Os(VIII) → Os(III) Reduction by Ligands Containing the Thioamido Group. A Kinetic Study of an Intermediate Step from Osmyl to Osmium(III) Complexes

FRANCO CRISTIANI, FRANCESCO A. DEVILLANOVA*, ANGELO DIAZ and GAETANO VERANI

Istituto di Chimica Generale Inorganica ed Analitica, Via Ospedale 72, 09100 Cagliari, Italy

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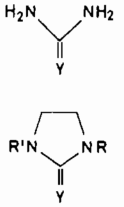
Osmyl complexes with the general formula $OsO_2L'_4(ClO_4)_2$ *(L' = N,N'-dimethylimidazolidine-2-thione and N,N'-diethylimidazolidine-2-thione) have been prepared by reacting* OsO_4 *with the ligand in acidified* ($HClO_4$) $H_2O/EtOH$ *(1:1 vol.) solutions. The reaction between these complexes and some ligands (HL) containing the –NH–CS– group (thiourea, imidazolidine-2-thione, N-methyl-imidazolidine-2-thione and N-ethyl-imidazolidine-2-thione) has been kinetically investigated. The osmyl compounds undergo reduction to Os(III), giving* $Os(HL)_6(ClO_4)_3$ *complexes. Three kinetic equations fit the experimental* k_{obs}*'s; however, the main process which involves one molecule of substrate, one of ligand and one of perchloric acid, is present in all the equations. The specific rate constants of this process are very close to those found in the* OsO_4 *reduction by HL carried out in the same conditions. This fact proves that the Os(VIII) → Os(III) reduction by HL occurs through an osmyl intermediate and that the rate-determining step regards the Os(VI) → Os(III) reduction.*

Introduction

The OsO_4 reduction in acidified $H_2O/EtOH$ (1:1 vol.) has been investigated recently [1–4] by using as reducing–complexing agents several ligands having the thio- or seleno-urea moiety, namely

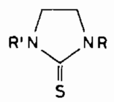


R'	R	Y = S	Y = Se
–	–	tu	su
H	H	dit	dise
H	Me	ditme	diseme
H	Et	ditet	diset

In all cases, the reduction occurs as follows:

$$2OsO_4 + 22HL + 6H^+ \rightarrow 2[Os(HL)_6]^{3+} + 5L_2 + 8H_2O \quad (1)$$

where HL is the ligand and L_2 its oxidation product, *i.e.* the disulphide or diselenide. Since this stoichiometry is complicated, reaction (1) must take place through several elemental processes; however, with the above-mentioned ligands we have isolated only the final osmium(III) complexes. On the other hand, it is well-known that the substitution of all the NH hydrogens with alkyl groups lowers the reducing power of Y; in fact, by reacting these ligands with copper(II) halides, only copper(I) complexes are obtained [5–7], whereas the reduction by the following disubstituted imidazolidines



R'	R	
Me	Me	diditme
Et	Et	diditet

is slow enough to obtain both copper(II) [8] and copper(I) [9] complexes.

With this in view, we have used diditme and diditet as reducing agents towards OsO_4 and, as expected, the reaction runs more slowly and a new complex containing the osmyl group $[OsO_2L'_4]^{2+}$ (L' = diditme or diditet) was obtained. By leaving this in the reaction medium, further reduction of osmium takes place in a very slow process. This fact suggests that the formation of the osmyl complex occurs also with HL ligands, and if so equation (1) may be written as a sum of the two following reactions:

$$OsO_4 + 6HL + 2H^+ \rightarrow [OsO_2(HL)_4]^{2+} + L_2 + 2H_2O \quad (2)$$

$$2[OsO_2(HL)_4]^{2+} + 10HL + 2H^+ \rightarrow 2[Os(HL)_6]^{3+} + 3L_2 + 4H_2O \quad (3)$$

In view of this, the main rate-determining step (which involves one molecule of substrate, one of perchloric acid and one of ligand), found for reaction (1) might be attributed either to the Os(VIII) →

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*Author to whom correspondence should be addressed.

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TABLE I. Some Important IR Bands in the 4000–200 cm^{-1} Range (Solid State).

	νCN	νCS	ν_{asym} OsO$_2$	ClO_4^-			
				ν_1	ν_2	ν_3	ν_4
diditme[a]	1505vs	508vs					
$[OsO_2(diditme)_4](ClO_4)_2$	1597vs	508ms	844vs neat	940w		1152vs	635s
	1577vs	487w				1115vs[b]	627s
						1085vs	623s
diditet[a]	1500vs	512ms					
$[OsO_2(diditet)_4](ClO_4)_2$	1583vs	512w	844vs neat	939w		1140s	636s
	1555vs	487w				1109vs[b]	625vs
						1087vs	

[a] Assignments according to ref. 12. [b] The bands at 1110vs cm^{-1} and 1121m cm^{-1}, present in the spectra of the free diditme and diditet respectively, contribute to these absorptions.

Os(VI) (Eqn. (2)) or to the Os(VI) → Os(III) (Eqn. (3)) reductions.

In order to ascertain this, we have studied the Os(VI) → Os(III) kinetics by using the osmyl complex of diditet (or diditme) as substrate and ligands having the NH group as reducing agent.

In this paper we report the study of the following reaction

$$2[OsO_2L'_4]^{2+} + 18HL + 2H^+ \rightarrow 2[Os(HL)_6]^{3+} + 8L' + 3L_2 + 4H_2O \qquad (4)$$

where HL is a ligand containing the NH group (tu, dit, ditme or ditet), whereas L′ is an N,N′-disubstituted imidazolidine (diditme or diditet).

Results and Discussion

$[OsO_2L'_4](ClO_4)_2$ and $[Os(HL)_6](ClO_4)_3$ Complexes

The details of the preparation of the osmyl complexes $[OsO_2L'_4](ClO_4)_2$ (L′ = diditme, diditet) together with the elemental analyses are reported in the Experimental Section. In Table I, some important i.r. bands of these complexes are compared with those of the free ligands. The shifts of νCN and νCS agree with the S-coordination to osmium, as already found for complexes of these ligands with other metals [8–11].

Among the four normal modes of vibration of the tetrahedral ClO_4^- ion, only ν_3 and ν_4 are infrared active. In our case, the presence of a weak band attributed to ν_1 and the splitting of the ν_3 and ν_4 bands indicate a lowering of the symmetry of the tetrahedral ion; however, the distortion of ClO_4^- is probably due to the crystal packing [3] and not to its coordination to metal.

The most significant i.r. band of the osmyl complexes is a neat strong band falling at 844 cm^{-1}, due to the antisymmetric stretching of the O=Os=O group.

By reacting the osmyl complexes of diditme or diditet with ligands containing the –NH–CS– group, Os(VI) is reduced to Os(III) giving the $[Os(HL)_6]^{3+}$ complexes, *i.e.* the HL ligands completely substitute the diditet (or diditme) in the coordination sphere, as proved by the elemental analyses and the infrared spectra of the final osmium complexes. In addition, the end product is also identified by its u.v. spectrum, recorded on the kinetic solution. In fact, by starting with either $[OsO_2(diditme)_4]^{2+}$, $[OsO_2(diditet)_4]^{2+}$ or OsO_4 we obtain the same final product.

Kinetic Results

The kinetic experiments were performed in H_2O/EtOH (1:1 vol.) by reacting the osmyl complex with a large excess of the ligand (tu, dit, ditme or ditet) and of perchloric acid, in order to assure pseudo-order conditions with respect to the substrate. The ionic strength was kept constant by means of sodium perchlorate. The kinetics were followed spectrophotometrically by recording the increase of the absorbance due to the product formation until a constant value (A_∞) was reached.

The plots ln ($A_\infty - A_t$) *versus* time are straight lines, whose slopes are the k_{obs}'s.

The pseudo-first order rate constants, obtained for each ligand (at different concentration ranging from 10^{-2} to 4×10^{-2} *M*) in presence of $HClO_4$ (0.60, 0.73, 0.87 and 1.00 *M*) at different temperatures (24, 30, 37 and 44 °C) using $[OsO_2(diditet)_4]^{2+}$

TABLE II. k_1 Specific Rates and Activation Parameters for the Reduction of Osmyl Complexes. In parentheses the corresponding values[a] for the same elementary process in the OsO_4 reduction are reported.

t (°C)	10^2 k_1 (mol^{-2} l^2 sec^{-1}) tu	dit	ditme	ditet
24	13.3 ± 0.3	2.34 ± 0.03	2.13 ± 0.06	2.00 ± 0.03
	(14.1)	(2.95)	(1.75)	(2.19)
30	19.3 ± 0.5	3.52 ± 0.08	2.99 ± 0.08	2.79 ± 0.04
	(23.0)	(4.35)	(2.61)	(3.22)
37	30.6 ± 0.6	6.00 ± 0.04	4.21 ± 0.09	4.05 ± 0.06
	(35.4)	(6.49)	(4.23)	(4.77)
44	43.0 ± 0.8	9.15 ± 0.12	5.70 ± 0.07	5.50 ± 0.08
	(57.4)	(9.99)	(6.58)	(7.02)
$\Delta H^{\ddagger}$	10.5 ± 0.3	12.3 ± 0.2	8.6 ± 0.3	8.9 ± 0.2
(Kcal/mol)	(12.5 ± 0.3)	(10.8 ± 0.1)	(11.8 ± 0.1)	(10.3 ± 0.2)
$-\Delta S^{\ddagger}$	27.1 ± 0.9	24.5 ± 0.7	37.2 ± 0.9	36.3 ± 0.6
(cal/(mol K))	(20.2 ± 1.1)	(29.2 ± 0.5)	(26.8 ± 0.3)	(31.5 ± 0.5)
r[b]	0.999	0.999	0.999	0.999

[a] The values at 24 and 44 °C are obtained from refs. 2 and 3 by linear interpolation of ln k_1 *versus* 1/T. [b] Correlation coefficient of the Eyring plots.

TABLE III. k_2 Specific Rates and Activation Parameters for the Reduction of Osmyl Complexes and Osmium Tetroxide with thiourea. k_3 and $[HL]_o$ for the osmyl reduction with ditme and ditet.

t (°C)	tu 10^3 k_2 (mol^{-1} l sec^{-1}) $[OsO_2(diditet)_4]^{2+}$	OsO_4	ditme k_3 (sec^{-1})	$[HL]_o$	ditet k_3 (sec^{-1})	$[HL]_o$
24	0.74 ± 0.08	0.86[a]				
30	1.34 ± 0.14	1.52				
37	2.68 ± 0.16	3.07				
44	7.33 ± 0.21	5.81[a]	3.8×10^{-4}	3.9×10^{-3}	2.3×10^{-4}	1.4×10^{-3}
$\Delta H^{\ddagger}$ (Kcal/mol)	20.6 ± 1.2	17.3 ± 0.5				
$\Delta H^{\ddagger}$ (cal/(mol K))	3.7 ± 3.8	14.4 ± 1.6				
r[b]	0.993	1.000				

[a] These values are obtained from ref. 2 by linear interpolation of ln k_2 *versus* 1/T. [b] Correlation coefficient of the Eyring plots.

as substrate* are available from the Editor (Tables A–D).

Although the ligands have the same thiourea moiety, they show different kinetic behaviours. In fact, we have found the following kinetic equations:

$$k_{obs} = (k_1[HL] + k_2)[HClO_4] \tag{5}$$

$$k_{obs} = k_1[HL][HClO_4] \tag{6}$$

$$k_{obs} = k_1[HClO_4]([HL] - [HL]_o) + k_3 \tag{7}$$

which fit the experimental data. Equation (5) is in good agreement with the data obtained for the thiourea; (6) is valid for dit at all temperatures investigated and for ditme and ditet only at 24, 30 and 37 °C. At 44 °C ditme and ditet obey equation (7).

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*Several kinetic experiments carried out on $[OsO_2(diditme)_4]^{2+}$ in the same conditions used for $[OsO_2(diditet)_4]^{2+}$ gave identical k_{obs}'s.

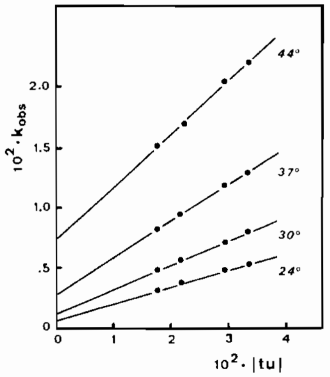


Fig. 1. Plots of k_{obs} *versus* the thiourea concentration at the reported temperatures (H_2O/EtOH 1:1 vol., [$HClO_4$] = 1.00, μ = 1.00).

A typical plot of the k_{obs}'s against the thiourea concentrations is reported in Fig. 1. These lines have positive intercepts whereas the straight lines k_{obs}/[$HClO_4$] cross the origin. Therefore, by using thiourea the Os(VI) → Os(III) reduction obeys the same kinetic law found for the reduction of osmium tetroxide in analogous conditions [2], *i.e.* there are two acid-dependent processes, one of which involves a ligand molecule. The k_1 and k_2 values are reported in Tables II and III respectively.

Equation (6) differs from equation (5) in that the k_2 term is missing. The k_{obs}'s against both [$HClO_4$] and [HL] are straight lines crossing the origin; therefore there is only one kineticallly-determining step in the reduction process. This behaviour (which has already been seen in the OsO_4 reduction with dit, ditme and ditet [3]) is present here in the case of dit at all temperatures investigated and ditme and ditet at 24, 30 and 37 °C.

At 44 °C ditme and ditet follow equation (7), as shown in Fig. 2 for ditme. k_{obs}/[$HClO_4$] are straight lines tending to one positive intercept, which is k_3; the k_{obs}/[HL] plots are also linear and intersect at a point of ($[HL]_o$, k_3) coordinates (for the k_3 and $[HL]_o$ values see Table III).

Clearly, k_3 represent a unimolecular process, which becomes kinetically important as the temperature increases. On the other hand, it is difficult to understand the inhibition role of $[HL]_o$.

We tried to enlarge the temperature range, but the non-optimal experimental conditions for an H_2O/EtOH mixture make these experiments unreliable.

The k_1 specific rate constants for the process dependent on acid and ligand concentrations are collected in Table II, together with the corresponding k_1 values of the same elementary process of the OsO_4 reduction.

The k_1 values obtained in the reductions of both OsO_4 and $[OsO_2(diditet)_4]^{2+}$ are very close, a fact which is not surprising since we were practically observing the kinetics of equation (3). In fact, as soon as the osmyl complex is added to the kinetic solution containing an excess of the ligand, an immediate substitution of L′ with HL occurs, as proved by the identical k_{obs} obtained from both $[OsO_2(diditet)_4]^{2+}$ and $[OsO_2(diditme)_4]^{2+}$. This is also confirmed by the closeness of the k_2 values of the reactions carried out with thiourea (see Table III). On the other hand, as said above, the final complex is always the same whether we start with OsO_4, $[OsO_2(diditme)_4]^{2+}$ or $[OsO_2(diditet)_4]^{2+}$.

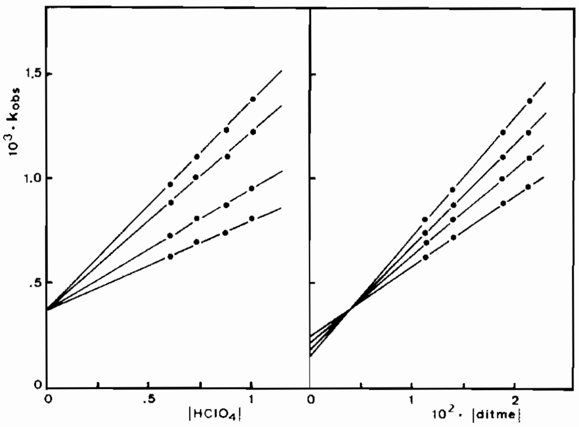
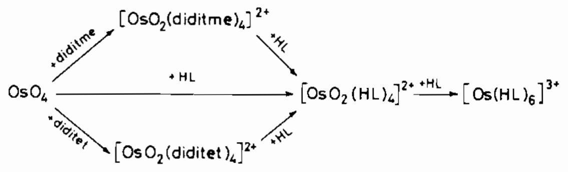


Fig. 2. Reaction between $[OsO_2(diditet)_4]^{2+}$ and N-methylimidazolidine-2-thione. Plots of k_{obs} *versus* [$HClO_4$] ([ditme] × 10^2 = 1.13, 1.38, 1.88, 2.13) and [ditme] ([$HClO_4$] = 0.60, 0.73, 0.87, 1.00).

The following scheme summarizes the reaction pathways:



where HL = tu, dit, ditme and ditet.

It is difficult to suggest a mechanism which can completely explain equations (5)–(7); however, their common process, characterized by k_1, might be interpreted according to the following idea. Since a trimolecular process is not probable, the rate determining step should involve an intermediate originating from an equilibrium reaction. From this point of view, it is possible to write several reactions in agreement with the kinetic equations. Two of them, *i.e.* a protonation of osmyl complex to give a hydroxo intermediate (I).

$$[OsO_2(HL)_4]^{2+} + H^+ \rightleftarrows [OsO(OH)(HL)_4]^{3+} \qquad (8)$$

or of the ligand

$$HL + H^+ \rightleftarrows H_2L^+ \qquad (9)$$

seem fairly realistic. Hence, the attack of HL on the hydroxo species (I) or of H_2L^+ on the osmyl complex would justify the trimolecular process. Here, k_1 of equations (5)–(7) should be the product of a specific rate and the equilibrium constant of equation (8) or (9) respectively.

As far as k_2 of equation (5) is concerned, this process does not involve any ligand molecule and it should be seen as a leaving of OH^- from the intermediate (I), promoted by the hydrogen bondings between OH and NH_2 groups of the bonded thiourea. This process is present only in the reaction with thiourea, which is not sterically hindered and which has two NH_2 groups more basic than the NH of the imidazolidines.

Experimental

Osmium Complexes

The osmyl complexes of the N,N′-disubstituted imidazolidine-2-thiones are prepared by reacting OsO_4 with the ligand (1:12 molar ratio) in absolute ethanol in presence of perchloric acid (~2 *M*). From the solution, kept at *ca.* 40 °C for 2 hours, ochreous crystals precipitate; the products are recrystallized from absolute ethanol/ethyl ether mixtures.

Anal. $[OsO_2(diditme)_4](ClO_4)_2$: Calcd. for $C_{20}H_{40}Cl_2N_8O_{10}OsS_4$: C 25.5, H 4.3, N 11.9; Found: C 25.6, H 4.3, N 11.8.

Anal. $[OsO_2(diditet)_4](ClO_4)_2$: Calcd. for $C_{28}H_{56}Cl_2N_8O_{10}OsS_4$: C 31.9, H 5.35, N 10.6, Found: C 32.2, H 5.4, N 10.6.

The osmium(III) complexes, obtained by reacting the osmyl compounds with HL ligands, have formulae $[Os(HL)_6](ClO_4)_3$. The elemental analyses and the infrared spectra are omitted here since they have been previously reported [2, 3].

Kinetic Measurements

To a pre-thermostatted H_2O/EtOH (1:1 vol.) solution of ligand, $HClO_4$ and $NaClO_4$ (added to maintain the ionic strength μ = 1.000 constant) a proper amount of the solid $[OsO_2L'_4](ClO_4)_2$ was added directly in the measurement cell. The ligand and $HClO_4$ concentrations were always chosen to assure pseudo-first order conditions.

The increase of the absorbance was recorded in 'time-drive' mode at the maximum wavelength of the final complex until a constant value was reached (λ_{max} = 481 nm for tu, 522 nm for dit, 530 nm for ditme and 525 nm for ditet).

Data Processing

The pseudo-first order rate constants were obtained from the slopes of the plots $\ln(A_\infty - A_t)$ *versus* time using the least squares method. In all cases in which the straight lines $k_{obs}/[HL]$ or $k_{obs}/[HClO_4]$ pass through the origin, coordinates (0, 0) have been introduced as an experimental point in the calculation.

Each k_{obs} value has been obtained by a unique kinetic experiment; in some cases, it was necessary to repeat the measurement and k_{obs} was calculated as an averaged value.

Acknowledgement

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