Notes

Oxo Transfer Reactions. Mechanistic Studies on the Oxidation of Triphenylphosphine by *trans*-$[Ru^{VI}L(O)_2]^{2+}$ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) †

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The mechanism for the oxidation of PPh_3 to $O{=}PPh_3$ by *trans*-$[Ru^{VI}L(O)_2]^{2+}$ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) in CH_3CN was studied from 280 to 299 K. The rate law for the reaction is $d[Ru^{VI}]/dt = k_2[PPh_3][Ru^{VI}]$. At 299 K, k_2 is $(1.28 \pm 0.1) \times 10^2$ dm^3 mol^{-1} s^{-1}. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are (8.7 ± 0.8) kcal mol^{-1} and -20 ± 2 cal K^{-1} mol^{-1} respectively. A direct comparison between the reactivities of *trans*-$[Ru^{VI}L(O)_2]^{2+}$ and $[Ru^{IV}(bipy)_2(py)(O)]^{2+}$ (bipy = 2,2′-bipyridine; py = pyridine) towards the oxidation of PPh_3 shows the ruthenium(IV) complex to react 1 000 times faster.

Oxo complexes of ruthenium-(VI), -(V), and -(IV) have received much attention in recent years because of their remarkable abilities as stoichieometric and catalytic oxidants.[1–6] Among the various oxoruthenium species, the ruthenium (IV) complex $[Ru(bipy)_2(py)(O)]^{2+}$ (bipy = 2,2′-bipyridine; py = pyridine) has been extensively studied by Meyer and co-workers.[2] Oxidation by this complex can proceed through a variety of pathways including O-atom transfer, H-atom and hydride abstraction. In contrast, although a number of *trans*-dioxoruthenium(VI) species have been synthesized[1c,d,3b,d,4,6] and shown to be good oxidants for quite some time, relatively few mechanistic details are known. We have thus initiated a programme to study the reactions of *trans*-dioxoruthenium(VI) complexes with various inorganic and organic substrates in order to elucidate the mechanistic pathways occurring under given conditions, and the factors governing these.

Herein we report the results of a kinetic study on the oxidation of PPh_3 to $O{=}PPh_3$ by *trans*-$[Ru^{VI}L(O)_2]^{2+}$ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane). The goal of this work is to obtain detailed kinetic, thermodynamic, and mechanistic information about the oxygen-atom transfer reactions of Ru^{VI}. The above system is particularly attractive because the redox and structural properties of the RuL oxo complexes have been well characterized.[1c] An analogous mechanistic study on the oxidation of PPh_3 by $[Ru^{IV}(bipy)_2(py)(O)]^{2+}$ was reported by Meyer and co-workers[7] a few years ago.

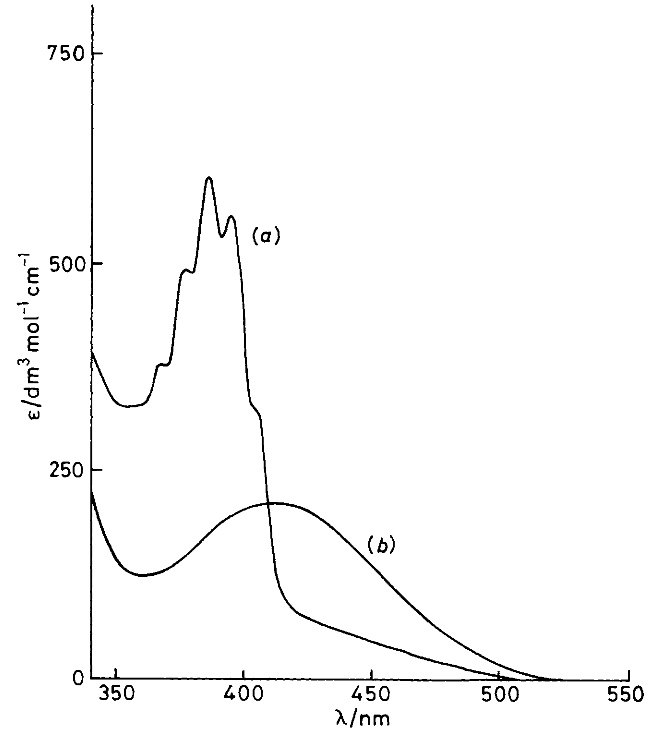

Figure. U.v.–visible spectra of *trans*-$[Ru^{VI}L(O)_2]^{2+}$ in acetonitrile before (*a*) and after addition of PPh_3 (*b*)

Experimental

Triphenylphosphine was recrystallized three times from absolute ethanol and dried in vacuum overnight. Infrared analysis showed that it was free from triphenylphosphine oxide [ν(P=O) $\approx$ 1 195 cm^{-1}]. Acetonitrile (Mallinkrodt, ChromAR) was distilled over $KMnO_4$ and CaH_4. The complex *trans*-$[Ru^{VI}L(O)_2][PF_6]_2$ was prepared as described previously.[1c]

Kinetics.—The kinetics of oxidation of PPh_3 by *trans*-$[Ru^{VI}L(O)_2]^{2+}$ was studied in acetonitrile by stopped-flow spectrophotometry. A HI-TECH stopped flow spectrophotometer equipped with an Aminco DASAR (data acquisition, storage, and retrieval) system directly linked to an Apple II microcomputer was used. Second-order rate constants and activation parameters were obtained by least-squares calculations.

Results

The Figure shows the u.v.–visible spectral changes when excess of PPh_3 is added to an acetonitrile solution of *trans*-

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† *Non-S.I. unit employed:* cal = 4.184 J.

Table. Kinetic data for the oxidation of PPh_3 by *trans*-$[Ru^{VI}L(O)_2]^{2+}$ (1.0×10^{-3} mol dm^{-3}) in CH_3CN *

T/K	$10^3[PPh_3]$/ mol dm^{-3}	$k_{obs.}$/s^{-1}	$k_{obs.}[PPh_3]^{-1}$/ dm^3 mol^{-1} s^{-1}
280.0	10	0.43	43.0
	20	0.79	39.5
	30	1.20	40.0
	40	1.72	43.0
	50	2.20	44.0
284.0	10	0.50	50.0
	20	1.00	50.0
	30	1.60	53.3
	40	2.20	55.0
	50	2.76	55.2
292.7	10	0.88	88.0
	20	1.60	80.0
	30	2.42	80.7
	40	3.40	85.0
	50	4.22	84.4
299.0	10	1.23	123.0
	20	2.45	122.5
	30	3.83	127.6
	40	5.30	132.5

* Each rate constant is the average of four or more experimental determinations under the same reaction conditions.

$[Ru^{VI}L(O)_2]^{2+}$ at room temperature. The vibronic structured absorption band of the ruthenium(VI) complex at 388 nm disappears with concomitant formation of a peak at 420 nm. The resulting species had been isolated and structurally characterized by *X*-ray crystallography as *trans*-$[Ru^{IV}L(O)(CH_3CN)]^{2+}$.[1a] By spectrophotometric analysis at 420 nm, the yield for the conversion of *trans*-$[Ru^{VI}L(O)_2]^{2+}$ into *trans*-$[Ru^{IV}L(O)(CH_3CN)]^{2+}$ is quantitative {$\varepsilon_{max.}$ for *trans*-$[Ru^{IV}L(O)(CH_3CN)]^{2+}$ = 190 dm^3 mol^{-1} cm^{-1} (λ = 420)}.[1c] The ruthenium(IV) product showed no reactivity toward PPh_3. As PPh_3 is a well-known oxygen-atom acceptor, the overall reaction is as in equation (1) with the $O{=}PPh_3$ product

$$trans\text{-}[Ru^{VI}L(O)_2]^{2+} + PPh_3 \xrightarrow{CH_3CN} trans\text{-}[Ru^{IV}L(O)(CH_3CN)]^{2+} + O{=}PPh_3 \quad (1)$$

identified by i.r. spectroscopy (1 195 cm^{-1}).

The kinetics of the PPh_3 oxidation [equation (1)] was monitored at 390 and 420 nm by stopped-flow spectrophotometry under pseudo-first order conditions {$[Ru^{VI}] = 10^{-3}$, $[PPh_3] = (1\text{—}5) \times 10^{-2}$ mol dm^{-3}}. Only a one-step reaction was observed; on mixing the absorbance at 390 nm rapidly decayed to a constant value that remained unchanged even over extended periods. The reaction has been found to obey the rate law: rate = $k_{obs.}[Ru^{VI}]$ where $k_{obs.} = k_2[PPh_3]$. The bimolecular rate constant k_2 was invariant in the presence of added electrolyte, such as 0.01 mol dm^{-3} $[NBu^n{}_4][PF_6]$. The kinetic data are presented in the Table. At 26 °C, the second order rate constant k_2 is $(1.28 \pm 0.1) \times 10^2$ dm^3 mol^{-1} s^{-1}. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained over a temperature range 280—299 K are 8.7 ± 0.8 kcal mol^{-1} and -20 ± 2 cal K^{-1} mol^{-1} respectively.

Discussion

The oxidation of PPh_3 to $O{=}PPh_3$ by ruthenium– and osmium–oxo complexes has been reported in several instances.[1a,6–9] For example, the reaction between $[Os(oep)(O)_2]$(H_2oep = octaethylporphyrin) and PPh_3 was found to give $[Os(oep)(OPPh_3)_2]$.[8] Meyer and co-workers[7] studied the mechanism of the PPh_3 oxidation by $[Ru^{IV}(bipy)_2(py)(O)]^{2+}$ in acetonitrile and concluded that the reaction involved concerted oxygen-atom transfer, as represented in equations (2)—(4).

$$M{=}O + PPh_3 \rightleftharpoons [M{=}O \cdots PPh_3] \quad (2)$$

$$[M{=}O \cdots PPh_3] \longrightarrow M\text{–}OPPh_3 \quad (3)$$

$$M\text{–}OPPh_3 + CH_3CN \longrightarrow M\text{–}N{\equiv}C\text{–}CH_3 + OPPh_3 \quad (4)$$

In this work, the outer-sphere one-electron oxidation of PPh_3 by *trans*-$[Ru^{VI}L(O)_2]^{2+}$ is not feasible because the $E_{\frac{1}{2}}$ value of the *trans*-$[Ru^{VI}L(O)_2]^{2+/+}$ couple occurs at 0.32 V *vs.* saturated calomel electrode (s.c.e.),[1c] which is substantially lower than that for the $PPh_3{}^{+/0}$ couple (> 1.32 V *vs.* s.c.e.).[7] The large negative $\Delta S^{\ddagger}$ of -20 ± 2 cal K^{-1} mol^{-1}, which is virtually identical to the value for the corresponding oxidation by $[Ru^{IV}(bipy)_2(py)O]^{2+}$ (-19 ± 3 cal K^{-1} mol^{-1}),[7] suggests that both *trans*-$[Ru^{VI}L(O)_2]^{2+}$ and $[Ru^{IV}(bipy)_2(py)(O)]^{2+}$ react by the same pathway. However, unlike the latter system,[7] only a one-step reaction was found in the present case, suggesting that the initial product *trans*-$[Ru^{IV}L(O)(OPPh_3)]^{2+}$, once formed, undergoes very rapid solvolysis to give *trans*-$[Ru^{IV}L(O)(CH_3CN)]^{2+}$. The lability of the ligand *trans* to the oxo group is consistent with the bond length found in the related complexes *trans*-$[Ru^{IV}L(O)(X)]^{n+}$ (X = CH_3CN, n = 2; X = Cl, NCO, n = 1).[1c]

A direct comparison between the reactivities of *trans*-$[Ru^{VI}L(O)_2]^{2+}$ and $[Ru^{IV}(bipy)_2(py)(O)]^{2+}$ toward oxidation of PPh_3 reveals that the latter complex is about 10^3 times more reactive than the former (Ru^{IV} 1.75×10^5, Ru^{VI} 1.28×10^2 dm^3 mol^{-1} s^{-1} at 26 °C). More importantly, this 10^3-fold difference in rate constants is primarily due to the difference in $\Delta H^{\ddagger}$ ($\Delta H^{\ddagger}$: Ru^{VI}, 8.7; Ru^{IV}, 4.7 kcal mol^{-1}).[7] Meyer and co-workers[7] suggested that $\Delta H^{\ddagger}$ is composed of two terms, ΔH_A for a pre-equilibrium association of the reactants [equation (2)] and $\Delta H^{\ddagger}_R$ for the redox step [equation (3)]. Since ΔH_A is usually very small (about 0.5 kcal mol^{-1}), the major contribution to $\Delta H^{\ddagger}$ comes from $\Delta H^{\ddagger}_R$. The much higher $\Delta H^{\ddagger}_R$ for *trans*-$[Ru^{VI}L(O)_2]^{2+}$ than for $[Ru^{IV}(bipy)_2(py)(O)]^{2+}$ can be attributed to the stronger Ru=O bond and the lower redox potential of the former system. Although the *X*-ray crystal structure of $[Ru^{IV}(bipy)_2(py)(O)]^{2+}$ is unknown, its Ru=O bond length is expected to be similar to that for *trans*-$[Ru^{IV}(py)_4(O)Cl]^{+}$,[10] which is $\approx$0.16 Å longer than the Ru=O bond in *trans*-$[Ru^{VI}L(O)_2]^{2+}$. On the other hand, $[Ru^{IV}(bipy)_2(py)(O)]^{2+}$ is also a stronger oxidant than *trans*-$[Ru^{VI}L(O)_2]^{2+}$ (0.99[11] *versus* 0.66V[1c] *vs.* s.c.e. at pH 1.0). In the redox step represented by equation (3), if the activation barrier mostly comes from the charge-transfer from PPh_3 to the metal centre, a stronger oxidant would lead to a faster rate.

Acknowledgements

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References

1 (*a*) C. M. Che, K. Y. Wong, and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1985, 546; (*b*) *ibid.*, p. 988; (*c*) C. M. Che, T. F. Lai, and K. Y. Wong, *Inorg. Chem.*, 1987, **22**, 2289; (*d*) C. M. Che, K. Y. Wong, W. H. Leung, and C. K. Poon, *ibid* 1986, **25**, 345.

2 W. K. Seok, J. C. Dobson, and T. J. Meyer, *Inorg. Chem.*, 1988, **27**, 5; 1986, **25**, 1415; R. A. Binstead and T. J. Meyer, *J. Am. Chem. Soc.*, 1987, **109**, 3287; J. Gilbert, L. Roecker, and T. J. Meyer, *Inorg. Chem.*, 1987, **26**, 1126; L. Roecker and T. J. Meyer, *J. Am. Chem. Soc.*, 1987, **109**, 746.

3 (*a*) A. M. El-Hendawy, W. P. Griffith, B. Piggott, and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 1983; (*b*) G. Green, W. P. Griffith, D. M. Hollinshead, S. V. Ley, and M. Schröder, *J. Chem. Soc., Perkin*

Trans. I, 1984, 681; (*c*) W. P. Griffith, S. V. Ley, and A. D. White, *J. Chem. Soc., Chem. Commun.*, 1987, 1625; (*d*) A. M. El-Hendawy, W. P. Griffith, B. Piggott, and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1988, 1983.
4 J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790, *Inorg. Chem.*, 1984, **23**, 3844.
5 M. E. Marmion and K. J. Takeuchi, *J. Am. Chem. Soc.*, 1988, **110**, 1472; 1986, **108**, 510.
6 T. C. Lau and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 1987, 179.
7 B. A. Moyer, B. K. Spe, and T. J. Meyer, *Inorg. Chem.*, 1981, **20**, 1475.
8 C. M. Che, W. C. Chung, T. F. Lai, W. P. Schaefer, and H. B. Gray, *Inorg. Chem.*, 1987, **26**, 3907.
9 F. C. Anson, J. A. Christie, T. J. Collins, R. J. Coots, T. J. Furutaini, S. L. Gipson, J. T. Keech, T. E. Krafft, B. D. Santarsiers, and G. H. Spies, *J. Am. Chem. Soc.*, 1984, **106**, 4460.
10 Y. Yukawa, K. Aoyagi, M. Kurihara, K. Shirai, K. Shimizu, M. Mukaida, T. Takeuchi, and H. KaKihana, *Chem. Lett.*, 1985, 283.
11 B. A. Moyer and T. J. Meyer, *Inorg. Chem.*, 1981, **20**, 436.

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