Substitution kinetics of some tetracarbonyl(η^2-alkene)osmium complexes ☆

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Abstract

The kinetics of displacement of the alkene from $Os(CO)_4(\eta^2$-alkene) by $P(OEt)_3$ or PPh_3 in heptane or dodecane have been studied (alkene = ethene, 1-octene, methyl acrylate). The reactions all proceed by dissociative paths with positive values of ΔS^* (60–80 J K^{-1} mol^{-1}) which contrast with the very small value 5.6 ± 0.1 J K^{-1} mol^{-1} (recalculated as -2 ± 10 J K^{-1} mol^{-1}) reported elsewhere for dissociative loss of CO from $Os(CO)_5$. Substantial amounts of the disubstituted products $Os(CO)_3L_2$ are produced by the reactions in addition to the expected $Os(CO)_4L$, a phenomenon also observed after similar reactions of $Fe(CO)_4(\eta^2$-alkene) complexes although the reasons for this seem to be different in the two cases. Comparison with data obtained elsewhere shows that the pronounced 'triad effect' exhibited by the $M(CO)_4(\eta^2$-methyl acrylate) complexes (M = Fe, Ru, Os) is caused entirely by the relative values of ΔH^* (152 ± 2, 116 ± 2, 149 ± 2 kJ mol^{-1}, respectively). The relationship between the activation enthalpies for alkene dissociation and the intrinsic strengths of the metal–(η^2-alkene) bonds is briefly discussed. What appears to be the complex $Os(CO)_4(\eta^2$-vinyl acetate) behaves quite differently from its methyl acrylate isomer.

Keywords: Kinetics and mechanism; Osmium complexes; Alkene complexes; Carbonyl complexes

1. Introduction

The bonding between metal atoms and alkenes has been a topic of interest for decades [1], not the less so because metal–alkene complexes are involved in a wide number of important catalytic reactions [1,2]. The strength of the bonding plays a pivotal role in some cases. Thus, hydrogenation of ethene using 'Wilkinson's catalyst' is not possible owing to the greater thermodynamic strength of the Rh–(η^2-C_2H_4) bond which prevents hydrogenation of the intermediate alkene complex [3]. Another feature of metal–alkene complexes is that metal–alkene bonds are very often more labile than metal–CO bonds in related complexes. Metal–alkene complexes can therefore provide a means of estimating the relative reactivities of metal complexes for which corresponding metal–CO bonds are so inert that their dissociative reactions cannot be studied. Thus $(\eta^5$-$C_5H_5)Mn(CO)_3$ is notoriously inert to substitution [4,5] yet the displacement of alkenes from $(\eta^5$-$C_5H_5)Mn(CO)_2(\eta^2$-alkene) complexes was studied in some detail as early as 1967 [5].

$Fe(CO)_5$ is an archetypal binary metal carbonyl yet no kinetic studies of its substitution reactions have been performed and only indirect quantitative estimates of its dissociative lability have been obtained [6]. On the other hand, a wide variety of $Fe(CO)_4(\eta^2$-alkene) complexes have received kinetic study by Cardaci [7] who found a good linear free energy relationship between log k (for the alkene dissociative process) and the Hammett σ_p parameter [7a].

The complex $Os(CO)_5$ is also very inert (but less so than $Fe(CO)_5$) and its substitution reactions have been studied [6]. They were concluded to proceed through a normal CO-dissociative path although the activation entropy was quite atypical [8], viz. 5.6 ± 0.1 J K^{-1} mol^{-1}. It therefore seemed to be of some interest to study the rate of replacement of alkenes from $Os(CO)_4(\eta^2$-alkene) complexes, both to see if they too showed unusual values of ΔS^* and to compare the rates with those for the corresponding Fe complexes. The results of such studies of several alkene complexes are reported here.
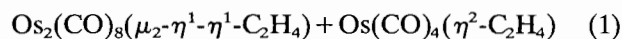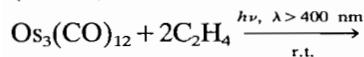
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2. Experimental

Os$_3$(CO)$_{12}$ (Strem Chemicals) was used as received. 1-Octene (1-oct, Sigma) and methyl acrylate (MA, Aldrich) were distilled under reduced pressure and stored under dry argon. Vinyl acetate (VA, Fluka) was used as received. Dichloromethane (DCM, BDH) and 1,2-dichloroethane (DCE, BDH) were distilled from P$_2$O$_5$. Heptane (Caledon) and dodecane (Aldrich) were predried over MgSO$_4$, distilled, and stored over molecular sieves. PPh$_3$ (Strem) was recrystallized from 95% ethanol, and dried under vacuum for 48 h. P(OEt)$_3$ (Baker) was distilled and stored over dry argon. Ethene (CP) was obtained from Matheson and Canox.

2.1. Synthesis of Os(CO)$_4$(η^2-C$_2$H$_4$)

This complex was synthesized photochemically from Os$_3$(CO)$_{12}$ in small quantities following the method described by Takats et al. [9] and illustrated in Eq. (1). Os$_3$(CO)$_{12}$ (4 mg, 4.2 μmol) was dissolved in DCM (5 cm^3) in a Schlenk tube, tightly sealed with a

$$Os_3(CO)_{12} + 2C_2H_4 \xrightarrow[\text{r.t.}]{h\nu,\ \lambda > 400\ nm}$$

$$Os_2(CO)_8(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-}C_2H_4) + Os(CO)_4(\eta^2\text{-}C_2H_4) \quad (1)$$

rubber septum cap. Ethene was bubbled through the solution until it was saturated and the atmosphere above the solution was pure ethene. The pressure was then raised to ~2 atm and the solution irradiated at room temperature (~22 °C) for ~2 h with light from a conventional slide projector. The solution was agitated periodically and reestablishment of the pressure of the ethene atmosphere was carried out at least once during the course of the reaction, the completion of which was indicated by the disappearance of the initial canary yellow colour of the solution.

Separation of the mononuclear complex from the reaction mixture was effected by a procedure based on that described by Norton and co-workers [10]. The solvent and the rather volatile Os(CO)$_4$(η^2-C$_2$H$_4$) were transferred from the Schlenk tube to a trap by application of a gentle-to-moderate vacuum, the trap being maintained at −15 to −20 °C. The solvent was then slowly removed by continued application of a gentle vacuum which, if carefully controlled, left behind flocculent crystals of the Os(CO)$_4$(η^2-C$_2$H$_4$) product. The yield was only ~25% (based on Eq. (1)) from each repeated procedure because of loss during solvent removal. However, large enough samples for kinetic study were obtained incidentally after repeated synthesis of the dinuclear complex, also wanted for kinetic study, which was produced in 80–100% yields from the residue after removal of the solvent and the mononuclear complex from the reaction mixture. The purity of the product was established by the close agreement of its

IR spectrum (Table 1) with that reported in the literature [10].

2.2. Synthesis of Os(CO)$_4$(η^2-alkene) (alkene = 1-octene, methyl acrylate, vinyl acetate)

In these syntheses Os$_3$(CO)$_{12}$ (4 mg, 4.2 μmol) was dissolved in either DCM or DCE (5 cm^3) to which a solution of alkene in DCM or DCE (~2 M, 5 cm^3) was added using degassed solutions and Schlenk tube techniques. Irradiation was carried out, under argon, as described above and, after completion of reaction, the solvent was removed under vacuum leaving behind a mixture of the mono- and dinuclear products together with the excess of alkene. The complexes were separated by thin layer chromatography (TLC) by elution with pure DCM (MA and VA complexes) or pure hexane (1-oct complex). Two strong, well-separated bands were usually seen, either directly (the dinuclear MA complex and the mononuclear 1-oct complexes were pale yellow) or by irradiation (254 nm) of fluorescent TLC plates. For alkene = MA or 1-oct the mononuclear complex eluted first but the putative dinuclear VA complex was the first to elute. The bands were removed from the plates, extracted with the appropriate eluent as solvent, and the solvent removed under vacuum. The purity of the 1-oct and MA compounds was established by their IR spectra (Table 1) in comparison with published data [9,11] and measurement of the molar absorptivity of a characteristic band (ϵ (2017.7 cm^{-1}) for the 1-octene complex in heptane = 3200 M^{-1} cm^{-1}; ϵ (2046.5 cm^{-1}) for the MA complex in dodecane = 2800 M^{-1} cm^{-1}) enabled the overall yields to be established as 80–100%. The molar ratios of mono- to dinuclear complexes were close to 1:1 for the MA complexes as reported [9] but the product of reaction with 1-oct was mainly the mononuclear complex.

The appearance of the IR spectrum of the mononuclear VA complex was very similar to those of the

Table 1
IR spectra of some mononuclear osmium carbonyl complexes [a]

Complex	IR bands (cm^{-1})			
Os(CO)$_4$(C$_2$H$_4$)	2108.5w	2021.1vs	1988.9s	
Os(CO)$_4$(1-oct)	2104.6w	2015.7vs	1985.0s	
Os(CO)$_4$(1-oct) [b]	2104.6w	2017.7vs	1986.9s	
Os(CO)$_4$(MA)	2125.6w	2046.5vs	2029.4s	2000.1vs
Os(CO)$_4$(VA)	2116.3w		2028.9vs	1998.1s
Os(CO)$_4${P(OEt)$_3$}	2068.0m	1990.8m	1957.6vs	1944.4vs
Os(CO)$_4$PPh$_3$	2062.2s	1981.0m	1944.4vs	
Os(CO)$_3${P(OEt)$_3$}$_2$	1919.0s	1905.8s		
Os(CO)$_3${P(OEt)$_3$}$_2$ [b]	1918.9s	1907.7s		
Os(CO)$_3$(PPh$_3$)$_2$	1900.0			
Os(CO)$_3$(PPh$_3$)$_2$ [b]	1899.8			

[a] In dodecane unless otherwise indicated.
[b] In heptane.

C_2H_4 and 1-oct complexes and the spectrum did not include an extra band similar to the one at 2046.5 cm^{-1} shown by the MA complex (see Table 3). Since the course of reaction of this complex was unusual (see below) no further characterization was undertaken.

2.3. Equipment

Nicolet 5DX or Perkin-Elmer 298 IR spectrophotometers were used with 1 mm path length cells with NaCl windows. Lauda thermostat baths of various types were used, depending on the temperatures of the reactions, and the reaction temperatures (± 0.1 °C) were measured with an iron–constantan thermocouple connected to a Fluke multimeter.

2.4. Kinetic procedures

Reactions were carried out in heptane or dodecane depending on the temperatures needed to obtain convenient reaction rates. Solutions were purged with a slow stream of argon in septum-sealed Schlenk tubes which were immersed in the temperature-controlled bath in a darkened fume hood, some of the reactants or products being photosensitive. The Schlenk tubes were small enough that there was only a minimal dead space above the reactant solution so that loss of complex by volatilization would be minimized.

Samples were removed, by means of steel-needled syringes, into ice-cooled vials where the reactions were quenched, and the spectra subsequently measured at leisure. The IR spectral changes were very clean, showing isosbestic points between pairs of close reactant and product bands. Absorbances of bands due to the reactant complex decreased essentially to zero over ~7 half-lives of reaction. Pseudo-first-order rate constants were obtained from the decreasing absorbance of a strong reactant band by application of the non-linear least-squares KORE programme [12], the precision of the rate constants indicated by the programme (i.e. the internal consistency of the data) generally being ~ $\pm 5\%$.

3. Results

3.1. The course of the reactions

For the complexes with the alkenes C_2H_4, MA and 1-oct the reactions with $L = P(OEt)_3$ or PPh_3 proceeded to form $Os(CO)_4L$ as the major product but some $Os(CO)_3L_2$ was always observed as well [1]. Measurement

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[1] The spectra (Table 1) of the $Os(CO)_4PPh_3$ and $Os(CO)_3(PPh_3)_2$ complexes were very close to those reported in Ref. 13, while those of the previously unreported complexes $Os(CO)_4\{P(OEt)_3\}$ and $Os(CO)_3\{P(OEt)_3\}_2$ were very close to those of their Ru analogues [14]. ϵ (1944.8 cm^{-1}) for $Os(CO)_4\{P(OEt)_3\} = 2900$ M^{-1} cm^{-1} and ϵ (1907.7 cm^{-1}) for $Os(CO)_3\{P(OEt)_3\}_2 = 1200$ M^{-1} cm^{-1} in heptane.

of the molar absorptivities of the isolated $P(OEt)_3$ complexes in heptane [1] enabled the molar ratios of the mono:bis products to be estimated. Thus for reactions of $Os(CO)_4(\eta^2\text{-}C_2H_4)$ in dodecane at 95 °C the ratio was 3.0 ± 0.2, independent of the concentration of the $P(OEt)_3$ over the range 0.035–0.14 M, and independent of whether the reactions were carried out under an atmosphere of C_2H_4 or CO or not. The standard error of each determination of the ratio was $\pm 20\%$ and it was assumed that the molar absorptivities in dodecane and heptane are the same. For reactions of the 1-oct complex in heptane the ratio was 5.7 ± 0.5, with a standard error of each measurement of $\pm 30\%$, independent of the $P(OEt)_3$ concentration (0.03–0.16 M), the presence of 1-octene (0.03–0.08 M) or the temperature (65–85 °C). Reactions of the MA complex in dodecane gave much more scattered results but the median value of the ratio was ~ 14 without there being any discernable correlation with the $P(OEt)_3$ concentration (0.04–0.16 M), the temperature (105–125 °C) or the presence of free MA (0.04–0.24 M). Although molar absorptivities were not measured the ratios of the intensities of the $Os(CO)_4PPh_3$ band at ~1945 cm^{-1} to that for $Os(CO)_3(PPh_3)_2$ at 1900 cm^{-1} were 4.7 (after reaction of the MA complex with PPh_3 in dodecane at 105 °C), 14 (C_2H_4 complex at 85 °C in dodecane) and 21 (1-oct complex at 85 °C in heptane).

The VA complex was exceptional in that, although it reacted eventually with $P(OEt)_3$ to form the mono- and bis-substituted products, the spectral changes, especially at the beginning of the reactions, showed the appearance of additional bands at 2116 and 1985 cm^{-1}. A product showing bands at 2104.6(w), 2015.7(vs) and 1985.0(s) cm^{-1} was seen when the complex was heated alone at 90 °C, and fairly clean isosbestic points were observed during the reaction. Owing to the uncertainty introduced by this anomalous behaviour no kinetic data were obtained for this complex.

3.2. The rate parameters

Rate constants for reactions of the various complexes under a variety of conditions are shown in Table 2. In the absence of free alkene they are independent of [L] except for the 1-oct complex in dodecane. These rate constants are slightly lower than those in heptane but increase gradually with increasing [L]. The activation parameters for reactions in the absence of any free alkene were obtained from an unweighted linear least-squares analysis of the dependence of ln k_{obs}/T on $1/T$ and are given in Table 3. The precision of the rate constants is seen to be quite acceptable and the occurrence of isosbestic points throughout the reactions, even at higher temperatures, shows that loss of complex by volatilization was negligible. The slight difference between the kinetic behaviour of the 1-oct complex in

Table 2
Observed rate constants for reactions of some $Os(CO)_4$ (η^2-alkene) complexes ([complex] = (4–8)×10^{-4} M)

T (°C)	L	10^2[L] (M)	$10^4\,k_{obs}$ (s^{-1})
Alkene = C_2H_4 in dodecane			
74.7	P(OEt)$_3$	10.0 [a]	0.185
		10.0	0.166
85.0	PPh$_3$	3.78	0.661
	P(OEt)$_3$	4.00	0.658
95.1		5.00	2.48
		10.0	2.65
		3.50 [b]	0.989
		5.00 [b]	1.16
		14.0 [b]	2.11
Alkene = 1-octene in heptane			
65.0	P(OEt)$_3$	5.16	1.45
		9.92	1.46
		13.9	1.60
75.0		4.76	5.87
		9.92	6.40
		13.9	6.61
		15.9	6.52
		2.72 [c]	3.40
		9.99 [d]	4.59
		5.00 [e]	2.84
		3.97 [f]	1.82
85.0	PPh$_3$	4.00	23.5
	P(OEt)$_3$	5.16	22.6
		9.98	23.5
		15.2	23.0
Alkene = 1-octene in dodecane			
65.0	P(OEt)$_3$	6.06	0.734
		8.27	0.830
		12.1	0.988
75.0		6.06	3.08
		12.1	3.96
85.0		6.06	12.4
		9.52	14.1
Alkene = methyl acrylate in dodecane			
104.8	PPh$_3$	4.04	0.845
105.3	P(OEt)$_3$	7.93	0.862
105.5		11.9	0.876
115.2		11.9	3.18
115.5		7.93	3.09
		15.9	3.16
124.9		3.97	9.45
		7.93	10.0
125.0		15.9	9.66
125.1		11.9	9.25
		7.93 [g]	7.41
		7.93 [h]	6.41
		5.55 [h]	4.44
		7.93 [i]	4.78
		7.93 [j]	3.94
		7.93 [k]	3.64

[a] Solutions equilibrated under 1 atm CO ([CO] = 7×10^{-4} M).
[b] Solutions equilibrated under 1 atm C_2H_4 ([C_2H_4] = 0.107 M).
[c–f] 10^2[1-oct] = 2.72, 5.00, 7.49 and 12.1 M, respectively.
[g–k] 10^2[MA] = 3.52, 8.21, 14.1, 16.4 and 23.5 M, respectively.

Table 3
Activation parameters [a] for dissociative loss of alkenes from some $Os(CO)_4(\eta^2$-alkene) complexes

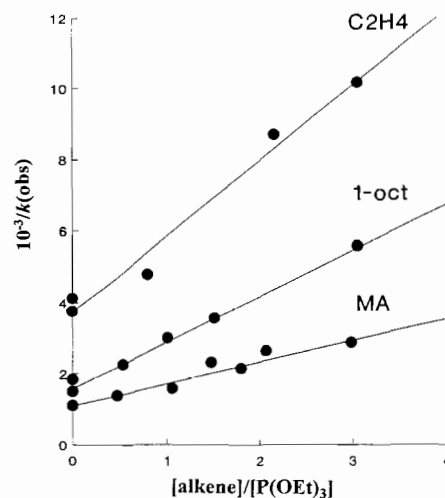| Alkene	k (50 °C) (s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	$\sigma(k)$ [b] (%)
C_2H_4 [c]	5×10^{-7}	136.8×2.9	56.5±8.8	8.4
1-Oct [d]	2×10^{-5}	134.3±1.7	78.2±5.0	5.2
1-Oct [e]	9×10^{-6}	135.6±5.4	77.4±15.5	14.9
MA [e]	2×10^{-8}	149.4±1.7	69.9±4.2	4.1

[a] For reactions in the absence of free alkene.
[b] Standard error of an individual determination of k_{obs}.
[c] In dodecane.
[d] In heptane.

Fig. 1. Dependence of $1/k_{obs}$ on [alkene]/[P(OEt)$_3$]. See Table 4 for temperatures of reaction.

Table 4
Rate parameters for reactions of $Os(CO)_4$ (η^2-alkene) with P(OEt)$_3$ in the presence of free alkene

Alkene	T (°C)	10^4a (s^{-1})	b	$\sigma(k)$ (%)
C_2H_4 [a]	95.1	2.66±0.18	1.86±0.22	14.1
1-Oct [b]	75.0	6.37±0.33	1.20±0.05	4.9
MA [a]	125.1	9.32±0.07	1.75±0.19	10.7

[a] In dodecane.
[b] In heptane.

heptane and dodecane has no perceptible influence on the activation parameters although those for reactions in dodecane are less precise.

Reactions with L = P(OMe)$_3$ in the presence of free alkene followed Eq. (2) quite closely as shown by the plots of $1/k_{obs}$ versus [alkene]/[L] in Fig. 1. The values of a and b were obtained from a weighted linear

$$k_{obs} = ab[L]/[alkene]/\{1 + b[L]/[alkene]\} \quad (2)$$

least-squares analysis of the dependence of $1/k_{obs}$ on [alkene]/[L] and are given in Table 4. The concentration

of C_2H_4 under 1 atm of the gas (Table 2) was estimated from data given by Wilhelm and Battino [15].

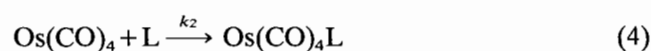## 4. Discussion

4.1. The products of the reactions

The fact that $Os(CO)_3L_2$ complexes are formed as products in addition to $Os(CO)_4L$ is reminiscent of the behaviour of analogous $Fe(CO)_4(\eta^2$-alkene) complexes [7]. In both cases the $M(CO)_4L$ complexes (M = Fe or Os) are too inert to undergo substitution reactions to form $M(CO)_3L_2$ and the facts that the $[Fe(CO)_4L]/[Fe(CO)_3L_2]$ ratio, $R(Fe)$, is constant throughout the reactions [7b], and that isosbestic points are observed throughout the reactions of the $Os(CO)_4(\eta^2$-alkene) complexes, both confirm that substitution into $M(CO)_4L$ does not play a role in the formation of $M(CO)_3L_2$. Cardaci has shown that $R(Fe)$ increases with increasing pressure of CO above the solutions and increases with increasing concentrations of PPh_3 in its reactions with $Fe(CO)_4(\eta^2$-$CH_2CHPh)$ [7c]. This was taken to imply that the $Fe(CO)_4$, formed by dissociation of the alkene, can undergo further loss of CO to form $Fe(CO)_3$ at a rate competitive with addition of L to form $Fe(CO)_4L$, the $Fe(CO)_3$ then reacting to form the $Fe(CO)_3L_2$ product. This suggestion is supported by the fact that $Fe(CO)_4$ in the gas phase is known to add CO relatively slowly [16], because of its triplet nature, so that it is possible for $Fe(CO)_3$ to be formed competitively by CO dissociation. No $Fe(CO)_5$ is formed, presumably because PPh_3 was in high enough concentration to compete successfully with CO for $Fe(CO)_4$. The proposal is also supported by the fact that $R(Fe)$ is independent of the source of $Fe(CO)_4$, i.e. whether it is formed from a range of different alkene complexes or from $Fe_2(CO)_9$ [7c]. An observation that is less easily accounted for is the formation only of $Fe(CO)_4L$ when L = $AsPh_3$ or $SbPh_3$ [7b]. If anything, these generally less nucleophilic ligands would be expected to compete less effectively for $Fe(CO)_4$, allowing more time for CO dissociation to occur and so leading to more $Fe(CO)_3L_2$.

The reactions of the $Os(CO)_4(\eta^2$-alkene) complexes have not been studied under high pressures of CO as were the Fe analogues [7c] so the role of CO dissociation from $Os(CO)_4$ is less clear. However, $Os(CO)_4$ is known to be much more reactive towards CO addition than $Fe(CO)_4$ in the gas phase [16] so one might expect more efficient scavenging of $Os(CO)_4$ and less formation of disubstituted products. Although the same alkenes were not involved in both studies this does not seem to be true. Further, the Os system differs in a major way from the Fe system in that $R(Os)$ depends significantly on the way the $Os(CO)_4$ is generated. No

$Os(CO)_3L_2$ is formed from $Os(CO)_5$ [6] and the value of $R(Os)$ when L = $P(OEt)_3$ depends on the nature of the alkene in the order alkene = C_2H_4 (3.0) < 1-octene (5.7) < MA (~ 14). It also depends on the alkene when L = PPh_3, but in a slightly different way, viz. MA < C_2H_4 < 1-oct so the relative effect of different alkenes also depends on the ligand involved. This raises the possibility that the disubstituted product is formed by reaction of $Os(CO)_4$ with unreacted alkene complex to form $Os_2(CO)_8(\mu_2$-η^1-η^1-alkene) (or its isomer $Os_2(CO)_7(\eta^2$-alkene)(μ-CO)) [17] which is known [18] to react with $P(OEt)_3$ to form $Os(CO)_4L$ and $Os(CO)_3L_2$ in an approximately 1:1 mole ratio. $Os(CO)_4$ is also known [16] to react with $Os(CO)_5$ in the gas phase to form $Os_2(CO)_8(\mu$-CO) and these reactions will all be expected to depend on the nature of the coordinatively saturated compound that is being attacked by $Os(CO)_4$ and by the nature of the ligand that attacks the dinuclear intermediate so formed. If it is this type of bimolecular reaction that is leading to the formation of $Os(CO)_3L_2$ then $R(Os)$ should increase with decreasing [complex] but such data are not yet available [2]. A further possible source of $Os(CO)_3L_2$, is dissociative loss of CO and formation of $Os(CO)_3L(\eta^2$-alkene), followed by loss of alkene and formation of $Os(CO)_3L_2$. This is unlikely since $Os(CO)_3L(alkene)$ is probably more stable to alkene loss than $Os(CO)_4(alkene)$ itself, because of enhanced π bonding, and it would therefore be seen as an intermediate. Also CO does not retard reaction of $Os(CO)_4(C_2H_4)$ with $P(OEt)_3$.

4.2. The mechanism of the reactions

In spite of the mechanistic complexities involved in the formation of the two products $Os(CO)_4L$ and $Os(CO)_3L_2$ the kinetics do strongly indicate that a classical reversible dissociative path is being followed as shown in Eqs. (3) and (4) for which the rate equation would be as shown in Eq. (5). This is identical in

$$Os(CO)_4(alkene) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Os(CO)_4 + alkene \qquad (3)$$

$$Os(CO)_4 + L \overset{k_2}{\longrightarrow} Os(CO)_4L \qquad (4)$$

form with Eq. (2) and implies that a (in Table 4) = k_1 and $b = k_2/k_{-1}$. The fact that the values of a are

$$k_{obs} = k_1(k_2/k_{-1})[L]/[alkene]/\{1 + (k_2/k_1)[L]/[alkene]\} \qquad (5)$$

the same as those of k_{obs} when $[L]/[alkene]$ is very large (i.e. when [alkene] = 0) supports the applicability of this equation even though it may only be approximate. Thus $Os(CO)_4$ may also be scavenged by $Os(CO)_4(alkene)$ (see above) in which case the rates

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[2] Evidence for the reaction of $Os(CO)_4$ with $Os(CO)_4$(propene) has been obtained [19], where the $Os(CO)_4$ was formed by dissociation of propene from the latter complex.

would not be precisely first-order in [Os(CO)₄(alkene)] and Eq. (4) would have to be supplemented to take account of this additional path for $Os(CO)_4$ scavenging. However, this is unlikely to change the form of the kinetics too much, especially since the yields of $Os(CO)_3L_2$ are not very high. It may be relevant that the fit to Eq. (4) is least good (Table 4) for alkene = C_2H_4 for which the yield of $Os(CO)_3L_2$ is highest. The slightly different kinetic behaviour of $Os(CO)_4(1$-oct) in dodecane is unexpected and no explanation is immediately obvious. Effects of retardation by free 1-octene might cast light on this phenomenon. However, it seems indisputable that the rate determining step is the dissociative loss of the alkene as shown in Eq. (3). The values of b listed in Table 4 are consistent with the expected low selectivity of highly reactive $Os(CO)_4$ and contrast with the values for the less reactive $Fe(CO)_4$ which depend considerably more on the nature of the alkenes [7a].

The reaction of the VA complex is obviously very different from that of the isomeric MA complex. It is clearly labile towards a spontaneous and quite clean reaction, even in the absence of added nucleophile, but neither the nature of the product nor the form of the kinetics are known so no further comment is justifiable.

4.3. The energetics of alkene dissociation

The first point to note from the data in Table 3 is that all the values of ΔS^* for displacement of the alkenes from the Os complexes are normal positive values as found generally for dissociative reactions [8] and as seen in Table 5 for some Fe and Ru complexes, i.e. none of them shows the anomaly found for $Os(CO)_5$ for which ΔS^* is ~0. If ΔS^* for $Os(CO)_5$ was ~70 J K⁻¹ mol⁻¹, in accord with the other complexes in Table 5, then the values of ΔH^* would be ~150 kJ mol⁻¹. This is much more in line with the trend shown by the MA complexes which give an excellent illustration of the enthalpic control of the 'triad effect' [4,6]. In terms of relative rate constants the triad effect changes from Ru ≫ Os > Fe for the pentacarbonyls to Ru ≫ Fe > Os for the MA complexes. This is because the values of ΔS^* do not fit with the triad effect, showing instead a monotonic decrease with increasing atomic number, at least for the MA complexes. These results contrast with those from studies of some substituted $M(CO)_4L$(alkene) complexes (M = Cr, Mo, W) where there is no triad effect, the rates being in the order Cr ≫ Mo ≫ W, and the enhanced rate of the Cr complex is ascribed to steric effects [22].

The data in Table 3 show a similar quantitative trend with changing alkene to that observed by Cardaci [7a] and others [5,22], i.e. substitution of alkyl groups into ethene increases the lability whereas electronegative

Table 5
Activation parameters for dissociative loss of L from some $M(CO)_4L$ complexes

M	L	k (50 °C) (s⁻¹)	ΔH^* (kJ mol⁻¹)	ΔS^* (J K⁻¹ mol⁻¹)
Fe	CO [a]	6×10⁻¹¹	167	75
Ru	CO [b]	3×10⁻³	115±2	64±5
Os	CO [c]	3×10⁻⁸	126±4	−2±10
Os	CO		~150 [d]	
Fe	MA	8×10⁻⁷	152±2 [e]	109±8
Ru	MA [f]	2×10⁻²	116±2	82±5
Os	MA [g]	2×10⁻⁸	149±2	70±4

[a] Estimate from Ref. [6].
[b] Ref. [20].
[c] From Ref. [6] (these values were recalculated from the original data to check on the unreasonably low error of 0.1 J K⁻¹ mol⁻¹ quoted for ΔS^*).
[d] If ΔS^* is ~70 J K⁻¹ mol⁻¹ as for $Fe(CO)_5$ and $Ru(CO)_5$.
[e] This value was quoted as 26.4 kcal mol⁻¹ in Ref. [7a]; this is clearly a misprint for 36.4 kcal mol⁻¹ as confirmed by inspection of the quoted value of ΔG^* and recalculation using the original data.
[f] Ref. [21].
[g] This work.

substituents decrease it. At 50 °C the 1-oct complex is 20 times more labile than the ethene complex while the latter is ~25 times more labile than the MA complex. These trends coincide with the relative extent of Os → alkene π bonding inferrable from the frequencies of the IR bands in Table 1. However, the greater lability of the 1-oct complex is almost entirely due to its more favourable value of ΔS^* whereas the greater inertness of the MA complex is clearly an enthalpy effect. The contribution of entropy effects to the dissociative lability of alkyl substituted alkenes was evident from early studies [5].

Although the values of ΔH^* for dissociative loss of MA and CO from corresponding complexes are not very different this certainly does not mean that the actual M–MA and M–CO bonds are intrinsically similar in strength. In general, as an alkene ligand moves away from a metal atom the C–C bond will increase in strength due to the restoration of electron density into the π bonding orbital and to the removal of electron density from the π* antibonding orbital, i.e. the transition state will be stabilized by some reasonably large proportion of the 264 kJ mol⁻¹ (for ethene) difference between the C–C and C=C bond strengths [23]. The intrinsic strengths of the M–alkene bonds are therefore much greater than those of M–CO bonds where the increase in bond strength in forming the free CO molecule is much less. The lower lability of the M–MA bonds compared with the M–(C_2H_4) bonds is usually ascribed to greater π bonding in the former caused by the electronegative COOMe group [7a,22]. The actual difference of 13 kJ mol⁻¹ in the $Os(CO)_4$(alkene) complexes must underestimate this effect. The incip-

iently free MA ligand will have gained a larger proportion of its π bond strength than a departing ethene ligand because it had lost a larger proportion of it in forming the bond in the first place. This effect will be enhanced because the π bond in MA is strengthened, by its delocalization into the COOMe substituent, to the extent of up to ~ 25 kJ mol^{-1} [24].

The absolute values, and the differences between them, of the activation barriers for loss of alkenes from metal–alkene complexes are the result of large opposing effects and the kinetic data do not, therefore, give a good measure of the *intrinsic* metal–alkene bond strengths in a way that is possible for more simply-bonded ligands. This does not detract from the importance of kinetic data in rather precisely quantifying the *effective* metal–alkene bond strengths in the sense of providing a measure of the energy needed to break them. They also provide a yardstick against which the reasonableness of thermochemically estimated bond strengths can be judged. Thus the value of 99 kJ mol^{-1} for the Fe–(C$_2$H$_4$) bond energy in Fe(CO)$_4$(C$_2$H$_4$) [25] seems to be very low in view of the 152 kJ mol^{-1} value of $\Delta H^{\ast}$ for removal of MA in spite of the slightly lower lability of the MA ligand (Tables 3 and 5).

Acknowledgements

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