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Lewis Acidity of Methyltrioxorhenium(VII) (MTO) Based on the Relative Binding Strengths of N-Donors

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Abstract: This article presents a σ acceptor strength scale for methyltrioxorhenium(VII) (MTO), one of the most versatile and useful high oxidation state organometallics ever described. The spectrophotometric titration of MTO with a series of N-donor bases in CCl_4 gives formation constants (K_f) and enthalpies for the adduct formation reactions. An excellent linearity of log K_f with respect to the Hammett σ constants of the substituents on the ligands was observed. The resulting ρ constant is proposed to be a good indication of the Lewis acidity of MTO. The enthalpies of adduct formation of N-donors with MTO also fit the ECW model to predict the values of E_A and C_A parameters for MTO. The parameters can be used to predict an acidity scale for MTO. These parameters also allow the chemists to predict and correlate quantitatively the enthalpies of MTO·Lewis base interactions. Significant chemical insights result from the fit of the data to the ECW model.

Introduction

Methyltrioxorhenium(VII) ($MeReO_3$ or MTO), a superstar compound, has been known for more than 2 decades. For a considerable part of this time, it has been widely regarded as a mere curiosity. This picture changed dramatically during the past decade. Today, many derivatives of MTO are known and easily accessible. Several of these compounds, most notably MTO itself, have found numerous very interesting applications in both catalysis and material science. The numerous different processes, in which MTO can be applied as a catalyst, are summarized as follows: oxidation of alkenes,[1−11] oxidation of conjugated dienes,[12] epoxidation of allylic alcohols and 1,3-transposition of allylic alcohols,[3−5,13−17] oxidation of aromatic compounds,[1−5,18−22] Baeyer−Villiger oxidation and Dakin reaction,[3−5,23−25] oxidation of sulfur compounds,[1−5,26−30] oxidation of phosphines, arsines, and stibines,[3−5,31] oxidation of anilines and amines,[3−5,32] oxidative cleavage of *N*,*N′*-dimethylhydrazones,[3−5,33−35] oxidation of halide ions,[1−5,36,37] oxidation of C−H and Si−H bonds,[1−5,38,39] oxidation of metal carbonyls,[40,41] aldehyde olefination, and related reactions,[1−5,8,42−47]

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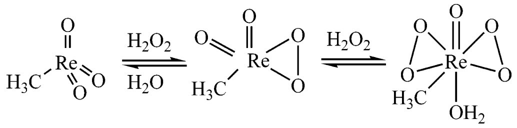
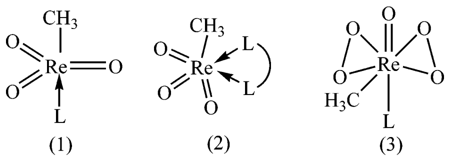
Scheme 1. Reaction of MTO with hydrogen peroxide



Scheme 2. Lewis base adducts of MTO



olefin metathesis,[8,44−47] and Diels−Alder reaction.[1−5,48] Despite the important applications of MTO, it is surprising that no quantitative information exists on the acidity strength of this important compound.

In the case of olefin epoxidation, full studies were made about the nature of the catalytically active species by using H_2O_2 as oxidizing agent. MTO reacts with H_2O_2 (see Scheme 1) to form mono- and bisperoxo complexes, depending on the amount of H_2O_2 used.[49]

The most important disadvantage of the MTO/H_2O_2 system is the parallel formation of diols instead of the desired epoxides, especially in the case of more sensitive substrates.[50] It was quickly detected that the use of Lewis base adducts of MTO (compounds 1 and 2 in Scheme 2) significantly decreases the formation of diols due to the reduced Lewis acidity of the catalytic system.[10]

In recent years, the catalytic activities of the Lewis base adduct of MTO have been studied. MTO forms trigonal bipyramidal adducts with monodentate N-bases and (distorted) octahedral adducts with bidentate Lewis bases.[7,51−56] The monodentate Lewis base adducts of MTO react with H_2O_2 to form mono- and bisperoxo complexes analogous to that of MTO, but coordinated by one Lewis base molecule instead of H_2O (compound 3 in Scheme 2). The activity of the bisperoxo complexes in olefin epoxidation depends on the Lewis bases, the redox stability of the ligands, and the excess of Lewis base used. The peroxo complexes of the MTO Lewis bases are, in general, more sensitive to water than MTO itself.[8,9]

On the other hand, nitrogen ligands are of great importance in homogeneous catalysis.[57−60] The substituted pyridines are also a set of ligands commonly used in coordination chemistry. The 2- and 2,6-substituted derivatives invariably have steric problems with Lewis acids. Pyridines substituted in the 3- and 4-positions provide a family of donors with a constant steric requirement toward bulky Lewis acids. Since steric problems are often encountered in transition metal ion chemistry, the pyridine family is often used to determine electronic influences on the chemistry. A recent review on the role of nitrogen ligands in homogeneous catalysis[57] states the bond dissociation energies of the adducts of some aliphatic amines with BMe_3[61−63] as the only quantitative data relevant to the coordination strength of nitrogen ligands, but these data are hardly of any use to predict the strength of the interaction between the usually employed ligands (most of which contain sp^2-hybridized nitrogen atoms) and a transition metal. Several papers, especially in the older literature, have been devoted to phenanthroline and bipyridine complexes,[64,65] but most of the available data were measured in aqueous solution, where protonation of the ligand becomes important. Thus, this information cannot be assigned to the low-to-medium polarity, often anhydrous, solvents commonly employed for catalytic processes.

Considering the important applications of MTO and its Lewis base adducts (compounds 1 and 2 in Scheme 2) in catalytic activity, a field where the Lewis acidity of MTO is well-known to play an important role, we have measured and extended the relative coordination ability of different N-donor ligands (shown in Scheme 3) toward MTO. The data obtained are used to present a scale of σ acceptor strength for MTO. We have also measured the enthalpies of the adduct formation in the poorly solvating solvent, CCl_4. The Drago's E_A and C_A parameters for MTO are also obtained. This is particularly significant because of the importance of MTO in inorganic, organometallic, and catalytic chemistry. These parameters also allow the chemists to predict and correlate quantitatively the enthalpies of MTO· Lewis base interactions.

Experimental Section

The compound methyltrioxorhenium ($MeReO_3$ or MTO) was prepared as reported.[66] The N-donor ligands (generically designated L) were purchased from commercial sources (Merck or Fluka) and were used as received. CCl_4 (Merck, quality; for spectroscopy) was used as solvent throughout this study, and the data were obtained at different temperatures. Equilibrium studies were carried out by using a Perkin Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant temperature bath. Typically, a 2×10^{-4} M solution of the MTO in CCl_4 contained in a quartz cuvette with a 1 cm path length was treated with successive aliquots of a solution of the N-donor ligand, of known concentration, in the same solvent. The values of formation constants (K_f) were determined by

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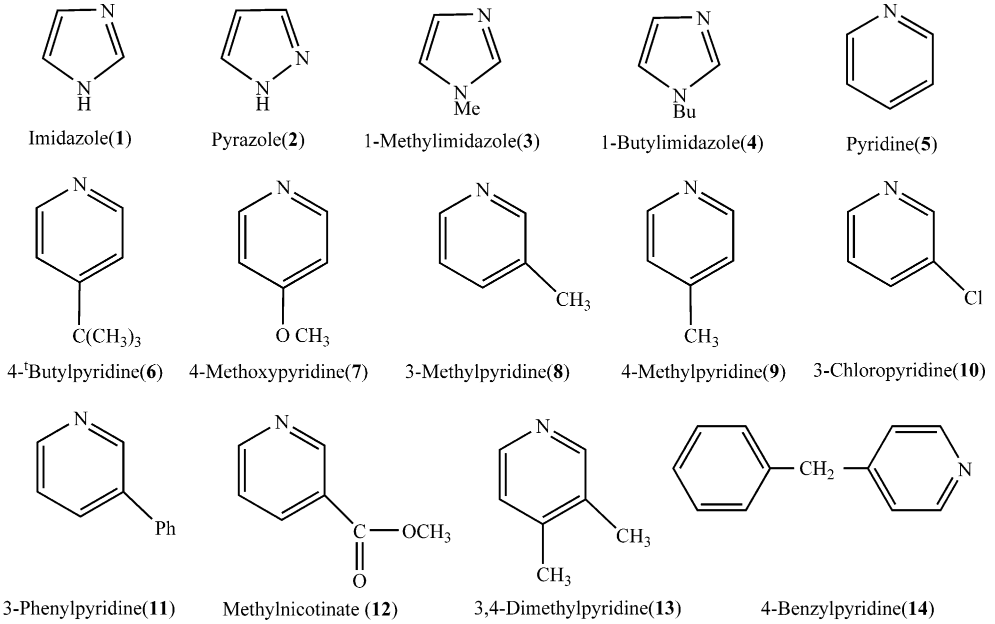
Scheme 3. Structural formulas of N-donor ligands



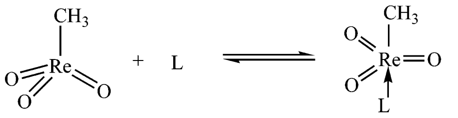
fitting the equilibrium absorbance to eq 1 by the method of nonlinear least squares.[53]

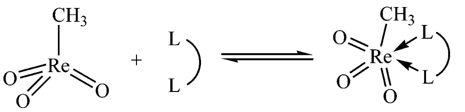
$$(\text{Absorbance})_{\text{eq}} = \left\{ \frac{\epsilon_{\text{MTO}} + \epsilon_{\text{MTO}\cdot\text{L}} K_f[\text{L}]}{1 + K_f[\text{L}]} \right\} [\text{MTO}]_0 \qquad (1)$$

Here, $(\text{Absorbance})_{\text{eq}}$ is the absorbance of a solution at equilibrium; ϵ_{MTO} and $\epsilon_{\text{MTO}\cdot\text{L}}$ are molar absorptivities for MTO and MTO·L species, respectively at corresponding wavelength; $[\text{MTO}]_0$ is the total concentration of MTO and MTO·L in the solution, and [L] represents the equilibrium ligand concentration.

Result and Discussion

Formation Constants and Linear Free-Energy Relationship (LFER). Very recently,[53–56] we have studied the interaction of MTO and different N-donor ligands (eqs 2 and 3) in $CHCl_3$ and benzene.


(2)


(3)

In this work, for reaction 2 in CCl_4 (a poorly solvating solvent to minimize the solvation effect), the program PSEQUAD[67] or KaleidaGraph 3.6 was used to determine K_f by a global fit of absorbance−concentration data taken at 8 wavelengths in the range of 300−400 nm. The values of K_f so calculated are given in Table 1. The corresponding Hammett σ value and the pK_a value of the ligands are also shown. Where two substituents were present, the sum of the individual σ constants is reported and was employed in the following fitting. The excellent linear relationships were observed between the formation constants and either the Hammett σ constants (see Figure 1) or the pK_a values of the ligands as $\log K_f = m(\text{p}K_a) + b$ (see Figure 2). The values for the ρ constant, the slope of the log K_f/ligand's pK_a plot (hereafter referred to as m), and the corresponding R^2 (correlation coefficient) values are collected in Table 2.

Very recently, Ragaini et al.,[73] for the first time, have pointed out that ρ can be considered as a measure of the Lewis acidity of the metal complexes bearing completely different ligands and having metals with different oxidation states. They have also stated that in the literature very little experimental quantitative information exists on the Lewis acidity of transition metal complexes. In this paper, we attempt to make a comparison between the ρ constants of different chemicals, including MTO (see Table 2). A series of formation constants has been measured for determination of the ρ constant. The data presented can be employed to give an experimental answer to an important question, that is, the acidity of MTO.

One important observation that is clear from the data in Tables 1 and 2 is that, although more basic ligands coordinate more strongly in all cases, the slope of the line describing the correlation is highly variable (ρ ranges from −1.0 to −5.6). The magnitude of the reaction constant, ρ, is essentially a measure of the susceptibility of a reaction to the polar effect of substituents in the adjacent benzene ring—the larger the value of ρ, the greater the susceptibility of the reaction. The sign of ρ is also of diagnostic use in that a negative ρ value indicates the development of a positive charge (or, of course, the disappearance of the negative charge) at the reaction center,

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Table 1. Formation Constants (K_f) for the Adduct Formation Reactions (eq 2) between MTO and Different N-Donor Ligands (shown in Scheme 3) and $\Delta H°$ Values in CCl_4

	K_f/L mol^{-1}									
ligand	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	pK_a[a]	σ[b]	$\Delta H°$/kJ mol^{-1}
1	8619.9 ± 929.9	6487.8 ± 436.1	5080.4 ± 166.8	3947.3 ± 148.9	3128.2 ± 117.3	2589.4 ± 95.1	2144.9 ± 56.5	6.99	c	−35.4 ± 0.6
2	105.3 ± 6.6	84.3 ± 3.6	60.5 ± 2.9	48.9 ± 3.0	37.8 ± 1.7	25.1 ± 1.9	19.8 ± 1.5	2.49	c	−38.9 ± 1.6
3	9723.6 ± 470.5	7307.7 ± 352.2	5736.5 ± 298.9	4444.5 ± 185.0	3526.6 ± 97.6	2935.3 ± 85.9	2430.6 ± 56.4	7.11	c	−35.3 ± 0.7
4	11110.0 ± 409.3	8440.7 ± 333.3	6330.0 ± 380.9	4890.9 ± 212.1	3601.2 ± 110.7	3000.9 ± 109.8	2410.6 ± 104.4	7.09	c	−38.6 ± 0.8
5	1500.9 ± 56.0	1175.6 ± 32.8	908.0 ± 13.5	720.7 ± 11.9	569.1 ± 64.1	450.6 ± 9.1	360.2 ± 12.0	5.23	0	−34.8 ± 0.2
6	3422.1 ± 157.7	2594.0 ± 138.6	1936.7 ± 56.6	1544.3 ± 68.0	1247.8 ± 90.4	996.9 ± 35.8	819.8 ± 27.9	5.98	−0.2	−36.2 ± 0.7
7	5887.0 ± 269.3	4412.7 ± 198.6	3396.6 ± 119.5	2649.6 ± 99.6	2103.9 ± 91.7	1700.7 ± 85.8	1314.8 ± 66.5	6.59	−0.27	−36.7 ± 0.4
8	1959.8 ± 101.8	1519.9 ± 96.4	1155.3 ± 46.4	914.0 ± 24.0	726.8 ± 54.8	562.2 ± 22.7	464.6 ± 12.9	5.52	−0.07	−35.8 ± 0.3
9	3038.8 ± 135.8	2301.3 ± 111.4	1764.2 ± 91.1	1388.0 ± 69.8	1103.1 ± 70.0	870.0 ± 18.6	719.3 ± 16.4	5.94	−0.17	−36.2 ± 0.4
10	130.6 ± 5.8	100.1 ± 3.9	80.0 ± 4.5	67.1 ± 5.2	55.6 ± 2.9	42.9 ± 1.6	36.0 ± 2.0	2.95	0.37	−31.4 ± 0.8
11	948.0 ± 50.0	719.3 ± 46.3	588.1 ± 29.0	469.4 ± 23.7	373.6 ± 9.5	280.2 ± 21.3	231.3 ± 15.8	4.85	0.06	−33.9 ± 0.8
12	160.9 ± 8.4	130.1 ± 7.9	103.9 ± 9.0	84.8 ± 6.9	67.7 ± 3.8	48.9 ± 2.8	39.6 ± 2.4	3.13	0.32	−32.6 ± 1.2
13	5199.3 ± 347.0	3945.9 ± 175.6	2979.5 ± 115.2	2328.2 ± 107.9	1849.0 ± 102.0	1493.6 ± 49.3	1135.7 ± 57.6	6.46	−0.24	−37.1 ± 0.4
14	2102.9 ± 144.0	1628.7 ± 123.9	1249.8 ± 99.4	979.9 ± 62.4	779.2 ± 35.9	621.7 ± 27.8	499.7 ± 29.4	5.59	c	−35.5 ± 0.2

[a] K_a applies to the reaction $HL^+ = H^+ + L$ in aqueous solution. [b] The σ_m parameter was used for substitution at C(3), and the σ_p parameter was used for substitution at C(4). The sum of the individual σ values is reported when two substituents are present on the pyridine ring. [c] Not defined.

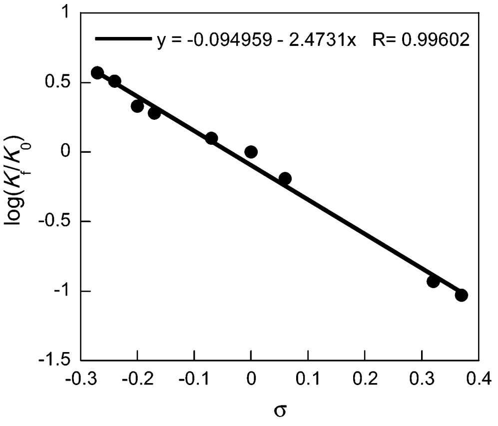

Figure 1. Plot of log(K_f/K_0) at 298 K for the adduct formation reaction of MTO with N-donors as a function of the Hammett σ constants for the substituents on the pyridine ring. Data are from Table 1.

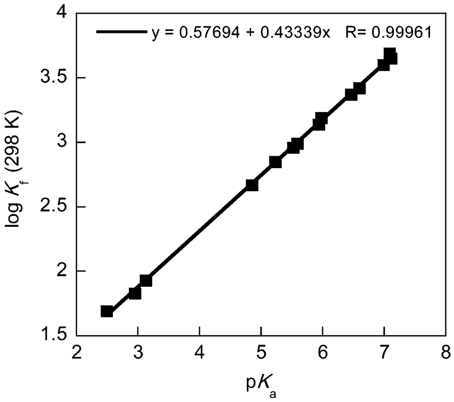

Figure 2. Plot of log K_f (at 298 K) for the adduct formation reaction of MTO with N-donors as a function of the pK_a of the N-donors. Data are from Table 1.

while vice versa, a positive ρ value indicates the development of a negative charge (or the disappearance of the positive charge) at reaction center.

Table 2. Values of ρ (reaction constant) and m (slope of the correlation log K_f versus N−donor pK_a Values) for Different Chemicals

Chemicals[a]	ρ	R^2 (ρ)	m	R^2 (m)	solvent	ref
MTO	−2.5	0.996	0.43	0.999	CCl_4	this work
MTO	−2.4	0.987	0.41	0.992	benzene	55
OsO_4	−1.9	0.991	0.34	0.996	toluene	68
C_{60}-fullerene	−2.9	0.997	0.71	0.997	CCl_4	69
o-Chloranil	−3.2	0.993	0.78	0.993	CCl_4	70
Zn(TPP)	−2.7	0.992	0.65	0.993	toluene	71a
Zn(OEP)	−2.0	0.987	0.49	0.987	toluene	71a
Phenol	−1.0	0.997	0.18	0.986	CCl_4	71b
$[Cu(PhMePh)_2]$	−1.7	0.998	0.34	0.980	$CHCl_3$	71c
H^+	−5.6	0.996	1.00	1.000	water	72

[a] o-Chloranil=3,4,5,6-Tetrachloro-1,2-benzoquinone, TPP=tetraphenylporphyrin, OEP=octaethylporphyrin, PhMePh=1-hydroxy-3-phenyl-4,5-dimethylpyrazole 2-oxide

The negative reaction constant for the pyridine equilibria with acids (Table 2) shows that a positive charge expands on the pyridine nitrogen in the adduct as compared with the free ligand. As expected, the metal center acts as an electron acceptor and attracts electrons upon coordination. To compare the Lewis acidity of MTO, the Hammett correlation for other chemicals has been used and is shown in Table 2. Note that the solvents used in the list (i.e., CCl_4, benzene, and toluene) are different, but their dielectric constants have close values. Clearly, acidity order is as follow:

$$H^+ > o\text{-chloranil} > C_{60}\text{-fullerene} > Zn(TPP) > MTO > Zn(OEP) > OsO_4 > [Cu(PhMePh)_2] > phenol$$

Thus, MTO has a greater Lewis acidity than OsO_4 toward pyridine derivatives.

Enthalpy Analysis with the ECW Model. In this section, we try to establish another scale for acidity of MTO. The formation constants (K_f) for reaction 2 with N-donors (L) were evaluated as a function of temperature over the range of 283−313 K. The enthalpy values were evaluated from the corresponding temperature data by applying a nonlinear K_f least-squares analysis according to the eq 4 (see Figure 3). The enthalpy values are listed in Table 1.

$$K_f = \exp\left(\frac{-\Delta H°}{RT}\right) \times \exp\left(\frac{\Delta S°}{R}\right) \qquad (4)$$

Chemists have long been interested in the interaction of acids with bases. To predict whether the magnitude of such an interaction will be large or small, acids and bases have traditionally been ranked in sequence according to their strength. Coordination chemists have recognized that there is no single order of acid strength, but rather the relative order within a group

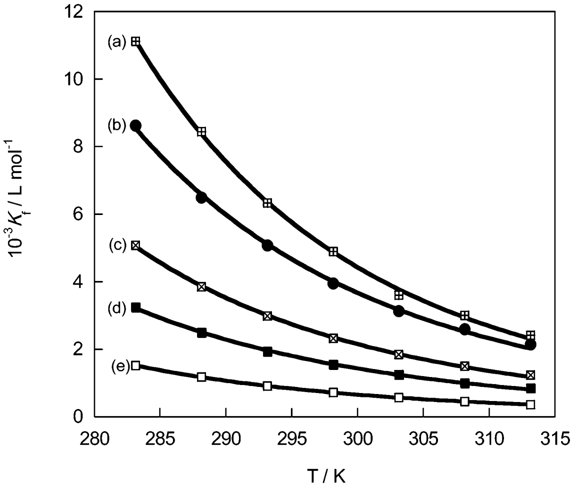

Figure 3. Plot of K_f versus *T* for adduct formation of MTO with N-donor ligands [(a) 1-butylimidazole; (b) imidazole; (c) 3,4-dimethylpyridine; (d) 4-*tert*-butylpyridine; (e) pyridine] in CCl_4.

of acids varies with the base being studied. The ECW approach has been successfully employed[74−77] for this case and to correlate many neutral base−neutral acid adduct formation enthalpies to the eq 5.

$$-\Delta H = E_A E_B + C_A C_B + W \qquad (5)$$

E_AE_B and C_AC_B describe electrostatic and covalent contributions for the donor (B)−acceptor (A) reaction. The *W* term is zero for simple donor−acceptor adduct reactions in poorly solvating media (e.g., CCl_4), but for a more complex reaction, it incorporates any constant contributions of a particular acid (or base) that is independent of the base (or acid) it reacts with. Equation 5 has, for the most part, been applied to 1:1 adduct formation enthalpies.

The most modern inorganic textbooks have also discussed the ECW model.[78] This approach[76,77] is the successful attempt at obtaining a quantitative scale of bond strengths that uses donor−acceptor enthalpies of formation measured in poorly solvating solvent. On the basis of a large database of *E* and *C* parameters, chemists and biochemists can predict and correlate quantitatively the enthalpies of Lewis acid−base interactions. In the present study, the values for E_A and C_A parameters of MTO are obtained. Thus we have used a graphical representation of the *E* and *C* equation that can result for MTO when the base is varied. Factoring and rearranging eq 5 (with $W = 0$) leads to[79]

$$\frac{-\Delta H}{C_B + E_B} = \left(\frac{C_A + E_A}{2}\right) + \left(\frac{C_A - E_A}{2}\right)\left(\frac{C_B - E_B}{C_B + E_B}\right) \qquad (6)$$

Table 3. Selected Parameters of the ECW Model[a]

Base	E_B	C_B	Acid	E_A	C_A
1-Methylimidazole	1.16	4.92	I_2	0.50	2.00
Pyridine	1.78	3.54	H_2O	1.31	0.78
3-Methylpyridine	1.81	3.67	BMe_3	2.90	3.60
3-Chloropyridine	1.66	3.08	BF_3	6.10	2.87
4-Methylpyridine	1.83	3.73	SO_2	0.51	1.56
4-Methoxypyridine	1.83	3.83	Zn(TPP)[b]	2.72	1.45
3,4-Dimethylpyridine	1.86	3.86	Phenol	2.27	1.07
4-^{t}Butylpyridine	1.84	3.70	Me_3SnCl	2.87	0.71
3-Phenylpyridine	1.75	3.41	Cu(HFacac)$_2$[c]	1.82	2.86
Methylnicotinate	1.70	3.24	VO(acac)$_2$[d]	1.60	1.96
4-Benzylpyridine	1.80	3.65	$Mo_2(PFB)_4$[e]	3.15	1.05

[a] Data from ref 77. Units for E_B, C_B, E_A and C_A are (kcal/mol)$^{1/2}$. [b] TPP=tetraphenylporphyrin. [c] HFacac=hexafluoroacetylacetonato. [d] Vanadyl acetylacetonate, data from ref 80. [e] PFB=perfluorobutyrate.

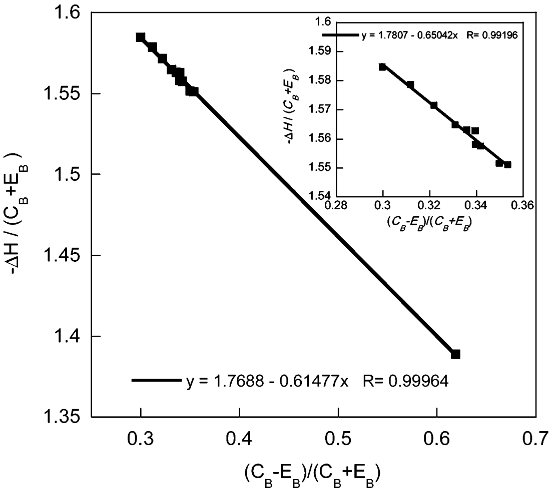

Figure 4. A plot of eq 6 for a series of N-donors (the inset: for pyridine derivatives only) reacting with MTO. MTO's E_A and C_A parameters from the slope and intercept of the plot are calculated as 2.38 (kcal/mol)$^{1/2}$ and 1.15 (kcal/mol)$^{1/2}$, respectively.

The value of $-\Delta H$ (in kcal/mol) divided by ($C_B + E_B$) for N-donors is plotted versus the value of ($C_B - E_B$)/($C_B + E_B$) calculated for N-donors from their parameters in Table 3 (see Figure 4). The data fit to eq 6 gives values of $E_A = 2.38$ (kcal/mol)$^{1/2}$and $C_A = 1.15$ (kcal/mol)$^{1/2}$ for MTO. It has been emphasized that in using eq 5 to solve for the unknown E_A and C_A, one should use donors with different C_B/E_B ratios. For this reason, we used a family of imidazoles (ligands 1−4 in Scheme 3) to extend this ratio, although the values of C_B and E_B are only known for 1-methylimidazole. The reactions of MTO with most of the donors (i.e. S- and P-donors) in the *E* and *C* correlation have not been included in this work because of the complexity of their interactions with MTO.[1] Even though the C_B/E_B ratios for ligands used in this study do not change appreciably and provide only tentative E_A and C_A values for MTO, the results are particularly important as they present an acidity scale for MTO. Another very important use of these parameters is the calculation of enthalpy of MTO interactions for hundred of systems which have not been examined experimentally.

To put the acidity of MTO on an external scale, it is necessary to make comparisons with other well-known acids; I_2, H_2O, BMe_3, BF_3, C_6H_5OH, SO_2, Me_3SnCl, Zn(TPP) {TPP=tetraphenylporphyrin}, Cu(HFacac)$_2$ {HFacac=hexafluoroacetylacetonato}, VO(acac)$_2$ {vanadyl acetylacetonate} and $Mo_2(PFB)_4$ {PFB=per-

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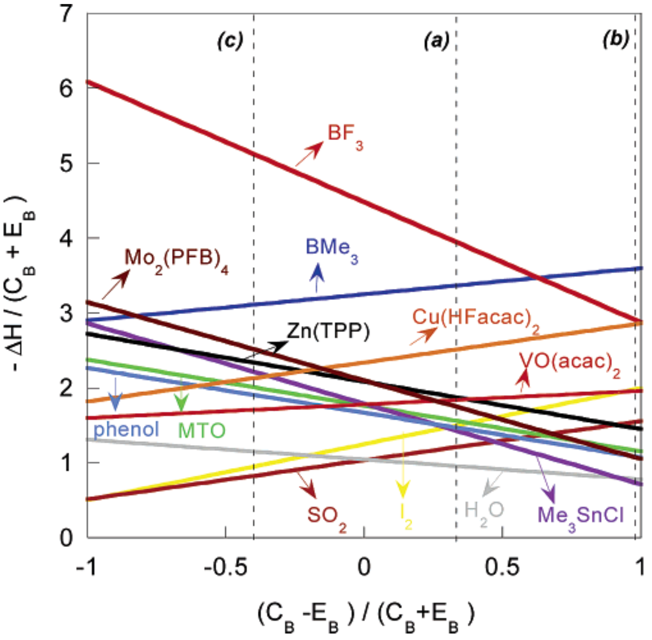

Figure 5. The E and C plot of the various acceptor orders for representative Lewis acids.

fluorobutyrate} were chosen for this purpose. E_A and C_A parameters of these acids are given in Table 3.

It is reported[77] that if both E_A and C_A are larger for one acid than another, the first acid is stronger toward any base. The difficulty arises if the comparison of C_A number yields the opposite rank order from the comparison of E_A number. Cramer and Bopp reported[79] a way in which the E and C numbers for a series of acids (or bases) could be plotted to facilitate such comparative discussion. Using the reported E_B and C_B parameters from Table 3 and eq 5, $-\Delta H$ is calculated for an acid of interest; for example I_2 interacting with some bases, listed in Table 3. The values of $-\Delta H$ (in kcal/mol) divided by (C_B+E_B) for bases are plotted versus the values of $(C_B - E_B)/(C_B+E_B)$ calculated from their parameters in Table 3. Equation 6 is that of a straight line and the calculated enthalpies for all bases interacting with this acid will fall on this line. The procedure is repeated for a series of acids (listed in Table 3) including MTO and the resulting plots are shown in Figure 5. The acceptor order toward any base whose E_B and C_B values are known can be determined from the corresponding plot.

Figure 5 shows the relative ordering of the acids when a common base is used. Different bases are located along the horizontal axis depending on their value of $(C_B - E_B)/(C_B+E_B)$. Then a line parallel to vertical axis at this point is drawn (the dashed lines in Figure 5). This line intersects the various acid lines in the proper sequence. Due to the large number of intersections of acid lines, it is clear that the ordering of acids will change from base to base. As pointed out above and graphically shown in Figure 5, BF_3 is, for example, a stronger acid than MTO with all bases; this is a direct result of the fact that these acid lines do not cross. Similarly, MTO is a stronger acid than phenol or H_2O with all bases. When the acceptor lines for two different acceptors cross, the order of acceptor strength changes toward bases on opposite sides of the intersection, which is the case for comparing of MTO with $Cu(HFacac)_2$, $VO(acac)_2$, $Mo_2(PFB)_4$, I_2, SO_2 and Me_3SnCl. Toward a base like pyridine (C_B=3.54, E_B=1.78 and $(C_B - E_B)/(C_B+E_B)$=0.33; the dashed line ***a*** in Figure 5) the acid strength order is

$$Cu(HFacac)_2 > VO(acac)_2 > Mo_2(PFB)_4 > MTO > I_2 > Me_3SnCl > SO_2$$

For a base like Me_2Se (C_B=4.24, E_B=0.05 and $(C_B - E_B)/(C_B+E_B)$=0.98; the dashed line ***b***) the order is

$$Cu(HFacac)_2 > I_2 > VO(acac)_2 > SO_2 > MTO > Mo_2(PFB)_4 > Me_3SnCl$$

and a base like CH_3CN (C_B=0.71, E_B=1.64 and $(C_B - E_B)/(C_B+E_B)$= −0.4; the dashed line ***c***) produces an acid strength order

$$Mo_2(PFB)_4 > Me_3SnCl > Cu(HFacac)_2 > MTO > VO(acac)_2 > I_2 > SO_2$$

Therefore it is clear that in order for the lines for two acids to cross, a necessary and sufficient condition is that a direct comparison of their E_A or C_A numbers yield opposite relative ordering.

Finally, it should be noted that the ECW model will predict the normal, sigma bond energy for adducts, including molecules which undergo drastic changes in their geometry upon adduct formation. When steric effect has an important role, systems are found that do not fit ECW model.[75,81] Acids such as BMe_3, BF_3, Me_3SnCl and MTO undergo extensive rearrangement from their structure as free acid when they form adducts. It is shown[75,81] that acids such as BMe_3, $AlMe_3$ and Me_3SnCl may encounter steric repulsion with certain bases such as $(CH_3)_3N$ and $(C_2H_5)_3N$. However excellent agreement between experimental enthalpies of adduct formation and the calculated one using ECW model, for these Lewis acids with pyridine derivatives indicates that steric effects are minimized with the N-donors selected for incorporation into our study in this work.

Conclusion

The results of this work can be summarized as follow:

a) In this work we have measured the relative coordination ability of different N-donor ligands toward MTO. A linear correlation between the relative coordination strength and either the Hammett σ constant of the substituents on the ligands or the pK_a of the N-donor was always found. This allowed one to measure the Lewis acidity of MTO using reaction constant, ρ. Clearly MTO is stronger acid than other metaloxo species OsO_4 toward pyridine derivatives.

b) On the basis of ECW model and comparing E_A and C_A parameters, obtained for MTO, with parameters for other well-known acids, the following results can be obtained: 1) Since both E_A and C_A values are greater for BMe_3, BF_3 and Zn(TPP) as compared to those for MTO, they are the stronger acids toward all bases. 2) Since both E_A and C_A values are greater for MTO than those for H_2O and phenol, MTO is the stronger acid toward all bases. 3) In the case of MTO, SO_2, $Cu(HFacac)_2$, $VO(acac)_2$, $Mo_2(PFB)_4$, Me_3SnCl and I_2, the situation is

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Table 4. MTO-Additive-Catalyzed Oxidation of Cyclooctene with Hydrogen Peroxide[a]

Additive	E_B	C_B	$-\Delta H$[b]	Yield %[c]
-	-	-	-	45
Pyridine	1.78	3.54	8.31	70
4-Methylpyridine	1.83	3.73	8.64	65
4-^{t}Butylpyridine	1.84	3.70	8.63	65
4-Cyanopyridine	1.53	2.94	7.02	75

[a] Data from ref 7; the reactions have been performed at room temperature with a MTO/H_2O_2/cyclooctene ratio of 0.01:1.5:1.0 and the MTO/additive ratio of 1:25. [b] ΔH (kcal/mol) is calculated using $\Delta H = E_{MTO} \cdot E_B + C_{MTO} \cdot C_B$. [c] Epoxide yield after 4 h.

ambiguous. Thus MTO is more acidic than I_2 toward bases with $E_B \gg C_B$, but is a weaker acid for bases where $C_B \gg E_B$.

The scales, suggested in this work, for Lewis acidity of MTO can be correlated to catalytic activity, a field where the Lewis acidity of the metal is well-known to play an important role. In MTO-catalyzed epoxidation reactions, the reactivity depends on the strength of interaction of MTO with additive. The extent of this interaction can be correlated to the enthalpy (i.e. the bond strength of Re−N) of the reaction. N-donors involving large enthalpy values tend to deactivate MTO and therefore decrease the epoxide yield. The reported MTO-additive-catalyzed oxidations of cyclooctene with hydrogen peroxide are presented in Table 4. As is clear from this table, 4-cyanopyridine is more efficient than 4-methylpyridine in epoxidation of cyclooctene. Generally, an additive acts as a Lewis base and reduces the acidity of MTO. This would prevents epoxide-ring opening and confirms the utility of MTO·N-donor in epoxidation. Despite huge studies on the role of additives in these systems, the effects of the basic additives are still a topic for conjecture.[82]

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