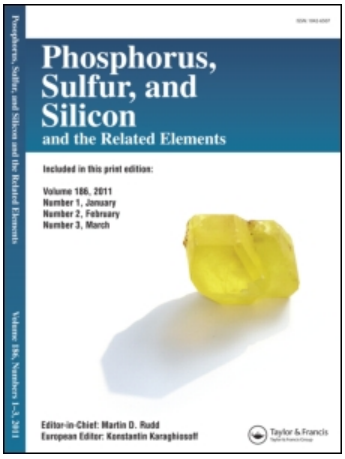

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THIO- AND SELENO-AMIDO GROUPS AS REDUCING AGENTS TOWARDS OsO_4. A KINETIC STUDY WITH SOME IMIDAZOLIDINE-2-SELONES†

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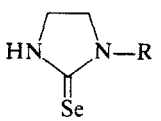
OsO_4 reacts with imidazolidine-2-selone and its *N*-methyl and *N*-ethyl-substituted derivatives in H_2O/EtOH (1:1 vol) in presence of perchloric acid to give $[OsL_6]^{3+}$. The infrared spectroscopy shows that the imidazolidines bind the metal ion through the selenium in the same way as the imidazolidine-2-thiones use the thioketonic sulfur. By spectrophotometric measurements, the formation of $[OsL_6)^{3+}$ has been followed in time, recording the increase of absorbance at the wavelengths of the maxima of absorption of the complex. The *pseudo*-first order rate constants are linear both with respect to the acid and the ligand concentrations, indicating that the rate determining step involves one proton and one molecule of the ligand. The reaction has also been followed with selenourea only at 6°C. The activation parameters for the sulfur and selenium compounds have been comparatively discussed.

INTRODUCTION

The kinetics of OsO_4 reduction in acidified media by thioureas and some ethylenethioureas have been recently investigated.[1-3] In all the cases studied, osmium (VIII) undergoes a reduction to Os(III) giving the $[Os(HL)_6]^{3+}$ complex according to the following reaction:

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

where HL is the ligand and L_2 indicates the product of the ligand oxidation, i.e. the disulfide. The kinetic experiments were carried out in presence of perchloric acid in H_2O/EtOH (1:1 vol) and for thiourea also in water. Now, this investigation has been extended to some parent selenium compounds, i.e.



R	
H	dise
Me	diseme
Et	diset

and selenourea (su), with the aim of comparing the reducing abilities of the selenium compounds with those of sulfur. On the other hand, the substitution of the sulfur with the more nucleophilic selenium atom affects the reaction rate and, sometimes, produces a change in the mechanism, as observed for example in the acid dependent decomposition of some dithio- and diselenocarbamates.[4-7]

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RESULTS AND DISCUSSION

As found for thiourea and imidazolidine-2-thiones, the aforementioned selonic ligands react with OsO_4 in H_2O/EtOH (1:1 vol) in presence of $HClO_4$ to give octahedral complexes of Os(III) in which the metal is surrounded by six molecules of ligands. The elemental analysis of the complexes are reported in the experimental section.

The coordinating bond occurs through the selenium atom as shown by the displacements of the i.r. significant bands of the complexes with respect to those of the free ligand (Table I). The shifts of ν(NH) and Δ(NH) exclude nitrogen as coordinating atom since in this case[8] larger downward shifts would be expected. On the other hand, the bands attributed to ν(CN) + δ(NH) undergo shifts towards higher frequencies, indicating an increase of the π-bond order on C⋯N, in agreement with a Se—metal bond. This coordination is also confirmed by the shifts of the bands arising from the >C=Se vibrations.

In the infrared spectra of the complexes, the presence of a peak at ~940 cm^{-1}, due to the ν_1 of the ClO_4^- ion, indicates a lowering of its tetrahedral symmetry caused by a distortion occuring in the crystal lattice. The symmetry lowering of perchlorate ion is also visible in the splittings of the ν_3 and ν_4 bands. This is very clear in the i.r. spectrum of the selenourea complex, where ν_1 is present as a medium peak at 938 cm^{-1}, and ν_3 and ν_4 are splitted in three well-defined bands (1142 vs, 1112 vs and 1088 vs for ν_3 and 636 s, 629 s and 625 s for ν_4).

In the visible spectrum, all the complexes show broad absorptions at around 600 nm, which are shifted towards higher wavelengths with respect to the corresponding sulphur compounds of *ca.* 100 nm; this well agrees with the major polarizability of the selenium atom. Due to the presence of these typical absorptions of the Os(III) complexes, we have been able to follow their formation kinetically.

The kinetic measurements have been performed in H_2O/EtOH (1:1 vol) in large excess of perchloric acid and ligand concentrations in order to assure the *pseudo*-order conditions with respect to osmium, buffering the solutions at ionic strength $\mu = 1.000$ by means of sodium perchlorate. The kinetics have been followed in time-drive by recording the absorbance increases in time until a constant value (A_∞) was obtained; the plots of ln ($A_\infty - A_t$) *versus* time are straight lines, whose slopes are the *pseudo*-order constants (k_{obs}).

The k_{obs}'s obtained at four temperatures and different acid and ligand concentrations are collected in Figures 1, 2 and 3 for dise, diseme and diset respectively.[9] The linearity of the k_{obs}'s with the ligand concentrations indicates that the reaction is of first-order with respect to the ligand.

Their slopes i.e. $k_{obs}/|L|$, plotted against the perchloric acid concentrations (see Table II), are still straight lines which pass through the origin; thus the reaction is of first order also with respect to the acid. Therefore, the rate determining step involves one molecule of osmium tetroxide, one of ligand and one of acid in accordance with the rate equation

$$v = k_{obs}[OsO_4] = k\,[L]\,[HClO_4]\,[OsO_4] \qquad (1)$$

This equation is the same as that found for the analogous reaction with imidazolidine-2-thiones.[3]

As far as regards the selenourea, the reaction is very fast and only measurements at low acid and ligand concentrations (in *pseudo*-order conditions) at 6°C have been carried out. Also in this case, the k_{obs}'s are straight lines with respect both to the ligand and to the acid concentrations and pass through the origin.

TABLE I

The most important IR bands in the 4000–200 cm^{-1} range (solid state)

Vibrations	dise	$[Os(dise)_6](ClO_4)_3$	diseme	$[Os(diseme)_6](ClO_4)_3$	diset	$[Os(diset)_6](ClO_4)_3$
ν(NH)	3250 vs	3310 m–3100 ms	3275 sh–3180 vs	3330 s	3260 sh–3190 vs	3340 vs
ν(CN) + δ(NH)	1515 vs–1500 vs	1539 vs–1524 vs	1528 vs–1501 vs	1550 vs–1505 vs	1509 s–1495 vs	1540 vs–1502 vs
ν(CSe)	357 s	340 m	580 ms–417 mw	525 sbr–402 vw	587 ms–450 mw	530 mbr–490 sh
Δ(NH)	668 s–588 vs	680 mbr–470 mbr	660 m	525 sbr–495 sh	680 mbr	
ClO_4^- ν_1	—	938 vw	—	940 sh	—	938 w
ClO_4^- ν_2	—	—	—	—	—	—
ClO_4^- ν_3	—	1122 vs neat–1008 s–1089 s	—	1090 vsbr	—	1122 neat–1090 vsbr
ClO_4^- ν_4	—	637 m–629 m–626 m	—	635 m–623 s	—	636 m–623 vs

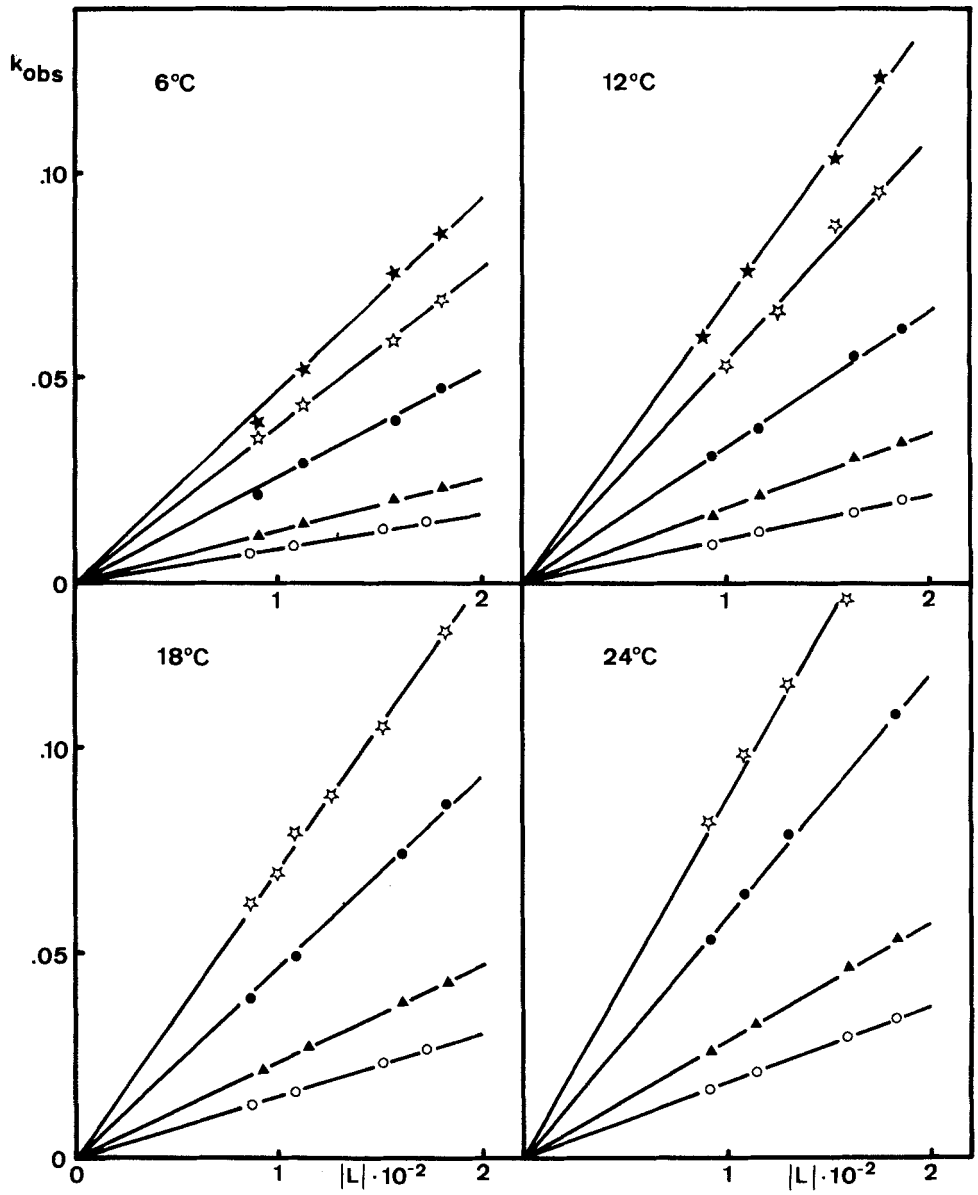

FIGURE 1 Plots of k_{obs}'s against the imidazolidine-2-selone concentrations at various temperatures and different acid concentrations ([$HClO_4$] = ○.137, ▲.212, ●.380, ☆.550, ★.700M; H_2O/EtOH 1:1 vol; μ = 1.000)

Hence the selenourea behaves differently from thiourea (tu)[2] since for this compound the rate equation was

$$v = (k_1[tu] + k_2)\,[HClO_4]\,[OsO_4] \qquad (2)$$

The Eq. (2) differs from (1) for the presence of a process which is non-dependent on the thiourea concentration. This should be explained by comparing the relative

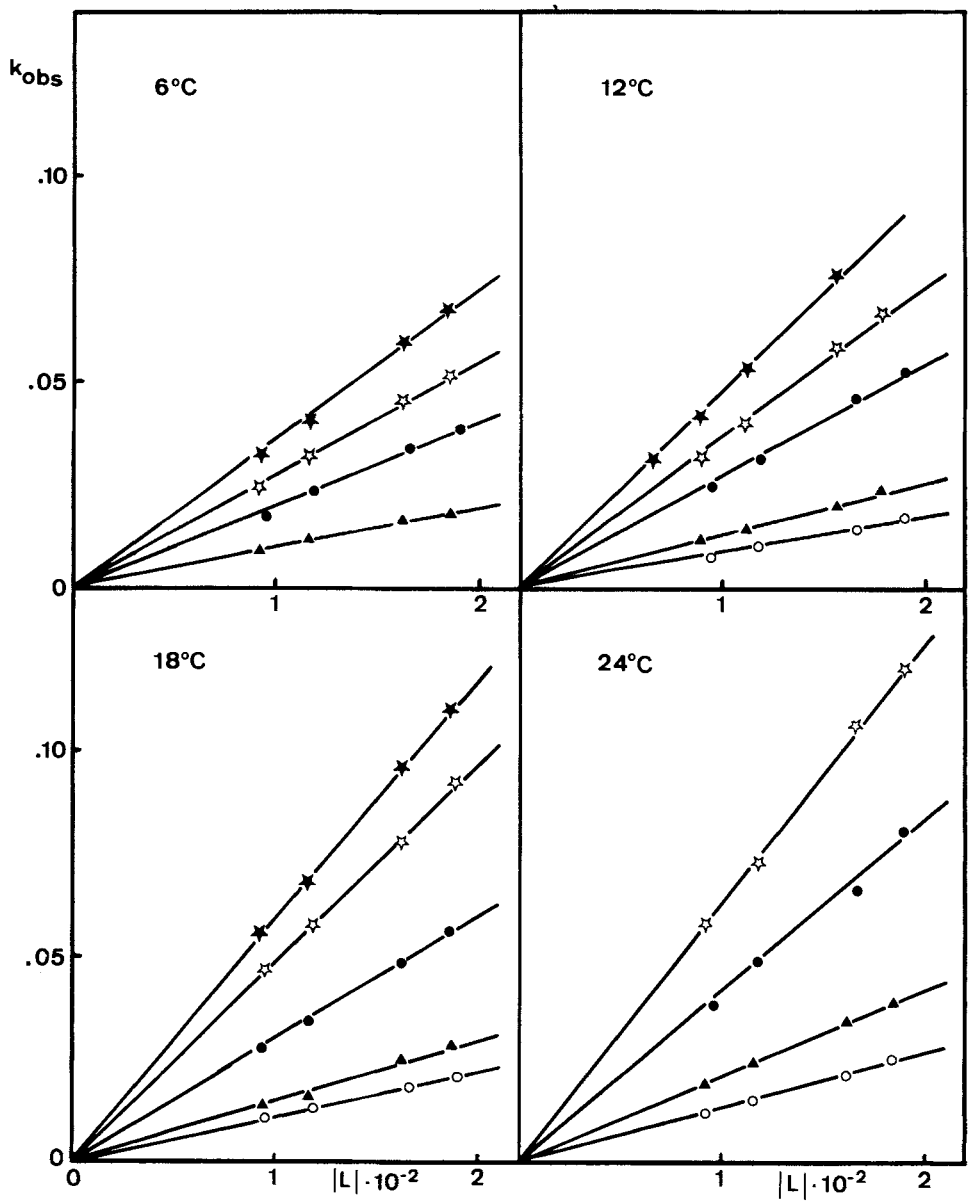

FIGURE 2 Plots of k_{obs}'s against the *N*-methyl-imidazolidine-2-selone concentrations at various temperatures and different acid concentrations ([$HClO_4$] = O.137, ▲.212, ●.380, ☆.550, ★.700M; H_2O/EtOH 1:1 vol; μ = 1.000)

specific rates for the same process, which are 20.6 ± 2 and 3.4 10^{-2} (l^2 mol^{-2} sec^{-1}) for selenourea and thiourea[10] respectively. Clearly the very high value of k_1 for su makes the term k_2 of Eq. (2) negligible.

The specific rate constants at 20°C and the activation parameters for the OsO_4 reduction both with the imidazolidine-2-thiones and 2-selones are reported in Table III. The OsO_4 reduction with the selenium compounds is *ca.* 600 times faster than

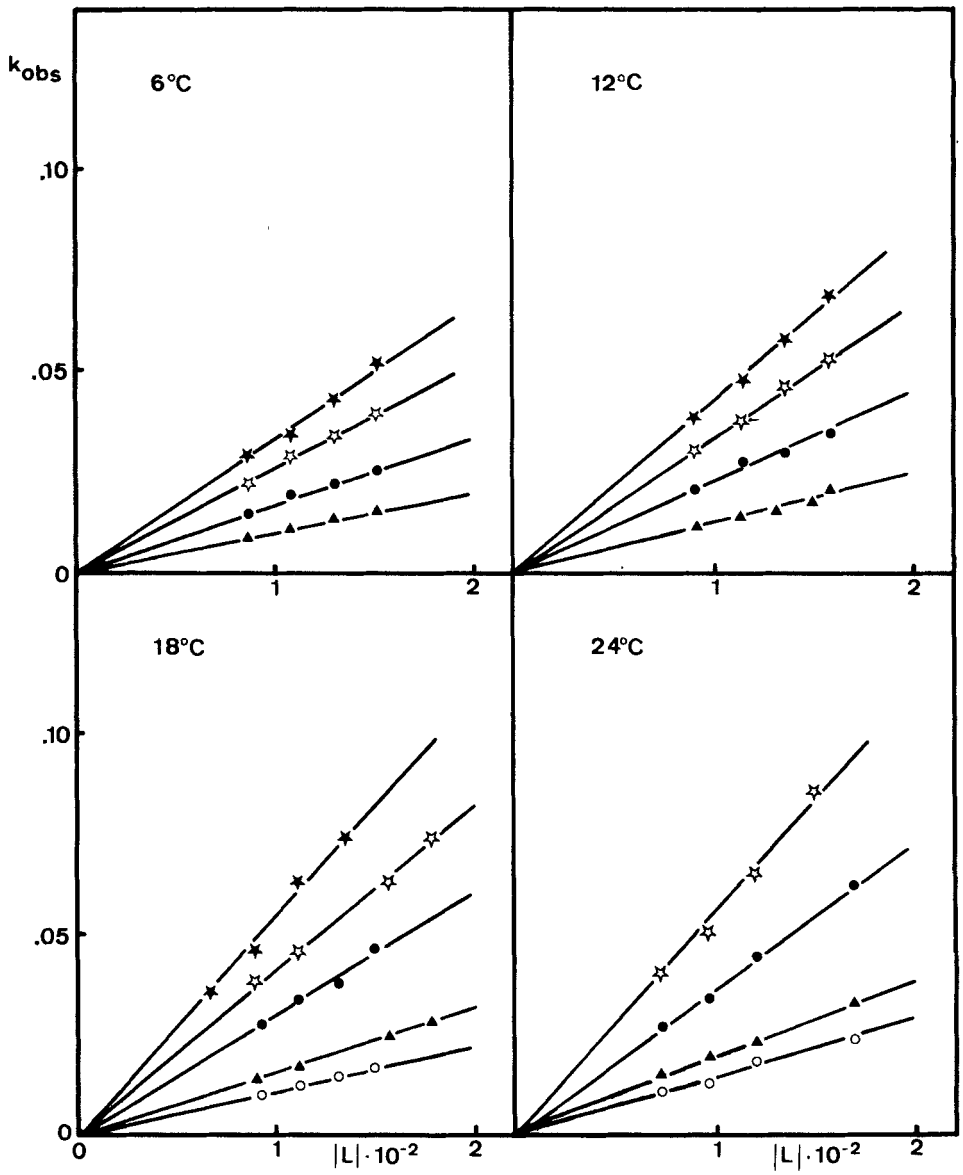

FIGURE 3 Plots of k_{obs}'s against the *N*-ethyl-imidazolidine-2-selone concentrations at various temperatures and different acid concentrations ([$HClO_4$] = ○.137, ▲.212, ●.380, ☆.550, ★.700M; H_2O/EtOH 1:1 vol; μ = 1.000)

that with the corresponding sulfur ones, in agreement with the higher nucleophilic properties of selenium with respect to sulfur. In fact this difference is due to the much lower values of $\Delta H^{\neq}$ for the selenium derivatives, while the $\Delta S^{\neq}$ values are similar for the corresponding compounds of the two series, thus confirming the same mechanism.

TABLE II

$k_{obs}/[LI](l \cdot mol^{-1}\ sec^{-1})$ as a function of the acid concentration at different temperatures and specific rate constants $k(l^2mol^{-2}sec^{-1})$ of the OsO_4 reduction with the imidazolidines-2-selone in H_2O/EtOH (1:1 vol)

t (°C)	Ligand	[HClO$_4$] .137	.212	.380	.550	.700	k ($l^2mol^{-2}sec^{-1}$)
6	dise	.87 ± .02	1.27 ± .01	2.60 ± .07	3.80 ± .06	4.75 ± .08	6.92 ± .14
	diseme	—	.99 ± .01	2.04 ± .06	2.80 ± .05	3.65 ± .06	5.23 ± .14
	diset	—	1.01 ± .03	1.69 ± .05	2.61 ± .03	3.32 ± .07	4.74 ± .11
12	dise	1.09 ± .03	1.84 ± .04	3.32 ± .03	5.53 ± .20	6.89 ± .14	10.08 ± .37
	diseme	.90 ± .03	1.31 ± .05	2.71 ± .04	3.73 ± .07	4.85 ± .08	6.97 ± .15
	diset	—	1.23 ± .05	2.24 ± .08	3.40 ± .15	4.30 ± .05	6.19 ± .10
18	dise	1.53 ± .02	2.35 ± .04	4.69 ± .08	6.94 ± .13	—	12.75 ± .37
	diseme	1.12 ± .01	1.52 ± .06	3.00 ± .03	4.83 ± .04	5.89 ± .04	8.62 ± .30
	diset	1.13 ± .01	1.59 ± .02	2.93 ± .06	4.08 ± .08	5.60 ± .21	7.80 ± .23
24	dise	1.87 ± .02	2.90 ± .03	5.90 ± .10	8.96 ± .09	—	16.46 ± .64
	diseme	1.36 ± .03	2.12 ± .02	4.19 ± .14	6.35 ± .08	—	11.63 ± .39
	diset	1.44 ± .06	1.92 ± .05	3.65 ± .05	5.39 ± .12	—	9.72 ± .25

TABLE III

Specific rate constants at 20°C and activation parameters for the OsO_4 reduction with imidazolidines-2-thione and 2-selone

R	Y	$k_{20°}$ ($mol^{-2}l^2sec^{-1}$)	$\Delta H^{\neq}$ (KJ/mol)	$-\Delta S^{\neq}$ (J/mol°K)
H	S	$2.28 \cdot 10^{-2}$	45.2 ± 0.6	122.2 ± 1.9
H	Se	13.99	30.2 ± 1.6	119.6 ± 5.5
Me	S	$1.32 \cdot 10^{-2}$	49.4 ± 0.4	112.1 ± 1.3
Me	Se	9.70	27.6 ± 1.5	131.7 ± 5.1
Et	S	$1.68 \cdot 10^{-2}$	43.1 ± 0.7	131.8 ± 2.2
Et	Se	8.41	25.0 ± 1.2	141.6 ± 4.1

EXPERIMENTAL

Os(III) complexes

The ligands have been prepared and purified as previously reported.[11-12] The complexes have been prepared by reacting osmium tetroxide with the ligand (1:15 molar ratio) in H_2O/EtOH (1:1 vol) in presence of perchloric acid (~3M).

Anal. $[Os(dise)_6](ClO_4)_3$: Calcd. for $C_{18}H_{36}Cl_3N_{12}O_{12}OsSe_6$: C, 15.6: H, 2.6: N, 12.2 Found: C, 15.6: H, 2.7: N, 12.1.

Anal. $[Os(diseme)_6](ClO_4)_3$: Calcd. for $C_{24}H_{48}Cl_3N_{12}O_{12}OsSe_6$: C, 19.7: H, 3.3: N, 11.5. Found: C, 19.6: H, 3.3: N, 11.4.

Anal. $[Os(diset)_6](ClO_4)_3$: Calcd. for $C_{30}H_{60}Cl_3N_{12}O_{12}OsSe_6$: C, 23.2: H, 3.9: N, 10.8. Found: C, 23.3: H, 3.9: N, 10.9.

The visible spectra of the complexes, recorded at the end of the reaction, show broad absorptions around 600 nm, where it is possible to identify the following three bands (nm), whose ϵ values are in parentheses. $[Os(dise)_6](ClO_4)_3$: 578sh(2700), 604(2850), 650(2530); $[Os(diseme)_6](ClO_4)_3$: 580(3050), 610(3150), 660(2660); $[Os(diset)_6](ClO_4)_3$: 590(3300), 618(3500), 660(3150); $[Os(su)_6](ClO_4)_3$: 560(2750), 604(2760), 650(2450).

Kinetic measurements

The osmium tetroxide solution was prepared in water by weighing. The perchloric acid solutions were prepared in H_2O/EtOH (1:1 vol) and tested by titrations with NaOH. The solutions of sodium perchlorate and imidazolidine-2-selones were prepared in H_2O/EtOH by weighing. The solutions for the kinetic experiments were prepared by mixing the appropriate amounts of ligand, $HClO_4$ and $NaClO_4$ (which was added to keep the ionic strength $\mu = 1.000$ constant). To a prethermostatted solution, 50 μl of the OsO_4 solution were added directly in the measuring cell under stirring. Experiments carried out with different amounts of OsO_4 (20–100 μl) gave the same k_{obs} values.

The increase of the absorbance was followed in time-drive at the maximum wavelength of the complex until a constant value was obtained.

Data processing

The k_{obs}'s were obtained from the slopes of the plots ln $(A_\infty - A_t)$ against time. All the straight lines were calculated by the least squares method.

Physical measurements

The infrared spectra were recorded on a Perkin Elmer 325 spectrophotometer as KBr discs (4000–400 cm^{-1}) and as Nujol mulls between CsI discs (450–200 cm^{-1}).

The visible spectra and the kinetic measurements were recorded with a Perkin Elmer mod. 402 spectrophotometer.

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9. The experimental k_{obs}'s as a function of the ligand concentration are supplied as Figures rather than numerical Tables, since the starting solutions of each ligand were different in concentration. In fact, both imidazolidine-2-selones and selenourea slightly decompose in solution; for this reason it was necessary to prepare them just before their employment (see Experimental).
10. This value has been extrapolated from Arrhenius' plot.
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