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Thermodynamics of Coordination of Pyridine and Its Substituted Derivatives to Osmium Tetroxide

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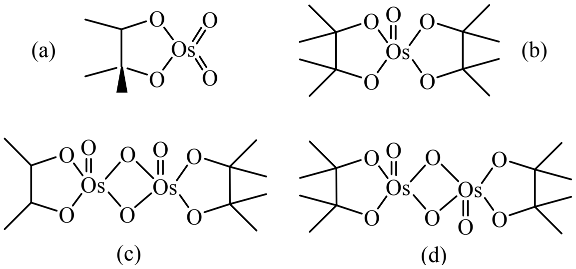
Complexation of osmium tetroxide (OsO_4) with pyridine and its substituted derivatives (i.e. 4-picoline, 3 -picoline, 4-tert-butylpyridine, methyl nicotinate, 3,4-dimethylpyridine, 3-chloropyridine, and 3-phenylpyridine) has been studied at different temperatures in benzene. Spectrophotometric measurements have been carried out to obtain the equilibrium constants and thermodynamic parameters. The equilibrium constants of the resulting 1:1 complexes are found to vary in the order 3,4-Me_2Py > 4-^{t}BuPy > 4-MePy > 3-MePy > Py > 3- PhPy > 3-C(O)OMePy ≈ 3-ClPy. All complexes are enthalpy stabilized whereas the entropy changes counteract the complexation. The results are discussed in terms of different basicities of the substituted pyridines.

Keywords: Osmium tetroxide, Pyridine derivatives, Thermodynamics, Spectrophotometry

INTRODUCTION

The oxidative functionalization of olefins is of major importance for both organic synthesis and the industrial production of bulk and fine chemicals. Among the different oxidation products of olefins, 1,2-diols are used in a wide variety of applications. OsO_4 is an effective reagent and used commercially in the important *cis*-hydroxylation of alkenes [1-15]. Interaction initially gives 1,2-diolato complexes. These include the mononuclear complexes (such as compounds **a** and **b** in Scheme 1) as well as binuclear complexes, that exist in *syn* and *anti* forms (such as compounds **c** and **d** in Scheme 1). All of these compounds can be reduced by Na_2SO_3 to give *cis*-diols. The oxide can also be used catalytically for the same conversion in presence of H_2O_2 or ClO_3^- [3].

When OsO_4 is reduced by ethanol in the presence of pyridine, the binuclear complex **a** in Scheme 2 is obtained [3]. This compound reacts with nucleosides *via* 2' and 3' hydroxyl groups of the sugar ring to give complexes like **b** in Scheme 2.



Scheme 1

The reactivity of OsO_4 toward carbon-carbon double bonds and the stability of the resulting osmate ester are dependent on the ligand present. Tertiary amine ligands offer considerable flexibility in the reactivity of the OsO_4/ligand mixture. Behrman and colleagues, in studies of the reaction of OsO_4 with nucleic acid and protein components, have shown that OsO_4/bipyridine is a highly

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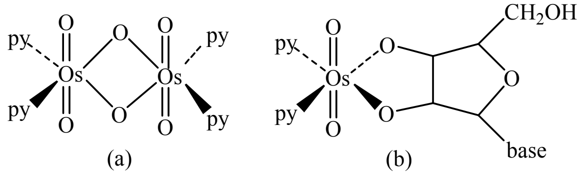
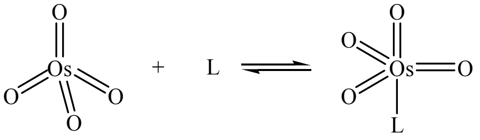


Scheme 2



Scheme 3

reactive and relatively nonselective reagent, whereas OsO_4/pyridine is a less reactive and more discriminating reagent [4,5]. In using OsO_4, as an effective reagent in *cis*-hydroxylation of alkenes as well as in a variety of catalytic systems, the critical step depends on the formation of an osmium(VI) cycloadduct which is promoted by bases such as pyridine [6-8] . Very recently, Mayer *et al.* have also pointed out that OsO_4 is reduced by H_2 in the presence of ligand such as pyridine and 1,10-phenanthroline, while in the absence of N-donors, OsO_4 is not reactive toward H_2 [16]. Although, it has been known for more than several decades that osmium tetroxide forms very stable 5-coordinate trigonal bipyramidal complexes with quinuclidine, hexamethylene tetramine and other N-donors [8,9], it is surprising that no information exists on the thermodynamics of complex formation of substituted pyridines with OsO_4. Considering this point, in this work we have fully studied the thermodynamics of the complex formation.

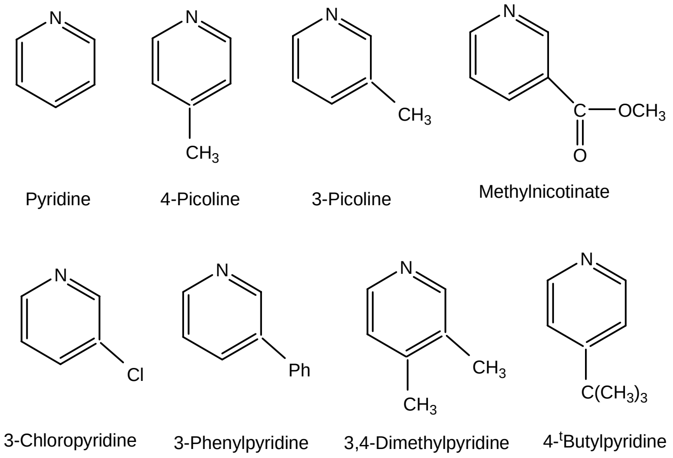
EXPERIMENTAL

Materials

Osmium tetroxide was obtained from Merck. It presents an especial hazard to the eyes and must be handled carefully. All substituted pyridines (see Scheme 4) were purchased from commercial suppliers and used without further purification. Spectroscopic grade benzene (Merck) was used as a solvent throughout this study. The pyridine ligands are sufficiently soluble in this solvent.

Instrumentation

UV-Vis spectra for equilibrium studies were recorded using a Perkin-Elmer Lambda 25 spectrophotometer, fitted with a temperature control system using an EYELA NCB-3 100 constant-temperature bath.



Scheme 4. Structural formulas of pyridine and its derivatives.

Determination of the Equilibrium Constants

A titration method was used for evaluation of equilibrium constants. The addition of substituted pyridines (generically designed as L) to OsO_4 was monitored by UV-Vis spectrophotometry. The values of equilibrium constants were determined by fitting the equilibrium absorbance to Eq. (4) by the method of nonlinear least squares using KaleidaGraph program [25]. The concentration ranges were $[OsO_4]_0$ = 0.35-1.00 mM and $[L]_T$ = 5-500 mM and were designed for each individual ligand specifically to optimize the precision of equilibrium measurements. Upon the addition of small amounts of pyridine to a benzene solution of OsO_4, the color of solution immediately discharged, undoubtedly due to the preferential coordination of the Lewis bases with the acceptor. (The value of $K_{eq} \approx 0.3$ l mol^{-1} for benzene [26] compares with 75.2 l mol^{-1} for the formation of OsO_4·pyridine in Scheme 3).

RESULTS AND DISCUSSION

Equilibrium Studies

Osmium tetroxide forms very stable 5-coordinate trigonal bipyramidal complexes with N-donors [8,9]. The values of the equilibrium constants at different temperatures were evaluated for the reaction represented in Scheme 3.

$$K_{eq} = \frac{[OsO_4 \cdot L]}{[OsO_4][L]} \tag{1}$$

The absorbance of a solution at equilibrium is the sum of the components from $OsO_4{\cdot}L$ and OsO_4:

$$Abs_{eq} = \varepsilon_{OsO_4}[OsO_4] + \varepsilon_{OsO_4 \cdot L}[OsO_4 \cdot L] \tag{2}$$

Using mass balance for osmium [Eq. (3)] and the simultaneous solution of Eqs. (1-3), an exact expression for the equilibrium absorbance can be obtained [Eq. (4)].

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$$[Os]_T = [OsO_4] + [OsO_4 \cdot L] \tag{3}$$

$$Abs_{eq} = \frac{\varepsilon_{OsO_4}[Os]_T + \varepsilon_{OsO_4 \cdot L} K_{eq}[L][Os]_T}{1 + K_{eq}[L]} \tag{4}$$

Here, ε_{OsO_4} and $\varepsilon_{OsO_4 \cdot L}$ are molar absorptivities for OsO_4 and $OsO_4{\cdot}L$ species, respectively, at corresponding wavelength and [L] represents the equilibrium ligand concentration. The values of K_{eq} were determined by fitting the equilibrium absorbances to Eq. (4) by the method of nonlinear least squares. Such solutions contained L at a known concentration because $[L]_T = [L]_{eq} >> [Os]_T$.

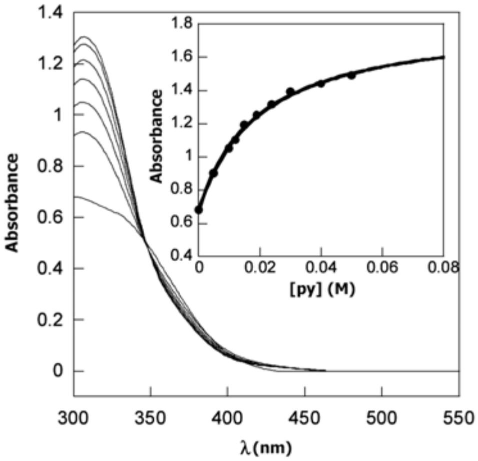

Fig. 1. Absorbance changes as a solution of OsO_4 was titrated with pyridine; the inset shows the analysis of spectrophotometric data to evaluate the equilibrium constant according to Eq. (4).

Figure 1 presents repetitive scan spectra showing the equilibrium progression from OsO_4 to $OsO_4{\cdot}L$ for L= pyridine, with increasing ligand concentration. To evaluate the equilibrium constant for the reaction shown in Scheme 3, a spectrophotometric titration was carried out. The inset of Fig. 1 shows the fit to Eq. (4) of the absorbance values at a wavelength of 307 nm. For L = pyridine, the value of K_{eq} thus determined is 51.6 (±4.1) l mol^{-1} in benzene at 35 °C. The values of the equilibrium constants for the given complex are summarized in Table 1.

Table 1. Equilibrium Data (K_{eq}/l mol^{-1}) for Complexation of OsO_4 with Pyridine and its Derivatives (XC_5H_4N) at Different Temperatures in Benzene

X	pK_a^{a}	K_{eq} (15 °C)	K_{eq} (25 °C)	K_{eq} (35 °C)	K_{eq} (45 °C)
H	5.23	111.1 ± 3.6	75.2 ± 2.6	51.6 ± 4.1	33.1 ± 1.3
4-Me	5.94	196.3 ± 7.1	134.2 ± 3.5	89.1 ± 2.7	59.5 ± 0.9
3-Ph	4.85	79.7 ± 0.7	54.1 ± 1.0	34.1 ± 0.4	22.2 ± 0.5
3-Me	5.52	135.0 ± 2.6	91.0 ± 4.4	61.6 ± 1.2	38.6 ± 1.6
4-*t*-Bu	5.98	188.6 ± 6.3	138.1 ± 3.9	92.8 ± 2.3	60.3 ± 0.7
3-Cl	2.95	29.7 ± 0.4	18.3 ± 0.5	11.1 ± 0.2	7.1 ± 0.2
3,4-Me_2	6.46	260.0 ± 8.8	169.0 ± 5.5	115.6 ± 6.9	83.1 ± 2.7
3-C(O)OMe	3.13	30.0 ± 0.7	18.3 ± 0.6	10.9 ± 0.4	7.1 ± 0.5

$^a K_a$ applies to the reaction $HL^+ = H^+ + L$ in aqueous solution [19].

Correlation between Equilibrium Constants and Ligand Basicities

Interestingly, the equilibrium data clearly reflect the electron-donating capability of the substituted pyridines. At 25 °C, the value of 75.2 l mol^{-1} for pyridine (pK_a = 5.23) increases to 134.2 l mol^{-1} for 4-picoline (pK_a = 5.94) due to the electron-donating nature of the methyl substituted resulting in an increase in the donor ability the alkyl-substituted pyridine. Thus 3-chloropyridine (pK_a = 2.95) undergoes only a relatively weak interaction with the Os(VIII) center, K_{eq} = 18.3 l mol^{-1}, due to the electron-withdrawing nature of the Cl substituted. For substituted pyridines, a linear relationship between logK_{eq} and pK_a at given temperatures is expected [17,18,20,21], as expressed by the following equation:

$$\log K_{eq} = m\,(pK_a) + b \qquad (5)$$

In Fig. 2, the values for logK_{eq} (Table 1) are plotted against pK_a at different temperatures. It is clear that the data for $OsO_4{\cdot}L$ fit to a straight line. The results listed in Table 1 were used to calculate the straight line equations shown in Fig. 2 by least-squares procedures. These equations allow the calculation of expected equilibrium constant for a complex of any substituted pyridine ligand from its pK_a at different temperatures.

Thermodynamic Parameters

The equilibrium constants (K_{eq}) for reaction shown in Scheme 3 were evaluated as a function of temperature, over the range 288-318 K (Table 1). The enthalpy and entropy changes were evaluated from the temperature dependence of the equilibrium constants by applying a linear least squares analysis according to the van't Hoff equation [Eq. (6) and Fig. 3] and are listed in Table 2. The Δ*G*° values, calculated from equation Δ*G*° = Δ*H*° - TΔS° at 25 °C, are also included in Table 2.

$$\ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (6)$$

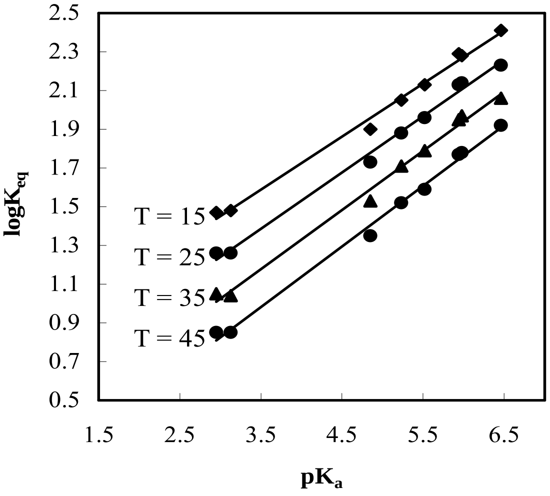

Fig. 2. Plot of log K_{eq} (at different temperatures) for the reaction of OsO_4 with pyridines as a function of the pK_a of the pyridines. Data are taken from Table 1.

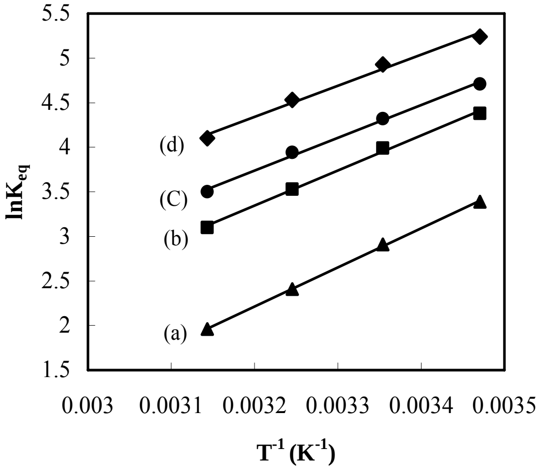

Fig. 3. van't Hoff Plots for complex formation of OsO_4 with (a) 3-chloropyridine, (b) 3-phenylpyridine, (c) pyridine and (d) 4-*tert*-butylpyridine in benzene.

From the data given in Table 2, it is readily obvious that the $OsO_4{\cdot}L$ complexes formed in benzene are enthalpy stabilized but entropy destabilized. It should be noted that, to the best of our knowledge, no published values of Δ*H*° and Δ*S*° for the complexation of OsO_4 with other ligands are available for comparison with the results obtained here.

Table 2. The Thermodynamic Parameter Values $\Delta H°$, $\Delta S°$ and $\Delta G°$ for Complex Formation of OsO_4 with Pyridines in Benzene Solvent

Ligand	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	$\Delta G°^{a}$ (kJ mol^{-1})
Pyridine	-30.5 ± 1.3	-66.6 ± 4.3	-10.7 ± 1.3
4-Picoline	-30.3 ± 1.0	-61.1 ± 3.0	-12.1 ± 1.0
3-Phenylpyridine	-32.7 ± 1.3	-77.0 ± 4.3	-9.8 ± 1.3
3-Picoline	-31.7 ± 1.6	-69.1 ± 5.2	-11.1 ± 1.6
4-*tert*-butylpyridine	-29.0 ± 2.1	-56.9 ± 2.9	-12.0 ± 2.1
3-Chloropyridine	-36.6 ± 0.6	-98.4 ± 1.9	-7.3 ± 0.6
3,4-Dimethylpyridine	-29.0 ± 0.6	-54.5 ± 2.0	-12.8 ± 0.6
Methyl nicotinate	-36.8 ± 0.5	-99.5 ± 1.7	-7.1 ± 0.5

^{a}At 25 °C.

Substituent Effects on the Thermodynamic Parameters

Gas phase studies allow the examination of intrinsic contribution to the thermodynamic functions separately in the absence of solvation effects. Spencer *et al.* have pointed out that the thermodynamic parameters for reactions occurring in a solvating medium also contain contributions from solute-solvent interactions [22]. It is believed that for a certain reaction the enthalpy and entropy changes are composed of intrinsic (ΔH^{i} and ΔS^{i}) and solvation (ΔH^{s} and ΔS^{s}) terms, which can be written as:

$$\Delta H° = \Delta H^{i} + \Delta H^{s} \tag{7}$$

$$\Delta S° = \Delta S^{i} + \Delta S^{s} \tag{8}$$

They have shown that, for reactions of the type considered in this work, ΔH^{i} is related to the strength of the donor-acceptor interaction and will be negative, due to bond formation in all interactions. They also reported that in determining the salvation entropy, the picture based on interaction of dissolved species with solvent is incomplete and any changes that may occur in the surroundings due to the presence of the solute molecule must also be considered. They concluded that "in general, both ΔH^{i} and ΔS^{i} will be negative while ΔH^{s} and ΔS^{s} will be positive [22]. Thus, ΔH^{i} favors complex formation but ΔS^{i} does not. Similarly, ΔS^{s} will favor complex formation while ΔH^{s} is unfavorable". Our results in the present study seem to be consistent with Spencer's studies. In the enthalpy term [Eq. (7)], the second term (ΔH^{s}, for the solvation energy) is probably proportional to the basicity of pyridine ligands.

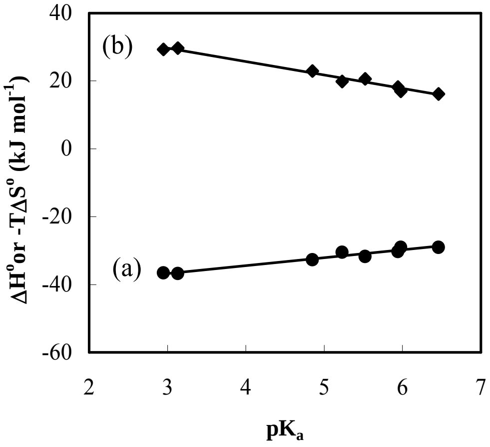

Fig. 4. Correlation between (a) $\Delta H°$ or (b) $-T\Delta S°$ and pK_a. Data are taken from Tables 1 and 2 at 25 °C and fitted to a linear relation.

The $\Delta H°$ values are plotted against pK_a (Fig. 4). The correlation is fully acceptable and shows a good linear dependence of $\Delta H°$ upon pK_a. That is, $\Delta H°$ is controlled by pK_a of the substituted pyridines. Since the electronic donating character of 3,4-dimethylpyridine is higher, its interaction with the solvent is stronger, hence the Δ*H*° value for this ligand is less negative (-29.0 kJ mol^{-1}) than the others (for example, for 3-chloropyridine, Δ*H*° = -36.6 kJ mol^{-1}), although the equilibrium constant is the greatest (K_{eq} = 169.0 and 18.3 l mol^{-1} at 25 °C for 3,4-dimethylpyridine and 3-chloropyridine, respectively). It seems that 3,4-dimethylpyridine is better solvated, because of its larger pK_a, and this factor decreases the overall enthalpy. The Δ*S*° values, which are negative in the association reaction of present study, possibly depend on the basicity of the ligands and vary from -99.5 to -54.5 J K^{-1} mol^{-1} as pK_a of ligand increases from 3.13 (methyl nicotinate) to 6.46 (3,4-dimethylpyridine). The relation between enthalpy change (ΔH^s) and entropy change (ΔS^s) can be qualitatively discussed by solvation.

Figure 5 shows the plot of Δ*H*° values against Δ*S*°. It seems that solvation controls not only Δ*H*° but also Δ*S*° because the absolute value of Δ*H*° (or exothermicity of the reaction) increases as the entropy change decreases. For substituted pyridines having small pK_a, the enthalpy changes of solvation ΔH^s for the reactants and the complex are negligible and the solvent molecules are loosely bounded to the reactants and the complex. Thus, the solvent molecules are not well aligned with the reactants and also with the complex (negligible ΔS^s). On the other hand, when the substituted pyridine has large pK_a, the solvation energy becomes much larger (negative and larger ΔH^s) and the solvent molecules are tightly trapped by the reactants and the complex. Thus, the solvent molecules are well aligned with the reactants and with the complex (negative and large ΔS^s). As a result, absolute magnitudes of Δ*H*° and Δ*S*° values decrease when pK_a values increase. This aspect is shown in Fig. 4 where Δ*H*° and TΔ*S*° are plotted against pK_a values of substituted pyridines. It should be noted that similar behavior for reaction of methyltrioxorhenium (MTO) with N-donor ligands was previously observed by us in organic solutions [18,21].

In Fig. 5, a plot of Δ*H*° *vs.* Δ*S*° (enthalpy-entropy compensation) for the complex formation of OsO_4 with pyridine and its derivatives yields a good straight line. Parallel changes in Δ*H*° and Δ*S*° are often found to occur for a series of reactions involving common or common-type reactants and indicate an evidence for operation of a common structure-activity relationship in the series of complexations [23,24].

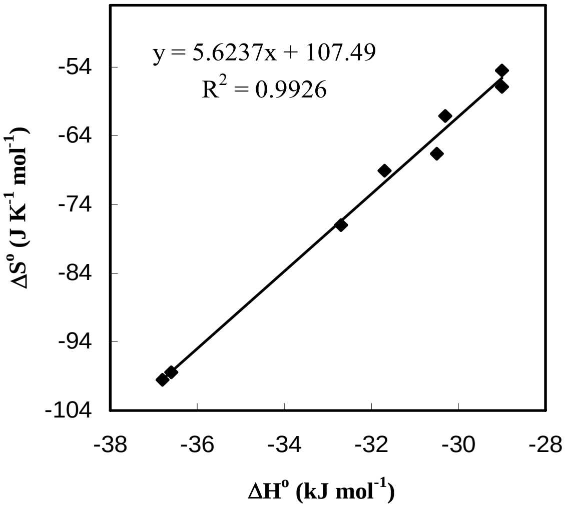

Fig. 5. The enthalpy-entropy compensation plot for complex formation of OsO_4 with pyridine and its derivatives. The data are taken from Table 2.

CONCLUSIONS

Equilibrium constants for reactions in which a series of substituted pyridines react with OsO_4 have been evaluated. The coordination of substituted pyridines to OsO_4 is governed by electronic effects. The values of K_{eq} correlate with the proton basicity of the ligands.

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