

NOTE

REACTIONS OF $\text{Os}_3(\text{CO})_{12}$ WITH HALOGENS

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The reaction of $\text{Os}_3(\text{CO})_{12}$, with X_2 , where $\text{X} = \text{Cl}$, Br and I in benzene and methylene chloride¹ has been found to yield $\text{Os}_3(\text{CO})_{12}\text{X}_2$, the structure of which contains a unique linear arrangement of osmium atoms². This reaction presumably involves the breakage of a single osmium–osmium bond. Qualitative observations in benzene have revealed that the rate of this reaction is slow³. As part of a programme to determine the properties of metal–metal bonds we have studied the kinetics of this reaction, and a suggested mechanism for the reaction is put forward.

EXPERIMENTAL

$\text{Os}_3(\text{CO})_{12}$ was prepared by the high pressure reaction of OsO_4 and CO in xylene³. Methylene chloride was dried (Molecular Sieve 4A) and distilled immediately before use. Estimation of halogen concentration was performed by adding excess KI and determining the amount of I_2 produced using a standard solution of $\text{Na}_2\text{S}_2\text{O}_3$.

Reaction rates were determined spectrophotometrically using a stopped-flow apparatus which was designed such that the solutions only came in contact with glass, polythene, Fluorosint*, and Kel-F**. Spectrophotometric measurements were performed at 400 and 350 $\text{m}\mu$. The relevant molar extinction coefficients are given in Table 1.

TABLE I

COMPLEX MOLAR EXTINCTION COEFFICIENTS

	400 $\text{m}\mu$	350 $\text{m}\mu$
$\text{Os}_3(\text{CO})_{12}$	~ 3000	~ 8000
$\text{Os}_3(\text{CO})_{12}\text{Cl}_2$	~ 250	~ 18000
$\text{Os}_3(\text{CO})_{12}\text{Br}_2$	~ 600	~ 17000

* A filled PTFE polymer (manufactured by Polypenco Ltd., Gate House, Welwyn Garden City, Herts, England).

** Poly(chlorotrifluoroethylene) (obtained from Fluorocarbon Company Ltd., Caxton Hill, Herts, England).

Good pseudo first order kinetics were obtained with $\text{Os}_3(\text{CO})_{12}$ concentrations $0.5\text{--}1.0 \times 10^{-4} M$, and halogen concentrations $5\text{--}50 \times 10^{-4} M$ (cf. Tables 2 and 3).

TABLE 2

FIRST ORDER RATE CONSTANTS^a FOR THE REACTION BETWEEN $\text{Os}_3(\text{CO})_{12}$ AND X_2 (WHERE $\text{X} = \text{Cl}$ OR Br)^b

$\text{Cl}_2(M)$	$k(\text{sec}^{-1})$	$\text{Br}_2(M)$	$k(\text{sec}^{-1})$
5×10^{-4}	5.31	5×10^{-4}	1.83
1×10^{-3}	5.48	7.5×10^{-4}	1.75
2.5×10^{-3}	5.58	1.25×10^{-3}	1.73
2.5×10^{-3} (13.7°)	2.23	2.5×10^{-3} (13.7°)	0.733
2.5×10^{-3} (22°)	3.49	2.5×10^{-3} (22°)	1.30
2.5×10^{-3} (27.9°)	5.90	2.5×10^{-3} (27.9°)	2.22
5×10^{-3}	5.74		

^a Unless otherwise stated, temperature = 25°. ^b In methylene chloride.

TABLE 3

ACTIVATION PARAMETERS

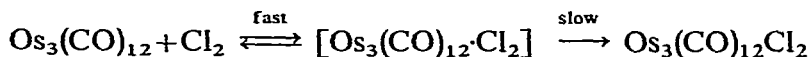
	ΔH^\ddagger (kcal/mole)	ΔS^\ddagger (e.u.)
$\text{Os}_3(\text{CO})_{12}/\text{Cl}_2$	11.8 (± 0.7)	-15.9 (± 2.4)
$\text{Os}_3(\text{CO})_{12}/\text{Br}_2$	12.7 (± 0.2)	-14.9 (± 1)

DISCUSSION

The preparative chemistry of the reaction between $\text{Os}_3(\text{CO})_{12}$ and halogen was performed in benzene². However it was not possible to study the kinetics of the reaction in benzene since at these low concentrations of halogen the photochemical reaction between benzene and halogen prevents the accurate determination of halogen concentration. Methylene chloride was chosen as the most suitable solvent since the UV and visible spectra of $\text{Os}_3(\text{CO})_{12}$ in this solvent is identical to that in benzene, and also no reaction between halogen and solvent occurs at room temperature. In carbon tetrachloride as the solvent media, the reaction pattern is different to that in methylene chloride. Initial observations in this solvent suggests that the reaction rate is dependent on halogen concentration. Carbon tetrachloride has not been used in these studies because of its known reaction with metal carbonyls⁴.

It can be seen from Table 2 that the first order rate constants are independent of halogen concentration in the range studied. Furthermore the reaction of $\text{Os}_3(\text{CO})_{12}$ with Cl_2 and Br_2 in methylene chloride is rapid, $t_{\frac{1}{2}} \sim 120$ and ~ 400 msec respectively.

On close inspection of the kinetic plots involving Cl_2 at 400 $m\mu$ (*i.e.* following the decrease in concentration of $\text{Os}_3(\text{CO})_{12}$) an initial, very fast, decrease in absorbance can be observed ($t_{\frac{1}{2}} \sim 5$ msec with $\text{Cl}_2 = 5 \cdot 10^{-4} M$). On increasing the Cl_2 concentration to $5 \cdot 10^{-3} M$, this particular reaction becomes too fast to measure ($t_{\frac{1}{2}} < 1\text{--}2$ msec). The rate for this reaction is therefore dependent on Cl_2 concentration. Assuming that the initial reaction rate has a first order dependence on Cl_2 , the following kinetic scheme could explain the above observations



The suggested intermediate $[\text{Os}_3(\text{CO})_{12} \cdot \text{Cl}_2]$, could be a charge-transfer or a Lewis acid/base complex between Cl_2 and $\text{Os}_3(\text{CO})_{12}$ respectively. Similar Lewis acid/base complexes may exist between OsO_4 and $\text{Os}_3(\text{CO})_{12}$ ⁵ and I_2 and $\text{Mn}_2(\text{CO})_{10}$ ⁶.

The rapid initial reaction could not be observed in corresponding reaction with Br_2 . This may indicate that the suggested Lewis acid/base intermediate decomposes rapidly. Indirect evidence for this intermediate is given by the rate constant being independent of Br_2 concentration, and also the fact that the first-order rate constants for the Cl_2 and Br_2 reactions are different.

The reactions between $\text{Os}_3(\text{CO})_{12}$ and I_2 in methylene chloride was complicated and was not studied kinetically in great detail. During reaction in benzene other minor products are formed¹ which may tend to interfere with electronic spectral observations. The reaction between $\text{Os}_3(\text{CO})_{12}$ and I_2 in decalin is photochemically initiated. A slow change in absorbance (at $330 \text{ m}\mu$) occurred in darkened flasks over several minutes, but during the determination of the absorbance of the reaction mixture a rapid decrease was observed.

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