Aerobic Epoxidation of Olefins Catalyzed by Electronegative Vanadyl Salen Complexes

Christopher J. Chang, Jay A. Labinger,* and Harry B. Gray*

Arthur Amos Noyes Laboratory and Beckman Institute, California Institute of Technology,
Pasadena, California 91125

Received July 2, 1997⊗

Vanadyl salen complexes bearing electron-withdrawing substituents have been prepared and characterized. Systematic substitutions on the ancillary ligand have allowed V^{5+}/V^{4+} reduction potentials to be tuned over a range of approximately 500 mV. The complexes are catalysts for the aerobic epoxidation of cyclohexene; catalytic activity roughly increases with increasing V^{5+}/V^{4+} reduction potential. The mechanism likely involves oxygen transfer from intermediate hydroperoxides that are formed by radical-chain autoxidation.

Introduction

Selective oxidation of hydrocarbons is of importance in the production of fuels, commodity chemicals, and fine chemicals.[1,2] The use of dioxygen as an oxidant for such processes is particularly attractive from both economic and environmental standpoints;[1−4] however, the triplet ground state of O_2 disfavors reactions with singlet organic compounds. Finding pathways for the selective oxidation of organic feedstocks using dioxygen could lead to improvements in the management of our natural resources.

Perhalogenated metal porphyrins are active catalysts for the oxidation of hydrocarbons by O_2 under mild conditions (25−60 °C, 4−8 atm).[5−7] Studies indicate that the mechanism involves radical-chain autoxidation, where the metal complex catalytically decomposes intermediate hydroperoxides formed from hydrocarbons and O_2.[8,9] Indeed, perhalogenated iron(III) porphyrin complexes are remarkably active catalysts for the decomposition of organic peroxides.[10,11]

Difficulty of synthesis is one problem limiting the use of perhalogenated metal porphyrins as catalysts in hydrocarbon oxidations. Therefore, we have embarked upon a program aimed at developing catalysts that mimic perhalogenated metal porphyrins but are more easily prepared. We chose salen for investigation, as its ligand framework is similar to that of a porphyrin;[12−14] in addition, the remarkable electronic and steric tunability of Schiff bases makes it possible to carry out systematic reactivity studies based on ancillary ligand modification.[13,15−18]

It is known that metal salen complexes catalyze the epoxidation of alkenes, using iodosylbenzene or *m*-chloroperbenzoic acid as an oxygen atom donor;[17−20] worthy of special mention is the work of Jacobsen[13,21,22] and Katsuki[23] employing chiral manganese(III) salen derivatives (with bleach or iodosylbenzene) for enantioselective reactions. In earlier work, we have shown that electronegative iron(III) salen complexes catalyze the aerobic oxidation of hydrocarbons under mild conditions.[15,16] Here we report that electronegative vanadyl salen complexes are moderately selective catalysts for aerobic olefin epoxidation.

Experimental Section

Physical Measurements. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer Paragon 1000 FT-IR. A Hewlett-Packard 5890 Series II gas chromatograph equipped with a Hewlett-Packard 3396 Series II integrator was employed for GC analyses. Fast atom bombardment (FAB) mass spectral analyses were performed at the UC Riverside mass spectrometry facility. Elemental analyses (C, H, N) were performed at the Caltech analytical facility. Cyclic voltammetry was performed using a BioAnalytical Systems (BAS) 100W 2.0. The working, auxiliary, and reference electrodes were glassy carbon, platinum wire, and AgCl/Ag, respectively. Electrochemical measurements were performed at room temperature (25 °C) under argon with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte.

Materials. Oxygen gas was passed through a calcium chloride drying tube before admission to the reaction system. Cyclohexene was distilled under nitrogen and stored over molecular sieves (4 Å) before use. *o*-Phenylenediamine was recrystallized at least twice from either ethanol or water. Reference samples of cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one (Aldrich) were distilled and stored over molecular sieves (4 Å) until use. Solvents (Burdick and Jackson)

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) *Selective Hydrocarbon Oxidation, Principles and Progress*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990.
(2) Hucknall, D. J. *Selective Oxidation of Hydrocarbons*; Academic Press: New York, 1974.
(3) *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simádi, L. I., Ed.; Elsevier: New York, 1991.
(4) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981.
(5) Ellis, P. E.; Lyons, J. E. *Catal. Lett.* **1989**, *3*, 389.
(6) Ellis, P. E.; Lyons, J. E. *Coord. Chem. Rev.* **1990**, *105*, 181.
(7) Lyons, J. E.; Ellis, P. E. *Catal. Lett.* **1991**, *8*, 45.
(8) Labinger, J. A. *Catal. Lett.* **1994**, *26*, 95.
(9) Grinstaff, M. W.; Hill, M. G.; Labinger, J. A.; Gray, H. B. *Science* **1994**, *264*, 1311.
(10) Grinstaff, M. W.; Hill, M. G.; Birnbaum, E. R.; Schaefer, W. P.; Labinger, J. A.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 4896.
(11) Lyons, J. E.; Ellis, P. E.; Myers, H. K.; Wagner, R. W. *J. Catal.* **1993**, *141*, 311.
(12) Schiff, H. *Ann. Chem. Suppl.* **1864**, *3*, 343.
(13) Jacobsen, E. N. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12.
(14) Lindroy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, U.K., 1989.
(15) Böttcher, A.; Grinstaff, M. W.; Labinger, J. A.; Gray, H. B. *J. Mol. Catal. A* **1996**, *113*, 191.
(16) Böttcher, A.; Birnbaum, E. R.; Day, M. W.; Gray, H. B.; Grinstaff, M. W.; Labinger, J. A. *J. Mol. Catal. A* **1997**, *117*, 229.
(17) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606.
(18) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.
(19) Yoon, H.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 4087.
(20) Koola, J. D.; Kochi, J. K. *J. Org. Chem.* **1987**, *52*, 4545.
(21) Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991**, *56*, 2296.
(22) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; p 159.
(23) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189.

© 1997 American Chemical Society

for electrochemical experiments were redistilled and passed through a column of activated alumina. TBAH (SACHEM) was recrystallized from methanol. All other chemicals were used as received from commercial suppliers.

Vanadyl Compounds 1−8. The Schiff bases were obtained by condensation of the appropriate diamine and substituted salicylaldehyde.[12,15,24,25] Ligands were recrystallized from ethanol at least once before metalation. Green vanadyl complexes **1**−**4** were prepared under ambient conditions by treatment of a dichloromethane solution of the ligand with $VO(acac)_2$, $VOSO_4{\cdot}H_2O$, or $V(acac)_3$ and dioxygen.[24−27] A modification of published procedures for the preparation of nitro-substituted complexes **5**−**8** was found to lead to analytically purer products in higher yields. The ligand (1 mmol) was dissolved in a warm methanol/nitromethane mixture (105 mL, 20:1). $VO(acac)_2$ (1 mmol, 1 equiv) in 15 mL of absolute methanol was added to the warm solution. The reaction mixture was refluxed for 30 min, concentrated, and cooled to room temperature. Orange products **5**−**8** were isolated by filtration, washed with cold methanol and water, and dried. Recrystallization from nitromethane/methanol mixtures gave analytically pure products (70−90% yield). Analytical data for **1**−**8** are as follows. (salen)VO (**1**) MS(FAB$^-$): *m/z* 333 (MH$^+$). Anal. Calcd (found) for $C_{16}H_{14}N_2O_3V$: C, 57.67 (56.79); H, 4.21 (4.48); N, 8.41 (8.06). (salchxn)VO (**2**) MS(FAB$^-$): *m/z* 387 (M$^+$). Anal. Calcd (found) for $C_{20}H_{20}N_2O_3V$: C, 62.03 (62.11); H, 5.17 (5.40); N, 7.24 (7.17). (salphen)VO (**3**) MS(FAB$^-$): *m/z* 381 (M$^+$), 382 (MH$^+$). Anal. Calcd (found) for $C_{20}H_{20}N_2O_3V{\cdot}0.5H_2O$: C, 61.55 (61.96); H, 3.84 (3.84); N, 7.18 (7.07). (saldpen)VO (**4**) MS(FAB$^-$): *m/z* 485 (M$^+$), 971 (2M$^+$). Anal. Calcd (found) for $C_{28}H_{22}N_2O_3V$: C, 69.29 (68.88); H, 4.54 (4.69); N, 5.77 (5.69). (3,3′,5,5′-$(NO_2)_4$salen)VO (**5**) MS(FAB$^-$): *m/z* 514 (MH$^+$). Anal. Calcd (found) for $C_{16}H_{10}N_6O_{11}V$: C, 37.40 (38.14); H, 1.95 (2.19); N, 16.38 (16.11). (3,3′,5,5′-$(NO_2)_4$salchxn)VO (**6**) MS(FAB$^-$): *m/z* 568 (MH$^+$). Anal. Calcd (found) for $C_{20}H_{16}N_6O_{11}V$: C, 41.03 (41.64); H, 3.08 (3.15); N, 14.36 (14.41). (3,3′,5,5′-$(NO_2)_4$salphen)VO (**7**) MS(FAB$^-$): *m/z* 562 (MH$^+$). Anal. Calcd (found) for $C_{20}H_{10}N_6O_{11}V{\cdot}0.5H_2O$: C, 42.11 (42.58); H, 1.93 (2.10); N, 14.73 (14.70). (3,3′,5,5′-$(NO_2)_4$saldpen)VO (**8**) MS(FAB$^-$): *m/z* 665 (M$^+$). Anal. Calcd (found) for $C_{28}H_{18}N_6O_{11}V{\cdot}0.5H_2O$: C, 47.90 (48.09); H, 3.14 (3.26); N, 11.98 (11.78).

Catalytic Oxidations. All glassware was oven-dried prior to use. In a typical experiment, the vanadyl catalyst (10 μmol) was added to a modified Kjeldahl flask[28] and the system was evacuated and purged with nitrogen. The flask was then charged with freshly distilled olefin (0.1 mol), and the system was saturated with 1 atm of O_2. Reactions were carried out at 80 °C for 24 h under 1 atm of O_2. Samples were withdrawn from the reaction solution at appropriate times and analyzed by GC. The oxidation products were identified by comparisons with authentic samples (retention time in GC; IR; NMR).

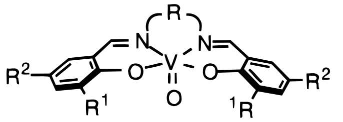
Results

Synthesis and Characterization of Oxovanadium(IV) Complexes. Salen ligands were readily prepared from commercially available starting materials by the Schiff-base condensation of 2 mol of a salicylaldehyde derivative with 1 mol of the appropriate diamine.[12,15,24,25] The yellow or orange crystalline products were isolated in excellent yields (>90%). Ligands were characterized by ^{1}H NMR spectroscopy. Treatment of the Schiff-base ligands with $VO(acac)_2$, $VOSO_4{\cdot}H_2O$, or $V(acac)_3$ under aerobic conditions gave the desired oxovanadium(IV) complexes.[24−27] Overall yields were reasonable (70−90%). The vanadyl compounds, which were identified by mass spectrometry and elemental analysis, are remarkably stable to air, water, and heat. The V═O IR stretching frequency is in the range 860−990 cm^{-1} for complexes **1**−**8** (Table 1).[29]

Table 1. Vibrational Parameters and Vanadium(V/IV) Reduction Potentials for **1**−**8**[a−c]

complex	V═O str (cm^{-1})	diatomic force const (mdyn/Å)	color	$E°(V^{5+}/V^{4+})$ (mV vs AgCl/Ag)
1	979	6.89	green	545
2	976	6.84	green	570
3	979	6.89	green	598
4	993	7.09	green	610
5	880	5.56	orange	insoluble
6	883	5.60	orange	insoluble
7	888	5.67	orange	975
8	860	5.31	orange	1039

[a] Infrared spectra measured as KBr pellets. [b] Electrochemical measurements made in anhydrous CH_2Cl_2 or DMF containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH). [c] Irreversible reduction was observed for the complexes at potentials less than −1600 mV accompanied by decomposition of the complex.



(**1**) R^1, R^2 = H, R = en
(**2**) R^1, R^2 = H, R = chxn
(**3**) R^1, R^2 = H, R = *o*-phen
(**4**) R^1, R^2 = H, R = dpen
(**5**) R^1, R^2 = NO_2, R = en
(**6**) R^1, R^2 = NO_2, R = chxn
(**7**) R^1, R^2 = NO_2, R = *o*-phen
(**8**) R^1, R^2 = NO_2, R = dpen

Electronic effects on the redox properties of the vanadyl complexes were investigated using cyclic voltammetry. Electrochemical studies were carried out in either dichloromethane or dimethylformamide solution at room temperature (complexes **5** and **6** were too insoluble for cyclic voltammetry). Compounds examined in both dichloromethane and dimethylformamide showed small shifts in redox potential between solvents (<0.05 V). The vanadyl complexes exhibited clean and quasi-reversible electrochemistry; a typical cyclic voltammogram is included in the Supporting Information. Overall, the V^{5+}/V^{4+} reduction potential shifts by approximately 500 mV from the parent (salen)VO (**1**) to the tetranitro derivative (3,3′,5,5′-$(NO_2)_4$-saldpen)VO (**8**) (Table 1). This is similar to the range of Fe^{3+}/Fe^{2+} potentials spanned by a series of iron(III) salen complexes[15,16] (e.g., (salen)FeCl to (3,3′,5,5′-$(NO_2)_4$saldpen)FeCl, 575 mV) and iron(III) porphyrins[10,16] (e.g., (TPP)FeCl to (TF_{20}-$PPBr_8$)FeCl, 600 mV). Irreversible ligand oxidation of the salen complexes occurs only at high potentials (>1.5 V), suggesting that these derivatives are oxidatively robust.

Aerobic Epoxidation of Cyclohexene. Investigations of **1**−**8** as oxidation catalysts utilized cyclohexene as substrate. In the presence of dioxygen and vanadyl catalyst, cyclohexene oxidation to a mixture of cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one was observed for all eight complexes. Similar product distributions (Figure 1) were observed for all the catalysts used (∼40% epoxide, ∼50% allylic alcohol, ∼10% allylic ketone). Typical catalyst/substrate reactions were run in solutions at elevated temperatures (80−85 °C) stirred under 1 atm of O_2. Under these conditions, complexes **1**−**8** are soluble in neat olefin solution; however, at room temperature, nitro-substituted complexes **5**−**7** are insoluble. As with electronegative iron(III) salen complexes,[15,16] incorporation of large

---

(24) Pfeiffer, P.; Breith, E.; Lübbe, E.; Tsumaki, T. *Liebigs Ann. Chem.* **1933**, *503*, 84.
(25) Pfeiffer, P.; Thielert, H. *J. Prakt. Chem.* **1937**, *149*, 242.
(26) Bonaides, J. A.; Carrano, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4088.
(27) Tsuchida, E.; Yamamoto, K.; Oyaizu, K.; Iwasaki, N.; Anson, F. C. *Inorg. Chem.* **1994**, *33*, 1056.
(28) Birnbaum, E. R. Ph.D. Thesis, California Institute of Technology, 1995.
(29) Abbreviations: en = ethylenediamine; chxn = 1,2-diaminocyclohexane; *o*-phen = *o*-phenylenediamine; dpen = 1,2-diphenylethylenediamine.

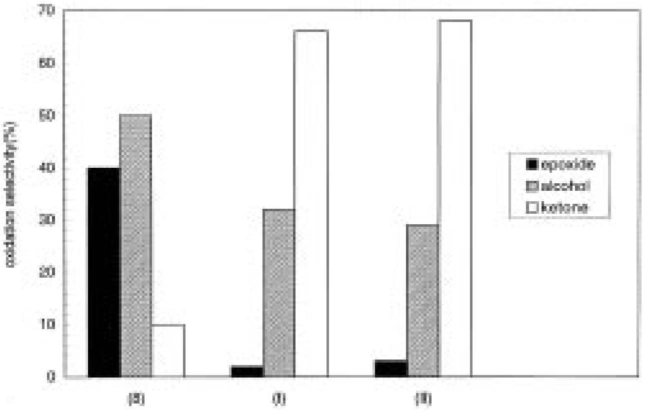


Figure 1. Product selectivity for the aerobic oxidation of cyclohexene catalyzed by (3,3′,5,5′-$(NO_2)_4$saldpen)V=O (**8**), (3,3′,5,5′-$(NO_2)_4$-saldpen)FeCl (**I**), and ($TF_{20}PPBr_8$)FeCl (**II**).

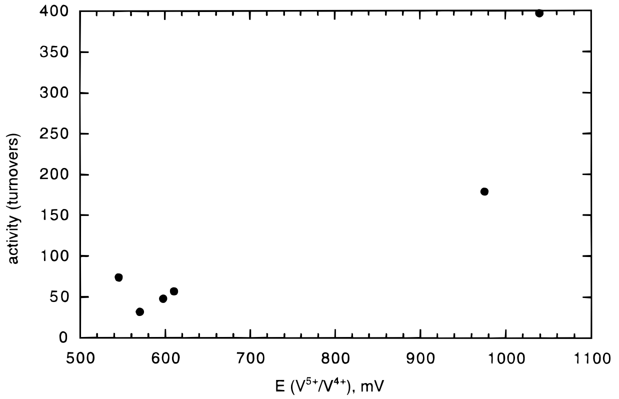


Figure 2. Plot of activity for catalytic cyclohexene oxidation (turnover number) vs V^{5+}/V^{4+} reduction potential (mV) for complexes **1**−**8**.

nonpolar groups into the diamine bridge greatly enhances the solubility of nitro-substituted derivatives. Complex **8** is the most active, achieving approximately 400 turnovers in a 24 h period. Its performance is compared to those of other salen derivatives in Figure 2.

Several control experiments were performed. In the absence of catalyst or in the presence of ligand alone, little or no oxidation occurs. Autoxidation by simple vanadyl salts (e.g., $VO(acac)_2$ or $VOSO_4$) under these conditions was much slower and occurs only at allylic positions. Catalysis was not affected by light. Finally, the catalysts are remarkably stable to oxidative degradation under reaction conditions.[30]

Discussion

Vanadyl complexes **1**−**8** catalyze the epoxidation of cyclohexene with moderate selectivity using molecular oxygen under mild conditions (80 °C, 1 atm of O_2). It is likely that the reactivity of **1**−**8** with O_2 as oxidant is related to the d^0 metal-catalyzed epoxidation of olefins by alkyl hydroperoxides.[1,31,32] We propose a dual-pathway autoxidation mechanism (Figure 3),[8,9] where one primary role of the metal is to generate radicals by catalyzing alkyl hydroperoxide decomposition. Initial autoxidation of cyclohexene generates allylic hydroperoxides. The vanadyl complexes can then decompose intermediate organic peroxides by acting either as radical oxidants to induce homolytic peroxide cleavage or as electrophilic oxygen-transfer reagents by promoting heterolytic peroxide cleavage. Homolytic cleavage of the peroxide by either oxovanadium(IV) or oxovanadium(V) yields allylic alcohol and α,*β*-unsaturated ketone products. An analogous pathway has been proposed for the aerobic oxidation of hydrocarbons catalyzed by electronegative iron(III) salen complexes on the basis of product distributions and sensitivity to radical initiators and inhibitors.[15]

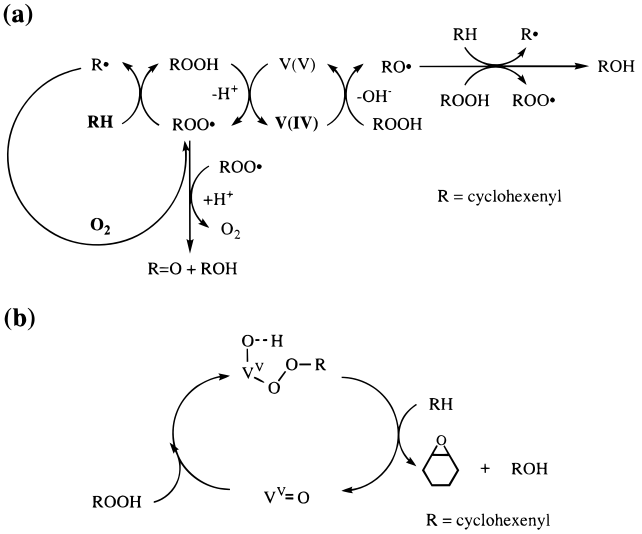


Figure 3. Proposed catalytic cycle for the oxidation of cyclohexene by vanadyl complexes **1**−**8** and dioxygen (1 atm): (a) generation of allylic hydroperoxides from cyclohexene and dioxygen; (b) epoxidation of cyclohexene by vanadium(V) and intermediate allylic hydroperoxides.

In contrast to that of their iron(III) salen counterparts, the vanadium-catalyzed aerobic oxidation of cyclohexene proceeds with moderate selectivity for epoxidation (40%, Figure 1). We propose this proceeds via a separate pathway, in which oxidation of the oxovanadium(IV) catalyst by cyclohexenyl hydroperoxide affords an oxovanadium(V) species, which can then react with another equivalent of organic peroxide and olefin to yield epoxide and allylic alcohol (Figure 3b).[33−38] Analogous intermediates have been proposed for the oxovanadium(IV)-catalyzed epoxidations of olefins using alkyl hydroperoxide oxidants.[36,39] EPR investigations of the reaction of several oxovanadium(IV) complexes with *tert*-butyl hydroperoxide (TBHP) indicate that an oxovanadium(V) complex is formed and is probably the active oxidizing species.[39] Preliminary experiments confirm that both complex **8** and its oxidized vanadium(V) counterpart catalyze the epoxidation of cyclohexene using TBHP or cumene hydroperoxide as oxidant. The last

---

(30) The absorption spectrum of **8** remains unchanged after reaction for 1 week.

(31) Landau, R.; Sullivan, G. A.; Brown, D. *CHEMTECH* **1979**, 602.

(32) *Aspects of Homogeneous Catalysis*; Ugo, R., Reidel, D., Eds.; Kluwer: Dordrecht, Holland, 1981, 1977; Vols. 4 and 3.

(33) The mechanism of epoxidation of olefins by alkyl hydroperoxides catalyzed by d^0 metal complexes remains a matter of debate, since the nature of the oxidizing species has not been clearly established. However, in view of its high selectivity and stereospecificity, it is generally accepted that it proceeds via peroxide heterolysis. Two mechanisms have been proposed: (A) nucleophilic attack of a noncoordinated olefin on the electrophilic peroxide oxygen atom bound to the metal;[34−36] and (B) insertion of the coordinated olefin into the metal−oxygen bond, forming a five-membered dioxametallocyclopentane.[37,38] We favor pathway A for the complexes studied here, on the basis of previous mechanistic studies of vanadyl Schiff-base/alkyl hydroperoxide systems.[39]

(34) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587.

(35) Nishida, Y.; Yamada, K. *Inorg. Chim. Acta* **1990**, *174*, 1.

(36) Talsi, E. P.; Chinakov, V. D.; Babenko, V. P.; Zamaraev, K. I. *J. Mol. Catal.* **1993**, *81*, 235.

(37) Chaumette, P.; Mimoun, H.; Saussine, L.; Fischer, J.; Mitscher, A. *J. Organomet. Chem.* **1983**, *250*, 291.

(38) Mimoun, H.; Mignard, M.; Brechot, P.; Saussine, L. *J. Am. Chem. Soc.* **1986**, *108*, 3711.

(39) Agarwal, D. D.; Rastogi, R.; Sangha, P. K. *Indian J. Chem.* **1995**, *34B*, 254.

result is hardly surprising, since vanadium(V)−peroxo complexes are active catalysts for the oxidation of a variety of organic substrates;[40,41] indeed, olefin epoxidation by alkyl hydroperoxides catalyzed by d^0 metal complexes (V^{5+}, Mo^{6+}, Ti^{4+}) is an industrial (Halcon) process.[31]

This "hybrid" mechanism, where the metal complex functions in two roles—to generate the hydroperoxide by a radical path and then to catalyze the epoxidation of the substrate—has previously been proposed for the aerobic oxidation of cyclohexene catalyzed by heteropolyacids.[42] It is also closely related to the mechanism proposed for the co-oxidation of olefins and aldehydes.[43] In the present system, the olefin functions as its own "sacrificial" cosubstrate, implying an optimal selectivity of 50%.

A striking feature of iron(III) halogenated porphyrin and electronegative salen autoxidation catalysts is the correlation of activity with redox potential. This is interpreted in the context of the radical-chain mechanism, with the key factor being the rate of reduction of Fe(III) by hydroperoxide, which is the slow step of hydroperoxide decomposition in the Haber−Weiss cycle. This rate is governed by the Fe^{3+}/Fe^{2+} potential, with an approximately linear relationship between log(rate) and potential.[8] The vanadyl salen complexes exhibit roughly similar behavior (Figure 2); the observation that the most oxidizing complexes are the most active catalysts suggests that the rate-determining step is the decomposition of an alkyl hydroperoxide by vanadium(V).

The unusual selectivity and reactivity of the vanadyl salen complexes for aerobic epoxidation of olefins are direct consequences of systematic electronegative substitution on the ligand skeleton. Replacement of ligand hydrogen atoms by nitro groups inhibits oxidative destruction of the catalysts; like their iron counterparts,[15,16] the electronegative vanadyl salen complexes are remarkably robust under reaction conditions. This is an important feature because deactivation appears to be a significant problem in other applications of salen derivatives as oxidation catalysts.[23] Infrared spectral analyses indicate that substitution of nitro groups on the ancillary ligand produce a more electrophilic metal−oxo center (Table 1). Green vanadyl complexes **1**−**4** have V═O stretching frequencies in the range 976−993 cm^{-1}, which are characteristic of monomeric five-coordinate structures. In contrast, orange nitro-substituted vanadyl complexes **5**−**8** have much lower V═O stretching frequencies (∼860−888 cm^{-1}). These complexes are six-coordinate in the solid state and in solution, as they form polymeric vanadium−oxygen (···V═O···V═O···) units. In the proposed autoxidation mechanism, vanadium(V) can selectively interact with cyclohexenyl hydroperoxide and cyclohexene to yield epoxide and allyl alcohol (Figure 3b). Hydroperoxide decomposition is most probably an inner-sphere process, requiring coordination of the peroxide to the metal center. Electronegative substitution endows the metal−oxo unit with enhanced electrophilicity and renders it more reactive toward nucleophilic addition of an organic peroxide (Figure 3b). The electron-withdrawing effect also activates the intermediate metal−peroxo complex for oxygen atom transfer to an olefin, by increasing the electrophilic character of the metal-bound peroxo oxygen (Figure 3b). Hence, the addition of electron-withdrawing groups affords a vanadyl center of high reduction potential that favors an olefin epoxidation pathway.

We have designed a family of robust catalysts for olefin epoxidation by dioxygen under mild conditions using inexpensive and readily available salen ligands. Systematic ancillary ligand substitutions with electron-withdrawing groups have allowed the reactivity of the catalysts to be modulated by control of redox potential and metal−oxo electrophilicity. Furthermore, since the complexes are not completely substituted with electron-withdrawing groups, it should be possible to increase both the reduction potential and metal−oxo electrophilicity, and hence the catalytic activity. Our findings suggest that the steps in the autoxidation mechanism may be manipulated to favor the heterolytic decomposition pathway and selectivity for epoxidation.

Acknowledgment. We thank Don Low, Mahdi Abu-Omar, and Jeff Rack for helpful discussions. C.J.C. thanks the Caltech SURF program and the A. A. Noyes Foundation for an award. This work was supported by the Bayer Foundation and the National Science Foundation.

Supporting Information Available: Representative electrochemical data for catalytic complexes (Figure S1) (1 page). Ordering information is given on any current masthead page.

IC970824Q

---

(40) *Organic Peroxides*; Ando, W., Ed.; Wiley: Chichester, U.K., 1992.

(41) Conte, V.; Di Furia, F. In *Catalytic Oxidations with Hydrogen Peroxide as an Oxidant*; Strukul, G., Ed.; Kluwer: Dordrecht, Holland, 1992.

(42) Neumann, R.; Dahan, M. *J. Chem. Soc., Chem. Commun.* **1995**, 171.

(43) Nam, W. W.; Kim, H. J.; Kim, S. H.; Ho, R. Y. N.; Valentine, J. S. *Inorg. Chem.* **1996**, *35*, 1045.