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METAL-CHAIN – METAL-RING TRANSITIONS IN THE REDUCTION OF TRINUCLEAR OSMIUM CARBONYL HALIDES

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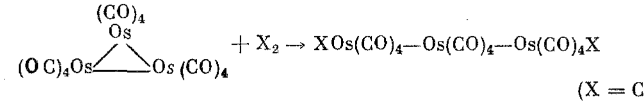
There are well-known reactions involving the opening of small carbon rings as a result of attachment of halogens and reverse reactions of ring formation in the reduction of normal α,ω-dihaloalkanes. In sufficiently mild conditions, triangulo-dodecacarbonyltriosmium $Os_3(CO)_{12}$ reacts similarly in nonpolar solvents with halogens, with dissociation of one of the metal–metal bonds, and is converted to linear carbonyl halides containing a chain of three Os atoms [1, 2],

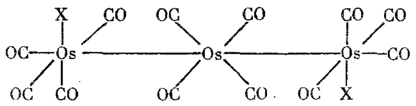


(X = Cl, Br, I).

There is only one known example of conversion of a linear osmium compound to a metal ring [3]: When the dihydride $H_2Os_3(CO)_{12}$ is heated at 165°C in the absence of a solvent, two H atoms split off forming $Os_3(CO)_{12}$.

In this article we report on the conversion of linear trinuclear osmium carbonyl halides $X_2Os_3(CO)_{12}$ (X = Cl, Br, I) to $Os_3(CO)_{12}$ as a result of chemical and electrochemical reduction.

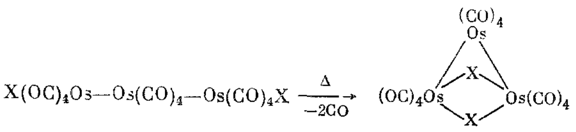
By x-ray structural analysis it has been found that in the crystalline state the diiodide $I_2Os_3(CO)_{12}$ contains a linear chain of three Os atoms, while the halogen atoms occupy equatorial positions on the terminal Os atoms in mutual trans positions [4]:



Dimethyldodecacarbonyltriosmium $Me_2Os_3(CO)_{12}$ [5] has a similar structure.

By comparing the vibrational spectra of compounds of the type $X_2Os_3(CO)_{12}$ in both the crystalline state and solutions, we can infer that these compounds are isostructural. In solutions we can expect the appearance of rotamers formed by rotation of the terminal groups $X(OC)_4Os$ about the Os–Os bond; however, the linear configuration of the molecule and the equatorial positions of the halogen atoms are then undoubtedly preserved.

Note that there is a possibility of bending of the linear Os–Os–Os chain owing to trans → cis isomerization. Similar isomerization is observed in reactions of intramolecular substitution of CO groups in $X_2Os_3(CO)_{12}$ complexes, leading to formation of compounds of the type $(\mu\text{-}X_2)Os_3(CO)_{10}$ [6]:



When linear carbonyl halides $X_2Os_3(CO)_{12}$ are reduced in mild conditions in an aprotic medium, we can expect dissociation of the osmium–halogen bonds and formation of an intermediate linear hypothetical biradical $[Os_3(CO)_{12}]^{\cdot\cdot}$. This biradical can later either take part in chain growth reactions leading to formation of tetracarbonylosmium oligomers or polymers, or be converted to a stable metal-ring compound:

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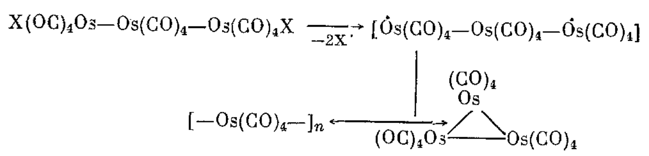
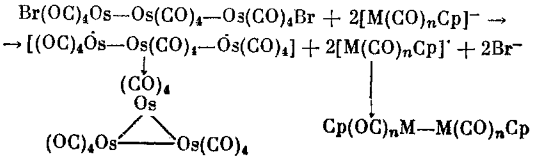


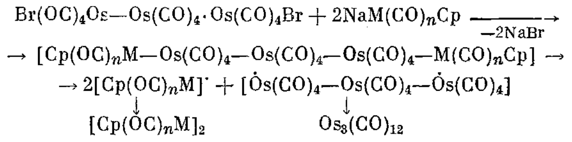
We found that reaction of $Br_2Os_3(CO)_{12}$ solution in acetonitrile with sodium amalgam at about 20°C quickly leads to quantitative formation of $Os_3(CO)_{12}$. When sodium amalgam acts on $Os_3(CO)_{12}$ solution in THF, it forms a complex mixture of mononuclear and polynuclear carbonylosmate anions [1]. The poor solubility of $Os_3(CO)_{12}$ in acetonitrile, which we used as solvent, hinders further reduction. Boiling $Br_2Os_3(CO)_{12}$ in toluene in the presence of excess pyridine unexpectedly led to the formation of $Os_3(CO)_{12}$ with a good yield (53%). In this case the pyridine probably acts as a reducing agent and the reaction can be of the one-electron transfer type [7].

When $Br_2Os_3(CO)_{12}$ reacts with $NaMo(CO)_3Cp$ and $NaFe(CO)_2Cp$, complex mixtures of products are formed in which there are appreciable amounts of $Os_3(CO)_{12}$ (about 30%) and the corresponding binuclear (η^5-cyclopentadienyl)metal carbonyls (about 40%). The formation of these compounds can be explained by means of two alternative mechanisms:

a) In the reaction an electron is transferred from the (η^5-cyclopentadienyl)carbonylmetallate anion to the antibonding σ^* orbital of the Os−Br bond, forming a halogen anion and corresponding metal carbonyl radicals:



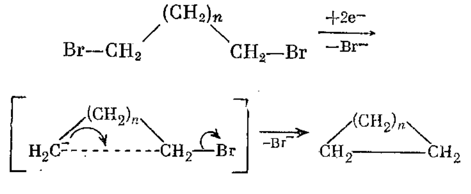
b) In the reaction conditions there is homolytic dissociation of the metal−metal bonds in the unstable linear heterometallic compounds formed as a result of substitution for the Br atoms:



$$\begin{aligned}&Br(OC)_4Os{-}Os(CO)_4{\cdot}Os(CO)_4Br + 2NaM(CO)_nCp \xrightarrow[-2NaBr]{} \\ &\to [Cp(OC)_nM{-}Os(CO)_4{-}Os(CO)_4{-}Os(CO)_4{-}M(CO)_nCp] \to \\ &\to 2[Cp(OC)_nM]^{\cdot} + [\dot{O}s(CO)_4{-}Os(CO)_4{-}\dot{O}s(CO)_4] \\ &\quad\ \downarrow \qquad\qquad\qquad\qquad \downarrow \\ &\ [Cp(OC)_nM]_2 \qquad\qquad\quad Os_3(CO)_{12}\end{aligned}$$

In order to elucidate the possible mechanism of reduction of linear trinuclear osmium carbonyl halides and to determine the relative lability of the osmium−halogen bonds, we undertook a study of the electrochemical reduction of these compounds and normal α,ω-dibromoalkanes. Polarographic reduction was effected at a dropping mercury electrode in absolute acetonitrile; the reference electrodes were Ag/Ag^+.

In the reduction of 1,3-dibromopropane and 1,4-dibromobutane, on the polarograms we observed one two-electron diffusion wave ($E_{1/2}$ = −2.49 and −2.52 V, respectively). The mechanism of polarographic reduction of these compounds, leading to the formation of cycloalkanes, is well known [8]; it is thought that the first stage of the process is heterolytic discharge of one of the C−Br bonds and that the resulting carbanion is stabilized by eliminating a halogen anion and giving the cyclic product



In the reduction of trinuclear osmium carbonyl halides $X_2Os_3(CO)_{12}$ (X = Cl, Br, I), on the polarograms we see three reversible diffusion waves: i_d is proportional to $\sqrt{H}$ and to the concentration of the test compound (Table 1). The potential of the first wave depends on the nature of the halogen atom and is undoubtedly related to the dissociation of the osmium−halogen bonds. The ease of reduction of the carbonyl halides decreases in the sequence I > Br > Cl. The observed sequence of change of the reduction potentials of Os−X bonds is evidence of a high degree of covalence of these bonds and is similar to that found previously both for organic halogen compounds [9] and for mononuclear carbonyl halides of transition metals [10, 11]. At the same time,

TABLE 1. Polarographic Characteristics of Reduction of Trinuclear Osmium Compounds (CH_3CN, 0.1 N Et_4NbF_4, $C = 1 \cdot 10^{-3}$ mole/liter, Ag/Ag^+)

Compound	$-E_{1/2}$, V	i_d, μA	αn	Compound	$-E_{1/2}$, V	i_d, μA	αn
$Os_3(CO)_{12}$	1,75	1,80	0,84	$Br_2Os_3(CO)_{12}$	1,44	1,40	0,47
	2,77	1,80	0,59		1,74	1,68	0,51
$Cl_2Os_3(CO)_{12}$	1,54	1,36	0,66		2,74	1,88	0,66
	1,78	1,60	0,66	$I_2Os_3(CO)_{12}$	1,24	1,88	0,96
	2,71	1,76	0,74		1,78	1,28	0,57
					2,71	1,96	0,70

the lower values of the potentials indicate easier polarizability of Os–X bonds in comparison with C–X bonds in dihaloalkanes.

The second and third reduction waves of the compounds $X_2Os_3(CO)_{12}$ coincide with the reduction waves of triangulo-dodecacarbonyltriosmium, and are evidently related to successive attachment of two electrons to this compound [12], which is formed in the first stage of reduction. The formation of $Os_3(CO)_{12}$ in polarographic reduction of $X_2Os(CO)_{12}$ complexes is confirmed by electrolysis of the dibromide $Br_2Os_3(CO)_{12}$ in acetonitrile at the controlled potential of the limiting current of the first reduction wave (−1.50 V).

Gubin and Denisovich [10] have established that mononuclear carbonyl halides of transition metals are easily subjected to polarographic reduction with dissociation of the metal–halogen bonds; according to the nature of these bonds, the process can follow either a one-electron mechanism

$$X - [M] + e^- \rightarrow X^- + [M]^{\cdot}$$
$$X = I,\ [M] = W(CO)_3Cp;\ X = Cl,\ Br,\ I,\ [M] = Fe(CO)_2Cp,$$
$$Fe(CO)_3(\eta^3\text{-}C_3H_5),$$

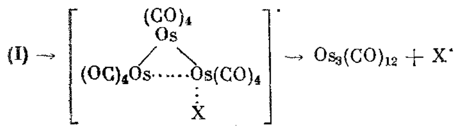
or a two-electron mechanism

$$X - [M] + 2e^- \rightarrow X^- + [M]^-$$

where X = Cl, Br, I, [M] = $Mn(CO)_5$, $Re(CO)_5$; X = Cl, Br, [M] = $W(CO)_3Cp$. On the basis of the equality of the heights of all the reduction waves of the compounds $X_2Os_3(CO)_{12}$ we can assume that one electron takes part in each stage of reduction. A similar conclusion is reached if we compare the heights of the waves of the compounds $X_2Os_3(CO)_{12}$ with the height of the two-electron wave of reduction of $BrRe(CO)_5$ [11]. Corresponding to this, we can propose the following scheme for the reduction of trinuclear linear carbonyl halides of osmium:

$$X{-}Os(CO)_4{-}Os(CO)_4{-}Os(CO)_4{-}X \xrightarrow[-X^-]{+e^-} \underset{(I)}{[\dot{O}s(CO)_4{-}Os(CO)_4{-}Os(CO)_4{-}X]} \xrightarrow[-HgX^{\cdot}]{+Hg}$$
$$\rightarrow \underset{(II)}{[Os(CO)_4{-}Os(CO)_4{-}Os(CO)_4]^{\cdot\cdot}} \rightarrow Os_3(CO)_{12} \xrightarrow{+e^-}$$
$$\rightarrow \underset{(III)}{[Os_3(CO)_{12}]^{\dot{-}}} \xrightarrow{+e^-} \underset{(IV)}{[Os_3(CO)_{12}]^{2-}}$$

When the first electron is attached to the $X_2Os_3(CO)_{12}$ molecule, one of the Os–X bonds is dissociated and a monohalododecacarbonyltriosmium radical (I) is formed. Detachment of a second halogen atom can occur without expenditure of electrons when radical (I) interacts with the surface of the mercury drop. The biradical (II) thus formed is rapidly stabilized, being converted to triangulo-dodecacarbonyltriosmium, which then successively acquires two electrons, being converted successively to anion radical (III) and dianion (IV). The possibility of synchronous splitting-off of a second halogen atom from radical (I) and formation of cyclic osmium carbonyl can apparently be eliminated, since this process, which to some extent resembles the conversion of the carbanion $BrCH_2CH_2CH_2^-$ to cyclopropane, involves the formation of a cyclic intermediate with a coordinately supersaturated Os atom:



Thus, the results of our chemical and electrochemical reduction of trinuclear linear osmium carbonyl halides indicate the possibility of formation of osmium carbonyl radicals, capable of being converted to stable metal rings, in these processes. Apparently, a similar behavior will also be characteristic of linear compounds of other transition metals. This feature of the linear compounds must certainly be taken into account in reactions of nucleophilic substitution of ligands at the terminal metal atoms.

EXPERIMENTAL

All operations were performed in absolute solvents in an atmosphere of argon. The compounds $X_2Os_3(CO)_{12}$ (X = Cl, Br, I) were obtained by the action of halogens on solutions of $Os_3(CO)_{12}$ in CCl_4, by methods similar to those described in [1].

Polarographs were recorded on an LP-7e electronic polarograph with a three-electrode thermostated cell. The anode and reference electrodes were of Ag/Ag^+; the cathode was a mercury dropping electrode with forced drop detachment, with the following characteristics: m = 0.53 mg/sec, t = 0.29 sec. Reduction was effected in anhydrous acetonitrile; the base electrolyte was a 0.1 N solution of Et_4NBF_4. The base electrolyte was discharged at −3.2 V. The error of measurement of the half-wave potential was ±0.03 V.

The IR spectra were recorded in an IR-75 instrument with a diffraction grating. Thin-layer chromatography (TLC) was carried out on Silufol plates (Czechoslovakia).

Reduction of $Br_2Os_3(CO)_{12}$ with Sodium Amalgam. A solution of 0.050 g (0.047 mmole) of $Br_2Os_3(CO)_{12}$ in 20 ml CH_3CN was shaken for 30 min with 2 ml of amalgam containing 0.010 g (0.43 mg-eq) of Na. The color of the solution quickly changed from pale yellow to orange, and a precipitate came down. After the end of shaking the suspension was carefully separated from the amalgam; the precipitate was filtered off and dried on the filter. We obtained 0.029 g (68%) of $Os_3(CO)_{12}$, identified by TLC and IR spectra.

Reaction of $Br_2Os_3(CO)_{12}$ with Na Salts of Metal Cyclopentadienylcarbonyls. a) To a solution of 0.440 g (0.41 mmole) of $Br_2Os_3(CO)_{12}$ in 30 ml of THF we added drops of $NaFe(CO)_2Cp$ solution obtained by reduction of 0.160 g (0.45 mmole) of $[Fe(CO)_2Cp]_2$ with 1% sodium amalgam in 10 ml of THF. The mixture was stirred for 2 h, and the solvent then driven off in vacuum. From the dry residue by successive extraction with hexane, benzene, and chloroform we separated 0.100 g (27%) of $Os_3(CO)_{12}$ and 0.070 g (44%) of $[Fe(CO)_2Cp]_2$, identified by means of the IR spectra and TLC.

b) By reacting 0.440 g (0.41 mmole) of $Br_2Os_3(CO)_{12}$ with $NaMo(CO)_3Cp$, obtained from 0.220 g (0.45 mmole) of $[Mo(CO)_3Cp]_2$, in similar conditions we separated 0.130 g (35%) of $Os_3(CO)_{12}$ and 0.080 g of $[Mo(CO)_3Cp]_2$.

Reaction of $Br_2Os_3(CO)_{12}$ with Pyridine. To a boiling solution of 0.100 g (0.094 mmole) of $Br_2Os_3(CO)_{12}$ in 50 ml of toluene we added drops of 0.023 g (0.29 mmole) of a solution of pyridine in 10 ml of toluene. The mixture was boiled for 2 h, then the solvent was driven off in vacuum and the residue recrystallized from a $CHCl_3$−hexane (1 : 3) mixture. We obtained 0.045 g (53%) of $Os_3(CO)_{12}$, identified from the IR spectrum.

CONCLUSIONS

1. As a result of chemical and electrochemical reduction the authors convert linear trinuclear osmium carbonyl halides to triangulo-dodecacarbonyl triosmium.

2. They study the polarographic reduction of linear compounds of osmium of the type $X_2Os_3(CO)_{12}$ (X = Cl, Br, I). In contrast with C−X bonds in dihaloalkanes, dissociation of Os−X bonds involves a one-electron stage and leads to the formation of osmium carbonyl radicals which are subsequently converted into metal rings.

3. The ease of reduction of compounds of the type $X_2Os_3(CO)_{12}$ depends on the electronegativity of the halogen atoms, and increases in the order X = Cl < Br < I.

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MECHANISM OF THE OXIDATION OF 12-MOLYBDOVANADOPHOSPHATE BLUES BY OXYGEN IN AQUEOUS SOLUTION

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Oxidation of blues of the composition $H_i[H_{3+n}PMo_{12-n}V_i^{IV}V_{n-i}^{V}O_{40}]$ (H_iHPA) by oxygen is one of the stages of liquid-phase oxidation of organic and inorganic substances catalyzed by corresponding heteropolyacids (HPA) of composition $H_{3+n}PMo_{12-n}V_n{}^{V}O_{40}$ [1]

$$H_iHPA + i/4O_2 \rightarrow HPA + i/2\ H_2O \tag{1}$$

Here n = 2-6 is the number of vanadium atoms in the polyanion; $i \leq n$ is the number of electrons which the blue acquires on reduction. The oxidation potential of HPA is fairly high (E_0 = 0.64-0.74 V [1]); therefore, reaction (1) takes place by a one-electron mechanism which is thermodynamically disadvantageous [2-4]. It appears that reaction (1) takes place via stages of multielectron transfers [2-4], but the details of the mechanism are obscure. To ascertain them, using a highly sensitive manometric method [5] we have investigated the kinetics of reaction (1) with $i < 1$ and n = 3, 4, 6 under the conditions usually realized in catalytic processes involving HPA. Previously [3, 4], data were obtained on the kinetics of reaction (1) in the presence of VO^{2+} ions with $[H_iHPA] \leq [VO^{2+}]$.

Blues of H_iHPA with $i < 1$ are a mixture of HPA and H_iHPA: $[H_iHPA] \approx [HPA] + [H_1HPA]$ and $i \approx [V^{IV}]/[H_iHPA]$, where $[H_iHPA]$ is the overall concentration of all forms of the polyanions, and $[V^{IV}]$ is the overall V^{IV} concentration. Particles of H_mHPA containing $m > 1$ V^{IV} atoms may also be present in equilibrium. The subscript m refers to the individual polyanions and takes integral values. We must distinguish m from the subscript i, characterzing the mean depth of reduction of the blue $i = \sum_{m=0} m\,[H_mHPA] \big/ \sum_{m=0} [H_mHPA]$ and acquiring a continuous series of values $0 < i \leq n$. Clearly, when $i < 1$ the following equations are correct:

$$[V^{IV}] \simeq [H_1\,HPA] > [H_2\,HPA] > [H_3\,HPA] \tag{2}$$

$$[HPA] \simeq [H_i\,HPA] - [V^{IV}] \tag{3}$$

Condition (2) is also confirmed by the fact that the equilibrium constant of the reaction $H_mHPA + V^{IV} + H^+ \rightleftharpoons H_{m+1}HPA + V^V$ does not depend on m and n [6].

EXPERIMENTAL

Aqueous solutions of Na salts of HPA and the corresponding blues were obtained as in [7] and kept in argon. Before an experiment the solutions were mixed in ratios to obtain a given i. Oxygen was obtained by decomposing H_2O_2 on an MnO_2 catalyst.

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