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Studies on the Formation and Hydrolysis of Osmate(VI) Esters

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3-Cyclohexenecarboxylic acid reacts with osmium tetraoxide in aqueous buffer solutions in the presence of a variety of pyridines to form osmate(VI) esters of the general formula $(RO)_2OsO_2L_2$, where L represents the monodentate ligand. The compounds appear to be octahedral osmyl complexes with a trans O=Os=O group. The general kinetic equation describing the formation of the esters is rate $= k_0[OsO_4][S] + k_1\beta_1[OsO_4][S][L] + k_2\beta_2[OsO_4][S][L]^2$ where S is the substrate, 3-cyclohexenecarboxylic acid, and β_1 and β_2 are the overall stability constants for the osmium tetraoxide–ligand system. The hydrolysis of the uncomplexed ester produces the expected diol and osmium-containing products whose nature is pH dependent. In strong alkali, the osmate(VI) ion is the sole product. At pH 9.5, the initially produced Os(VI) species is oxidized by oxygen to osmium tetraoxide. In water or acid, 1 mol of the initially produced Os(VI) species dismutes to $^1/_3$ mol of OsO_4 and $^2/_3$ mol of Os(V), the latter perhaps present as a dimeric oxide. On long standing, both of these products, when present together, are reduced by water to osmium dioxide, $OsO_2 \cdot 2H_2O$. The hydrolysis is pH dependent and is catalyzed by both acid and alkali. $H_2{}^{18}O$ experiments show that the hydrolysis proceeds exclusively with osmium–oxygen bond cleavage.

Our studies[1] on the reaction of osmium tetraoxide–pyridine complexes with nucleic acid components left unanswered a number of fundamental questions about the reaction of olefins with osmium tetraoxide and with osmium tetraoxide complexes. In this paper, we examine the kinetics of the reactions between a single olefin, 3-cyclohexenecarboxylic acid (CCA), and osmium tetraoxide in aqueous solutions in the presence and absence of pyridine and some of its derivatives. We also report some observations on the hydrolysis of the uncomplexed osmate ester.

Results and Discussion

Properties of the Osmate(VI) Esters.—Table I gives analytical data for a number of osmate esters. The analyses correspond well with the general formula $(RO)_2OsO_2L_2$, where L represents a monodentate ligand. Table I also gives iodometric titration data which show 1 mol of I_2 produced per mole of ester corresponding to reduction of hexavalent osmium to Os(IV).[2]

Ir Spectra.—Griffith has suggested that the bis(pyridine) osmate esters are osmyl compounds,[3] that is, of octahedral geometry with a trans O=Os=O arrangement. He has assigned a strong band between 800 and 850 cm^{-1} to the asymmetric stretch of the osmyl group.[4] This band is present in the bis(pyridine) ester of CCA (830 ± 5 cm^{-1}, KBr) unshifted by deuteration and absent in both CCA and its *cis*-diol.

Nmr Spectra.—The nmr spectra of the esters showed chemical shifts which were qualitatively similar to those reported previously for the thymine and uracil esters.[1] The spectra of the bis(pyridine), the bis(3-picoline), bis(4-picoline), bis(3-chloropyridine), and the 2,2′-dipyridyl osmate esters of CCA in DMSO-d_6 at 35° all showed an upfield shift for the 3 and 4 protons of about 1.20 ppm as compared with the olefinic protons in CCA. The pyridine and substituted pyridine protons all showed a downfield shift of about 0.1–0.3 ppm. For the case of the 2,2′-dipyridyl ester, the pyridine protons were shifted downfield by about 0.5 ppm. Integration of these spectra confirmed the stoichiometry of Table I. We note, in addition, that the lack of any large chemical shift or line-broadening suggests that the osmate esters are diamagnetic, as expected. This was confirmed by measurement of the magnetic susceptibilities by the Faraday method.[5] Both the osmate ester of CCA and its bis(pyridine) adduct were diamagnetic.

Kinetics of Formation of the Osmate Esters.—We have analyzed our kinetic results according to the three-term equation suggested by our previous work[1]

$$\text{rate} = k_0[OsO_4][S] + k_1\beta_1[OsO_4][S][L] + k_2\beta_2[OsO_4][S][L]^2 \quad (1)$$

where S is the substrate and β_1 and β_2 are the successive stability constants for the osmium tetraoxide–ligand system.[1] Values for k_0 were obtained by studying the reaction in the absence of ligands. Table II gives these results for the temperature range 40–15° together with an extrapolated rate constant for 8°. The hydrolysis of the ester is sufficiently slow so as to give no interference under the conditions we have used; at 25°, the half-time for hydrolysis was of the order of 100 min while that for formation was of the order of 3 min.

Evaluation of k_0 allows evaluation of k_1 and k_2. From eq 1, with limiting osmium tetraoxide concentration, we can write for k_ψ, the pseudo-first-order rate constant

$$k_\psi = k_0[S] + k_1\beta_1[S][L] + k_2\beta_2[S][L]^2 \quad (2)$$

and hence

$$(k_\psi - k_0[S])/[L] = k_1\beta_1[S] + k_2\beta_2[S][L] \quad (3)$$

Accordingly, plots of $(k_\psi - k_0[S])/[L]$ *vs.* [L] should give straight lines with slopes equal to $k_2\beta_2[S]$ and intercepts equal to $k_1\beta_1[S]$. Plots of this kind are shown in Figure 1 for the ligands pyridine, 3-picoline, and 4-picoline. If a ligand forms no bis complex or if β_2 is sufficiently small, then

$$\text{rate} = k_0[S][OsO_4] + k_1\beta_1[S][OsO_4][L] \quad (4)$$

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TABLE I

ANALYSIS OF OSMATE ESTERS OF CCA

Compound	Medium of preparation	Analysis	% calcd	% found	I^-/Os
Bis(pyridine) ester	Petroleum ether	N	5.19	4.98	
	H_2O	C	37.91	37.52, 37.76	2.05, 1.97
	H_2O	H	3.74	3.69, 3.90	
	H_2O	Os	35.32	35.23, 35.18	
	H_2O	Pyridine	29.4	28.9, 29.7	
Bis(4-picoline) ester	H_2O	4-Picoline	32.86	33.2, 32.82	2.02, 1.90, 1.99
Bis(3-picoline) ester	H_2O	3-Picoline	32.86	33.14, 32.60	2.06, 1.99
Bis(3-chloropyridine) ester	H_2O	3-Chloropyridine	37.41	35.93	
	CCl_4	3-Chloropyridine	37.41	36.65	
2,2′-Dipyridyl ester	H_2O	Os	35.45	34.86, 34.8	
OsO_4–CCA ester	CCl_4	Os	50.01	49.4, 49.7, 48.0	2.02, 2.09

TABLE II

THE REACTION OF OsO_4 AND CCA[a]

T, °C	k_0, M^{-1} min^{-1}	T, °C	k_0, M^{-1} min^{-1}
40	142	20	50
30	87	15	35
25	68	8	25

[a] $[OsO_4] = 1.5–3 \times 10^{-4}$ M, $[CCA] = 2–6 \times 10^{-3}$ M, pH 9.4–9.6, λ 230 nm. Each rate constant is the average of five runs. The variation is of the order of 5%. $E_a = 9.5 \pm 0.6$ kcal/mol.

TABLE III

VALUES OF $k_1\beta_1$ AND $k_2\beta_2$ FOR OsO_4–LIGAND–CCA SYSTEMS[a]

	$10^{-3}k_1\beta_1$					$10^{-4}k_2\beta_2$		
10^4[CCA], M	3-Cl(py)	py	3-pic	4-pic	2,2′-dipy	py	3-pic	4-pic
5			5.7	6.5			3.41	9.23
10	0.97	2.60	5.8	6.45	128.9	1.7	3.28	9.19
15		2.75	5.87	6.37		1.67	3.33	9.20
20	0.93	2.68			127.5	1.63		
30	0.95				130.3			
Av	0.95	2.68	5.8	6.44	129	1.67	3.34	9.21

[a] 8°, pH 9.4–9.6 (carbonate buffer), $\mu \simeq 0.08$ M. $[OsO_4] = 1.5–2.5 \times 10^{-4}$ M, ligand concentration was $1 \times 10^{-2}–2 \times 10^{-1}$ M except for [2,2′-dipy] $= 1–7 \times 10^{-3}$ M.

TABLE IV

COMPARISON BETWEEN OBSERVED AND CALCULATED SLOPES OF k_ψ *vs.* [S] PLOTS

	Slope									
	3-Chloropyridine[a]		Pyridine[b]		3-Picoline[b]		4-Picoline[b]		2,2′-Dipyridyl[a]	
10^2[L], M	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
0.3									413	412
0.4									554	541
0.5									667	670
5	73	72	200	201	377	398	577	579		
10	119	120	438	435	941	938	1595	1589		
15			799	803						

[a] Slope $= k_0 + k_1\beta_1[L]$. [b] Slope $= k_0 + k_1\beta_1[L] + k_2\beta_2[L]^2$. For experimental conditions, see Table III, $[CCA] = 5–50 \times 10^{-4}$ M.

TABLE V

STABILITY CONSTANTS AND RATE CONSTANTS FOR THE OsO_4–CCA–LIGAND SYSTEMS, 8°

Compound	pK_a[a]	β_1,[b] M^{-1}	k_1,[c] M^{-1} min^{-1}	β_2,[d] M^{-2}	k_2,[e] M^{-1} min^{-1}
Pyridine	5.2	0.46	5.8×10^3	0.28	6×10^4
4-Picoline	6.0	2.6	2.5×10^3	*8*	1×10^4
3-Picoline	5.7	1.2	4.8×10^3	*2*	1.6×10^4
3-Chloropyridine	2.8	$\sim\mathit{10}^{-3}$	$\sim 10^6$	$\sim\mathit{10}^{-5}$	
2-Fluoropyridine	−0.44	$\sim\mathit{10}^{-6}$		$\sim\mathit{10}^{-11}$	

[a] The data are thermodynamic values in water from A. Albert and E. P. Serjeant, "The Determination of Ionization Constants," Chapman and Hall, London, 1971, p 94. [b] The data are from ref 1 or by linear extrapolation from a plot of log β_1 *vs.* pK_a (italics). [c] The values for $k_1\beta_1$ (Table III) were divided by β_1 values. [d] The value for pyridine is from ref 1. The values in italics are by extrapolation from a plot of log K_2 *vs.* pK_a assuming a slope of unity. K_2 for pyridine = 0.6.[1] [e] The values for $k_2\beta_2$ (Table III) were divided by β_2 values. $\beta_1 = [OsO_4 \cdot L]/([OsO_4][L])$. $\beta_2 = [OsO_4 \cdot L_2]/([OsO_4][L]^2)$. $K_2 = \beta_2/\beta_1$.

and

$$k_\psi - k_0[S] = k_1\beta_1[S][L] \qquad (5)$$

In this case, plots of $k_\psi - k_0[S]$ *vs.* [L] will be linear with slopes given by $k_1\beta_1[S]$. This behavior is shown by 2,2′-dipyridyl and by 3-chloropyridine. Plots of this kind are also given in Figure 1. Since no spectral changes are observed upon mixing 2-fluoropyridine with osmium tetraoxide, we can conclude that only very weak complexes are formed. In addition, we observe no acceleration of the rate of reaction of CCA with osmium tetraoxide following addition of 2-fluoropyridine in the concentration range $2.5–14.5 \times 10^{-2}$ M. Table III gives the values for $k_1\beta_1$ and for $k_2\beta_2$ for the reaction of CCA with various ligands at 8°. This table also shows the good first-order dependence on CCA concentration. The rates were independent of pH in the range 7–10.5 using pyridine as ligand. Comparison of the data shows, for example, that the ob-

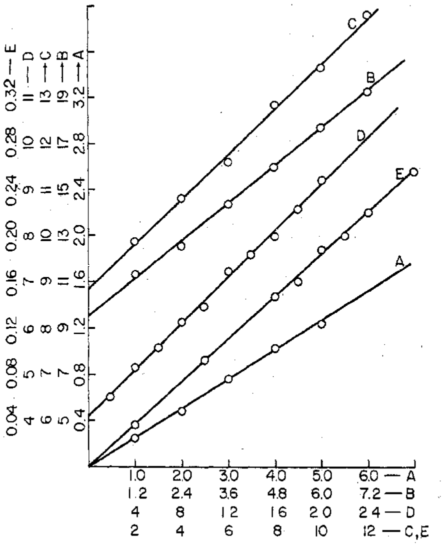

Figure 1.—Variation of rate with ligand concentration: pH 9.4–9.5, temperature 8°, $[OsO_4] = 1.5\text{–}4 \times 10^{-4}$ *M*. A, E: the *y* axis is $k_\psi - k_0[\mathrm{CCA}]$; $[\mathrm{CCA}] = 2 \times 10^{-3}$ *M*. A: *x* axis = 10^3[2,2′-dipyridyl], λ 340 nm. E: *x* axis = 10^2[3-chloropyridine], λ 300 nm. B, C, D: the *y* axis is $(k_\psi - k_0[\mathrm{CCA}]/[\mathrm{base}]$; λ 300 nm; $[\mathrm{CCA}] = 1.5 \times 10^{-3}$ *M*. *B*: *x* axis = 10^2[4-picoline]. C: *x* axis = 10^2[3-picoline]. D: *x* axis = 10^2[pyridine].

served rate constant ($k_1\beta_1$) for the formation of the 2,2′-dipyridyl ester is about 5200 times larger at 8° than the rate constant for the formation of the uncomplexed ester. Equation 2 also predicts that plots of k_ψ *vs.* [S] will give straight lines whose slopes will be given by $k_0 + k_1\beta_1[\mathrm{L}] + k_2\beta_2[\mathrm{L}]^2$ (or $k_0 + k_1\beta_1[\mathrm{L}]$, if the k_2 term is negligible).

Table IV gives the calculated and observed values for these slopes as a function of ligand concentrations.

Stability Constants of the Ligands with Osmium Tetraoxide and Calculation of the True Rate Constants.—Table V lists previously measured[1] values of β_1 for the ligands pyridine, 3-picoline, and 4-picoline. Since a plot of log β_1 *vs.* pK_a is reasonably linear with a slope of unity, we can estimate values of β_1 for 3-chloropyridine and 2-fluoropyridine. These estimates are also given in the table. Values for k_1 were computed from the measured values of $k_1\beta_1$ (Table III) and the values for the stability constant, β_1. It is noteworthy that although the values for $k_1\beta_1$ increase with increasing basicity of the ligand, the values for k_1 change in the opposite direction. This is reasonable in view of the two-step mechanism proposed for ester formation.[1,6] We have been unable to measure β_2 for any of the substituted pyridines because of solubility limitations so that an experimental correlation for this parameter has not been possible. However, the assumption of a slope of unity for a plot of log K_2 *vs.* pK_a as well[7] allows the estimates for β_2 and k_2 given in Table V. k_2, like k_1, decreases with increasing basicity of the ligand.

Products of the Hydrolysis of the CCA–Osmate Ester.—The expected glycol, *cis*-3,4-dihydroxycyclohexane-1-carboxylic acid, was found in good yield (80–95%) as the only organic product of the hydrolysis over the entire pH range investigated (0.1 *N* H_2SO_4–10 *N* KOH). The diol was detected on paper chromatograms using the benzidine–periodate reaction.[8] It had an R_f in 1-butanol–acetic acid–water (4:1:5) of 0.7. Only one spot was observed. It was identified as *cis*-3,4-dihydroxycyclohexanecarboxylic acid as follows: the diol was crystallized from ethyl acetate or acetone following trituration of the dried, acidified reaction mixtures with ethyl acetate. Titration with standard NaOH gave an equivalent weight of 160 ± 1 (theory, 160.1). It sintered at 150–152° and gave mp 185° (dec) (lit. 187°).[9] Its diacetyl derivative was prepared and gave mp 85° (lit. 84°).[9]

Osmium-Containing Products.—Analysis of the osmium-containing products of the hydrolysis is complicated by the occurrence of a series of pH-dependent oxidation–reduction reactions. Since we expected that an Os(VI) species, related to the osmate ion, would be the initial product of the hydrolysis, we examined the behavior of the ester and of potassium osmate as a function of pH in parallel.

10 *N* KOH.—Potassium osmate is stable in strong base.[2] When the osmate ester of CCA was treated at room temperature with 10 *N* KOH, a violet-pink solid began to precipitate within a few minutes. After standing overnight, the material was filtered, washed with alcohol, and dried under vacuum over concentrated H_2SO_4. The ultraviolet and visible spectrum of this material was identical with that of potassium osmate. The weight corresponded to a 90% yield. Spectrophotometric experiments in 0.1 *N* KOH confirmed this quantitative conversion of the ester to potassium osmate. The extinction coefficients for potassium osmate in 0.1 *N* KOH were the following: 520 nm, 26; 300 nm, 1200; 233 nm, 6050. Bardin and Goncharenko[10] have reported the reduction of osmium tetraoxide to Os(VI) in strong alkali. Norkus, *et al.*,[11] however, have shown that the reduction is due to reducing impurities.

pH 9.5 Carbonate Buffer.—At this pH, in air, solutions of potassium osmate in the concentration range 1×10^{-3}–1×10^{-4} *M* were oxidized in 95–98% yield to osmium tetraoxide in 24 hr at room temperature. The ester behaved in the same way. These results are consistent with the observations of Périchon, *et al.*,[12] and of Cairns and Roberts.[13] If the reaction is carried out under nitrogen or if the concentration of the Os(VI) species exceeds the solubility of oxygen in water (*ca.* 10^{-3} *M*), a very slow conversion to osmium tetraoxide and a black precipitate is observed. We have not investigated the disproportionation quantitatively at this pH because it is so slow. In semiquantitative terms, the initial rate of decrease in the absorbancy at 235 nm for equimolar concentrations is about 650 times slower under nitrogen than in air for both the ester and osmate. In addition, the rate for osmate is about twice that for the ester. We assume, however, that the black precipitate is, initially at least, an Os(V) oxide as is the

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case at lower pH values. Neither this black precipitate nor osmium dioxide, prepared separately, is stable at this pH in the presence of air. A $1 \times 10^{-4}\ M$ suspension of the dioxide is converted to a 90% yield of osmium tetraoxide in about 1 week at room temperature. In 0.1 M KOH, the dioxide is oxidized to the osmate ion. The dioxide is stable in 0.05 M sulfuric acid.

Reactions of Os(VI) in Water and Dilute Acid.—Both the ester and potassium osmate disproportionate in dilute acid (0.001–0.1 N H_2SO_4) to give OsO_4 and a black precipitate. The ester behaves similarly in water. Analyses showed the formation of between 0.24 and 0.37 mol of OsO_4 per mole of ester or osmate. The average value for 17 runs was 0.3 mol of OsO_4.

Iodometric titration of the washed precipitate (see methods) shows that the black precipitate formed from either potassium osmate or the ester oxidizes 1 equiv of iodide per equivalent of osmium according to the equation

$$\mathrm{Os(V)} + \mathrm{I}^- = \mathrm{Os(IV)} + {}^1/{}_2\mathrm{I}_2 \qquad (6)$$

The overall disproportionation in water or acid thus corresponds to

$$3\mathrm{Os(VI)} \longrightarrow \mathrm{Os(VIII)} + 2\mathrm{Os(V)} \qquad (7)$$

The Os(IV) species produced by reduction was washed, dried, and weighed. The amount formed corresponded to $^2/_3$ mol of $OsO_2 \cdot 2H_2O$ (Table VIA). The titration would have given the same results had the precipitate been a 1:1 mixture of Os(IV) and Os(VI) species. There are, however, two lines of evidence which support the contention that it is an Os(V) oxide. An Os(IV)–Os(VI) mixture would be expected to give rise to some osmium tetraoxide by disproportionation of Os(VI). This is not observed. Magnetic susceptibility measurements on the black precipitate show that it is diamagnetic. We have measured the susceptibility of $OsO_2 \cdot 2H_2O$ and find that it is paramagnetic, as predicted by Figgis and Lewis,[14] with a susceptibility of 2.25 BM at 301°K. All known Os(VI) oxides are diamagnetic so that a 1:1 mixture should still show a paramagnetism of the order of 1.6 BM. A possible explanation is a dimeric Os(V) oxide such as Os_2O_5 which might be diamagnetic as observed.

Osmium tetraoxide is not stable in the presence of this black precipitate, but the rate of disappearance of the tetraoxide in these heterogeneous mixtures depends upon the physical state of the precipitate. The precipitate formed from the ester in water or dilute acid, in the absence of salts, is very finely divided and, in this case, the stoichiometry of eq 7 is observed for only a few hours. After 1 or 2 weeks, all of the osmium is converted to a different insoluble black oxide (Table VIB) which can no longer oxidize iodide and whose properties correspond to the osmium dioxide dihydrate described by Ruff and Rathsburg.[15] It is this material which is paramagnetic. The precipitate which results from the disproportionation of the ester (in the presence of salts) or potassium osmate in 0.1 N sulfuric acid is much coarser. The wet mixtures of osmium compounds prepared in this way still show appreciable amounts of the tetraoxide after 7 weeks (Table VIA, Figure 2).

TABLE VI

THE DECOMPOSITION OF POTASSIUM OSMATE AND CCA ESTER IN WATER AND DILUTE ACID. ANALYSES OF OSMIUM OXIDES

A. The Initial Precipitate

		I^-, 10^5 equiv[a]		$OsO_2 \cdot 2H_2O$, 10^5 mol[b]	
Compd	10^5 mol	Found	% theory[h]	Found	% theory[h]
Ester	12.36[c]	8.10	98	8.21	99
Ester	10.52[c]	6.70	96	7.02	100
Ester	7.89[c]	5.1	97	5.24	99
Ester	12.18[c]	6.12	76	8.00	99
Osmate	15.08[d]	10.0	94	9.98	94
Osmate	13.58[d]	8.8	97	8.91	98
Osmate	11.41[d]	7.50	99	7.58	100
Osmate	10.86[d]	7.01	97	7.25	100
Osmate	10.86[e]	6.1	84	7.01	97
		OsO_4, 10^5 mol[f]		Os_2O_5, 10^5 mol[i]	
		Found	% theory[h]	Found	% theory[h]
Osmate	13.96[g]	4.49	97	5.28	116
Osmate	10.89[g]	2.9	80	3.97	109
Osmate	15.08[d]			4.99	99

B. The Final Precipitate

			$OsO_2 \cdot 2H_2O$, 10^4 mol[n]	
Medium	Ester, 10^4 mol	OsO_4 added, 10^4 mol	Found	% theory
Water, air	1.323[j]		1.301	98[m]
Water, air	1.610[j]		1.596	99[m]
Water, air	2.662[j]		2.533	95[m]
Water, N_2	1.407[j]		1.344	96[m]
0.1 N H_2SO_4, air	1.323[j]		1.286	97[m]
0.1 N H_2SO_4, N_2	1.317[j]		1.290	98[m]
Water, air	1.328[k]	0.590	1.851	97[o]
Water, air	1.189[k]	0.484	1.619	97[o]
Water, air	1.610[k]	0.669	2.216	97[o]
0.1 N H_2SO_4, air	1.328[l]	0.602	1.890	98[o]
0.1 N H_2SO_4, N_2	1.366[l]	0.728	2.061	99[o]

[a] Analysis by thiosulfate titration, see methods. [b] Analysis by weight after iodide reduction. [c] In water, analysis after 30–60 min. [d] In 0.1–0.2 N H_2SO_4, analysis after 10 min. [e] pH 3 with H_2SO_4, analysis after 55 days. [f] Analysis by titration, see methods. [g] In 0.1 N H_2SO_4, analysis after 3 weeks. [h] Based on eq 6 and 7. [i] Analysis by weight. [j] Analysis after 7–10 days. [k] Analysis after 10–15 days. [l] Analysis after 15–20 days. [m] Based on eq 11b. [n] Analysis by weight. [o] Based on eq 11b assuming also reduction of added OsO_4. The total volume of reaction mixture was 10 ml, 25°, no external salt added.

Since all of the osmium in these mixtures can be reduced to $OsO_2 \cdot 2H_2O$, we examined disproportionating mixtures in the Warburg apparatus to see if we could detect the evolution of oxygen. Reproducibility in these experiments was poor because of the long time periods necessary (Table VIB, Figure 2). The increase in volume corresponded to between $^1/_2$ and $^1/_6$ mol of gas per g-atom of Os(VI). When these experiments were carried out in the presence of oxygen-trapping agents such as Fieser's solution or the indigo carmine reagent,[16] most of the gas evolution was prevented. There was, however, always a small residual quantity which we have not accounted for.

The disproportionation of osmates in aqueous solution has been documented since the discovery of these Os(VI) compounds. The review by Charonnat[17] should be consulted for a concise history. The final oxidized product of the disproportionation is osmium tetraoxide, but the identity of the black, insoluble, reduced product, although generally assumed to be OsO_2 or one of its

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(17) R. Charonnat in "Nouveau Traité de Chimie Minerale," P. Pascal, Ed., Vol. 19, Masson, Paris, 1958, p 228.

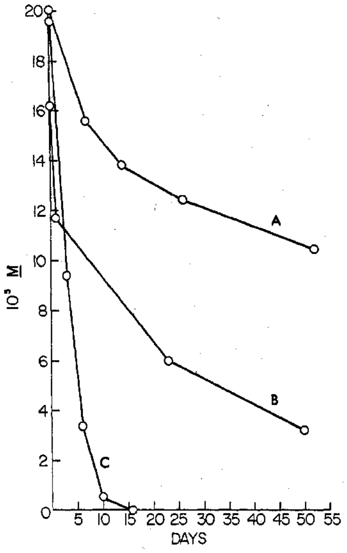

Figure 2.—Rate of disappearance of osmium tetraoxide from disproportionating mixtures of potassium osmate and CCA ester. All mixtures contained 0.2–0.4 *M* sodium sulfate. Temp = 23°. A: 6.7 × 10^{-4} *M* potassium osmate in 0.1 *N* sulfuric acid. B: 5.3 × 10^{-4} *M* CCA ester in 0.1 *N* sulfuric acid. C: 7.2 × 10^{-4} *M* CCA ester in water. The osmium tetraoxide concentration was measured spectrophotometrically using ϵ_{260} 2500.

hydrates, has never been established with certainty. Hofmann, *et al.*, reported in 1913[18] that the black, insoluble material which precipitated from neutral or weakly acidic solutions of potassium osmate corresponded in composition to an Os(V) oxide. Their evidence was based on the number of equivalents of potassium chlorate necessary to produce 1 equiv of osmium tetraoxide. Bavay, *et al.*,[19] have also suggested that the black, insoluble precipitate produced in this dismutation is an Os(V) species. These authors find that the initial disproportionation is to an Os(VII) species and, by stoichiometric implication, an Os(V) species. The Os(VII) species is soluble and there is good spectrophotometric evidence for its existence.[19-21] The Os(VII) species undergoes further dismutation to osmium tetraoxide and Os(V). The Os(V) species which forms the black, insoluble precipitate is said to undergo a slow further reaction to Os(IV) and Os(VI).[19]

Our proposed scheme is

$$6\mathrm{Os(VI)} \longrightarrow 3\mathrm{Os(VII)} + 3\mathrm{Os(V)} \qquad (8)$$

$$3\mathrm{Os(VII)} \longrightarrow 2\mathrm{Os(VIII)} + \mathrm{Os(V)} \qquad (9)$$

$$4\mathrm{Os(V)} + 2\mathrm{Os(VIII)} + 6\mathrm{H_2O} \longrightarrow 6\mathrm{Os(IV)} + 12\mathrm{H^+} + 3\mathrm{O_2} \qquad (10a)$$

or

$$4\mathrm{Os(V)} + 2\mathrm{H_2O} \longrightarrow 4\mathrm{Os(IV)} + 4\mathrm{H^+} + \mathrm{O_2} \qquad (10b)$$

The sum of eq 8 and 9 corresponds to the stoichiometry observed after short reaction times (Table VIA)

$$3\mathrm{Os(VI)} \longrightarrow \mathrm{Os(VIII)} + 2\mathrm{Os(V)}$$

After longer reaction times, the overall stoichiometry corresponds either to the sum of eq 8, 9, 10a or eq 8, 9, 10b or to some intermediate stoichiometry

$$3\mathrm{Os(VI)} + \mathrm{H_2O} \longrightarrow \mathrm{Os(VIII)} + 2\mathrm{Os(IV)} + {}^1/{}_2\mathrm{O_2} + 2\mathrm{H^+} \qquad (11a)$$

$$\mathrm{Os(VI)} + \mathrm{H_2O} \longrightarrow \mathrm{Os(IV)} + 2\mathrm{H^+} + {}^1/{}_2\mathrm{O_2} \qquad (11b)$$

Osmium(VI) Equilibria.—There are a number of acid–base equilibria which might account for the fact that the osmate ion disproportionates in solutions more acidic than pH 10.5.[19] We have measured the pH of solutions of potassium osmate in water in an attempt to define the equilibria involved. The data are presented in Table VII. The interesting fact which these data show is that the ratio $[\mathrm{OH^-}]/[\mathrm{osmate}]$ is approximately constant. We interpret this observation as reflecting dimerization of the osmate ion followed by dissociation (Scheme I). The table also shows that the assumption of a simple stepwise dissociation of the monomer is inconsistent with the data.

TABLE VII

EQUILIBRIA OF POTASSIUM OSMATE SOLUTIONS

$10^3[\mathrm{osmate}]_i$, *M*	pH[a]	10^3KK_D[b]	$10^5\beta_1$[c]	$10^9\beta_2$[d]
1.708	9.95	3.03	0.49	0.44
3.571	10.30[e]	3.50	1.18	2.34
6.519	10.55	3.31	2.04	7.25
7.761	10.65	3.73	2.73	12.20
11.64	10.80	3.28	3.61	22.81
15.52	10.90	2.91	4.28	34.02
27.38	11.20	3.77	9.74	154.4
	Av	3.36		

[a] Measured under nitrogen at 25°. [b] $KK_D = [\mathrm{OH^-}]^2/([\mathrm{osmate}]_i - [\mathrm{OH^-}])^2$, see Scheme I ($[\mathrm{osmate}]_i$ is the initial concentration of osmate). [c] $\beta_1 = [\mathrm{OH^-}]^2/([\mathrm{osmate}]_i - [\mathrm{OH^-}])$, $\mathrm{OsO_2(OH)_4^{2-}} \rightleftarrows \mathrm{OsO_2(OH)_3^-} + \mathrm{HO^-}$. [d] $\beta_2 = [\mathrm{OH^-}]^3/([\mathrm{osmate}]_i - [\mathrm{OH^-}])$, $\mathrm{OsO_2(OH)_4^{2-}} \rightleftarrows \mathrm{OsO_2(OH)_2} + 2\mathrm{HO^-}$. [e] Adjustment of the ionic strength to 0.05 *M* with sodium sulfate changed the pH to 10.35.

SCHEME I

$$2\mathrm{OsO_2(OH)_4^{2-}} \xrightleftharpoons{K_D} [\mathrm{OsO_2(OH)_3O(OH)_3OsO_2}]^{4-} + \mathrm{H_2O}$$

$$[\mathrm{OsO_2(OH)_3O(OH)_3OsO_2}]^{4-} \xrightleftharpoons{K} [\mathrm{OsO_2(OH)_2O(OH)_3OsO_2}]^{3-} + \mathrm{HO^-}$$

$$KK_D = [\mathrm{OH^-}]^2/[\mathrm{OsO_2(OH)_4^{2-}}]^2$$

CCA Ester Hydrolysis. Kinetics.—A summary of the rate data is given in Table VIII. The rate increases in both the acid and alkaline regions, but we have not pursued the details of the pH dependency because of optical interference from the disproportionation intermediates. A comparison of these data with the rate of

TABLE VIII

pH DEPENDENCE OF THE HYDROLYSIS OF THE OSMATE ESTER OF 3-CYCLOHEXENECARBOXYLIC ACID AT 25°

pH	10^3k_ψ, $\mathrm{min^{-1}}$	pH	10^3k_ψ, $\mathrm{min^{-1}}$
5.6[a]	11.48 ± 0.2	7.8[a]	5.37 ± 0.15
6.45[a]	8.68 ± 0.2	8.9[b]	3.77 ± 0.10
6.85[a]	6.39 ± 0.2	9.5[b,c]	5.86 ± 0.10
		10[b]	9.46 ± 0.10

[a] Phosphate buffer. [b] Carbonate buffer. [c] Data at other temperatures are the following: 45°, 4.34 × 10^{-2} $\mathrm{min^{-1}}$; 35°, 1.77 × 10^{-2} $\mathrm{min^{-1}}$; 8°, 8.71 × 10^{-4} $\mathrm{min^{-1}}$; E_a = 19 kcal $\mathrm{mol^{-1}}$.

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(18) K. A. Hofmann, O. Ehrhart, and O. Schneider, *Chem. Ber.*, **46**, 1657 (1913).

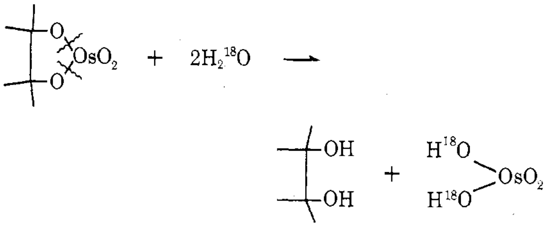
(19) J. C. Bavay, J. Nicole, G. Nowogrocki, and G. Tridot, *C. R. Acad. Sci., Ser. C*, **266**, 1293 (1968).

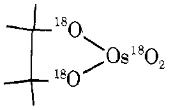
(20) J. C. Bavay, G. Nowogrocki, and G. Tridot, *Bull. Soc. Chim. Fr.*, 2030 (1967).

(21) J. P. Beaufils, M. Hellin, and F. Coussemant, *C. R. Acad. Sci., Ser. C*, **266**, 496 (1968).

hydrolysis of the bis(pyridine) osmate ester of CCA at pH 9.5, 25°, shows that the bis(pyridine) ester hydrolyzes more slowly by about a factor of 30.

Hydrolysis of the CCA Ester in $H_2{}^{18}O$.—The CCA ester (4.5×10^{-3} mol) was hydrolyzed with 5.5×10^{-2} mol of $H_2{}^{18}O$. The resulting 3,4-dihydroxycyclohexanecarboxylic acid was examined after 5 days. Analysis of the *m/e* ratio at 116, 117, 118 showed no oxygen-18 incorporation. The hydrolysis must therefore proceed with 100% Os–O cleavage according to eq 12 and differs, therefore, from the osmium tetraoxide catalyzed hydroxylation of olefins by hydrogen peroxide studied by Sulima.[22] The presence of oxygen-18 in the Os(VI) species formed as a result of the hydrolysis was demonstrated by running the hydrolysis in the presence of an olefin. The Os(VI) species disproportionates in part to osmium tetraoxide (*vide ante*) which in turn reacts with the olefin


(12)



The reaction was carried out by allowing 3×10^{-5} mol of the ester to hydrolyze in 5.5×10^{-2} mol of $H_2{}^{18}O$ containing 1.5×10^{-5} mol of allyl alcohol. The reaction mixture was filtered after 2 days and the reaction solution containing both glycerol and the cyclohexanecarboxylic acid diol was analyzed by mass spectrometry. Glycerol is much more volatile than the diol and can be analyzed without interference by examining only the initial scans and by keeping the probe temperature low. The glycerol peaks at *m/e* 61, 62, 63 gave an oxygen-18 content of 4.8 ± 0.1% unchanged when the ester:allyl alcohol ratio was either $^1/_2$ or 14.5. There was no exchange between water and either allyl alcohol alone or glycerol under these conditions. In order to account for this incorporation, we must assume complete exchange of the oxygens of the hypothetical molecule $OsO_2(OH)_2$ with water. On this assumption, one can show that the expected incorporation into the two carbon fragment from glycerol is $3x/2\%$, where x is the percentage oxygen-18 enrichment of the water. Since we must assume complete exchange for the species $OsO_2(OH)_2$, the only evidence for the position of bond cleavage is the negative set of results showing no incorporation into the initial diol.

Experimental Section

Chemicals.—3-Cyclohexenecarboxylic acid (CCA) from Aldrich Chemical Co. was distilled and the middle fraction used in all experiments. Osmium tetraoxide was obtained from Research Organic/Inorganic Chemical Co. Potassium osmate, $K_2OsO_2(OH)_4$, was a product of Alfa Inorganics Inc. or was prepared by ethanol reduction of the tetraoxide in KOH.[2] Pyridine, 3- and 4-picolines, and 3-chloropyridine were obtained from Aldrich Chemical Co. and Fisher Scientific Co. These were purified by distillation over KOH and stored over Fisher molecular sieve 4A. 2-Fluoropyridine and 2,2′-dipyridyl (Aldrich Chemical Co.) were used without further purification. Dimethyl sulfoxide-d_6 from Norell Chemical Co., Inc., was dried over Fisher molecular sieve, Type 4A. Tetramethylsilane was obtained from Aldrich Chemical Co.; H_2O^{18} was obtained from Prochem, Ltd.; allyl alcohol was from Eastman Organic Chemicals; glycerol and benzoic acid were Baker analyzed products. All other chemicals were of reagent grade. Sodium phosphate buffers were used in the pH range 6–8.15 and sodium carbonate buffers in the pH range 9–10.7.

Instruments.—Ultraviolet and visible spectra were recorded on a Perkin-Elmer Model 202 instrument. The same instrument was used with the time-drive attachment and a thermostated cell compartment held to within 0.1° of the indicated temperature for kinetic runs and stability constant measurements. Capped silica cells of 1-cm path length were used. Ir spectra were measured on a Perkin-Elmer 237B grating instrument. Proton magnetic resonance spectra were recorded on a Varian Associates T-60 instrument (60 MHz). Spectra were obtained at 35° using tetramethylsilane as an internal standard in dimethyl sulfoxide. The mass spectra were obtained on a Finnigan (1015 S/L) mass spectrometer. Samples in capillary tubes were introduced through a solid probe into the system. Measurements were carried out at an electron energy of 75 V and a current of 350 μA.

Oxygen-18 Measurements.—The oxygen-18 content of H_2O^{18} was measured both by direct estimation of the water spectrum at m/e = 18, 19, and 20 and by complete exchange with benzoic acid. In this latter method, 5 mg of benzoic acid was heated with $H_2{}^{18}O$ in 1 *N* HCl at 80° for 26 hr. The benzoic acid crystallized on cooling. The ^{18}O analysis was carried out by examination of the *m/e* ratios at 105, 106, and 107 and at 122, 123, and 124. The same ratios were obtained after 70 hr of heating. Calculations were made according to the procedure described by Biemann.[23] Both methods gave an oxygen-18 content of 3.3 ± 0.1%.

Kinetics of CCA Ester Hydrolysis.—The kinetics of CCA ester hydrolysis were followed by measurement of the decrease in the absorbancy of the ester in the vicinity of 230 nm. Runs were made in the temperature range 25–45° and for the pH range 6–10.6 using 1×10^{-4}–4.5×10^{-4} *M* substrate. Weighed quantities of the ester were dissolved in prethermostated buffer solutions contained in 25-ml volumetric flasks. Aliquots were transferred to capped silica cells for measurement of the absorbancy changes. Pseudo-first-order rate constants were calculated from the initial slopes of plots of log absorbancy *vs.* time since the plots deviated from linearity after about 20–40% of reaction.

The Kinetics of Ester Formation.—The formation of the osmate ester of CCA was followed by measuring the increase in absorption at 230 nm with time. With limiting concentrations of osmium tetraoxide, plots of log $[(A_\infty - A_0)/(A_\infty - A_t)]$ *vs.* time were linear. The k_ψ values obtained from the slopes of these plots varied linearly with CCA concentration. Values for k_0 were estimated from plots of k_ψ *vs.* CCA concentration. The formation of the pyridine and substituted pyridine esters was measured similarly except that the analytical wavelength was 300 nm (330 or 340 nm for 2,2′-dipyridyl). There was no significant variation in the slopes of the k_ψ plots when the limiting osmium tetraoxide concentration was varied in the range 5–40 $\times 10^{-5}$ *M*.

Preparation and Analysis of the Esters.—The bis(pyridine), bis(3-picoline), bis(4-picoline), bis(3-chloropyridine), and 2,2′-dipyridyl osmate esters of CCA were prepared in water by the procedure already described,[1] except that the reaction mixtures were allowed to stand for 2–3 hr instead of overnight. CCA was used in slight excess except for the case of 2,2′-dipyridyl for which the ratio OsO_4:dipyridyl was exactly 1. Dark brown solutions were obtained. The reaction mixtures were evaporated to dryness with air, finely powdered, and finally washed several times with ether. The washed powders were dried under vacuum overnight. The pyridine, 3-picoline, 4-picoline, and 3-chloropyridine content of the esters were determined by Ang's method.[24] The osmate ester of CCA was prepared in nonaqueous medium as follows: 1.97 mmol of osmium tetraoxide was dissolved in 100 ml of reagent grade carbon tetrachloride. To this, 1.7 mmol of CCA was added and dissolved by stirring. The solution turned

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[22] L. V. Sulima, *Russ. J. Org. Chem.*, **1**, 73 (1965).

[23] K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962, p 223 ff.

[24] K. P. Ang, *Anal. Chem.*, **38**, 1411 (1966).

light yellow and then pale green with fluorescence. After 1 hr, an olive green powdery solid began to separate. The mixture was left overnight at room temperature. The solid was filtered on a Büchner funnel, washed with ice-cold CCl_4, and dried *in vacuo* over P_2O_5. Osmium was determined by our slight modification of Criegee's method.[1] The oxidation state of osmium in the esters and other compounds was determined by iodometric analyses as follows (Table I): 15–85 mg of the compound was dissolved in water. Ten milliliters of 0.4 *N* KI was added followed by 5 ml of 2 *N* sulfuric acid and 25 ml of chloroform. The pyridine and picoline esters gave a violet-brown chloroform layer and a dark green aqueous layer. The mixtures were titrated with 0.1 *N* thiosulfate to a light olive green end point in the chloroform layer. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Determination of Osmium Tetraoxide Formed Following the Hydrolysis of the Esters.—A spectrophotometric or a titrimetric method was used depending on the amount of ester. Ester (2-60 mg) was added to water or to dilute sulfuric acid in 25-ml standard flasks. Acid solutions rapidly gave a clear supernatant fluid and a black precipitate. Anhydrous sodium sulfate was added to coagulate the solid. The mixture was filtered through a sintered glass funnel using as little suction as possible (OsO_4 is volatile). The absorbancy ratio, 240/300, can be used to demonstrate the absence of Os(VI) species from these solutions. For OsO_4, the ratio is 2.0 and ϵ_{240} 3150 ± 50. The Os(VI) species all have maxima in the vicinity of 300 nm; *e.g.*, potassium osmate has ϵ_{300} 1200 ± 100. The titrimetric method was used for larger quantities. In this case, the filtrate was collected directly into a mixture of 10 ml of 0.4 *M* KI, 5 ml of 2 *N* H_2SO_4, and 25 ml of chloroform. A violet chloroform layer and a dark green aqueous layer were formed. The mixture was titrated to a colorless end point in the chloroform layer using 0.1 *N* thiosulfate.

Analysis of the Black, Insoluble Osmium Oxides. (a) **The Initial Precipitate.**—Thirty to fifty milligrams of the CCA ester was added to 150–200 ml of water and allowed to stand at room temperature for 30–45 min to ensure complete hydrolysis. A blue-black colloidal suspension formed within a few minutes. After 30–45 min to ensure complete hydrolysis, solid sodium sulfate was added to flocculate the suspension. A clear, colorless supernatant liquid remained. If hydrolysis was incomplete, the supernatant liquid was brownish yellow. The mixture was filtered on a tared sintered-glass funnel and washed several times with water. The washings were discarded. The oxide on the filter was stirred with a 20% KI solution acidified with sulfuric acid. The filtrate was collected and the process repeated until liberation of I_2 ceased. I_2 in the combined filtrates was titrated with thiosulfate. The remaining precipitate was washed thoroughly with water and ether, dried *in vacuo* over P_2O_5 and weighed. Similar experiments were carried out with potassium osmate except that the initial solution must be acidified because of the alkalinity of potassium osmate solutions.

(b) **The Final precipitate.**—The black precipitate initially formed is allowed to stand in a glass-stoppered flask (total volume 10–15 ml) for 10–15 days together with the osmium tetraoxide initially formed. The precipitate was washed, dried, and weighed.

Warburg Experiments.—CCA ester (4–5 mg) was weighed into a small glass boat which was designed to balance on top of the center well of a single-arm Warburg flask. The main compartment of the flask contained 2.5 ml of water or buffer. In some experiments, oxygen-trapping solutions were placed in the side arms. In these cases, the air in the flask was replaced with nitrogen. The ground-glass joints were sealed with syrupy phosphoric acid at the lower edge and lanolin at the upper edge. After thermal equilibration, the boat and its contents were tipped into the main compartment. Readings were taken at 30 min intervals for about 12 hr.

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The Magnetic Circular Dichroism and Absorption Spectra of Nickel(II) Oxide

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The absorption and MCD spectra of a thin film of NiO have been measured at ~8°K and the results interpreted in terms of an exchange field splitting of the spin–orbit states using molecular field theory. The results agree well with calculation and assignments have been made. It is noted that a single ion approach is inadequate to explain both the absorption and the MCD spectra in contradiction to previous work on thin film and single crystal NiO.

Introduction

Most studies of the electronic spectra and structure of octahedral Ni(II) complexes have been directed toward obtaining crystal-field theory information: Δ, covalency parameters, electron repulsion parameters, low symmetry or lattice distortions, etc.[1] Inorganic chemists have generally tended to ignore the spectra of the binary compounds and instead have examined crystals whose spectra are similar in the solid state and in solution. In the binary oxides, for example, strong cooperative effects are a special feature of the physical properties of the compounds and in this work we have examined a crystal of markedly antiferromagnetic Ni(II) in order to characterize the electronic states in the presence of a strong exchange field.

Nickel oxide is a particularly interesting and important compound. By contrast to the early iron group oxides it does not exhibit metallic type conduction having a conductivity of 10^{-8} ohm^{-1} cm^{-1}.[2] This fact necessitated some rethinking of the approach to the theory of electrons in solids since according to the band theory, NiO should have a partly filled d band and thus be an excellent conductor. However, it is not and, furthermore, the electronic spectrum is similar to that of $NiSO_4 \cdot 7H_2O$, say, or to Ni(II) in aqueous solution. Thus a Heitler–London or localized electron model of the electronic structure of NiO is more

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(1) See for example J. Ferguson, *Progr. Inorg. Chem.*, **12**, 159 (1970).

(2) J. P. Suchet, "Crystal Chemistry and Semiconduction," Academic Press, New York, N. Y., 1971, p 169.