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Preliminary communication

The Kinetics of Iodide Attack on the Cluster $Os_6(CO)_{18}$.

by Glyn R John, B F G Johnson,
Jack Lewis and Alastair L Mann
(University Chemical Laboratory,
Lensfield Road, Cambridge)

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SUMMARY

The reduction of the cluster $Os_6(CO)_{18}$ to $[Os_6(CO)_{18}]^{2-}$ by iodide has been found to obey the rate law, Rate = $k_1k_2[Os_6(CO)_{18}][I^-]^2/k_{-1} + k_2[I^-]$. This is most easily explained in terms of a pre-equilibrium association between the cluster and iodide, followed by rate-determining attack of a second iodide ion.

We have previously[1] demonstrated that the cluster $Os_6(CO)_{18}$ undergoes reversible reduction to produce $[Os_6(CO)_{18}]^{2-}$ under mild conditions. In the course of reaction the Os_6 unit changes from a bicapped tetrahedral geometry to that of a regular octahedral arrangement. Mechanistic studies in cluster chemistry are very few and, apart from the study of CO exchange processes[2], mechanisms have generally been proposed on the basis of selective synthesis and product stereochemistry alone. Here we wish to report preliminary findings from a detailed kinetic investigation of the reduction of $Os_6(CO)_{18}$ to $[Os_6(CO)_{18}]^{2-}$ by iodide (equation 1).

$$Os_6(CO)_{18} \underset{I_2}{\overset{I^-}{\rightleftarrows}} [Os_6(CO)_{18}]^{2-} \qquad (1)$$

Using an excess of iodide the reduction appears to proceed to completion in dichloromethane and may be conveniently followed by the slow (*i.e.*, of the order of minutes) disappearance of the original neutral carbonyl bands at 2075(vs), 2061(vs), 2037(s), 2029(ms, sh), 1999(w) and 1958(w) cm^{-1} and growth of product bands at 1992(vs) and 1915(w) cm^{-1}. Good linear *pseudo*-first order plots were obtained for 75-85% of reaction. However, in other solvents the reaction is not as simple. Other products have also been observed[3] and the course of this reaction is significantly solvent dependent.

The rate of attack of iodide upon $Os_6(CO)_{18}$ is found to be proportional to $[I^-]^2$ for iodide concentrations in the range $2.5 \times 10^{-3} - 5.0 \times 10^{-2}$ and for temperatures 10-30°C. This may be most easily rationalised in terms of a pre-equilibrium association between $Os_6(CO)_{18}$ and I^-, followed by rate-determining attack by a second I^- ion, as shown in equations 2 and 3.

$$Os_6(CO)_{18} + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [INT] \qquad (2)$$

$$[INT] + I^- \xrightarrow[slow]{k_2} [Os_6(CO)_{18}]^{2-} + I_2 \qquad (3)$$

The rate expression for such a mechanism is:-

$$Rate = \frac{k_1k_2[Os_6(CO)_{18}][I^-]^2}{k_{-1} + k_2[I^-]}$$

which reduces to the experimentally observed form:-

$$\text{Rate} = k[Os_6(CO)_{18}][I^-]^2$$

$$(\text{where } k = k_1k_2/k_{-1})$$

provided $k_2[I^-] << k_{-1}$ (i.e., low iodide concentrations).

The observed trimolecular rate constants at the different temperatures studied are given in Table 1. Since these rate constants consist of a combination of terms (k_1, k_{-1}, k_2), the calculated activation parameters so derived, $\Delta H^{\ddagger}_{app} = 90.7 \pm 4.3$ kJ mol^{-1} and $\Delta S^{\ddagger}_{app} = +53.4 \pm 1.4$ J k^{-1} mol^{-1}, have limited mechanistic significance. Further support for the proposed mechanism is gained from the observation that at higher iodide concentrations plots of k_{obs} versus $[I^-]^2$ tend to level off.

Table 1

Temperature dependence of observed trimolecular rate constants in dichloromethane.

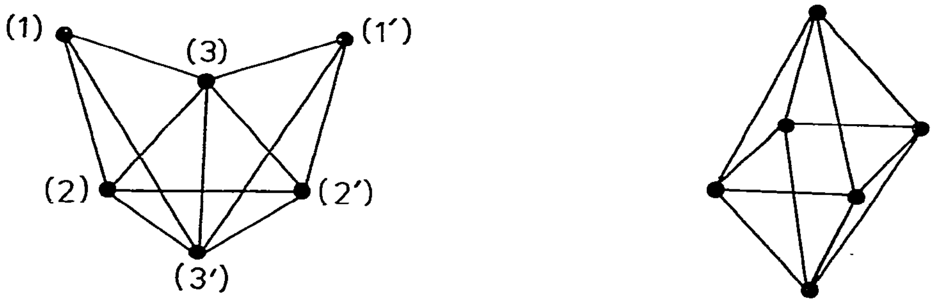
T/°C	k/l^2 mol^{-2} s^{-1}
30	15
25	7.5
20	4.1
15	2.3
10	1.1

At present we have no firm experimental evidence to elucidate the exact nature of the intermediate species postulated. Two modes of initial attack by iodide may be envisaged:-

(i) attack at a carbonyl carbon to yield an acyl-iodide derivative,

and (ii) direct attack at an osmium atom.

Thus, an intermediate of the type $[Os_6(CO)_{17}(COI)]^-$ or $[Os_6(CO)_{18}I]^-$ would be involved. Attack at a carbonyl carbon to form acyl-type intermediates has been frequently proposed[4,5,6] in metal carbonyl chemistry and would at first appear the more likely. However, $Os_6(CO)_{18}$ (an 84-electron species) has three pairs of osmium atoms (Os(1), Os(2) and Os(3)) which differ in their coordination number (6-, 7- and 8- coordinate, respectively) and the electron density associated with them. In contrast, $[Os_6(CO)_{18}]^{2-}$ (an 86-electron species) is electron precise according to cluster bonding ideas (e.g., Wade theory[7]); all six osmium atoms are in the same environment (Figure 1).



(I)

(II)

Figure 1

Whatever the precise nature of this initial iodo-intermediate complex may be, it is believed that electron density is withdrawn from the coordinated iodide into the cluster framework. Then a second iodide ion attacks the bound (δ+) iodide moiety to release free iodine (confirmed by t.l.c.). At one or other stage during the electron transfer process the rearrangement in cluster geometry takes place.

Interestingly, the reverse oxidation reaction is a much more rapid process (*i.e.*, of the order of seconds) in dichloromethane and a preliminary analysis indicates that the overall oxidation takes place at least ca. 10^2 times faster than reduction. Again, the mechanistic implications should prove interesting, since the I-I bond must be cleaved by $[Os_6(CO)_{18}]^{2-}$. It seems feasible that here the highly charged (symmetrical) sheath of oxygen atoms effects the initial polarisation, resulting in the loss of electrons from the cluster core. A full kinetic investigation of this oxidation process is currently being undertaken using stopped-flow techniques.

ACKNOWLEDGEMENTS

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