Complexation of Osmium Tetroxide with Tertiary Amines

S. F. KOBS and E. J. BEHRMAN*

Department of Biochemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.

(Received August 11, 1986)

Abstract

We report data on the rate of formation of OsO_4 complexes with tetramethylethylenediamine and two phenanthrolines. Buffer and pH effects and energies of activation were studied as well. Data for the stoichiometry of $OsO_4 \cdot L$ complexes and stability constants are reported for these as well as other ligands. ^1H NMR chemical shifts were determined for three OsO_4·pyridine complexes.

Introduction

Osmium tetroxide reacts with alkenes to form cyclic osmate esters. These adducts can be hydrolyzed to the corresponding *cis*-dols [1, 2]. Rates of such reactions are accelerated in the presence of tertiary amines [3]. The mechanism of this rate enhancement has been recently discussed [4]. The reaction may follow the general scheme shown in Fig. 1. The work described here concerns the first reaction in this series, the formation of an $OsO_4 \cdot L$ complex.

Complexes of OsO_4 with tertiary amines (e.g., pyridine [4–7], triethylenediamine [8], hexamethylenetetramine [8–10], pyrazine [8], 3- and 4-picoline [5], isoquinoline [8], quinuclidine [8, 10], pyridazine [8] and 5-methyl pyrimidine [8]) have been characterized by UV–Vis [4, 5], Raman [7, 8] and IR [6–8, 11] spectroscopy, and X-ray crystallography [10]. Single crystal X-ray analysis of OsO_4·quinuclidine and $(OsO_4)_2$·hexamethylenetetramine shows a change in OsO_4 geometry from tetrahedral to trigonal bipyramidal upon coordination to a ligand nitrogen [10]. The osmium–nitrogen bond is unusually long [10]. The aromatic tertiary amines coordinate one OsO_4 per nitrogen atom where sterically allowed. Pyridazine and phthalazine each contain two adjacent nitrogen atoms but coordinate only one OsO_4 molecule for steric or electronic reasons [8]. Hexamethylenetetramine binds two OsO_4 molecules [10] even though it contains four equivalent nitrogen atoms.

No NMR data are available for $Os(VIII)O_4$ adducts nor have the kinetics of complex formation been reported. During studies of imidazole oxidation by OsO_4 we observed that the reaction to form $OsO_4 \cdot L$ is slow enough to be measured by conventional techniques for a number of ligands.

$$OsO_4 + L \rightleftharpoons OsO_4 \cdot L$$

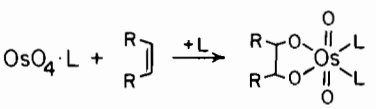

Fig. 1. General reaction scheme for OsO_4 addition to an olefin in the presence of a ligand. R = alkyl side chain, L = tertiary amine ligand.

Experimental

Materials

N,N,N′,N′-tetramethylethylenediamine (TMEN) (Aldrich) was distilled (boiling point (b.p.) 119–121 °C, 760 mm Hg); 4-picoline (4-pic) and pyridine (py) were also obtained from Aldrich and were of analytical grade or better and were used without purification, as were 1,10-phenanthroline, (phen) (Sigma), 2,2′-bipyridine (bipy) and 4,7-diphenyl-1,10-phenanthroline disulfonate (BPDS) (GFS Chemicals). Hexamethylenetetramine (HMT) and triethylenediamine (DABCO) (from Aldrich) were 99% pure and used without purification. OsO_4 (>99.8%) was obtained from Ventron Chemicals and CCl_4 (analytical grade) from Fisher Scientific.

Instrumentation

NMR spectra were obtained on a Varian Model T-60 (60 MHz) instrument; UV and visible spectral determinations were done on either a Cary Model 15 or a Varian DMS 70. The kinetics were run on the Cary 15 with temperature control (±0.1 °C) by means of a circulating water bath (Forma Scientific Model

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

2095) and water-jacketed cell holders. pH determinations were made on a Radiometer Model 26.

Methods

Solutions of OsO_4 were calibrated before each set of determinations using the following $\lambda(\epsilon)$ values: 304 (1202), 297 (1442), 282 (1738), 275 (1733), 250 (3116) for aqueous solutions [12] and 321 (522), 312 (1068), 305 (1541), 298 (1751), 290 (1826) for CCl_4 solutions [13]. Ligand solutions were prepared by dissolving the weighed ligand in buffer and titrating with HCl or NaOH to the desired pH. The pH values of solutions in CCl_4 were not adjusted. Sodium phosphate buffers were used in the pH range 7.8–8.2 and 9.6–11.5, sodium borate buffers in the pH range 8.0–9.6 and sodium carbonate at pH 9.5 and 11.5.

The kinetics were run as follows. An aliquot of the ligand solution in buffer, at the appropriate temperature, was used to blank the spectrophotometer. To begin the reaction, an aliquot of temperature-equilibrated OsO_4 solution was added, the contents of the cuvette rapidly mixed by inversion, and absorbance measurements immediately and continuously recorded. The absorbance at 450 nm was determined because these complexes exhibit a weak maximum around this wavelength. Reactions were monitored until a stable infinity value was obtained. Plots of log $(A_{450,\infty} - A_{450,t})$ *versus* time were linear for at least two half-lives. Slopes of these lines (k_ψ values) were calculated using a linear regression program (Texas Instruments TI-55). Since these reactions were run under pseudo-first order conditions ($[OsO_4]$ limiting), rate = $k_{app}[OsO_4][L]^n = k_\psi[OsO_4]$. Values of n (the order in ligand) were determined by varying n and fitting plots of k_ψ *versus* $[L]^n$ to the best straight line through zero. Rate constants (apparent) were calculated from $k_{app} = k_\psi/[L]^n$, derived from the initial rate expressions (see above).

Activation energies were also determined under pseudo-first order conditions ($[OsO_4]$ limiting). The temperature was increased by 2–5 °C increments over the range 9–36 °C using identical reactant concentrations. Plots of ln k_{app} *versus* $1/T$ (K^{-1}) yielded straight lines with slopes = $-E_a/R$.

Stability constants were determined either in aqueous or organic solvents. In aqueous solution, the ligand was buffered and [L] varied while $[OsO_4]$ was held constant; the solutions were reacted for 60 min at 20 °C by which time A_{450} was constant. In CCl_4 (for the NMR and stoichiometric determinations), [L] was varied and $[OsO_4]$ held constant (to conserve OsO_4). Reaction time was ⩾60 min at 25 °C; A_{450} values were determined at this temperature. The stability constants for aqueous solutions were calculated by using the equations of Rossotti and Rossotti [5, 14]; those for reactions in CCl_4 were derived from mole–ratio plots according to Meyer and Ayers [15].

The NMR determinations were performed as follows. The solution of ligand in CCl_4 was equilibrated at 35 °C in the NMR instrument. An aliquot of OsO_4 in CCl_4 was added, the contents of the tube mixed by inversion, and spectra taken at intervals until, for consecutive spectra, proton chemical shifts were constant. The proton chemical shifts for the complex were recorded relative to a spectrum of the parent compound (also equilibrated at 35 °C) using the equation: $\Delta\delta(Hz) = \delta(Hz)$, complex $- \delta(Hz)$, parent where δ = chemical shift.

The stoichiometry of $OsO_4 \cdot L$ complexation was determined using mole–ratio plots [15]. General conditions were: constant [L], varying $[OsO_4]$, reaction for ⩾60 min at 20 °C (aqueous solution buffered at pH 8.2 with 0.1 M sodium phosphate) or, for solutions in CCl_4, at 25 °C (A_{450} determination) or 35 °C (NMR determination).

Results and Discussion

Although a vast literature exists on the kinetics of formation of metal ion–ligand complexes, corresponding studies for uncharged metal oxide–ligand compounds do not appear to have been made. Table I gives apparent rate constants ($k_{app} = k_\psi/[L]^n$) for the coordination of OsO_4 with TMEN, BPDS and phen. We were unable to determine corresponding data for py, 4-pic and bipy as these rates were too rapid for our techniques.

TABLE I. Kinetics of $OsO_4 \cdot L$ Formation[a]

Ligand	[L] (10^2 M)	Range of $[OsO_4]$ (10^3 M)	Number of runs	k_{app} (M^{-n} min^{-1})[b]
TMEN	1.33 2.66	0.44–1.09	6	467 ± 32
BPDS	1.33	0.56–1.40	4	3.17 ± 0.35
phen	0.75	0.33–0.76	5	8.00 ± 0.19

[a]General conditions: reactions were run in 0.1 M sodium phosphate, pH 8.2, at 20 °C. The reactions with phen were run in the same buffer containing 10% (*v/v*) acetone. [b]n = Order in [L] (TMEN = 2; BPDS, phen = 1); k_{app} is the mean value ± one standard deviation.

A plot of log k_{app} *versus* pH (Fig. 2) shows a linear rate increase with increasing pH values for reactions of TMEN with OsO_4 in both borate and phosphate buffers, but with different slopes. Extrapolation of the line for the reactions in phosphate buffer to pH 9.5 gives a value of 22 000 M^{-2} min^{-1} which approximates values (21 500 and 21 700 M^{-2} min^{-1}) determined at pH 9.5 in 0.1 M sodium carbonate buffer.

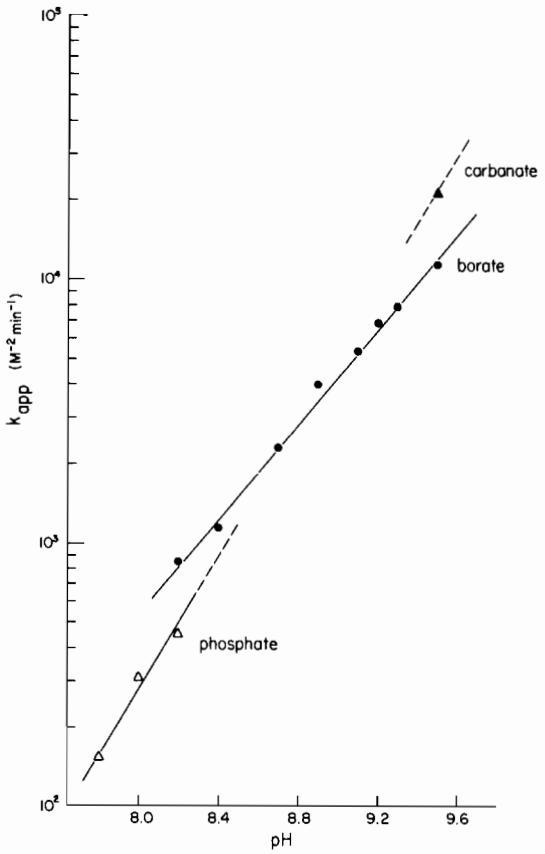

Fig. 2. Effect of pH on TMEN·OsO_4 complex formation. Buffers are the sodium salts, 0.1 M; TMEN stock solutions, buffered to the appropriate pH, were used; T = 20 °C. Each point is the mean of 5–7 determinations at Δ[L], constant and limiting [OsO_4]. The dotted line extrapolates data for reactions in phosphate buffer to that determined in carbonate buffer. ● = borate, ▲ = carbonate, △ = phosphate.

The slope of the line for the reaction of OsO_4 with TMEN in 0.1 M sodium borate is smaller. A plot of log k_{app} *versus* [borate] (Fig. 3) shows an increase in rate with increasing borate concentration, suggesting the formation of a borate·OsO_4 species analogous to the perosmate ion, $OsO_4(OH)_2^{2-}$ [16–18].

The rate of formation of OsO_4·buffer species is too rapid to measure by our techniques. Figure 4 shows a typical kinetic run. We attribute the small, very rapid initial rise in absorbance, A_i (shown in the inset) either to the formation of perosmate [19], or to an OsO_4·buffer complex, or to both. For borate buffers, our kinetic evidence suggests the formation of a borate·OsO_4 species distinct from perosmate. For phosphate and carbonate buffers there is no corresponding kinetic evidence, either in this paper or in ref. 20, for the formation of an OsO_4·buffer complex. Figure 4 also shows that the rapid initial rise in absorbance at 450 nm increases with pH for all three buffer systems. This is qualitatively consistent with the observations of Galbács *et al.* [19] for perosmate or with the formation of OsO_4·buffer species. Quantitative estimates from the data of Galbács *et al.*, however, suggest that the increases in A_{450} which we observe are about ten times larger than those expected for perosmate formation. Spectra of solutions of OsO_4 in 0.1 M sodium carbonate, borate, phosphate and hydroxide

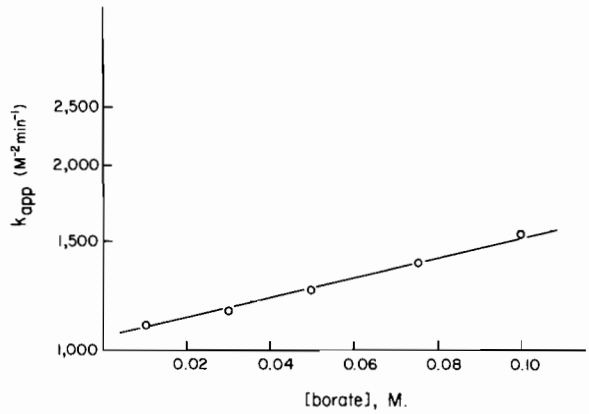

Fig. 3. The effect of [borate] on rate of OsO_4·TMEN complexation. [L] = 1.36–4.77 × 10^{-3} M, [OsO_4] = 1.03–1.22 × 10^{-4} M, pH = 9.5, sodium borate molarity as indicated. T = 20 °C.

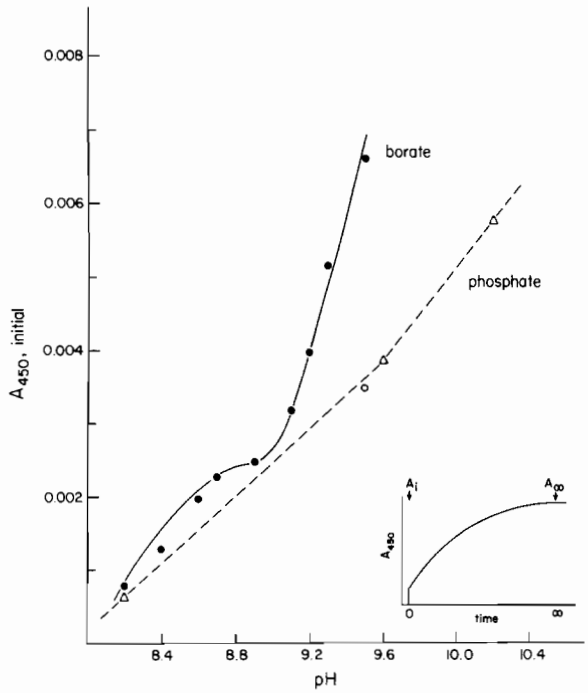

Fig. 4. The effect of pH on A_{450}, initial for OsO_4·TMEN complex formation. [TMEN] = 8.33 × 10^{-3} M, [OsO_4] = 2.6 × 10^{-4} M; all buffers prepared from the sodium salts, 0.1 M; T = 20 °C. ● = borate, ○ = carbonate, △ = phosphate. Inset illustrates a typical kinetic run.

are qualitatively similar in the range 350–650 nm. Thus, for OsO_4·L complex formation in carbonate or phosphate buffers, rate = $k_{app}[OsO_4][L]^n$; for borate, rate = $k_1[OsO_4][L]^n + k_2[OsO_4][B_4O_7^{2-}]^m \cdot [L]^n + k_3[OsO_4][B_4O_7^{2-}]^m$, where L represents the neutral species. A plot of k_{app} *versus* % un-ionized TMEN (Fig. 5) has two linear portions that intersect at a value corresponding to pH 9.0. This is the pK_a of borate, and is close to the pK_2 (9.1) of TMEN [21]. Little variation in k_{app}, as a function of pH, is observed for OsO_4·phen complex formation (k_{app} = 9.66 ± 0.25 M^{-1} min^{-1} in 0.1 M sodium phosphate, pH 7.0; 8.00 ± 0.19 M^{-1} min^{-1} in the same buffer, pH 8.2).

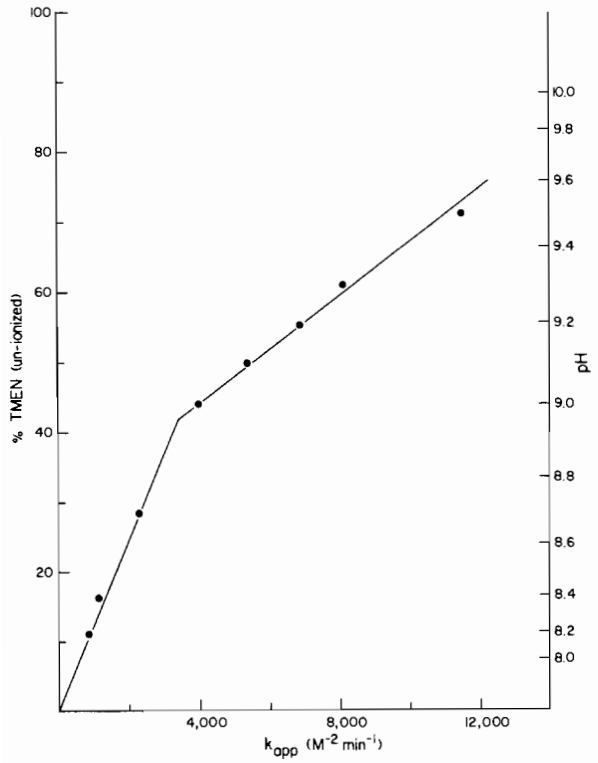

Fig. 5. Observed rate constant for OsO_4·TMEN complex formation as a function of ligand ionization state. Reactions were run under pseudo-first order conditions ([OsO_4] limiting) in 0.1 M sodium borate, pH as indicated, T = 20 °C. TMEN solutions were buffered to the appropriate pH.

The activation energies for coordination are low. E_a for phen (8400 ± 160 cal/mol) is lower than that for BPDS (15 220 ± 300 cal/mol); the sulfonate and/or phenyl groups on BPDS probably impede complexation. Activation energies for OsO_4·TMEN complexation decrease with increasing pH (Fig. 6). The values (cal/mol) are as follows: 3290 ± 70 (0.1 M sodium phosphate, pH 8.2), 2630 ± 40 (0.1 M sodium borate, pH 8.2), 2110 ± 50 (0.1 M sodium borate, pH 9.5) and 1680 ± 130 (0.1 M sodium carbonate, pH 9.5).

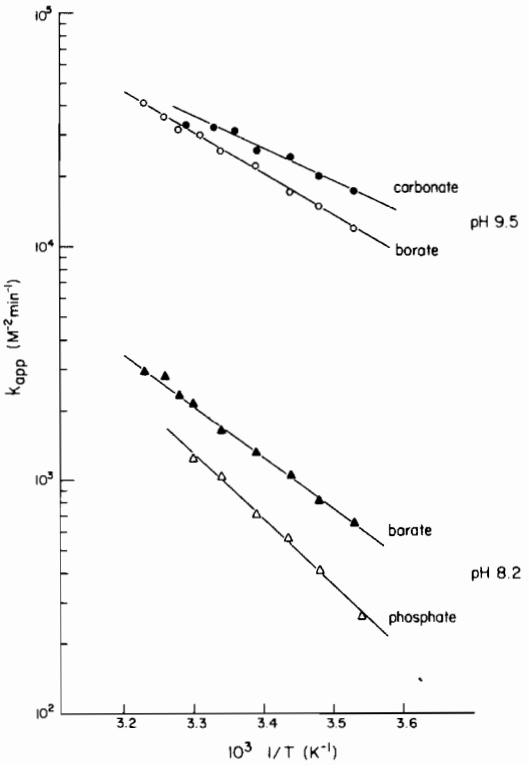

Fig. 6. Activation energies for OsO_4·TMEN complexation as a function of buffer and pH. [buffer] = 0.1 M, all were prepared from the sodium salts. Reactions were run under pseudo-first order conditions ([OsO_4] limiting). ● = carbonate, ○ = borate at pH 9.5; △ = phosphate, ▲ = borate at pH 8.2.

Data for the stoichiometry of complex formation are given in Table II. Aromatic tertiary amines form 1:1 complexes with OsO_4 (one OsO_4/N atom) where sterically allowed. Studies with molecular models indicate that BPDS should bind only one OsO_4. The observed value of 1.4 indicates impurity in the sample, most likely due to incomplete sulfonation during preparation of the disulfonate derivative. The pK_a values for the nitrogen atoms are too low for their ionization to interfere with measurements at pH 8.2. This is not the case with TMEN. That approximately two TMEN molecules are required to produce one molecule of OsO_4·TMEN is further evidence for involvement of a TMEN-mediated proton transfer step to yield a stable complex

$$TMENH^+ + OsO_4 \rightleftharpoons OsO_4 \cdot TMENH^+$$

$$TMENH^+ \overset{TMENH_2^{2+}}{\longrightarrow} OsO_4 \cdot TMEN$$

Table III gives data for stability constants of OsO_4·L complexes. The constants for TMEN in aqueous solution are exceptionally large, and similar

TABLE II. Stoichiometry of OsO_4·L Complexes[a]

Ligand	[L] (10^2 M)	[OsO_4] (10^2 M)	T (°C)	Solvent[b]	L/OsO_4	Method
TMEN	0.10–3.98	0.40	20	aq	2.2	A_{450}
	0.13–1.07	0.51	25	aq	1.8	A_{450}
BPDS	0.10–3.98	0.40	20	aq	1.4	A_{450}
4-pic	21.1	4.25–48.3	35	CCl_4	1.3	NMR
	1.91	0.39–4.4	25	CCl_4	1.2	A_{450}
py	32.7	6.2–61.8	35	CCl_4	1.1	NMR
	2.97	0.56–5.62	25	CCl_4	1.1	A_{450}
bipy	45.4	11–125	35	CCl_4	0.93, 0.63[c]	NMR
	4.12	1.0–11.5	25	CCl_4	0.50	A_{450}

[a]General conditions: reactions in aqueous solution were in 0.1 M sodium phosphate, pH 8.2, using ligand solutions buffered at the same pH. Determination of the stoichiometry of the complex was done by use of mole-ratio plots [15]. [b]aq = Aqueous solution. [c]bipy exhibited upfield proton shifts in the region between binding of one to two OsO_4 molecules, yielding a curve with two inflection points (see Fig. 7 and text).

TABLE III. Stability Constants for OsO_4·L Adducts[a]

Ligand	T (°C)	Solvent[b]	β_1 (M^{-1})[c]	ϵ_{450}	Reference
py	20	aq (pH 8.2)	0.23	148	e
py	23	aq (pH 7.5)	0.27	[d]	5
TMEN	20	aq (pH 8.2)	33.3	68	e
TMEN	20	aq (pH 11.5)	21.0	90	e
BPDS	20	aq (pH 8.2)	18.1	650	e
DABCO	20	aq (pH 8.2)	17.7	450	e
HMT	20	aq (pH 8.2)	2.4	486	e
py	30	CCl_4	12.0	[d]	4
py	20	CCl_4	22.0	[d]	6
py	25	CCl_4	18.0	[d]	e
4-pic	25	CCl_4	32.5	[d]	e
bipy	25	CCl_4	24.5	[d]	e

[a]General conditions: [L] = 0.1–1.4 M, [OsO_4] = $0.26–1.67 \times 10^{-3}$ M; reaction mixtures were allowed to equilibrate for ≥60 min at the temperature given. [b]aq = 0.1 M sodium phosphate, pH as indicated. [c]β_1 values were calculated according to equations given in ref. 5 (aqueous solutions); those in organic solvent were determined from mole–ratio plots according to equations in ref. 15. The estimated error for these determinations: ±5% [5] in aqueous solution, 6% [15] for reactions run in CCl_4. [d]Not determined. [e]This work.

to other OsO_4·L complexes in less polar solvents. The stability decreases approximately 35% when determinations are made at pH 11.5 rather than 8.2 (0.1 M sodium phosphate buffers). This may be due to perosmate ion formation at the higher pH value.

Proton chemical shifts for the py, bipy and 4-pic complexes are given in Table IV. No NMR data for OsO_4·L adducts have been reported in the literature, although chemical shifts for a few similar metal oxide–ligand complexes have been determined [22]. Downfield proton shifts of roughly the same magnitude have been reported for Os(VI)–ligand complexes [5]. OsO_4·bipy shows more complicated behavior than py and 4-pic (Fig. 7). The nature of the unusual upfield shifts (between binding one and two OsO_4 to bipy) may be rationalized by use of molecular models. Bipyridine exhibits almost free rotation around the 2,2′ C–C bond, but when one OsO_4 is bound, this rotation is limited to about 90°. When two OsO_4 molecules are bound to bipy, rotational freedom is eliminated and the rings are locked into approximately a mutually perpendicular configuration. In this position, the OsO_4 coordinated to one of the pyridine rings is held so that the α-hydrogen of the other pyridine ring is directly in the shielding cone of one or more of the Os=O groups. This may apply to some extent as well to the β and γ protons. This mutual shielding is sufficient, evidently, to override the normal deshielding.

Previous work from this laboratory has dealt with the kinetics of formation and stability of oxo-

TABLE IV. NMR Data for OsO_4·L Complexes[a]

Ligand	Δ Chemical shift (Hz)[b]			
	α-H	β-H	γ-H	$-CH_3$
py	+1.5	+10.5	+12.5	–
4-pic	+0.5	+11.0	–	+3.5
bipy	+4.5	+4.0	+2.5	–
	(+3.5)[c]	(+3.0)[c]	(+3.0)[c]	

[a]General conditions: these reactions were run in CCl_4 at 35 °C; [py] = 0.327 M ([OsO_4] = 6.18×10^{-2} to 0.618 M), [4-pic] = 0.211 M ([OsO_4] = 4.25×10^{-2} to 0.483 M) and [bipy] = 0.454 M ([OsO_4] = 0.112 to 1.26 M) in the appropriate reaction mixture. A spectrum of each parent compound was taken (at 35 °C) for reference. The change in chemical shift was calculated as described in 'Experimental'. Tetramethylsilane was used as an internal standard. [b]These are observed values, as corrections for β_1 would be ≤5% (see Table III). [c]This value is calculated for the second inflection point ([OsO_4]/[L] ~ 1.7, see Fig. 7). [d]These values are similar in direction and magnitude for a number of Os(VI) esters [5] and several MoO_5·L complexes [22].

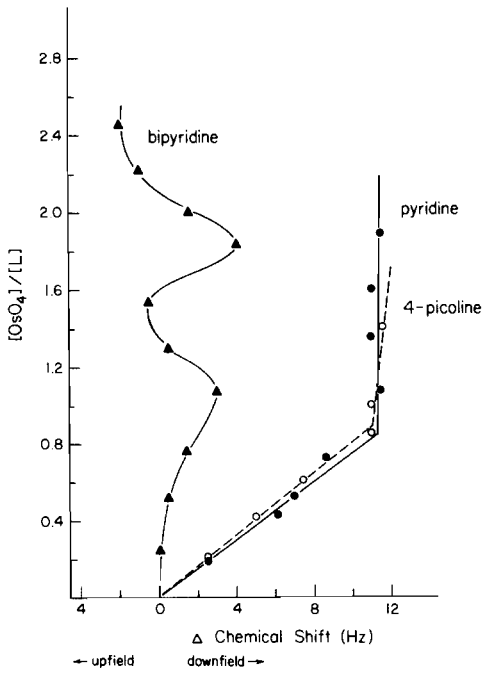

Fig. 7. NMR data for OsO_4·L complexes. Δ Chemical shift values (calculated as described in 'Experimental') are for the β hydrogen atoms of the pyridine rings; solvent is CCl_4, T = 35 °C, TMS internal standard. —●— = py; —▲— = bipy; —○— = 4-pic.

osmium(VI) esters as a function of ligand structure [23]. Our present studies on the corresponding properties of osmium(VIII) ligand species show a rough correlation witht he osmium(VI) data on stability. We see, however, no similar correlation of the kinetic data. Steric factors may well dominate the rates of formation of the Os(VIII)·L species.

References

1 R. Criegee, *Justus Liebigs Ann. Chem., 522,* 75 (1936).
2 M. Schröder, *Chem. Rev., 80,* 187 (1980).
3 R. Criegee, B. Marchand and H. Wannowius, *Justus Liebigs Ann. Chem., 550,* 99 (1942).
4 R. L. Clark and E. J. Behrman, *Inorg. Chem., 14,* 1425 (1975); K. A. Jørgensen and R. Hoffmann, *J. Am. Chem. Soc., 108,* 1867 (1986).
5 L. R. Subbaraman, J. Subbaraman and E. J. Behrman, *Bioinorg. Chem., 1,* 35 (1971).
6 A. B. Nikol'skii and Y. I. D'yachenko, *Russ. J. Inorg. Chem., 19,* 1031 (1974).
7 W. P. Griffith and R. Rossetti, *J. Chem. Soc., Dalton Trans.,* 1449 (1972).
8 M. Cleare, P. C. Hydes, W. P. Griffith and M. J. Wright, *J. Chem. Soc., Dalton Trans.,* 941 (1977).
9 L. Tschugajeff and J. Tschernjajeff, *Z. Anorg. Allg. Chem., 172,* 216 (1928).
10 W. P. Griffith, A. C. Skapski, K. A. Woode and M. J. Wright, *Inorg. Chim. Acta, 31,* L413 (1978).
11 A. J. Nielson and W. P. Griffith, *J. Chem. Soc., Dalton Trans.,* 1084 (1979).
12 A. A. Waldrop, *Ph.D. Dissertation,* The Johns Hopkins University, 1978, p. 27 (University Microfilms #7806279).
13 P. R. Hammond and R. R. Lake, *J. Chem. Soc. A,* 3819 (1971).
14 F. J. Rossotti and H. Rossotti, ' The Determination of Stability Constants', McGraw-Hill, New York, 1961, pp. 270–285.
15 A. S. Meyer and G. H. Ayres, *J. Am. Chem. Soc., 79,* 49 (1957).
16 W. P. Griffith, *J. Chem. Soc.,* 245 (1964).
17 R. K. Panda, G. Neogi and D. Ramaswamy, *Int. J. Chem. Kinet., 13,* 1001 (1981).
18 H. C. Jerviss, W. Levason, M. Tajik, M. Webster and N. P. C. Walker, *J. Chem. Soc., Dalton Trans.,* 199 (1985).
19 Z. M. Galbács, A. Zsednai and L. J. Csányi, *Transition Met. Chem., 8,* 328 (1983).
20 R. L. Clark and E. J. Behrman, *Bioinorg. Chem., 5,* 359 (1976).
21 R. Rometsch, A. Marxer and K. Miescher, *Helv. Chim. Acta, 34,* 1611 (1951).
22 H. Mimoun, I. Seree de Roch and L. Sajus, *Bull. Soc. Chim. Fr.,* 1481 (1969).
23 W. R. Midden, C.-H. Chang, R. L. Clark and E. J. Behrman, *J. Inorg. Biochem., 12,* 93 (1980).