Reaction of Osmium Tetroxide with Alkenes, Glycols, and Alkynes; Oxo-osmium(VI) Esters and Their Structures

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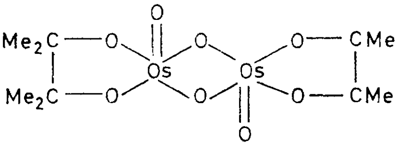
Osmium tetroxide reacts with mono-alkenes (R) to give five-co-ordinate mono- or di-esters of the saturated diolato-ligand $(O_2R)^{2-}$, *viz.* $[Os_2O_4(O_2R)_2]$ (I) and $[OsO(O_2R)_2]$ (II); (II) may also be obtained by the reaction of OsO_4 with the glycol $R(OH)_2$. With alkenes (R) or acetylene in the presence of tertiary nitrogen bases, L, the octahedral ' osmyl ' species $[OsO_2L_2(O_2R)]$ (III) and $[Os_2O_4L_4(O_4C_2H_2)]$ (IV) are formed. Spectroscopic and other data are used to assign structures to these complexes; ^{18}O and ^{2}H substitution has been used to help the interpretation of i.r. data.

It has long been known that osmium tetroxide reacts with mono-alkenes (R) to give cyclic osmium-containing esters which, on hydrolysis, yield *cis*-diols $R(OH)_2$.[1,2] We have recently reported the *X*-ray crystal structure of $[Os_2O_4(O_2C_2Me_4)_2]$,[3] but apart from this, most of these esters have been characterised by osmium analyses only,[2] and their structures are not known. As part of a more general study of the role of osmium tetroxide as a *cis*-hydroxylating agent for olefins and as a specific staining reagent for lipids we report the chemical and structural characterisation of a number of mono- and di-esters and related complexes.

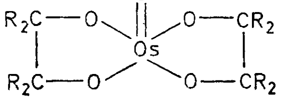
Cyclic Mono-esters (I).—A number of structures involving either four-[2] or six-co-ordinate[4] osmium has been suggested for these. The *X*-ray crystal structure of the complex derived from tetramethylethylene showed it to be dimeric with square-based pyramidal osmium(VI) linked in a centrosymmetric structure *via* a dioxo-bridge. The terminal oxo-ligands (Os–O 1·673 Å) are *trans* to each other across the planar Os_2O_2 bridge (Os–O 1·92 Å).[3] The correct formula is therefore $[Os_2O_4(O_2C_2Me_4)_2]$.

We have prepared a number of mono-esters from non-aqueous solvents using Criegee's methods[2] and fully characterised them for the first time. They are dimeric in solution and have the stoicheiometry $[Os_2O_4(O_2R)_2]$, where the parent alkene R is tetramethylethylene, cyclopentene, 2,3-dimethylpent-2-ene (DMP), camphene, cholesterol, or ergosterol; the DMP complex is reported for the first time. Titration of the complexes by Kirschman and Crowell's method[5] shows the osmium to be sexivalent, and they are diamagnetic as expected for osmium(VI) complexes with terminal oxo-ligands.[6] The ^{1}H n.m.r. spectra of $[Os_2O_4(O_2C_2Me_4)_2]$ in deuteriochloroform or in carbon tetrachloride shows two methyl resonances (τ 8·71 and 8·87) arising from pairs of methyl groups above and below the Os_2O_2 plane. This, molecular weight measurements, and the similarity of the i.r. spectra in solid and solution suggest that the Os_2O_2 bridge is retained in solution. The i.r. spectra (see below) are also consistent with all the mono-esters studied having the dimeric structure (I).

Cyclic Di-esters (II).—Reaction of pinacol with $K_2[OsO_2(OMe)_4]$ followed by acid hydrolysis[2] gives a product, $[OsO(O_2C_2Me_4)_2]$, identical with that obtained from reaction of osmium tetroxide with an excess of tetramethylethylene; *X*-ray studies on the product show it to be monomeric in the solid state.[7] The ^{1}H n.m.r. spectrum in deuteriochloroform has two methyl resonances (τ 8·60 and 8·73). The complex (and the ester $[OsO(O_2C_2H_4)_2]$ derived from ethylene) is diamagnetic, contains osmium(VI) and is monomeric in benzene solution. The i.r. spectra are similar for the solids and their carbon tetrachloride solutions. We therefore propose the simple five-co-ordinate square-based pyramidal structure (II) as originally suggested by Criegee[2] for these species.



(I)



(II)

We find that osmium tetroxide will react slowly with ethylene glycol or a solution of pinacol in carbon tetrachloride to give the corresponding di-esters. Studies on the electronic spectra and also of the Raman spectra of mixtures of osmium tetroxide and these glycols show that the di-ester appears to be the only product, although there is a report that such mixtures give osmium(VIII) esters.[8]

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[7] F. L. Phillips and A. C. Skapski, unpublished work.

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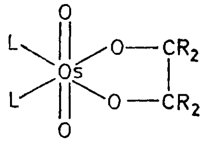
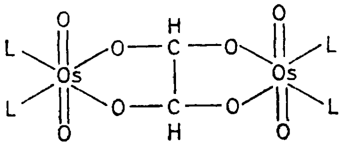
Cyclic Esters with Tertiary Nitrogen Bases (III, IV).—Osmium tetroxide reacts with mono-alkenes in the presence of pyridine or isoquinoline (L) to give $[OsO_2L_2(O_2R)]$, which stabilises the mono-esters.[2] The kinetics



(III)



(IV)

of such reactions have been studied.[9] The i.r. spectra of the pyridine complexes with R = ethylene, tetramethylethylene, and cyclopentene suggest that these are 'osmyl' complexes (III) (species containing the *trans* $O{=}Os^{VI}{=}O$ unit), as we have already suggested for the ethylene complex $[OsO_2(py)_2(O_2C_2H_4)]$.[4,10] Reaction of osmium tetroxide with an excess of ethane-1,2-diol in the presence of pyridine gives a product of empirical formula $[OsO_2(py)_2(glycol)_2]$ rather than the expected $[OsO_2(py)_2(O_2C_2H_4)]$. The product is diamagnetic and contains sexivalent osmium; the i.r. spectrum shows, in addition to 'osmyl' bands, unco-ordinated glycol O–H stretches at 3320 cm^{-1} (shifting to 2480 cm^{-1} on deuteriation). We propose that this is a six-co-ordinated osmyl complex, $[OsO_2(py)_2\{OC_2H_4(OH)\}_2]$.

TABLE 1

Infrared spectra [a] of oxo-osmium(VI) esters

Complex	ν(OsO terminal)	ν(Os_2O_2)	ν(OsO ester)	Ligand modes ν(C–O)	ν(C–C)
(a) *Mono-esters*					
$[Os_2O_4(O_2C_2Me_4)_2]$	982s	655s	588s	1122s	860s
	981s [b]	649s [b]	572s [b]	1106s [b]	831s [b]
	932s [c]	617s [c]	565s [c]	1121s [c]	839s [c]
$[Os_2O_4(O_2C_2Me_3C_2H_5)_2]$	979s	656m	575m	1122s	853s
$[Os_2O_4(O_2C_5H_8)_2]$	991s	651s	583m		837m
$[Os_2O_4(O_2C_{10}H_{16})_2]$	988s	632m	586m		
$[Os_2O_4(O_3C_{27}H_{46})_2]$	985s	621m			
$[Os_2O_4(O_3C_{23}H_{44})_2]$	989s	615m			
(b) *Di-esters*					
$[OsO(O_2C_2H_4)_2]$	992s		622m	1016s	868s
	990s [b]		591m [b]	932s [b]	769m [b]
$[OsO(O_2C_2Me_4)_2]$	978s		631m	1121m	859s
	935s [c]		612m [c]	1125m [c]	847s [c]
(*c*) *Complexes with tertiary bases*	ν(OsO_2)	δ(OsO_2)			
$[OsO_2(C_5H_5N)_2(O_2C_2H_4)]$	833vs	295m	593s	1041s	867s
	822vs [d]	294m [d]	591m [d]	1042s [d]	847m [d]
	789vs [c]	281m [c]	561s [c]	1028s [c]	801m [c]
$[OsO_2(C_9H_7N)_2(O_2C_2H_4)]$	833s	291m	589m	1029m	814m
$[OsO_2(C_5H_5N)_2(O_2C_2Me_4)]$	829s	291m	609m	1126s	862m
$[OsO_2(C_5H_5N)_2(O_2C_5H_8)]$	821s	291m	612m	1029m	839m
$[OsO_2(C_5H_5N)_2\{OC_2H_4(OH)\}_2]$	840s	287m	589s	1011m	860m
	845s [b]	289m [b]	579s [b]	893m	700m
$[Os_2O_4(C_5H_5N)_4(O_4C_2H_2)]$	835s	280m	590m	1005s	821m
$[Os_2O_4(C_9H_7N)_4(O_4C_2H_2)]$	837s		575m	990s	

[a] In cm^{-1}. [b] Deuterium substituted. [c] Oxygen-18 substituted. [d] Pyridine only deuterium substituted.

With acetylene in the presence of pyridine or quinoline (L), osmium tetroxide gives species formulated[2] as $2OsO_4,L_4,C_2H_2$. On the basis of their i.r. spectra (Table 1) we formulate these as osmyl complexes with a bridging 'tetrolato' unit (IV), *i.e.* $[Os_2O_4L_4(O_4C_2H_2)]$; the C–C (single bond) stretching mode appears near 830 cm^{-1} as a weak band close to the very intense O=Os=O stretching mode. The C–H bands lie near 2900 cm^{-1}, as expected for alkanes.

Infrared Spectra of the Complexes.—These are summarised in Table 1. Their assignment is helped by ^{18}O-substitution and ^{2}H-substitution of selected complexes: the former greatly affects metal–oxo modes while leaving predominantly ligand modes largely unaffected, the reverse holding for deuteriation.

(i) *Metal–oxo modes*. In (I) and (II) the Os=O (terminal) stretch is easily identified as a sharp band *ca.* 980 cm^{-1} shifting downwards by 52 cm^{-1} on ^{18}O-substitution (calculated shift, 57 cm^{-1}) and remaining unchanged on deuteriation. In solid $OsOCl_4$ which also has a five-co-ordinate structure, this band appears at 1020 cm^{-1}.[11] In (III) and (IV) the i.r.-active stretch ν(OsO_2) of the *trans* O=Os=O 'osmyl' group is clearly recognisable[10] as a very strong, sharp, band *ca.* 830 cm^{-1} shifting downwards some 44 cm^{-1} on ^{18}O-substitution, while the deformation δ(OsO_2) appears[10] *ca.* 300 cm^{-1}. A band *ca.* 650 cm^{-1} in the mono-esters, not found in the

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monomeric species (II)—(IV), is tentatively assigned to a stretching mode of the Os_2O_2 bridge. All the complexes have bands *ca.* 580 cm^{-1} which we tentatively assign to a predominantly Os–O (ester) stretch on the basis [12] of their large shifts on ^{18}O-substitution and smaller shifts on deuteriation of the complexes (such bands have been noted in ethane-1,2-diol complexes, but assigned [13] to torsional modes).

(ii) *Ligand modes.* Bands assigned as arising predominantly from C–C or C–O stretching modes are given in Table 1 and are so assigned on the basis of their absence in the parent olefins and also on the basis of their shifts on deuteriation (using published data on ethane-1,2-diol [12,14]). In all the complexes the C–H stretching frequency lies near 2850—2900 cm^{-1}, as expected for alkanes.

TABLE 2

Analyses and molecular weights of oxo-osmium(VI) esters

Complex	C (%)	H (%)	N (%)	O (%)	*M*
$[Os_2O_4(O_2C_2Me_4)_2]$	20·7 (21·3)	3·7 (3·6)		19·0 (18·9)	674 (677) [a]
$[Os_2O_4(O_2C_2Me_3C_2H_5)_2]$	24·0 (23·9)	4·1 (4·0)		18·3 (18·2)	
$[Os_2O_4(O_2C_5H_8)_2]$	18·7 (18·6)	2·6 (2·5)		20·1 (19·9)	672 (645) [a]
$[Os_2O_4(O_2C_{10}H_{16})_2]$	30·9 (30·7)	4·3 (4·1)		16·3 (16·4)	
$[Os_2O_4(O_3C_{27}H_{46})_2]$	51·9 (50·6)	7·0 (7·3)		11·2 (12·5)	1285 (1282) [b]
$[Os_2O_4(O_3C_{28}H_{44})_2]$	51·9 (51·7)	6·8 (6·8)		12·2 (12·3)	
$[OsO(O_2C_2H_4)_2]$	14·7 (14·7)	2·6 (2·5)		24·4 (24·5)	328 (326) [a]
$[OsO(O_2C_2Me_4)_2]$	33·1 (32·9)	5·7 (5·5)		18·4 (18·2)	451 (439) [a]
$[OsO_2(C_5H_5N)_2(O_2C_2H_4)]$	31·5 (32·7)	3·2 (3·2)	6·7 (6·3)	14·9 (14·5)	
$[OsO_2(C_9H_7N)_2(O_2C_2H_4)]$	44·6 (44·4)	3·5 (3·4)	5·2 (5·2)	11·8 (11·8)	
$[OsO_2(C_5H_5N)_2(O_2C_2Me_4)]$	38·6 (38·7)	4·6 (4·5)	5·6 (5·6)	13·1 (12·9)	
$[OsO_2(C_5H_5N)_2(O_2C_5H_8)]$	37·6 (37·5)	3·8 (3·8)	5·8 (5·8)	13·4 (13·3)	
$[OsO_2(C_5H_5N)_2\{OC_2H_4(OH)\}_2]$	33·4 (33·3)	4·1 (4·4)	5·7 (5·6)	19·0 (19·0)	
$[Os_2O_4(C_5H_5N)_4(O_4C_2H_2)]$	31·1 (30·9)	3·2 (3·0)	6·7 (6·6)	14·9 (15·0)	
$[Os_2O_4(C_9H_7N)_4(O_4C_2H_2)]$	43·3 (43·6)	3·1 (2·9)	5·3 (5·3)	12·3 (11·9)	

[a] In benzene. [b] In chloroform. Calculated values in parentheses.

Staining and Fixation Properties of Osmium Tetroxide.—It is generally held [15-17] that the valuable staining properties of osmium tetroxide for the study of tissue and membrane structure is primarily associated with the initial reaction between the double bond in unsaturated lipids and osmium tetroxide. Our studies on 'model' alkenes reported here show that small molecules will give either mono- or di-esters with osmium tetroxide, but larger ones such as cholesterol and ergosterol may only give dimeric mono-esters. This may help to resolve the argument as to whether mono-esters [15,16] or di-esters [17] are formed with tissue lipids; we suggest that mono-ester formation is more likely due to the size of the lipids. If this is so, the important fixation properties of osmium tetroxide become understandable since, if such mono-esters are dimeric with an Os_2O_2 bridge as in our model systems, cross-linking of lipids at double bond sites *via* such bridges may occur.

Further studies are in progress on the reaction of osmium tetroxide with water-soluble unsaturated lipids, and also on its reactions with amino-acids, peptides, and lipoproteins.

EXPERIMENTAL

Mono-esters, (I).—These were made by Criegee's general procedure [2] using the alkene and osmium tetroxide in stoicheiometric proportions in carbon tetrachloride or cyclohexane solutions. The analyses are listed in Table 2 and the main features of the i.r. spectra in Table 1.

*Di-μ-oxo-dioxobis(tetramethylethane-*1,2-*diolato)osmium* (VI), $[Os_2O_4(O_2C_2Me_4)_2]$, was made in the ^{18}O-substituted form by reaction of tetramethylethylene with a stoicheiometric quantity of $Os^{18}O_4$ (75% enrichment, prepared as described below) in carbon tetrachloride; the deuteriated form was made by reaction of $K_2[OsO_2(OMe)_4]$ in carbon tetrachloride with $[^2H_{14}]$pinacol followed by acid hydrolysis.

Di-esters, (II).—*Oxobis(tetramethylethane-*1,2-*diolato)-osmium*(VI), $[OsO(O_2C_2Me_4)_2]$, was prepared by Criegee's procedure.[2] The product was also obtained by recrystallisation of the mono-ester, $[Os_2O_4(O_2C_2Me_4)_2]$, from a concentrated solution of tetramethylethylene in carbon tetrachloride. This method was used to prepare the ^{18}O-substituted product, using a solution of $Os^{18}O_4$ in carbon tetrachloride (see below).

*Oxobis(ethane-*1,2-*diolato)osmium*(VI), $[OsO(O_2C_2H_4)_2]$. This was made by Criegee's method from $K_2[OsO_2(O_2C_2H_4)_2]$ [2]. A more crystalline solid was however obtained by treating osmium tetroxide with an excess of ethane-1,2-diol. The black crystals separated from the mother liquor after standing for *ca.* 10 days. Criegee's method was used to isolate the deuteriated product, using $[^2H_6]$ethane-1,2-diol.

Complexes with Tertiary Bases, (II, IV).—These were prepared using the methods described by Criegee.[2]

*(Ethane-*1,2-*diolato)dioxobis(pyridine)osmium*(VI), $[OsO_2(C_5H_5N)_2(O_2C_2H_4)]$ was made in the ^{18}O-substituted form by passing ethylene gas into a solution of $Os^{18}O_4$ (75%

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[16] J. C. Riemersma, *Biochim. Biophys. Acta*, 1968, **152**, 718.

[17] E. D. Korn, *J. Cell Biol.*, 1967, **34**, 627.

enrichment) in carbon tetrachloride in the presence of an excess of pyridine; the [$^2H_5$]pyridine form was made using deuteriated pyridine.

Bis(2-hydroxyethoxo)dioxobis(pyridine)osmium(VI), [$OsO_2(C_5H_5N)_2(OC_2H_4OH)_2$], was prepared by mixing pyridine (1 ml), ethanol (1 ml), and ethane-1,2-diol (1 ml) with a solution of osmium tetroxide (0·1 g) in carbon tetrachloride (5 ml). The brown solid formed in the upper pyridine–diol layer was separated off, washed with ether, and dried. Deuteriated products were made using [$^2H_5$]pyridine and [$^2H_6$]ethane-1,2-diol.

Osmium tetroxide enriched in ^{18}O was made by hypochlorite oxidation of the metal. A solution of $Na^{18}OCl$ in $H_2{}^{18}O$ (0·5 ml, 97% enrichment) was made by passing dry chlorine gas through an ice-cold solution of $Na^{18}OH$ until it was saturated. Freshly prepared, finely divided, osmium metal (0·4 g) was then added and the mixture allowed to warm to room temperature and the flask flushed with nitrogen gas. The $Os^{18}O_4$ was then extracted into carbon tetrachloride (10 ml) and its concentration determined spectrophotometrically.

Analytical and molecular weight data are summarised in Table 2. Microanalyses were performed by Alfred Bernhardt, Munich; molecular weights were determined in benzene or chloroform using a Hitachi–Perkin-Elmer vapour pressure osmometer.

I.r. spectra were run as Nujol mulls between caesium iodide plates over the range 200—4000 cm^{-1} on Perkin-Elmer 325 and 457 instruments.

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