would give the desired solvent composition. After thermal equilibration, the sodium hydroxide was added, and the reaction was allowed to proceed to the desired degree of completion as calculated from rate data obtained under the same conditions. Where possible the degree of completion was monitored by withdrawing small aliquots, diluting them with ethanol, and measuring absorbance at 248 nm; in highly aqueous media the styrene began to separate at an early stage, and this check could not be employed. The reaction was quenched by cooling to 0 °C and adding sufficient acid to neutralize the remaining base.

For faster reactions, an insufficiency of base was used, and the reaction was allowed to proceed until all of the base was consumed. A control experiment showed no reaction occurs in the absence of base. The ammonium salt (2.0 g, 0.003 mol) was dissolved in ca. 22 mL of solvent in a 25-mL volumetric flask and equilibrated thermally before diluting to the mark with more solvent. Approximately 0.15 mL of concentrated (ca. 23 M) sodium hydroxide was added to the flask and the contents mixed well. The reaction was allowed to proceed until all of the base was consumed, and the concentration of styrene was determined by withdrawing a small aliquot, diluting it with ethanol, and measuring the absorbance at 248 nm. For very fast reactions, there is a danger of error from local depletion of the faster-reacting isotopic species during mixing. Consequently, some of the fastest reactions in 60% Me_2SO were also carried out in a simple rapid-mixing apparatus, a T of stainless-steel tubing of 0.125-in. i.d. with syringes attached vertically to the two ends of the horizontal tube and a receiver flask to the vertical tube. The mixing time for such an apparatus is claimed to be in the range of 10–20 ms.[32] Base solution was placed in one syringe and substrate solution in the other, and the entire apparatus was equilibrated in the constant-temperature bath before the syringe plungers were driven down simultaneously by means of a horizontal connecting bar. The final styrene concentration was determined as above. Results obtained with this apparatus did not differ significantly from those obtained by the conventional mixing procedure, so mixing time was evidently not a source of error in any of our experiments.

For the reactions in ethanol, 1.5 g of substrate was dissolved in 100 mL of dry ethanol and the solution thermally equilibrated. To it was added 10 mL of equilibrated 1.1 M sodium ethoxide solution. At the desired fraction of reaction, three 1.0-mL aliquots were withdrawn and diluted with ethanol to determine the absorbance at 248 nm. The remainder was quenched with hydrochloric acid, cooled in an ice bath, and added to 200 mL of ice-cold ether. The precipitated ammonium salt was removed by suction filtration and dissolved in water for oxidation with potassium permanganate as described below.

The following workup procedure was used in all the reactions in Me_2SO–H_2O. The reaction mixture was poured into 200 mL of distilled water and the solution extracted five times with benzene to remove styrene. A control experiment showed no radioactivity in the benzene extract after the fourth extraction. To the solution was added 2.0 g (0.019 mol) of sodium carbonate, and then potassium permanganate was added cautiously with stirring (a great deal is needed to oxidize both substrate and Me_2SO). Addition was continued until the purple color persisted after 3 h of heating on a steam bath. The solution was cooled and sodium sulfite added to discharge the purple color. Then more sodium sulfite and concentrated hydrochloric acid were added to convert the Mn^{IV} to water-soluble Mn^{II}.[33] The clear solution was cooled and extracted with ether. The extracts were dried over magnesium sulfate, and the ether was removed to yield benzoic acid, which was recrystallized 5–10 times from water. It was dried in vacuo, and ca. 50 mg was dissolved in the scintillation cocktail (15 mL of a solution of 26.5 g of BuPBD in 8 parts of toluene) for activity determination on a Beckman LS-100C liquid scintillation counter. Counting was to the 0.2% (2σ) level of precision, and quench corrections were made by the external standard channels ratio method[34] by using a Beckman standard set of quenched ^{14}C samples to determine the quench correction curve. Counting efficiency was high (ca. 94%) in all cases. Control experiments showed that oxidation of the ammonium salt in water and in 40% Me_2SO gave benzoic acid samples of the same molar activity within 0.1%. The k_{12}/k_{14} values from eq 4 are given in Table I, where each value is the average of two or three separate experiments.

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[32] Caldin, E. F. "Fast Reactions in Solution", Blackwell: Oxford, 1964.

[33] Fieser, M.; Fieser, L. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 942.

[34] Neame, K. D.; Homewood, C. A. "Liquid Scintillation Counting"; Halsted-Wiley: New York, 1974; pp 106–110.

Activation of Cobalt–Nitro Complexes by Lewis Acids: Catalytic Oxidation of Alcohols by Molecular Oxygen

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Abstract: Lewis acids dramatically enhance the oxidation power of cobalt–nitro complexes. Thus, in the presence of $BF_3{\cdot}Et_2O$ or $LiPF_6$, cobalt–nitro complexes such as $pyCo(saloph)NO_2$ or $pyCo(TPP)NO_2$ oxidize primary alcohols to aldehydes and secondary alcohols to ketones. No reaction is observed in the absence of Lewis acids. The effect of Lewis acids is attributed to their association with the nitro ligand, thereby increasing its electrophilicity. The results strongly suggest that the oxidation proceeds via an "ester-like" intermediate, which in a nonradical pathway collapses to the carbonyl product, water, and the corresponding nitrosyl complex. Importantly, it has been found that the reoxidation of the nitrosyl complexes by molecular oxygen is facile in the presence of Lewis acids. This finding facilitated the conversion of the stoichiometric oxidation of alcohols into a catalytic system using molecular oxygen as the oxidant. Initial oxidation rates are rapid. However, the rates decline as the byproduct, water, accumulates in the reaction mixture.

Previously, we advanced a new approach to specific, catalytic oxidations of organic substrates by molecular oxygen.[1] In this approach, the critical step consisted of oxygen atom transfer from a nitro ligand of metal–nitro complexes to organic substrates. This concept (eq 1 and 2) was demonstrated[1] by us in the oxidation

$$M\text{-}NO_2 + S \rightarrow SO + M\text{-}NO \qquad (1)$$

$$2M\text{-}NO + O_2 \rightarrow 2MNO_2 \qquad (2)$$

of triphenylphosphine catalyzed by cobalt–nitro complexes.[2] The importance of this finding lies in the fact that the catalytic cycle exhibits features which are helpful in preventing Haber–Weiss, metal-assisted, nonspecific radical oxidations: (a) The oxidation and reduction occur exclusively at the nitro ligand. (b) The cobalt–nitro and –nitrosyl complexes formally exist in the form of Co(III)–NO^- and Co(III)–NO_2^-. Thus, the oxidation state

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[1] Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 270.

[2] Oxidation of certain cobalt–nitrosyl complexes by molecular oxygen to cobalt–nitro complexes has been reported by Clarkson, S. G.; Basolo, F. *Inorg. Chem.* **1973**, *12*, 1528.

0002-7863/81/1503-3522$01.25/0

Table I. Stoichiometric Oxidation of Alcohols by a Combination of Cobalt-Nitro Complexes with Lewis Acids[a]

run no.	complex	Lewis acid/Co (ratio)	T, min	yield, %[b]
		Cycloheptanol		
1	I	none	60	0
2		$BF_3 \cdot Et_2O$ (5.0)	45	84
3		$LiPF_6$ (5.0)	30	69
4		$NaPF_6$ (5.0)	60	0
5	II	none	60	0
6		$BF_3 \cdot Et_2O$ (1.5)	60	10
7		(2.9)	60	34
8		(5.0)	45	84
9		(10.0)	10	84
		Benzyl Alcohol		
10	I	$BF_3 \cdot Et_2O$ (5.0)	45	99
11		$LiPF_6$ (5.0)	45	85
12		$LiBF_4$ (5.0)	45	47
13	II	$BF_3 \cdot Et_2O$ (5.0)	30	52[c]
14	Co(TPP)NO	$BF_3 \cdot Et_2O$ (5.0)	60	0
15	Co(TPP)I	$BF_3 \cdot Et_2O$ (5.0)	60	5.7
16	Co(TPP)	$BF_3 \cdot Et_2O$ (5.0)	60	0
		Cyclohexanol		
17	I	$BF_3 \cdot Et_2O$ (4.7)	20	47
		Cyclopentanol		
18	I	$BF_3 \cdot Et_2O$ (5.1)	60	26
		Cyclohexyl Ethyl Ether		
19	II	$BF_3 \cdot Et_2O$ (5.0)	60	0
		Cyclopentanol/Cycloheptanol (1:1)		
20	I	$BF_3 \cdot Et_2O$ (5.0)	30	54[d]

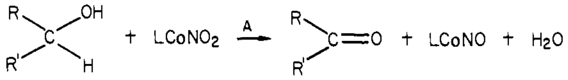
[a] The reaction was run in deoxygenated 1,2-dichloroethane under argon at 60 °C. [b] The yield is based on the amount of the cobalt complex. [c] In addition to benzaldehyde, 39% of salicylaldehyde was formed. [d] Only cycloheptanone was found in the reaction mixture.

of cobalt remains constant throughout the catalytic cycle and metal-centered, one-electron redox reactions are avoided.[3] (c) The regeneration of the oxidant by the reaction with molecular oxygen (eq 2) is a discrete and separate step from the subsequent oxidation of the organic substrate (eq 1). This precludes the assembly of oxygen and a substrate on the same metal which very often leads to facile, metal-assisted formation of peroxy compounds—the source of radicals.[4] Thus, extension of the above concept to substrates other than phosphine appeared extremely desirable.

Our previous work indicated that cobalt-nitro complexes are weak oxygen-transfer agents. Nevertheless, we did observe that the oxidation occurred only in hydrogen-bonding solvents. No oxidation was observed in inert (benzene) or slightly nucleophilic (acetonitrile) solvents. We have sought to amplify this mild solvent effect by employing strong Lewis acids. Now, we would like to report that Lewis acids do convert cobalt-nitro complexes to more potent oxidants. Thus, in deoxygenated media, the combination of Lewis acids with cobalt-nitro complexes readily oxidizes primary and secondary alcohols to the corresponding aldehydes or ketones and functions as a catalyst for the oxidation of alcohols by molecular oxygen.

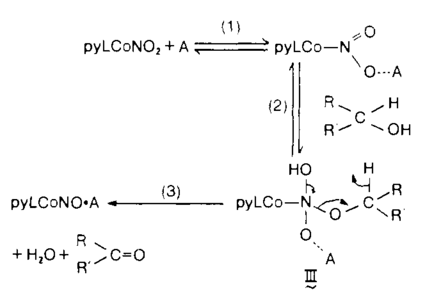
Results and Discussion

Cobalt-Nitro Complexes as Stoichiometric Oxidants. In the absence of Lewis acids, the cobalt-nitro complexes pyCo(TPP)NO_2 (I) and pyCo(saloph)NO_2 (II) (TPP = tetraphenylporphyrin, saloph = *N*,*N*′-bis(salicylidene)-*o*-phenylenediamino) show no evidence of alcohol oxidation (Table I). Addition of Lewis acids A to a solution of the nitro–cobalt complexes I or II in deoxygenated 1,2-dichloroethane (DCE) promotes the oxidation of alcohols (Table I) with concomitant reduction of the nitro–cobalt complexes to their nitrosyl analogues (eq 3). Control experiments employing the four-coordinate Co(TPP) parent complex, the oxidized parent complex Co(TPP)I, or the nitrosyl complex Co(TPP)NO did not produce any significant amount of aldehydes or ketones (Table I, runs 14–16). These facts clearly establish that the presence of the nitro ligand is essential and that it serves as the site of the alcohol oxidation.



(3)

Scheme I. Mechanism of Alcohol Oxidation by a Combination of Cobalt-Nitro Complexes with Lewis Acids (A)



The generality of the reaction is demonstrated by the finding that two different cobalt-nitro complexes, I and II, exhibit similar reactivity toward primary and secondary alcohols. Of the alcohols tested, benzyl alcohol appears to react faster and gives higher yields of the product (benzaldehyde) than the secondary alcohols (Table I). The yields of ketones from the cycloalkanols reach a maximum when studied as a function of time. This is caused by the ability of the Lewis acids to catalyze subsequent aldolizations of the carbonyl products. It is especially reflected by the low yield of cyclohexanone.

Benzyl alcohol is oxidized cleanly to benzaldehyde by I. However, oxidation of benzyl alcohol by complex II yields a mixture of the expected benzaldehyde (52%) and salicylaldehyde (39%) after 30 min. The latter product is the result of an aldehyde exchange between benzaldehyde and the salicylidenimine moiety of the saloph ligand.[5]

Different types of Lewis acids, including neutral molecules (e.g., $BF_3 \cdot Et_2O$) and metal cations (e.g., Li^+), promote the stoichiometric oxidations. In the case of cations, the charge/ionic radius ratio[6] plays an important role as suggested by the fact that $NaPF_6$ possesses no activating effect (Table I, runs 3 and 4).

A mechanism of alcohol oxidation consistent with our observations is summarized in Scheme I. The Lewis acids coordinate to the oxygen of the nitro group (Scheme I, step 1) as well as to other bases (e.g., alcohols) present in the reaction mixture. Thus, the coordination of the Lewis acids to the nitro ligand must be an equilibrium process. This is supported by the increased yield and the shortened reaction time when a larger excess (relative to I or II) of a Lewis acid is employed (Table I, runs 5–9).

Under identical conditions, ethers such as cyclohexyl ethyl ether are not oxidized by cobalt-nitro complexes (Table I). A difference of several orders of magnitude in the reactivity of alcohols and the corresponding ethers is encountered whenever the oxidation proceeds via ester formation as in the case with vanadium and chromium oxides.[7] Nitric acid as well as N_2O_3 is also known to react with alcohols to form nitrates and nitrites, respectively.

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[3] See for example Sheldon, R. A.; Kochi, J. K. *Oxid. Combust. Rev.* **1973**, *5*, 135. "Advances in Catalysis"; Academic Press, New York, 1976; Vol. 25.

[4] See for example Lyons, J. E. *Adv. Chem. Ser.* **1974**, *No. 132*, 64.

[5] The possibility of salicylaldehyde formation by oxidation of benzaldehyde has been eliminated. The amount of benzaldehyde and salicylaldehyde formed in the reaction mixture would require ~30% more of II than the amount originally added. Benzaldehyde is not oxidized by a mixture of II and $BF_3 \cdot Et_2O$. No salicylaldehyde is formed when I is employed as the oxidant.

[6] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley: New York, 1972; p 198.

[7] Brownell, R.; Leo, A.; Chang, Y. W.; Westheimer, F. H. *J. Am. Chem. Soc.* **1960**, *82*, 406. Rocek, J.; Aylward, D. E. *Ibid.* **1975**, *97*, 5452.

Alkyl nitrates are known to decompose into carbonyl compounds and lower valent nitrogen oxides.[8] The Lewis acid coordination to the nitro ligand decreases the electron density at the nitrogen of the nitro group and makes it more susceptible to a nucleophilic attack by alcohols. This may lead to an ester-like intermediate III (Scheme I, step 2) in analogy to the behavior of nitric acid.

The inability of I or II to oxidize ethers strongly suggests that the alcohol oxidation is a two-electron, nonradical process. This is corroborated by the predominant formation of cycloheptanone when a 1:1 mixture of cyclopentanol and cycloheptanol is treated with a deficient amount of I. Previously, it had been demonstrated that in a nonradical, two-electron oxidation a 1:1 mixture of cyclopentanol and cycloheptanol yields predominantly cycloheptanone, while cyclopentanone predominates in a radical, one-electron oxidation.[9] The collapse of the intermediate III leads to the observed formation of a carbonyl product, water, and the cobalt-nitrosyl complex (Scheme I, step 3). In agreement with our data and in analogy to esters of inorganic acids, this decomposition of III can best be described as a hydride transfer from the α carbon of the alcohol moiety to the oxygen of the nitro group.

In the course of this study, we attempted to isolate the boron trifluoride adduct of I responsible for the alcohol oxidation. It was found, however, that in the absence of alcohol and in deoxygenated media, I disproportionates to the cobalt nitrosyl and cobalt nitrate analogues (eq 4). The exact mode of bonding of

$$2\mathrm{LCoNO_2} \xrightarrow{\mathrm{A}} \mathrm{LCoNO} + \mathrm{LCoNO_3} \qquad (4)$$

the nitrate ligand to the cobalt is not known. However, the IR bands ($\nu_{\mathrm{CoNO_3}}$ = 990, 1265, and 1530 cm^{-1}) are very similar to those observed in (t-Bu(py))Co(DH)$_2$NO$_3$ (DH = dimethylglyoximato; $\nu_{\mathrm{CoNO_3}}$ = 980, 1275, 1504, and 1512 cm^{-1}) in which the nitrato ligand is oxygen bound.[10] This disproportionation is additional evidence for the ability of $BF_3{\cdot}Et_2O$ to promote oxygen transfer from cobalt-nitro complexes. In this case the oxidizable substrate is a second molecule of cobalt-nitro complex. This disproportionation of cobalt-nitro complexes (with or without pyridine as the axial base) may have affected the yields of carbonyl products reported in Table I. We have observed that I, which has been mixed with 5 equiv of $BF_3{\cdot}Et_2O$ and allowed to disproportionate for 1 h in deoxygenated DCE and in the absence of an oxidizable substrate, will yield only 30% of the amount of benzaldehyde expected under the conditions reported in Table I. Thus, systems where the disproportionation can compete with the alcohol oxidation can be expected to exhibit lower yields. The oxidation of certain secondary alcohols (Table I) appears to fit into this category.

Precedent for the above disproportionation behavior may be found in the chemistry of [ClRu$^{\mathrm{III}}$(bpy)$_2$NO$_2$]$^+$.[11] The parent ClRu$^{\mathrm{II}}$(bpy)$_2$NO$_2$ complex is stable and shows no tendency for oxygen transfer. However, upon electrochemical oxidation to the Ru(III) analogue (which oxidizes phosphine to phosphine oxide), it rapidly disproportionates to Ru$^{\mathrm{III}}$NO and Ru$^{\mathrm{III}}$NO$_3$. Here the analogy between the chemistry of ruthenium- and cobalt-nitro complexes ends. Thus, attempts to oxidize alcohols via alkyl-nitro complexes such as [Ru$^{\mathrm{III}}$(bpy)$_2$(py)N(O)OR]$^{2+}$ fail to give carbonyl products.[12] Instead, the facile, one-electron reduction of Ru(III) to Ru(II) causes formation of alkoxy radicals which abstract hydrogen from the solvent.

Table 11. Oxidation of Alcohols Catalyzed by a Combination of Cobalt-Nitro Complexes with Lewis Acids[a]

run no.	complex	Lewis acid/Co (ratio)	T, min	mol of product[b]/ mol of Co
		Benzyl Alcohol		
1	1	none	240	0
2		$BF_3{\cdot}Et_2O$ (5.0)	60	7.9
			240	11.9
3		$LiPF_6$ (5.0)	60	6.2
			240	7.9
4	Co(TPP)NO	none	240	0
5		$BF_3{\cdot}Et_2O$ (5.0)	60	10.1
			240	14.3
6	Co(TPP)	$BF_3{\cdot}Et_2O$ (5.0)	60	0.2
7	Co(TPP)1	$BF_3{\cdot}Et_2O$ (5.0)	60	0.8
		Cycloheptanol		
8	1	$BF_3{\cdot}Et_2O$ (5.0)	90	1.5[c]
9		$BF_3{\cdot}Et_2O$ (5.0)	60	4.2
			90	4.6
10	11	$BF_3{\cdot}Et_2O$ (5.0)	90	1.5[c]
		Cyclopentanol/Cycloheptanol (1:1)		
11	1	$BF_3{\cdot}Et_2O$ (5.0)	270	3.5[d]

[a] Unless stated otherwise, the oxidation was run at 60 °C under 344.7 kPa (50 psig) of O_2. [b] The product is either benzaldehyde or cycloheptanone. [c] At 103.4 kPa (15 psig) of O_2. [d] Only cycloheptanone was found in the reaction mixture.

Addition of Lewis acids to Co(saloph)NO yields adducts which were characterized by ν_{NO} infrared bands which were shifted to higher frequencies by ~15 to 30 cm^{-1}. In fact, the Lewis acid adducts of Co(saloph)NO can be isolated from the reaction media when II is used as the oxidant. The isolated materials are simple adducts rather than decomposition products, as verified by comparison with an authentic sample prepared from the original Co(saloph)NO (ν_{NO} = 1660 cm^{-1}) and the corresponding Lewis acids (BF_3 adduct ν_{NO} = 1689 cm^{-1}; $LiPF_6$ adduct ν_{NO} = 1679 cm^{-1}). The shift of ν_{NO} to higher frequencies is consistent with the coordination of the Lewis acids at the nitrosyl ligand resulting in a decrease of electron density at the formally NO$^-$ ligand. This coordination of Lewis acids to bent nitrosyl ligands has no precedent. However, protonation at the nitrogen atom of some bent cobalt-, rhodium-, and iridium-nitrosyl complexes has been observed.[13] The addition of Lewis acid to I or II exerts comparable effects (Table I). Nevertheless, we were unable to isolate Lewis acid adducts of Co(TPP)NO either from the reaction mixture or by direct combination of the authentic Co(TPP)NO and the appropriate Lewis acid.

Cobalt-Nitro Complexes as Catalysts for the Oxidation of Alcohols by Molecular Oxygen. Our interest in cobalt-nitro complexes is predicated on the ability of the corresponding nitrosyl complexes to be reoxidized by molecular oxygen.[2] In principle, for any stoichiometric oxidation by a nitro complex, a catalytic analogue employing molecular oxygen as the oxidant should be feasible. The presence of oxygen in a mixture containing nitro complex I or II together with a Lewis acid does indeed result in a catalytic oxidation of alcohols (Table II). As in the stoichiometric reaction, the catalytic oxidation of benzyl alcohol is faster (7.9 mol of benzaldehyde (mol of Co)$^{-1}$ h^{-1}) than that of secondary alcohols (e.g., cycloheptanol, 4.2 mol of cycloheptanol (mol of Co)$^{-1}$ h^{-1}). It is not a radical process as demonstrated by the predominant formation of cycloheptanone when an equimolar mixture of cyclopentanol and cycloheptanol is oxidized (Table II, run 11). Control experiments with Co(TPP) and Co(TPP)I demonstrate that routes such as radical autoxidation or nonradical

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(8) For example, see March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure"; McGraw-Hill: New York, 1968; p 326. Waters, W. A. "Mechanism of Oxidation of Organic Compounds"; Wiley: New York, 1964; p 49. Recently nitric acid has been shown to oxidize alcohols cleanly to aldehydes or ketones in high yields. McKillop, A.; Ford, M. E. *Synth. Commun.* **1972**, *2*, 307.

(9) Jacobson, S. E.; Muccigrosso, D. A.; Mares, F. *J. Org. Chem.* **1979**, *44*, 921. Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *Ibid.* **1975**, *40*, 1860. Cella, J. A.; McGrath, J. P. *Tetrahedron Lett.* **1975**, 4115. Dobson, A.; Robinson, S. D. *Inorg. Chem.* **1977**, *16*, 137.

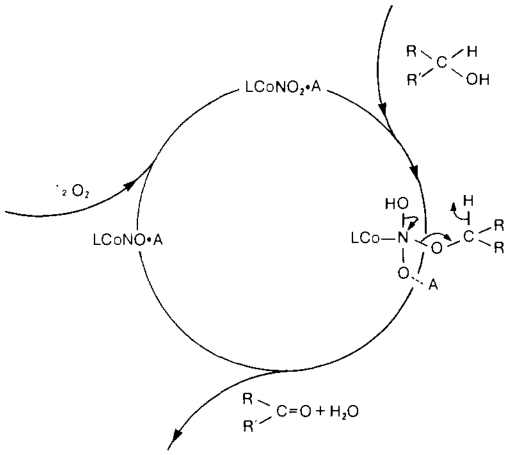
(10) Trogler, W. C.; Marzilli, L. G. *Inorg. Chem.* **1974**, *13*, 1008.

(11) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2384.

(12) Walsh, J. L.; Bullock, R. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 865.

(13) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1969**, 155. Grundy, K. R.; Reed, C. A.; Roper, W. R., *Ibid.* **1970**, 1501. Dolceti, G.; Hoffman, N. W.; Collman, J. P. *Inorg. Chim. Acta* **1972**, *6*, 531. Collman, J. P.; Hoffman, N. W.; Morris, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 5659. Enemark, J. H.; Feltham, R. D.; Riker-Nappier, J.; Bizot, K. F. *Inorg. Chem.* **1975**, *14*, 624.

Scheme II. Mechanism of Alcohol Oxidation by O_2 Catalyzed by Cobalt-Nitro Complexes



processes involving the metal center cannot account for the oxidations catalyzed by the nitro complexes (Table II, runs 6 and 7). In agreement with the stoichiometric oxidations, the presence of Lewis acids is essential. During the early stages of the catalytic oxidation, the integrity of the complex is preserved. Thus, the IR spectrum of the complex isolated from the reaction mixture after 5 min at room temperature (no oxidation observed) is analogous to that of the complex isolated after five molar turnovers. The oxidation rate is dependent on the partial pressure of oxygen. We feel that these observations are consistent with the mechanism summarized in Scheme II. This scheme incorporates the features of the stoichiometric oxidation of alcohols by cobalt–nitro complexes (Scheme I) and the reoxidation of cobalt–nitrosyl complexes by molecular oxygen.

The rate of alcohol oxidation declines with time (Table II). This decline may be caused by several factors. Water is the necessary byproduct of alcohol oxidation.[14] It may mute the effect of the Lewis acids by hydrolysis (e.g., $BF_3{\cdot}Et_2O$) and/or by coordination (e.g., Li^+). When $BF_3{\cdot}Et_2O$ is employed as the cocatalyst, disproportionation of cobalt–nitro complexes I or II to a mixture of reoxidizable cobalt–nitrosyl and an inactive, oxygen-bound cobalt–nitrato species (eq 4) may also contribute to the observed decrease in the reaction rate.

Previously, cobalt–nitrosyl complexes were oxidized only in the presence of *Lewis bases*, which in the course of oxidation are incorporated into the cobalt–nitro complexes as an axial ligand.[2] The interesting feature of the catalytic cycle in Scheme II is the oxidation of cobalt–nitrosyl complexes in the presence of *Lewis acids*. In fact, the presence of strong bases such as pyridine inhibits the catalytic oxidation. This is evident by comparison of runs 2 and 5 in Table II. When I is used as the catalyst, 1 equiv of pyridine is liberated after the first turnover since Co(TPP)NO has very little affinity for the formation of a six-coordinate pyridine adduct. The liberated pyridine then interacts with the Lewis acid and decreases its effective concentration and, therefore, the reaction rate. This is corroborated by the finding that in the stoichiometric oxidations of alcohols by cobalt–nitro complexes (Table I, runs 5–9), a lower BF_3/Co ratio results in a slower rate. When Co(TPP)NO is used as the catalyst (Table II, run 5), no pyridine is liberated, the concentration of Lewis acid remains constant, and superior results in comparison with I are obtained.

The relatively facile oxidation of the nitrosyl ligand in the presence of Lewis acids has been verified by an independent experiment. At room temperature in an oxygen-saturated DCE solution containing benzyl alcohol, Co(TPP)NO, and 5 equiv of $BF_3{\cdot}Et_2O$, a relatively fast reaction yields a complex which was isolated after solvent evaporation. The IR spectrum of this complex, containing no nitrosyl bands, displays new bands at 1208, 1313, and 1490 cm^{-1} together with a broad and intense band at 950–1180 cm^{-1} ascribed to BF_3 and benzyl alcohol. The IR bands of the oxidized complex cannot be directly compared to those of I (ν_{CoNO_2} = 820, 1220, and 1318 cm^{-1}) since the latter is a six-coordinate complex with pyridine occupying one axial position. Nevertheless, the IR spectrum suggests the presence of an oxidized nitrogen-bound ligand.[15] The study of the nitrosyl ligand oxidation in the presence of Lewis acids is not completed at this time and will be reported in the future.

There are only a few examples of alcohol oxidations catalyzed by homogeneous catalysts.[16] The common mechanistic path appears to be formation of metal alkoxide followed by β-hydride elimination to form the carbonyl product and a metal hydride. The hydride is then oxidized by oxygen, probably via a hydroperoxy intermediate, to water and the metal complex in the original oxidation state. Nitrosyl complexes, in which the site for the reaction with oxygen as well as for the subsequent alcohol oxidation is at the nitrogen-containing ligand, provide a new mechanistic approach to selective oxidations. The scope of the chemistry of cobalt–nitro complexes has recently been substantially broadened and includes catalytic oxidation of olefins.[17] These results are being reported elsewhere.

Experimental Section

Materials. Ethyl cyclohexyl ether[9] and cobalt complexes Co(TPP),[18] Co(TPP)NO,[19] and pyCo(saloph)NO_2[1] were prepared by published procedures. Vacuum distillation was found satisfactory for purification of $BF_3{\cdot}Et_2O$.[20] Dichloromethane and 1,2-dichloroethane (both from MCB) were dried over 4-Å molecular sieves. Cyclohexanol (Eastman), all the alcohols, and pyridine (Aldrich) were used without purification.

pyCo(TPP)NO₂ was prepared by vigorous bubbling of dry oxygen through a solution of Co(TPP)NO (0.600 g, 0.86 mmol) in dichloromethane (30 mL) and pyridine (1.2 mL, 14.9 mmol) for 4 h. The product (0.600 g, 0.75 mmol) was precipitated by addition of a 1:1 petroleum ether–hexane mixture (100 mL). The precipitate was filtered, washed with hexane, and dried under vacuum at room temperature. The compound exhibits new IR bands at 820, 1220, and 1320 cm^{-1} but no IR bands at 1690 cm^{-1} attributable to Co(TPP)NO. Anal. Calcd for $C_{49}H_{33}CoN_6O_2$: C, 73.87; H, 4.15; N, 10.55. Found: C, 72.61; H, 4.61; N, 10.19.

[Co(saloph)NO]₂·LiPF₆. Under argon, $LiPF_6$ (0.942 g, 6.20 mmol) was added to a solution of Co(saloph)NO (0.500 g, 1.24 mmol) in deoxygenated dichloromethane (5 mL). The mixture was stirred at 25 °C for 15 min at which time the undissolved $LiPF_6$ was filtered off. Most of the solvent was evaporated from the filtrate until about 2 mL was left. The product was precipitated by addition of deoxygenated hexane, filtered, washed with hexane, and dried under vacuum at room temperature. The IR spectrum exhibits a shifted nitrosyl band at 1679 cm^{-1} as well as a broad P–F band at 840 cm^{-1}. Anal. Calcd for $C_{40}H_{28}Co_2F_6LiN_6O_6P$: C, 50.12; H, 2.94; Co, 12.29; F, 11.89; Li, 0.73; N, 8.77; P, 3.23. Found: C, 49.45; H, 3.23; Co, 11.84; F, 11.97; Li, 0.71; N, 8.51; P, 3.32.

A similar reaction of $BF_3{\cdot}Et_2O$ (0.25 mL, 2.03 mmol) with Co(saloph)NO (0.168 g, 0.42 mmol) produced an adduct of approximately 2 mol of BF_3 per mol of the nitrosyl complex (based on the ratio of Co to B). The IR spectrum shows a shifted nitrosyl band at 1689 cm^{-1} as well as a broad B–F band at 1100–1200 cm^{-1}.

Disproportionation of pyCo(TPP)NO₂. Under argon, $BF_3{\cdot}Et_2O$ (0.125 mL, 1.02 mmol) was added to a solution of pyCo(TPP)NO_2 (0.159 g, 0.20 mmol) in deoxygenated 1,2-dichloroethane (5 mL). After the so-

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[14] Notice that after ten molar turnovers 2 mol of water for every molecule of $BF_3{\cdot}Et_2O$ is formed. Thus the Lewis acid is effectively quenched and the reoxidation of the nitrosyl complex is strongly inhibited.

[15] The oxidation of cobalt–nitro complexes in our system requires the presence of alcohols which may fulfill the function of the axial ligand in the resultant nitro complexes. This suggestion is in qualitative agreement with the observation of Clarkson and Basolo (ref 2) that Co(acacene)NO can be oxidized to the nitro complex in methanol. However, the rate of nitrosyl oxidation in methanol is extremely slow and not directly comparable with the rates observed in the presence of alcohols and Lewis acids.

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lution was stirred for 1 h at 25 °C, an aliquot was withdrawn. The solvent from the sample was evaporated under vacuum. The isolated material exhibits new IR bands at 990, 1265, 1530, and 1690 cm^{-1}. A deoxygenated mixture of benzyl alcohol (0.53 mL, 5.1 mmol) and biphenyl (0.440 g, 0.29 mmol) was added under argon to the remaining solution. The resulting mixture was immersed into a bath heated to 60 °C. At different time intervals, samples were removed by a gas-tight syringe and analyzed by GC. Only 30% of the expected amount of benzaldehyde was formed.

Oxidation of Co(TPP)NO by O_2 in the Presence of Lewis Acids. Under argon, first Co(TPP)NO (0.139 g, 0.20 mmol) was added to deoxygenated 1,2-dichloroethane, followed by benzyl alcohol (0.53 mL, 5.1 mmol) and then $BF_3 \cdot Et_2O$ (0.125 mL, 1.02 mmol). Then a slow stream of O_2 was passed through the solution at room temperature. After 1 h, the solvent was evaporated under vacuum, and the residue was treated with a 1:1 mixture (20 mL) of dichloromethane and *n*-heptane under argon. The resulting precipitate was filtered off, washed with 4 portions of dichloromethane–*n*-heptane mixture (20 mL), and dried under vacuum. The IR spectrum of this material shows no Co–NO band. Instead, new bands are observed at 1208, 1313, and 1490 cm^{-1} as well as a broad band at 950–1100 cm^{-1} ascribed to BF_3 and benzyl alcohol.

Oxidation Procedures and Product Analysis. Stoichiometric Oxidation of Alcohols by Cobalt–Nitro Complexes. All stoichiometric alcohol oxidations were carried out in the same manner. Oxidation of benzyl alcohol is chosen as an example. The internal standard, biphenyl (0.760 g, 0.49 mmol), and pyCo(TPP)NO_2 (0.320 g, 0.40 mmol) were placed in a flask and deaerated with argon. A deaerated solution of benzyl alcohol (1.05 mL, 10.1 mmol) in 1,2-dichloroethane (10 mL) was added under an argon flow. The reaction mixture was placed in an argon-filled glovebag where $BF_3 \cdot Et_2O$ (0.25 mL, 2.03 mmol) was added. The reaction solution was capped with a serum stopper and immersed in a 60 °C oil bath. Samples for GC analysis were removed at *t* = 0, 5, 10, 15, 30, 45, and 60 min with a gas-tight syringe. Prior to injection on a GC column, $BF_3 \cdot Et_2O$ was neutralized to avoid decomposition of the column packings. This was accomplished by adding 1 drop of pyridine and 1 mL of hexane to a 0.5-mL reaction solution aliquot, followed by filtration to remove the precipitated $BF_3 \cdot$pyridine complex. GC analysis was performed on either a Hewlett-Packard 5830A equipped with a flame ionization detector or on a Hewlett-Packard 5710A equipped with a thermal conductivity detector. Analysis of the products of cyclohexanol, cycloheptanol, and cyclopentanol oxidations was carried out with a 1.83-m (6 ft) column containing 10% Carbowax on 80/100 Supelcoport. The benzyl alcohol oxidation mixtures were analyzed on a 1.22-m (4 ft) column containing 5% Silar 5 CP supported on 80/100 Gas-Chrom Q. Concentrations of the solution components were determined by computer integration employing biphenyl as the internal standard. Product identities were determined by coinjection with authentic materials and by GC/MS analyses. Complexes from a reaction solution were isolated by removing the solvent under vacuum from a reaction mixture aliquot. The resulting oils were triturated with petroleum ether, yielding a solid which was filtered and dried under argon.

Oxidation of Alcohols by O_2 Catalyzed by Cobalt–Nitro or –Nitrosyl Complexes. An oxygen-saturated solution of the substrate (~10 mmol), biphenyl (internal standard, ~0.5 mmol), and the appropriate cobalt–nitro or –nitrosyl complex (~0.4 mmol) in oxygen-saturated 1,2-dichloroethane (10 mL) was placed into a Fisher-Porter bottle equipped with a Teflon-coated stirring bar. At this time, the reactor was closed, pressurized with O_2 to the required pressure, and immersed into a controlled-temperature bath. Samples were withdrawn through a septum with a glass-tight syringe. The analysis of the samples is described above.

Gas-Phase Reactions of O(^{3}P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 1. Rate Constants and Arrhenius Parameters[1]

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Abstract: Absolute values of rate constants have been determined for the reaction of ground-state oxygen atoms, O(^{3}P), with CH_3SH, C_2H_5SH, CH_3SCH_3, and CH_3SSCH_3 by using a phase shift technique in which oxygen atoms are generated by mercury-photosensitized decomposition of N_2O and monitored by the chemiluminescence from their reaction with NO. Between 298 and ~560 K, the rate constants are represented by the following equations: $k_{CH_3SH} = (1.52 \pm 0.17) \times 10^{-12} + (64 \pm 40) \times 10^{-12} \exp[(-1673 \pm 322)/T]$; $k_{C_2H_5SH} = (2.28 \pm 0.11) \times 10^{-12} + (145 \pm 74) \times 10^{-12} \exp[(-2075 \pm 268)/T]$; $k_{CH_3SCH_3} = (1.11 \pm 0.12) \times 10^{-11} \exp[(460 \pm 41)/T]$; $k_{CH_3SSCH_3} = (4.35 \pm 0.70) \times 10^{-11} \exp[(251 \pm 61)/T]$ in units of cm^3 molecule^{-1} s^{-1}.

Introduction

The detailed role of organic sulfides in the atmospheric portion of the global sulfur cycle is not well understood,[3] and even the rate of emission of biogenic organic sulfides, relative to that of H_2S, is in question.[4-6] The concentration of dimethyl sulfide has been determined in the atmosphere on the eastern coast of the United States[7] and has been shown to be released, along with other organic sulfur compounds (CH_3SH, CH_3SSCH_3), from various biogenic sources (algae, bacteria, plants)[3,8] and from anthropogenic sources (wood pulp mills, petroleum refineries, sewage treatment plants).[8] The homogeneous gas-phase reactions of the organic sulfides in the atmosphere probably involve oxidation by hydroxyl radicals and oxygen atoms.[8-10] Although the rates of the reactions O + H_2S[11] and O + CH_3SH[12] are too slow to compete significantly with the corresponding hydroxyl radical reactions[13,14] for the average ambient concentrations of O and OH, the reactions O + CH_3SCH_3[12,15,16] and perhaps O + CH_3SSCH_3 may be sig-

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