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Competition of methyltrioxorhenium (MTO) with osmium tetroxide (OsO₄) for pyridines binding: Ligand binding assay

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ABSTRACT

Competition of methyltrioxorhenium (MTO) with osmium tetroxide (OsO₄) toward L = pyridine and its derivatives, based on the equilibrium constant for the reaction OsO_4 ·L + MTO = MTO·L + OsO_4 , has been measured. A successful correlation of $\log K_{eq}$ with the Hammett σ constants of the substituents on the ligands was realized. A negative reaction constant, obtained for the reactions, shows that a more positive charge expands on the pyridine nitrogen in the complex MTO·L as compared with the complex OsO_4 ·L. So, the rhenium center acts as a better electron acceptor than osmium center. The thermodynamic parameters have been obtained and an excellent linear relationship was observed between the enthalpy and entropy of the reactions.

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1. Introduction

Osmium tetroxide has been widely used for the *cis*-dihydroxylation of olefins under mild conditions, which is of fundamental importance in nature. Many oxidation systems have been developed for this transformation [1]. In the first step of this transformation, OsO_4 reacts with alkenes to yield a cyclic osmate ester (Scheme 1). Subsequent reductive hydrolysis of ester in solution gives the *cis*-1,2-diol. The presence of a tertiary amine that coordinates to osmium accelerates the dihydroxylation reaction [2]. The oxidation can be carried out under both catalytic and stoichiometric conditions. The stoichiometric reaction is studied by Criegee who has shown that pyridine accelerates the reaction considerably [3]. In addition, osmium tetroxide could be used in catalytic amounts in the presence of stoichiometric amounts of a cooxidant, such as hydrogen peroxide or *N*-methylmorpholine *N*-oxide (NMO), which reoxidises osmium *in situ* [1c,4].

Methyltrioxorhenium CH₃ReO₃ or MTO, containing a metalmethyl bond, is a reactant stable to hydrolysis, and can act in the presence of H_2O_2 or O_2 as a highly efficient and selective catalyst for a number of reactions, such as epoxidation of alkenes [5], oxidations of aromatic compounds [6], primary and secondary amines [7], alkynes [8], anilines [9], sulfur compounds [10], phosphines, arsines, stibines [11], symmetric disulfides [12], alcohols [13], ketones [14], halide ions [15], alkanes [16], aldehyde olefination [17] and olefin metathesis [18]. The mono-peroxo complex **A** and the bis-peroxo complex **B** shown in Scheme 2 are the active species for the catalytic oxidation of methyltrioxorhenium with H_2O_2 [19]. However, in the case of olefin epoxidation, depending on the constitution of the epoxide, a hydrolytic ring opening catalyzed by the electropositive Re(VII) center can also occur to give 1,2-diols [20]. This problem can be overcome by replacing aqueous hydrogen peroxide with the hydrogen peroxide–urea adduct as primary oxidant in non aqueous media [21] or by adding pyridine [19,22], 3-cyanopyridine [23] or 2,2'-bipyridine (compounds **1** and **2** in Scheme 3) that reduce the Lewis acidity of the catalytic system and thus preserve the epoxide from destruction [24].

Therefore, transition metal-based oxidants have been successfully used for oxidation of unsaturated organic compounds. It is important to use environmentally friendly oxidants, such as molecular oxygen or hydrogen peroxide, which give no waste products [25]. However, direct oxidation of the catalyst by O₂ or H_2O_2 is often kinetically unfavored, since the energy barrier for electron transfer can be high. The problem has been solved by introduction of efficient electron transfer mediators (ETMs) between the substrate selective redox catalyst and the terminal oxidant $(O_2 \text{ or } H_2O_2)$ [26]. Several compounds have been used as ETM in the hydrogen peroxide-based osmium-catalyzed dihydroxylation of various alkenes (see Scheme 4). The mechanism of these oxidation systems is that the hydrogen peroxide reacts with a cocatalyst (electron transfer mediator) to give a reactive peroxo or hydroperoxide intermediate, which can efficiently reoxidize Os(VI) to Os(VIII).

For the first time, Bäckvall and his coworkers [27] have reported a novel and robust system for osmium-catalyzed asymmetric





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Scheme 2. Reaction of MTO with hydrogen peroxide.



Scheme 3. Lewis base adducts of MTO.



Scheme 4. Electron transfer mediators (ETMs).

dihydroxylation of olefins by aqueous H_2O_2 with methyltrioxorhenium (MTO) as electron transfer mediator (ETM). The mechanism has been shown in Scheme 5 where MTO acts as an ETM. In this scheme, *N*-methyl morpholine (NMM) was also used as an additional ETM to facilitate electron transfer from MTO to OsO₄. It was demonstrated that in some cases direct electron transfer from MTO to OsO₄ is efficient without added NMM [28].

Considering the important applications of these two metal oxo compounds, MTO and OsO_{4} , in catalytic activities and also concurrent application of them in H_2O_2 -based OsO_4 -catalyzed dihydroxylation of alkenes, we have decided to measure their competition and coordination ability toward Lewis bases such as pyridine and its derivatives according to reaction shown in Scheme 6.

2. Experimental

2.1. General

Methyltrioxorhenium(VII) [29] and pyridines adducts of osmium tetroxide [2a,30] were synthesized according to literature procedures. Osmium tetroxide was obtained from Merck. Pyridine and its derivatives were purchased from Aldrich or Fluka and used as received. Benzene (ACS grade, Aldrich) was used as the solvent for UV–Vis spectroscopy.

Values of equilibrium constant (K_{eq}) for reaction shown in Scheme 6 were determined by UV–Vis spectrophotometric titration. The spectra were recorded using a Perkin–Elmer UV Lambda 25 spectrophotometer equipped with a circulating water thermostatic system (EYELA NCB-3100 constant temperature bath). Quartz cuvettes with 1 cm optical path lengths were used. Typically the equilibrium constant of the reaction was determined by titrating 3 ml a solution of OsO₄·py in benzene with successive aliquots of a known concentration solution of MTO in the same solvent at 25 °C. This procedure was repeated until the spectra remained unchanged with further addition of MTO. The software PSEQUAD [31] was used to analyze the multiwavelength absorbance data to obtain the equilibrium constant.

The same method was used at other temperatures and thermodynamic parameters were obtained from Eq. (1).

$$\ln K_{\rm eq} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{1}$$



Scheme 5. Catalytic system for osmium-catalyzed dihydroxylation of olefins using H₂O₂.



Scheme 6. Ligand exchange between MTO and OsO4.

2.2. Theoretical calculations

GAUSSIANO3 [32] was used to fully optimize all the structures reported in this paper at the B3LYP level of density functional theory (DFT). The effective core potential of Hay and Wadt with a double- ξ valence basis set (LANL2DZ) [33] was chosen to describe Re and Os. The 6-311++G^{**} basis set was used for other atoms. To evaluate and ensure the optimized structures of the molecules, frequency calculations were carried out using analytical second derivatives. In all cases only real frequencies were obtained for the optimized structures.

3. Results and discussion

3.1. Equilibrium constants and substituent effects

The equilibrium constants (K_{eq}) for pyridine and five ringsubstituted pyridines exchange between OsO4 and MTO (Scheme 6) are given in Table 1. The program PSEQUAD [31] is used to determine K_{eq} by a global fit of absorbance-concentration data taken at 14 wavelengths. The values of K_{eq} are >1, with a magnitude that increases as the Py ligand becomes more electron-donating. For example, the presence of CH₃ group at the para position of pyridine enhances the stability of MTO adducts by a factor of about 1.5 with respect to Cl group. The adduct stability of MTO with pyridines respect to OsO_4 follows the order 4-methoxy > 4-methyl > 3methyl > 4-phenyl \sim 4-H > 3-chloro pyridine. The electronic effect is examined more closely using the Hammett correlation for para and meta substituted pyridine, as shown in Fig. 1. The linear correlation between $\log(K_{\rm X}/K_{\rm H})$ and σ , according to equation $\log(K_{\rm X}/K_{\rm H})$ $K_{\rm H}$) = $\rho\sigma$, shows that the equilibrium constant increases with the donating ability of the pyridine ligand. To confirm more this phenomenon, theoretical studies using DFT calculations were performed to calculate the charge on nitrogen atoms of the L ligands [32]. The data were used in connection with the equilibrium data to confirm the electronic effect of the pyridines ligands on the equilibrium behaviors. The graph of $log(K_X/K_H)$ for the reaction of complexes OsO4·L and MTO at 25 °C in benzene versus charges on the L ligands, the inset of Fig. 1, is linear for the series of L ligands, pyridine, 4-methylpyridine, 3-methylpyridine, 3-chloropyridine, 4-methoxypyridine and 3-phenylpyridine, and this confirms that the equilibrium constants of the reactions correlates linearly with the charges on the L ligands.

It has been reported [34] 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. A negative reaction constant, obtained for reaction shown in Scheme 6 ($\rho < 0$) means that a more positive charge expands on the pyridine nitrogen in the complex MTO-L as compared with the complex OsO₄-L. The rhenium center, so, acts as a better electron acceptor than osmium center.

To consider the influence of the remote substituents on the structural properties of the OsO₄·L and MTO·L complexes, DFT cal-



Fig. 1. The linear correlation between $\log(K_X/K_H)$ and σ (the inset, plot showing a correlation between $\log(K_X/K_H)$ and the charge of the nitrogen atom on the L ligands).

culations are performed with the program suite GAUSSIANO3 [32] for six different pyridine complexes. The calculated bond distances from DFT-optimized structures for the compounds OsO_4 ·L and MTO·L along with DFT-optimized structures for these complexes are shown in Fig. 2. In each case the geometry at the metal is distorted trigonal bipyramidal, but the bond lengths of the Os(VIII)–N and Re(VII)–N are influenced significantly by the substituent on the pyridine ring as is clear from Fig. 3 (M–N bond length versus pK_a of pyridines). The M–N (M = Os or Re) bond lengths of the OsO₄·L and MTO·L complexes apparently depend on the basicity of the pyridine ligands. For example the Re–N bond length of the 4-methylpyridine complex is more than 0.043 Å shorter than the corresponding bond length for the 3-chloropyridine complex (2.445 Å versus 2.488 Å, respectively).

3.2. Sensitivity of metal center to ligand

To find the sensitivity of metal center, in OsO_4 and MTO, to pyridine and its derivatives, we have used equilibrium constants reported for the reactions [M] + L = ML, where [M] = MTO or OsO_4 [35] (Eqs. (2) and (3)) to derive values of K_{ex} that refer to reactions (4) and (5). We choose pyridine as the constant reference point.

The K_{ex} values, calculated from Eqs. (4) and (5) at 298 K, are collected in Table 2. We then have constructed a plot of log $K_{ex}(OsO_4)$ against log $K_{ex}(MTO)$ for pyridines transfer. The result is shown in

Table 1

Equilibrium data ($10 K_{eq}/L mol^{-1}$)^a for the reaction OsO₄·L + MTO = MTO·L + OsO₄ (L = pyridine and its derivatives) at different temperatures in benzene.

Ligand	10 K _{eq} at different temperatures					$\Delta H (\mathrm{kJ}\mathrm{mol}^{-1})$	ΔS (J mol ⁻¹ K ⁻¹)
	10 °C	20 °C	25 °C	30 °C	40 °C		
Pyridine	111.1	82.4	73.3	61.5	50.1	-19.7 ± 0.7	-49.9 ± 2.3
4-Methylpyridine	157	104.9	87.1	76.4	54.9	-25.6 ± 0.6	-67.7 ± 2.4
3-Methylpyridine	143.8	100.1	85.1	73.0	54.4	-23.8 ± 0.3	-62.2 ± 1.0
3-Chloropyridine	96.9	64.3	53.8	45.1	31.3	-27.6 ± 0.3	-78.8 ± 1.1
4-Methoxypyridine	165.1	120.1	99.9	88.4	65.7	-22.6 ± 0.4	-56.6 ± 1.5
3-Phenylpyridine	111.0	81.7	72.7	60.0	47.3	-21.2 ± 0.7	-54.8 ± 2.3

^a Estimated error in K_{eq} given based on least squares regression analysis is ±10%.



Fig. 2. The DFT-optimized structures and calculated bond distances for the compounds OsO4·L and MTO·L.



Fig. 3. Relationship between M–N(L) bond length (M = Os or Re) and pK_a of L (L = pyridine and its derivatives) for OsO₄·L and MTO-L complexes.

Fig. 4 and the correlation is fully acceptable. The slope of the line is 0.83 ± 0.03 , that is, the equilibrium of ligand exchange at the osmium center is less sensitive to the ligand than at the rhenium center.

3.3. Temperature profiles

In order to have a better understanding of the thermodynamics of reaction shown in Scheme 6, it is useful to consider the enthalpic and entropic contributions to these reactions. The temperature dependence of the reactions between OsO_4 ·Py and MTO are studied

 Table 2

 Equilibrium constants for ligand exc

Equilibrium	constants	for	ligand	exchange	processes	$(K_{ex},$	Eqs.	(4)	and	(5))	at
T = 298 K.											

L	$K_{\rm ex}$ (MTO)	$K_{\rm ex} ({\rm OsO}_4)$
4-Methylpyridine	1.93 ± 0.10	1.72 ± 0.24
3-Methylpyridine	1.27 ± 0.04	1.24 ± 0.16
3-Chloropyridine	0.13 ± 0.01	0.17 ± 0.02
4-Methoxypyridine	3.68 ± 0.15	2.71 ± 0.38
3-Phenylpyridine	0.65 ± 0.03	0.75 ± 0.10



Fig. 4. Correlation of the equilibrium constants (at 298 K) for exchange of pyridines at a rhenium center vs. the equilibrium constants for pyridines exchange at an osmium center, both on logarithmic scales.



over the temperature range of 283–313 K. The ΔH and ΔS values for these reactions are evaluated by applying a linear ln K_{eq} leastsquares analysis according to the van't Hoff equation (Fig. 5 and Eq. (1)) and presented in Table 1. In general, the pyridines transfer from OsO₄ to MTO is not entropy controlled as $T\Delta S$ is in general not greater than ΔH . For more investigations, a series of DFT calculations has been performed and enthalpy and entropy changes during the ligand exchange reactions were determined. The results show that the values of calculated enthalpies are more negative for reactions with more electron donating substituent on pyridine ring (i.e. 4-methoxypyridine) than those for electron withdrawing group on L (i.e. 3-chloropyridine). On the other hand, the reactions are accompanied by an entropy production indicating that the entropy of MTO-L complexes are systematically lower than the entropy of OsO_4 ·L complexes in benzene solution. However it seems that the entropy changes for the reactions can be positive when the corresponding MTO-L complexes compare to OsO_4 ·L. To investigate the intrinsic entropy changes of the reactions, DFT calculations have been done in the gas phase and found that ΔS values are positive, although no correlation found between the calculated entropy changes and the basicity of the pyridine ligands. This confirms again that the ligand exchange process, shown in Scheme 6, is enthalpy controlled, not entropy controlled.



Fig. 5. van't Hoff plots for ligand exchange between MTO and OsO_4 [(a) 4-methoxypyridine, (b) 3-methylpyridine, (c) pyridine and (d) 3-chloropyridine] in benzene.



Fig. 6. $\Delta H - \Delta S$ compensation plot for pyridines exchange between OsO₄ and MTO.

3.4. $\Delta H - \Delta S$ compensation plot

Enthalpy–entropy compensations between ΔH and ΔS are a type of thermodynamic relationship that is widely used for numerous chemical equilibriums and kinetic processes to discuss their mechanisms [36]. An enthalpy-entropy compensation is demonstrated by a linear correlation between ΔH and ΔS . The slope of the linear plot of the enthalpy change versus the entropy change is called the compensation temperature (T_c) . Chemical reactions or equilibrium processes that have a similar compensation temperature are considered to be fundamentally related and mechanistically similar. These compensation temperatures are, respectively, called isokinetic or isoequilibrium processes. An enthalpy-entropy compensation is usually represented as $\Delta H = T_c \Delta S + \Delta G_{T_c}$ where ΔG_{T_c} is the Gibbs free energy change at temperature T_c . This equation means that, at temperatures close to T_{c} , changes in ΔH are offset by changes in ΔS , so that ΔG remains independent of the temperature [36].

Thermodynamic parameters indicate that the enthalpy–entropy compensation effect holds in general for ligand exchange between MTO and OsO₄. As shown in Fig. 6, an acceptable linear relationship between ΔH and ΔS for this reaction is observed. The graph of enthalpy versus entropy values for reactions shown in Scheme 6 in benzene generates a highly linear trend and can be expressed by

 $\Delta H = T_{\rm c}\Delta S - 6.55 \text{ kJ/mol}$

The value of T_c is derived from the slope of the slope of the plot and has unit of temperature [37] and is equal to 273 ± 24 K. At this temperature, any variation in the standard enthalpy for a series of pyridines is balanced by a compensating variation in the standard entropy, such that the total free energy (ΔG) of the reaction (the *y* intercept of the plot) remains constant at -6.55 kJ/mol.

To test the reliability of enthalpy–entropy compensation correlation, Krug's method can be applied [38] which suggests that the observed compensation temperature T_c must be significantly different from the mean experimental temperature. For the reactions shown in Scheme 6 with pyridine and its derivatives, the mean experimental temperature is significantly different from the observed T_c (298 versus 273 ± 24 K). Furthermore the compensation effect between ΔH and ΔS may be indicative of chemical fact rather than simply an artifact of statistical correlation.

4. Conclusion

Equilibrium constants for reactions in which a series of pyridine ligands transfer from OsO_4 to MTO have been evaluated. The exchange reaction is governed by electronic effect and the values of equilibrium constants correlate with the Hammett reaction constant. The enthalpy and entropy of the reactions were measured and an acceptable linear relationship between ΔH and ΔS is observed.

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