mol relative to the (doublet) reactants. Several possible mechanisms were explored, but the lowest-energy pathway on the doublet surface corresponds to stepwise formation of the C−O bonds with a diradical intermediate (Figure 2).[12]

The first barrier on the doublet PES is 20.0 kcal/mol and involves C−O σ-bond formation and cleavage of the ethylene π-bond. This leads to an intermediate with an unpaired electron on the distal ethylene carbon atom. The carbon-centered electron is spin-opposed

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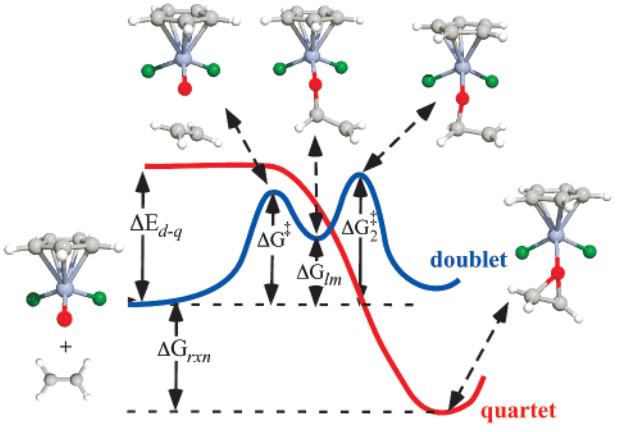

	ΔG$_{rxn}$	ΔG‡	ΔG$_2^‡$	ΔG$_{lm}$	ΔE$_{d\text{-}q}$
CpCr(O)Cl_2	-16.3	+20.0	+24.6	+11.2	+34.0
Cp*Cr(O)Cl_2	-10.7	+22.3	-----	+13.6	+36.2

Figure 2. Reaction paths for the reactions of **1** and **3** with ethylene. All energies are reported in kcal/mol; Free energy changes are at 298 K.

to two unpaired electrons on the Cr center to form an overall spin doublet. To complete formation of the epoxide adduct on the doublet potential-energy surface, a barrier of 24.6 kcal/mol must be overcome to form the second C−O bond. The overall free energy of reaction on the doublet PES is +5.9 kcal/mol. At the optimal geometry for **3** in the doublet spin state, the quartet spin state is ∼34 kcal/mol higher in energy. The reaction of the oxo complex in the quartet spin state with ethylene proceeds without a barrier from the optimal doublet geometry to form the expected Cr(III) quartet product, **4**. The MECP, which connects the doublet and quartet potential-energy surfaces, was fully optimized and found to correspond to a geometry near the local minimum between the transition states on the doublet PES. At the MECP geometry, the two spin states differ by the spin pairing of the radical on the ethylene carbon atom to the unpaired electrons on the chromium center. The energy difference between the MECP and the local minimum on the doublet PES is 0.9 kcal/mol. The highest energy barrier that must be overcome, therefore, is the first 20.0 kcal/mol barrier on the doublet PES. The reaction can cross onto the quartet PES at the MECP and proceed to the final product without the need to overcome the second barrier on the doublet surface. With the assumption of a rapid crossing rate between the two spin states at the MECP,[13] the kinetic barrier to the formation of the epoxide adduct is 20.0 kcal/mol. The barrier energy was further refined by the addition of solvent effects (at the gas-phase geometries) using the polarizable continuum model (PCM) with dichloromethane as the solvent. The barrier height with solvent effects is raised to 21.5 kcal/mol. Applying an Eyring model, a pseudo-first-order reaction rate constant of $k = 1.1 \times 10^{-3}$ s^{-1} is estimated, with a corresponding half-life of 11 min.

According to these calculations, **3** should readily epoxidize alkenes. Returning to the reactivity of **1** itself, further calculations show that it follows the same mechanism as **3**. However, the rate-limiting step for the epoxidation of ethylene by **1** is 24.4 kcal/mol (including solvent effects), significantly higher than the barrier to reaction with **3**. The predicted pseudo-first-order rate constant is $k = 7.9 \times 10^{-6}$ s^{-1}, and the corresponding half-life is 24.3 h. Thus, the reaction of ethylene with **1** is expected to be significantly slower than the reaction with **3**.

In light of these computational results, we have prepared CpCr(O)Cl_2 (**3**, Cp = η^5-C_5H_5), by the reaction of [CpCr(μ-Cl)Cl]$_2$ with O_2. This reaction was significantly slower than the analogous formation of **1**, but the yield of **3** was high, and its thermal stability in solution markedly exceeded that of **1**. **3** is a stronger oxidant than **1**, as indicated by its rapid and quantitative reaction with [Cp*Cr(μ-Cl)Cl]$_2$ to yield **1** and [CpCr(μ-Cl)Cl]$_2$. More importantly, **3** oxidizes olefins stoichiometrically. For example, an equimolar mixture of **3** and norbornene in methylene chloride ([**3**], [norbornene] = 0.028 M) after 2 h at room temperature had produced *exo*-norbornene oxide (22% yield at 45% conversion) as the major product, along with lesser amounts of two other organic products. The latter may well be secondary products resulting from the Lewis acid-catalyzed ring opening of the epoxide. An investigation of the scope of this oxygen atom transfer reaction and its potential for catalysis is now in progress.

These results show that chromium oxo species generated by the direct activation of O_2 are capable of epoxidizing olefins.[14] Computational chemistry has efficiently guided the choice of complexes for experimental investigation. Finally, there is no "spin-blocking" of the oxygen transfer reaction. Spin surface crossing at the MECP is fast and, if anything, opens a lower barrier pathway.

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Supporting Information Available: An X-ray crystallographic file for **1**, in CIF format, full characterization of **1**, **2a**, **2b**, **3**, and experimentals for some of their reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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