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Adduct Formation of Methyltrioxorhenium with Mono- and Bidentate Nitrogen Donors: Formation Constants

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The coordination of N-donor ligands to MTO (methyltrioxorhenium) is governed by both electronic and steric effects. For example, the binding constant of pyridine to MTO is 196.6 L mol^{-1}, whereas that of the better donor 4-picoline is 732 L mol^{-1} and that of the sterically encumbered 2,6-di-*tert*-butyl-4-methylpyridine is <1 L mol^{-1}. Equilibrium constants have been evaluated for this reaction, MTO + L = MTO•L, where L comprises mono- and bidentate N-donor ligands. The values of log *K* for monodentate ligands range from <0 for 2-substituted pyridines to 3.3 for 1-butylimidazole and for bidentate ligands from 2.2 for 2,2′-bipyridine to 5.27 for 4,7-dimethyl-1,10-phenanthroline at 25 °C in chloroform. A successful correlation of log *K* with pK_a of L was realized except in the case of 2-substituted ligands, where steric effects make *K* smaller than expected from the proton basicity of L.

Introduction

Methyltrioxorhenium (MTO) has excellent catalytic properties in numerous oxy functionalizations,[1−6] some examples being the oxidation of olefins,[7,8] alcohols,[9,10] arenes,[11] and carbonylmetal compounds.[12,13] The epoxidation of olefins has received particular attention, using MTO to activate H_2O_2. Due to the Lewis acidity of the rhenium center, a major limitation of this system is the opening of the epoxide ring, leading to the formation of diols in the presence of water.[1−6,14] It was soon found, however, that amine additives, such as pyridine,[15,16] pyrazole,[17] and 3-cyanopyridine,[18−20] enhance the efficiency and selectivity of MTO-catalyzed oxidations. The aromatic N-base ligands work by coordinating to the metal center, thereby reducing the Lewis acidity of the catalyst and additionally accelerating the catalytic reactions.[21−25] MTO forms trigonal-bipyramidal adducts with pyridines and related bases[26] and distorted octahedral adducts

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with bidentate Lewis bases, e.g. 4,4′-dimethyl-2,2′-bipyridine and 1,10-phenanthroline.[27] In the presence of H_2O_2 these complexes form very active and highly selective epoxidation catalysts.

Considering the importance of azole and azine compounds in catalytic processes by MTO, we obtained the equilibrium constants between MTO and mono- or bidentate nitrogen donors. A successful correlation of log K with pK_a of L was realized except in the case of 2-substituted ligands, where steric effects make K smaller than expected from the proton basicity of L. The chelating effect in bidentate ligands also has an important role.

Experimental Section

The compound $MeReO_3$, or MTO, was synthesized according to the literature procedure.[28] Other reagents, including the nitrogen donor ligands, were purchased from commercial sources. They were used without further purification. Chloroform was used as the solvent in these studies, and the data were obtained at 25 °C.

Spectrophotometric methods were used for equilibrium studies. A Philips PU 7850 spectrophotometer with temperature control using a Polyscience 900 constant-temperature bath was used. Reagent-grade chloroform was used as the solvent for these studies. The ethanol stabilizer that accompanies the commercial solvent has no effect.

Results

Values of the equilibrium constants have been evaluated for the reactions represented by this chemical equation:

$$\mathrm{MTO} + \mathrm{L} = \mathrm{MTO{\cdot}L}$$

$$K = \frac{[\mathrm{MTO{\cdot}L}]}{[\mathrm{MTO}][\mathrm{L}]} \tag{1}$$

The absorbance of a solution at equilibrium is the sum of the larger component from the adduct of MTO•L and the smaller one from MTO:

$$\mathrm{Abs}_{\mathrm{eq}} = \epsilon_{\mathrm{MTO}}[\mathrm{MTO}] + \epsilon_{\mathrm{MTO.L}}[\mathrm{MTO{\cdot}L}] \tag{2}$$

Mass balance for rhenium must also be maintained:

$$[\mathrm{Re}]_{\mathrm{T}} = [\mathrm{MTO}] + [\mathrm{MTO{\cdot}L}] \tag{3}$$

The simultaneous solution of these equations, which is presented in the Supporting Information, affords an exact expression for the equilibrium absorbance in which the indicated equilibrium is sustained:

$$\mathrm{Abs}_{\mathrm{eq}} = \frac{\epsilon_{\mathrm{MTO}}[\mathrm{Re}]_{\mathrm{T}} + \epsilon_{\mathrm{MTO.L}}K[\mathrm{L}][\mathrm{Re}]_{\mathrm{T}}}{1 + K[\mathrm{L}]} \tag{4}$$

Here [L] represents the equilibrium ligand concentration. The values of K were determined for most of the ligands by fitting the equilibrium absorbances to eq 4 by the method of nonlinear least squares. Such solutions contained L at a known concentration because $[\mathrm{L}]_{\mathrm{T}} \cong [\mathrm{L}]_{\mathrm{eq}} \gg [\mathrm{Re}]_{\mathrm{T}}$. Figure 1 shows the fit to eq 4 of the absorbance values at the corresponding wavelength (see Table 1) for L = 4.4′-dimethyl-2,2′-bipyridine and 4-phenylpyridine, respectively. The values of K so determined are 883.4 and 309 L mol^{-1} in chloroform at 25.0 °C, respectively.

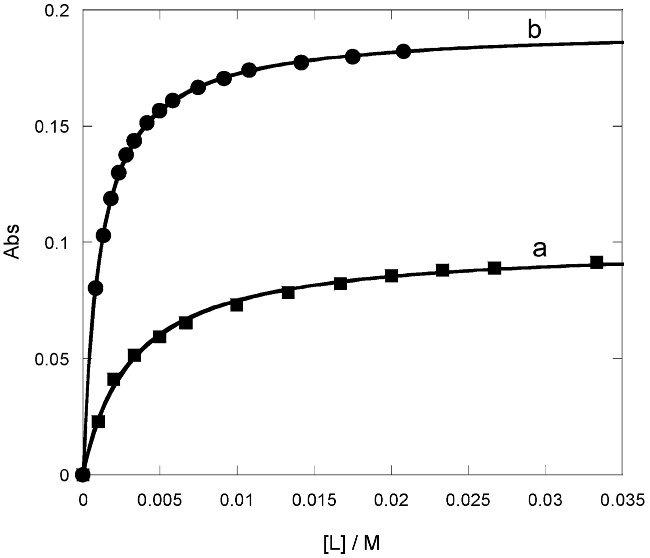

Figure 1. Analysis of the spectrophotometric data to evaluate the equilibrium constants according to eq 4 for (a) L = 4-phenylpyridine and (b) L = 4,4′-dimethyl-2,2′-bipyridine.

A more complex situation arises when K is quite large, as was the case for 4,7-dimethyl-1,10-phenanthroline. Then, $[\mathrm{L}]_{\mathrm{T}}$ must not be $\gg [\mathrm{Re}]_{\mathrm{T}}$ to realize the balance between MTO and MTO•L needed for the evaluation of K. That is, $[\mathrm{L}]_{\mathrm{T}} \neq [\mathrm{L}]_{\mathrm{eq}}$. This situation requires an iterative solution. To do so, we made use of the program PSEQUAD.[29] The data for pyridine were checked by both methods of calculation, and the agreement in the values of K was, within the experimental error, 196.6 ± 9.4 and 197.8 ± 7.2, by nonlinear least squares and by using the program PSEQUAD, respectively. The values of the equilibrium constants by the method most appropriate for the given adduct are summarized in Table 1. The Supporting Information lists the initial concentration of MTO and the range of each ligand L used in the determination of the values of K.

If one wishes, one further correction could be applied.[33] For a detailed comparison of the acidity constant of HL^+ species, it is important to note that for release of a proton from HL'^+, where L′ is imidazole, pyrazole, 3,5-dimethylpyrazole, and benzimidazole, two possibilities exist whereas there is only a single for other ligands listed in Table 1. This

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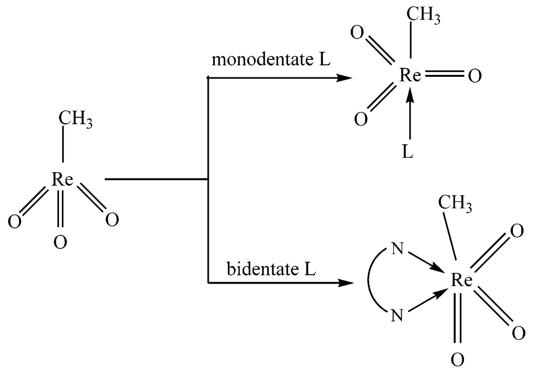
Table 1. Equilibrium Data for the Coordination of Nitrogen Donor Ligands to MTO at 25 °C in $CHCl_3$ and PK_a Values of the Ligands

entry	ligand	K_{eq} [a]/L mol^{-1}	pK_a [b] (pK_{corr})	λ/nm[c]
1	imidazole	714.9 ± 39.5	6.99 (7.29)	315
2	pyrazole	28.40 ± 1.2	2.49 (2.79)	305
3	3,5-dimethylpyrazole	62.7 ± 8.4	4.26 (4.56)	305
4	benzimidazole	300.8 ± 13.3	5.53 (5.83)	315
5	1-methylimidazole	1079.6 ± 78.3	7.11	300
6	1-butylimidazole	1999.5 ± 52.2	7.09	340
7	pyridine	196.6 ± 9.4	5.23	320
8	4-*tert*-butylpyridine	677.4 ± 32.9	5.98	320
9	4-methoxypyridine	821.3 ± 16.6	6.59	330
10	4-phenylpyridine	309 ± 18	5.44	345
11	3-cyanopyridine	7.21 ± 0.14	1.78	
12	3-bromopyridine	23.3 ± 0.2	2.87	
13	3-chloropyridine	21.8 ± 0.3	2.95	
14	pyridine-4-aldehyde	36.8 ± 0.9	3.30	
15	3-phenylpyridine	156 ± 4	4.85	
16	3-methylpyridine	254 ± 11	5.52	
17	4-methylpyridine	732 ± 20	5.94	
18	2-chloropyridine	<1	0.62	
19	2,6-dimethylpyridine	<1	6.67	
20	2,6-di-*tert*-butyl-4-methylpyridine	<1	6.88	
21	2,2-bipyridine	162.2 ± 2.2	3.62	360
22	4,4-dimethyl-2,2-bipyridine	883.4 ± 6.3	4.40	360
23	1,10-phenanthroline	5464.3 ± 454.9	5.16	370
24	5-methyl-1,10-phenanthroline	13097.0 ± 505.1	5.43	400
25	5-chloro-1,10-phenanthroline	1470.2 ± 24.9	3.98	405
26	4,7-dimethyl-1,10-phenanthroline	189234.4 ± 13132.9	6.39	370

[a] K was evaluated by use of the nonlinear least-squares method for ligands 1−10, 21−25, the program PSEQUAD for ligand 26, and from ref 30 for ligands 11−20. [b] K_a applies to the reaction $HL^+ = H^+ + L$ in aqueous solution. Data are from refs 27, 31, and 32. [c] λ specifies the wavelength used for fitting data from equilibrium studies.

Scheme 1



means the symmetric acids, HL'^+, are favored by a factor of 2 in their deprotonation reactions and hence for comparisons one can add the corresponding pK_a values 0.3 (=log 2) to obtain the corrected acidity (pK_{corr}) which actually quantify the acid−base properties of HL'^+. This is expressed in a general form in eq 5. The corresponding results for this system mentioned are listed in column 4 of Table 1 (entries 1−4).

$$pK_{corr} = pK_a + 0.3 \qquad (5)$$

Interpretation and Discussion

Adduct Formation with Electron Donors. (η^1-Organo)-rhenium(VII) trioxides are Lewis acids with two free coordination sites. Reaction with Lewis bases leads to electronic and steric saturation of the Re center (Scheme 1). Ligands, especially those with oxygen or nitrogen donor atoms, form Lewis acid−base adducts with MTO.[34−36] Although both sites of bidentate ligands can bind to the rhenium center to form a distorted octahedral complex, usually only a single monodentate ligand coordinate to the rhenium atom when a monodentate ligand was used. Special attention has been paid to these adducts because they have proven to be highly selective oxidation catalysts.[34]

Interestingly, the equilibrium data clearly reflect the electron-donating capability of the monodentate ligands. The pyrazole ligand with 2 nitrogens (pK_a = 2.49) is considerably less basic than imidazole and 1-methylimidazole (pK_a = 6.99 and 7.11, respectively), because of the aza effect, and thus undergoes only a relative weak interaction with the Re(VII) center. The value of K for pyridine (pK_a = 5.23), 196.6 L mol^{-1}, increases to 732 L mol^{-1} for 4-methylpyridine (pK_a = 6.05) due to the electron-donating nature of the methyl substituted resulting in an increase of the donor ability the alkyl-substituted pyridine.

The bidentate ligands show an analogous correlation. The equilibrium constant values for 2,2′-bipyridine (pK_a = 3.62) and 4,7-dimethyl-1,10-phenanthroline (pK_a = 6.39) are 162.2 and 1.89×10^5, respectively. This can be explained on the basis of the relative donating ability of these ligands. The coordination of bidentate Lewis base ligands to MTO is governed not only by electronic but also by steric effect. One can find in the literature that the synthesis of a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline MTO adduct was not successful.[27] This indicates that the methyl groups in positions 2 and 9 of 1,10-phenanthroline lead to an excessively bulky ligand which cannot coordinate to MTO.

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Table 2. Logarithms of the Equilibrium Constants of the Adducts Formed between Metal Ions and N-Donors (L)[a]

entry	ligand	Cu_{aq}^{2+}	Zn_{aq}^{2+}	Re^{7+} (MTO)	Re^{5+} ($\{MeReO(edt)\}_2$)
1	imidazole	4.18		2.85	6.29
2	pyrazole			1.45	1.98
4	benzimidazole	3.42		2.48	4.70
5	1-methylimidazole	4.22		3.03	6.12
7	pyridine	2.54		2.28	4.01
10	4-phenylpyridine	2.54		2.49	
15	3-phenylpyridine	2.25		2.19	
16	3-methylpyridine	2.77		2.40	
17	4-methylpyridine	2.88		2.86	
21	2,2-bipyridine		5.13	2.21	
23	1,10-phenanthroline		6.40	3.74	
24	5-methyl,1,10-phenanthroline		6.62	4.11	
25	5-chloro,1,10-phenanthroline		5.85	3.17	
26	4,7-dimethyl,1,10-phenanthroline		6.90	5.28	

[a] Data are from refs 32, 33, and 37 and this work.

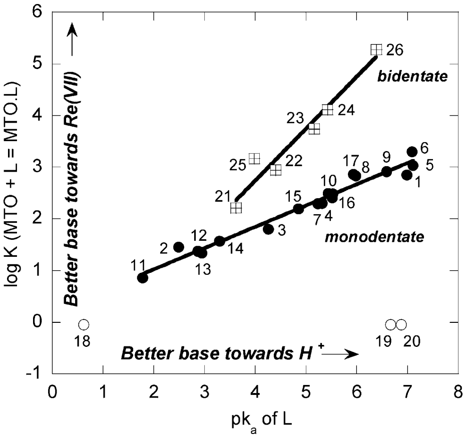

Figure 2. Plot showing a correlation between the equilibrium constants (on the logarithmic scale) for adducts formation of MTO with different ligands L in chloroform and pK_a of the same ligands. Ligands 18, 19, and 20 (Table 1) were omitted from the linear fit.

Correlation between Formation Constants and Ligand Basicities. Figure 2 displays a plot of log K for reaction 1 versus pK_a, for the acid ionization of HL^+. Except for ligands 2-chloropyridine, 2,6-di-*tert*-butyl-4-methylpyridine, and 2,6-dimethylpyridine, a good correlation was found; the slopes of the lines in Figure 2 for monodentate and bidentate ligands are 0.41 ± 0.02 and 1.00 ± 0.12, due to chelating effect, respectively. Exceptions for those three ligands are logical as well, in that they present a steric barrier for coordination to rhenium which is absent in the proton basicity. No deviation was found for benzimidazole and 3,5-dimethylpyrazole, where a steric effect for rhenium might have been expected to exist. That steric effect would be smaller than the ones for 2-chloropyridine, 2,6-di-*tert*-butyl-4-methylpyridine, and 2,6-dimethylpyridine, because the bond angle between N, the ring carbon, and the carbon in the 2-position is about 132° in benzimidazole and 3,5-dimethylpyrazole and 120° in 2-chloropyridine, 2,6-di-*tert*-butyl-4-methylpyridine, and 2,6-dimethylpyridine. The same behavior has been observed for reaction of benzimidazole with $\{MeReO(edt)\}_2$, where edt is 1,2-ethanedithiolate.[37]

For N-donor ligands a linear relationship between log K and pK_a is expected as expressed by the following:

$$\log K = m(\mathrm{p}K_a) + b \qquad (6)$$

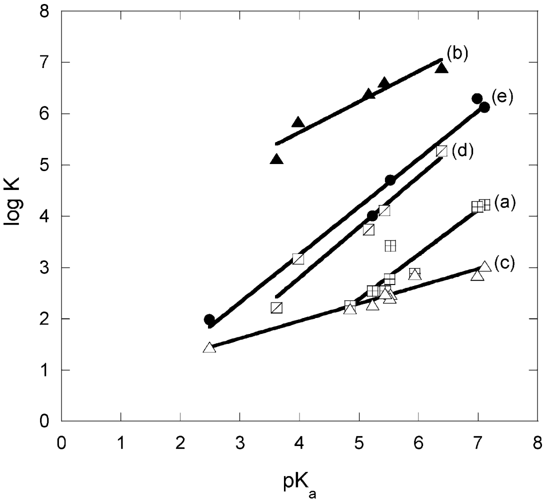

Figure 3. Relationship between log K and pK_a for the reactions of (a) Cu_{aq}^{2+} + monodentate N-donors, (b) Zn_{aq}^{2+} + bidentate N-donors, (c) Re^{7+} (MTO) + monodentate N-donors, (d) Re^{7+} (MTO) + bidentate N-donors, and (e) Re^{5+} ($\{MeReO(edt)\}_2$) + monodentate N-donors, based on the data given in Table 2. The least-squares lines are drawn through the indicated sets (when available).

Table 3. Straight-Line Correlations for Formation Constants and Ligand Basicities[a]

adduct	m	b	R[b]
Cu_{aq}^{2+} + monodentate N-donors[c]	0.87 ± 0.13	−1.98 ± 0.78	0.94
Zn_{aq}^{2+} + bidentate N-donors[c]	0.60 ± 0.11	3.25 ± 0.54	0.95
Re^{7+} (MTO) + monodentate N-donors[d]	0.41 ± 0.02	0.20 ± 0.10	0.98
Re^{7+} (MTO) + bidentate N-donors[d]	1.00 ± 0.12	−1.28 ± 0.60	0.97
Re^{5+} ($\{MeReO(edt)\}_2$) + monodentate N-donors[d]	0.93 ± 0.07	−0.49 ± 0.42	0.99

[a] The slopes (m) and intercepts (b) for the straight reference lines from plots of log K versus pK_a were calculated by the least-squares procedure from the data listed in Tables 1 and 2. [b] Correlation coefficient. [c] At 25 °C in aqueous solution. [d] At 25 °C in $CHCl_3$.

In Figure 3 the values from Table 2 for log K versus pK_a are plotted for two metal ions (Cu_{aq}^{2+} and Zn_{aq}^{2+}), MTO (Re^{7+}), and $\{MeReO(edt)\}_2$ (Re^{5+}) as examples. It is evident that the data for a given metal ion fit on a straight line. The results listed in Tables 1 and 2 provide five or more data

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(37) Nabavizadeh, S. M.; Espenson, J. H. *Eur. J. Inorg. Chem.* **2003**, 1911−1916.

points for each metal ion. These were used to calculate the straight line equations summarized in Table 3 by least-squares procedures. These equations allow calculation of the expected stability constant for an adduct of any N-donor ligand, provided its pK_a.

Summary. Equilibrium constants for reactions in which a series of N-donor ligands react with MTO, leading to adduct formation, have been evaluated. The coordination of N-donor ligands to MTO is governed by electronic and steric effects. The values of K correlate with the proton basicity of the ligands.

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Supporting Information Available: Concentrations used for the determination of the equilibrium constants and the derivation of eq 4. This material is available free of charge from via the Internet at http://pubs.acs.org.

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