Aerobic Oxidations Catalyzed by Chromium Corroles

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The selective oxidation of organic molecules solely by molecular oxygen is one of the holy grails in chemistry.[1,2] Processes that rely on metal-oxo species are usually selective, but there is an intrinsic problem: when the reducing power of a given metal complex is sufficient to activate O_2, the oxidizing power of its higher valent form is usually not great enough to allow oxidation of organic substrates (Scheme 1a: M^n, $M^{n+2}(O)$, and S, respectively).

One of nature's solutions, exemplified by cytochrome P-450, is to supply two reducing equivalents to catalyze the reduction of O_2 by an otherwise inert iron(III) porphyrin (Scheme 1b),[3] an approach that is very hard to mimic in synthetic systems.[4] An artificial route is to use 4d and 5d metals that have a larger number of accessible oxidation states. The most outstanding example is olefin epoxidation by dioxoruthenium(VI) porphyrin in a process that involves disproportionation of oxoruthenium(IV) to dioxoruthenium(VI) and dioxygen-activating ruthenium(II) (Scheme 1c).[5] The limitation of this system is product inhibition: the reactivity of the ruthenium(II) intermediate is gradually diminished during the process due to epoxide coordination.

The failure to achieve a catalytic aerobic oxidation reaction (under nonradical conditions)[1] by 3d metal porphyrins calls for investigations with other ligands.[2] A particularly appealing candidate is the 5,10,15-tris(pentafluorophenyl)corrolato trianion (**1**,[6] Scheme 2), whose iron, manganese, and rhodium complexes were recently shown to be potent catalysts.[7] Metal-oxo species have been obtained so far with manganese(V) (spectroscopy)[7b] and chromium(V) (spectroscopy and X-ray crystallography).[8a] In addition, chromium corroles have been isolated in four oxidation states.[8b] Importantly, aerobic oxidation of the chromium(III) complexes **2a** and **2b** to the (oxo)chromium(V) complex **3** and the reduction of **3** by PPh_3 suggest that the Cr^VO/Cr^{III} cycle could be used for catalytic oxygenation of substrates. We have looked into this possibility, focusing on fully characterized **2b** and **3**,[8] and have gathered mechanistic information that has shed new light on the requirements that must be met in a functional system.

We first examined the reactivity of chromium(III) and (oxo)-chromium(V) complexes under noncatalytic conditions. Investigations of the aerobic oxidation of **2a** in the absence of substrate revealed that intermediates do not accumulate (indicated by the isosbestic points in Figure 1a) and that there is an inverse dependence on ligand concentration (Figure 1b). These results are consistent with a fast preequilibrium between six- and five-coordinate chromium(III), the latter of which reacts with O_2 in the rate-limiting step (Scheme 2: K_1 and k_2, respectively). Support for this reaction sequence is provided by the much lower reactivity of **2b**, whose pyridine ligands are much more strongly bound than the triphenylphosphine oxide in **2a**. In addition, a very large solvent effect was found for **2b**: its transformation to **3** requires minutes in acetonitrile, hours in methanol, and weeks in toluene and THF.
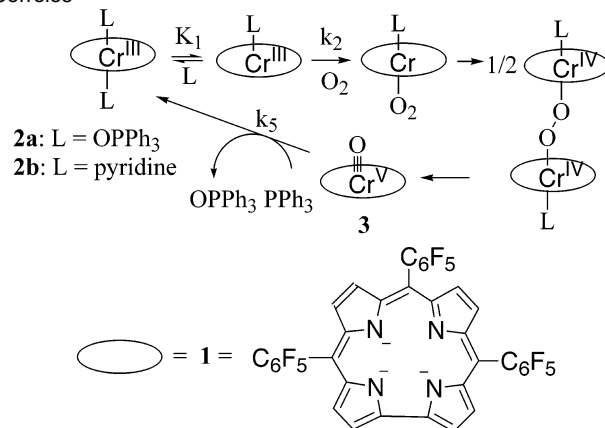
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Scheme 1. Mechanisms for Metal-Catalyzed Oxygenation of Substrates
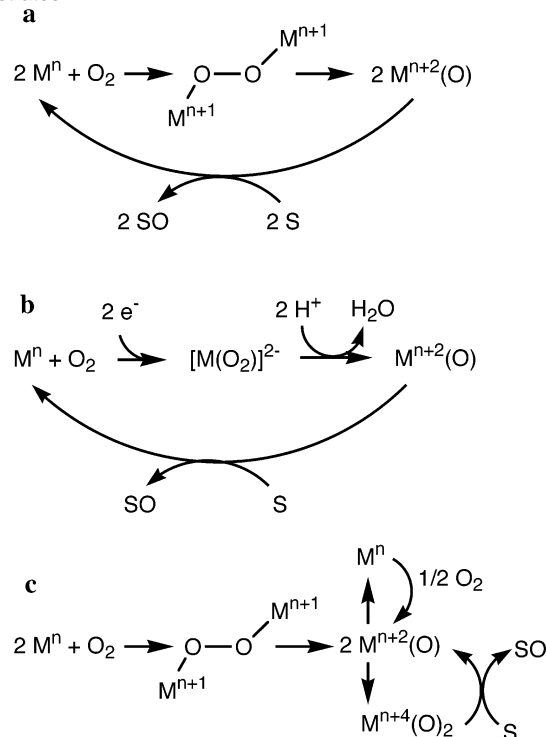
Scheme 2. Interconversion of Chromium(III) and Oxochromium(V) Corroles

2a: L = $OPPh_3$
2b: L = pyridine

The stoichiometric reaction of isolated **3** with PPh_3 (k_5 of Scheme 2, measured in the presence of 0.7% pyridine to avoid reoxidation of **2a** to **3**) also revealed a solvent effect: the second-order rate constants are 5.5, 14.7, 29.5, and 61.0 M^{-1} s^{-1} in THF, toluene, methanol, and acetonitrile, respectively. The beneficial effect of acetonitrile on both processes is a very important observation, as
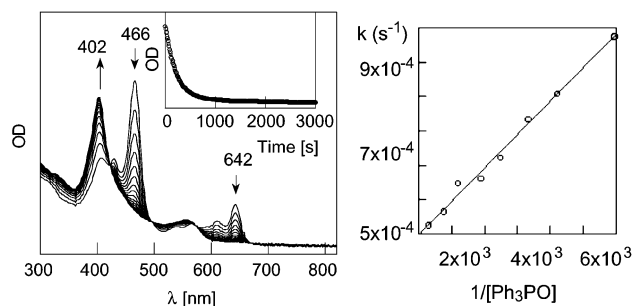
Figure 1. Spectral changes during aerobic oxidation of (tpfc)Cr(OPPh$_3$)$_2$ (**2a**, 12.8 μM in 1.69 mM OPPh$_3$/CH$_2$Cl$_2$) to (tpfc)Cr(O) (**3**), kinetic trace (at 466 nm) of the same reaction, and the effect of OPPh$_3$ on the kinetics.

other conceivable modifications to increase the reactivity of the metal-oxo corrole toward substrates will necessarily have an opposite effect on the activation of dioxygen by the low-valent state. Support for this idea came from an analogue of **3** in which all eight β-pyrrole positions were substituted by bromine atoms (Br$_8$-**3**).[9] The electrochemical reduction potential of Br$_8$-**3** is positively shifted by 0.5 V relative to **3**, and its reactivity toward PPh$_3$ (8200 M^{-1} s^{-1} in CH$_3$CN) is more than 2 orders of magnitude greater than that of **3**. What is more, Br$_8$-**3** is able to oxidize olefins, but aerobic oxidation of the corresponding chromium(III) complex to Br$_8$-**3** is extremely slow.

The catalytic aerobic oxidation of PPh$_3$ (66.4 mM) in the presence of **3** (1.2 mM) was examined in THF, toluene, methanol, and acetonitrile.[10] The total turnover numbers (TON, mol product/mol catalyst) after 17 h were 3, 4, 6, and 12, respectively, reflecting the solvent effect on the elementary steps. With ^{18}O$_2$ instead of air, the TON in acetonitrile increased to 33, and ^{18}OPPh$_3$ (>95% ^{18}O) was produced. The low efficiency in the other solvents is due to product inhibition, indicated by the formation of the six-coordinate complex **2a** (UV–vis). Yet, a different scenario was revealed for the reaction in acetonitrile by monitoring product formation and electronic spectra as a function of time. The initial catalytic reaction is very fast, with a strong decline after about 10 min (Figure 2, inset). Product inhibition is not the reason for incomplete conversion: the characteristic spectrum of **3** changes almost immediately (Figure 2a,b), but not to that of **2a**. Of all known oxidation and coordination states of chromium corroles, the final spectrum (Figure 2d) with λ_{max} of 430 nm resembles only that of [(**1**)Cr^{IV}(O)]$^-$.[8b] Further support came from ^{19}F NMR spectroscopy of a reaction mixture in CD$_3$CN, where residual diamagnetic resonances due to [(**1**)Cr^{IV}(O)]$^-$ are evident. Finally, we found a system that did not suffer from any of the aforementioned problems: thiophenol (66.4 mM in benzene) is fully converted in quantitative yield into diphenyl disulfide within 24 h in the presence of **3** (1.2 mM).

We have demonstrated catalytic aerobic oxidation of substrates by a corrole-based Cr^{V}O/Cr^{III} cycle, the first in which both the reduced and the oxidized 3d metal complexes were fully characterized at ambient conditions. The mild oxidative power of Cr^{V}O may be beneficial for catalytic processes in biological systems, the focus of our current research efforts.
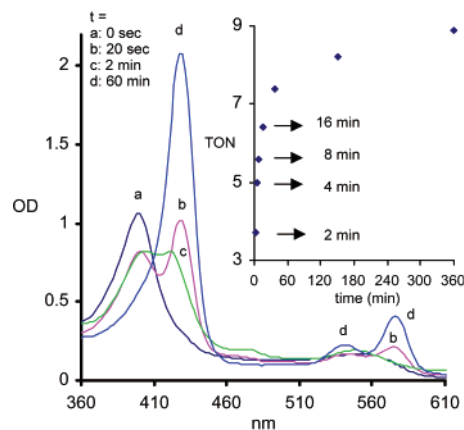

Figure 2. UV–vis spectra taken at different times during the aerobic oxidation of Ph$_3$P to Ph$_3$PO in the presence of **3** in CH$_3$CN. Inset: the catalytic turnovers (TON, mol product/mol catalyst) versus time.

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(9) Preparation and reactivity of 2,3,7,8,12,13,17,18-octabromo-5,10,15-tris-(pentafluorophenyl)corrolato-oxochromium(V), Br$_8$-**3**: NBS (200 mg) and **3** (18 mg, 21 μmol) were heated for 4 h in methanol (20 mL) under N$_2$. Column chromatography (silica; 1:1 CH$_2$Cl$_2$/n-hexane for unreacted material and CH$_2$Cl$_2$/n-hexane/ethanol (2:1:0.01) for the product) was followed by titration of the green fraction (Cr(Br$_8$-tpfc), redissolved in 5 mL of CH$_2$Cl$_2$) by a concentrated m-CPBA/CH$_2$Cl$_2$ solution to achieve oxidation to Br$_8$-**3**. Flash chromatography (silica, CH$_2$Cl$_2$) allowed for the isolation of a red product in 96% yield (30 mg, 20.1 μmol). ^{19}F NMR (CDCl$_3$): −137.0 (br s, 6F), −150.7 (s, 3F), −161.4, −161.9, −162.7 (3 br s, 6F). UV–vis (toluene): λ_{max} (ϵ, M^{-1} cm^{-1}): 424 (76 000), 584 (14 000) nm. MS: DCI$^-$ (isobutane, m/z) 1476.3 [M$^-$ − O, 60%]. $E_{1/2}$ (TBAP, CH$_2$Cl$_2$, vs Ag/AgCl): 0.58 V. The reactions of Br$_8$-**3** with excess PPh$_3$ and norbornene in toluene produced OPPh$_3$ (1 min, 100%; 2 days, 300%; 3 days, 500%) and exo-norbornene oxide (6 h, 70%), respectively. With cyclohexene, allylic oxidation products (6 h: 300% cyclohexene oxide, 9000% 2-cyclohexene-1-ol, 8000% 2-cyclohexene-1-one) indicate a radical mechanism. Yields were determined by GC relative to an internal standard and are reported after subtraction of products obtained in control reactions.
(10) Yields of OPPh$_3$ were determined by GC (control experiments in the absence of catalyst revealed negligible amounts) and of ^{18}OPPh$_3$ by GC/MS as well.

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