Polyhedron Vol. 12, No. 12, pp. 1443–1451, 1993
Printed in Great Britain

0277–5387/93 \$6.00+.00

OXIDATION OF TERTIARY PHOSPHINES BY MOLECULAR OXYGEN CATALYSED BY Ru^{III}-EDTA COMPLEX. ELECTRONIC EFFECT OF PHOSPHINE SUBSTITUENT ON THE OXYGEN ATOM TRANSFER REACTION; X-RAY CRYSTAL STRUCTURE OF THE COMPLEX $[Ru^{III}(EDTA\text{-}H)PPh_3]$

M. M. TAQUI KHAN,†‡ DEBABRATA CHATTERJEE, M. R. H. SIDDIQUI, S. D. BHATT, H. C. BAJAJ, K. VENKATASUBRAMANIAN and M. A. MOIZ

Discipline of Coordination Chemistry and Homogeneous Catalysis,
Central Salt and Marine Chemical Research Institute, Bhavnagar 364002, India

(*Received* 30 *September* 1992; *accepted* 10 *February* 1993)

Abstract—The catalytic oxidation of tertiary phosphines, PR_3 (R = *p*-fluorophenyl, phenyl and cyclohexyl), by molecular oxygen to the corresponding phosphine oxide, (PR_3O), catalysed by $Ru^{III}(EDTA\text{-}H)(H_2O)$ is reported as a function of catalyst, substrate (PR_3) and molecular oxygen concentration at a constant pH 3.0 in water–dioxan (50% v/v) medium. The reactivity of PR_3 towards catalytic oxidation by molecular oxygen decreases in the order tris(*p*-fluorophenyl)phosphine > triphenylphosphine > tris-(cyclohexyl)-phosphine. A reverse reactivity order was observed in the case of stoichiometric oxidation of PR_3 by $[O{=}Ru^{V}(EDTA)]^-$. The proposed mixed-ligand complex Ru^{III}-EDTA-PR_3 intermediate in the catalytic oxidation of PR_3 with molecular oxygen has been isolated and its structure solved by single-crystal X-ray diffraction. The experimental results are discussed in terms of the σ-basic and π-acidic character of the phosphine substrates in the homolytic bond cleavage of O—O bonds of the μ-peroxo intermediate and oxygen atom transfer to the substrate. The bond dissociation energy for O—O bond cleavage is computed by the kinetic data obtained for oxygen atom transfer from the oxo complex $[O{=}Ru^{V}(EDTA)]^-$.

The oxidation of phosphines by transition-metal oxo complexes has been the subject of much current interest.[1–5] In our laboratory we have been engaged in developing non-porphyrinic ruthenium(III) complex catalysts for the oxidation of a variety of organic substrates.[6–10] These non-porphyrinic ligands involve aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), Schiff bases and dimethylglyoxime, which do not undergo self-oxidation during the catalytic processes. In our earlier contribution[11] we reported the oxidation of PPh_3 to PPh_3O with molecular oxygen catalysed by the Ru^{III}-EDTA complex where we proposed the formation of a mixed-ligand Ru-EDTA-PPh_3 intermediate in the catalytic cycle. We have now successfully isolated the complex $Ru^{III}(EDTA\text{-}H)PPh_3$ and determined its structure.

In order to gain an insight into the mechanistic details of the reaction, such as coordination of the phosphine ligand to the metal ion and the nature of the oxygen atom transfer, we have studied the oxidation of various phosphines (PR_3; R = *p*-fluorophenyl, phenyl and cyclohexyl) by molecular oxygen catalysed by complex **1**. We have also studied the stoichiometric oxygen atom transfer reaction in the oxidation of PR_3 by the $Ru^{V}(EDTA)(O)^-$ complex. The experimental results are discussed in terms of σ-basicity and π-acidity of PR_3 substrates, which governs the reactivity of Ru^{III} and Ru^{V} complexes.

EXPERIMENTAL

The complex $K[Ru^{III}(EDTA\text{-}H)Cl]$ (**1**) was prepared following the published procedure.[12] Dis-

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† Author to whom correspondence should be addressed.

‡ Present address: 17-3-479 Yakutpura, Hyderabad 500023, A.P., India.

tilled dioxane (HPLC grade) and doubly distilled water were used to prepare all solutions. All other chemicals used were of A.R. grade.

Synthesis of K[Ru^V=O(EDTA)]·2H$_2$O

The complex K[Ru^V=O(EDTA)] was prepared by interacting K[Ru^{III}(EDTA-H)Cl] with iodosylbenzene.[13] To a stirred solution of K[Ru(EDTA-H)Cl] [1 mmol in 10 cm^3 water–dioxane (1 : 1)] was added iodosylbenzene (1.1 mmol) and the solution was stirred for 1 h in the dark. The greenish-brown product, [Ru^V=O(EDTA)]$^-$, thus formed was precipitated by adding acetone, immediately filtered and washed with a cold acetone–water mixture (9 : 1) and dried. Found: C, 24.9; H, 3.3; N, 5.8. Calc.: C, 25.0; H, 3.3; N, 5.8%. UV–vis spectra, λ_{max} (nm) [ε_{max} (mol^{-1} dm^3 cm^{-1})] = 390(1860). IR spectra: ν(Ru=O), 870 cm^{-1}. $E_{1/2}$ (determined by cyclic voltammetric studies) for Ru^{5+}/Ru^{4+}, Ru^{4+}/Ru^{3+} and Ru^{3+}/Ru^{2+} redox couples are 0.91, 0.14 and −0.21 V (vs S.C.E.), respectively.

Synthesis of [Ru(EDTA-H)(PR$_3$)] *complexes*

[Ru(EDTA-H)(PPh$_3$)] (**2**). To a refluxing solution of K[Ru^{III}(EDTA-H)Cl] (500 mg, 1 mmol) was slowly added triphenylphosphine (260 mg, 1 mmol) dissolved in a minimum volume of dioxane. The mixture was refluxed (under nitrogen) for a period of 2 h until the colour of the solution changed from yellow to orange–yellow. The solution was then allowed to cool down and an orange–yellow product precipitated. The product was filtered, washed with cold water several times and finally with ether and dried *in vacuo* (yield: 89%). Found: C, 51.0; H, 4.8. Calc.: C, 51.5; H, 4.3%. UV–vis in H$_2$O, λ_{max} (nm) [ε_{max} (mol^{-1} dm^{3}cm^{-1})]: 485 (3.8 × 10^2), 375 (1.6 × 10^3), 260 (6.7 × 10^3). IR: ν(Ru—P) = 532 cm^{-1}, μ_{eff} (Evans' method): 1.78 B.M. at 300 K.

Complexes [Ru^{III}(EDTA-H)(P(C$_6$H$_4$—F)$_3$)] (**3**) and [Ru^{III}(EDTA-H)(C$_6$H$_{11}$)$_3$] (**4**) were prepared following a similar procedure as described for the preparation of **2**. Found: C, 49.4; H, 5.8; N, 3.9. Calc. for [Ru^{III}(EDTA-H)P(C$_6$H$_4$—F)$_3$]: C, 50.1; H, 6.9; N, 4.3%. UV–vis, λ_{max} (nm) [ε_{max} (mol^{-1} dm^3 cm^{-1})] = 481 (3.67 × 10^2).

[Ru^{III}(EDTA-H)P(C$_6$H$_{11}$)$_3$]. Found: C, 47.5; H, 3.4; N, 3.9. Calc.: C, 47.6; H, 3.5; N, 4.0%. UV–vis, λ_{max} (nm) [ε_{max} (mol^{-1} dm^3 cm^{-1})] = 487 (4.1 × 10^2).

The redox potentials for the Ru^{3+}/Ru^{2+} couple of complexes **2**, **3** and **4** determined by cyclic voltammetric studies (vs S.C.E.) are −0.11, −0.14 and −0.27 V, respectively. The ^{31}P NMR spectra of complexes **2**, **3** and **4** give a singlet at δ (ppm) = 25.79, 23.51 and 52.3, respectively. The shifts are in accordance with the decreasing shielding on the phosphorus atom in the phosphines in the order **4**, **2**, **3**.

Instrumentation and techniques

Microanalyses were performed using a Carlo–Erba elemental analyser. The electronic spectra of the complexes were recorded with a Shimadzu-160 UV–vis spectrophotometer. The IR and far-IR spectra were recorded on Beckman Aculab-10 (4000–600 cm^{-1}) and Perkin–Elmer-621 (600–200 cm^{-1}) spectrometers, respectively. pH measurements were performed using a Digisun pH meter with an accuracy of ±0.01 unit. Electrochemical studies were performed with PAR 174A electrochemical apparatus. Cyclic voltammetric studies were performed in 0.1 M HClO$_4$ medium using a glassy carbon working electrode.

Kinetic studies

Kinetics of the catalytic oxidations of PR$_3$ with molecular oxygen were followed by measuring the absorption of oxygen with time as described earlier.[11] Stoichiometric oxygen atom transfer from Ru^V(EDTA)O$^-$ to PR$_3$ was studied spectrophotometrically by following the decrease in the peak at 393 nm of the complex Ru^V(EDTA)O$^-$ with time. For this purpose equal volumes (1 cm^3) of solutions (pre-equilibrated at the desired temperature) of the oxo complex (5 × 10^{-4} M) and PR$_3$ (2.5 × 10^{-3}–2.5 × 10^{-2} M) were mixed in a spectrophotometric cell and the corresponding pseudo-first-order rate constant (k_{obs}) values were obtained from the absorbance vs time trace by the usual procedure. The rate constant data are reproducible to within ±4%.

Product analysis

The oxidation products PR$_3$O were analysed by ^{31}P and ^{19}F [(*p*-fluorophenyl)$_3$P] NMR spectra recorded on a JEOL FX-100 NMR spectrometer using phosphoric acid and trifluoroacetic acid, respectively, as standards. The formation of tertiary phosphine oxide with time is shown in Fig. 1.

X-ray crystallographic studies

Large yellowish-orange crystals of the complex could be obtained by recrystallization from an aqueous solution. A crystal of the dimensions 0.19 × 0.28 × 0.31 mm was used for data collection. Crystal data are summarized in Table 1. Density

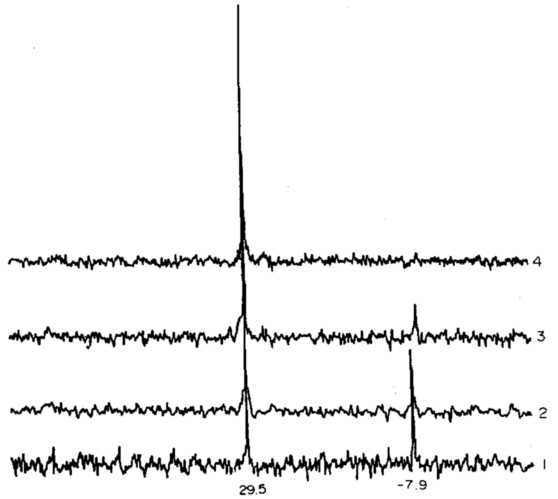


Fig. 1. ^{31}P NMR spectra for the formation of $(C_6H_4—F)_3PO$ with time at 35°C: (a) $t = 30$, (b) 60, (c) 90 and (d) 120 min.

considerations (Table 1) indicated the presence of two independent [Ru(EDTA-H)PPh_3] moieties with some solvent of crystallization. Two sets of reflection controls were used to monitor orientation and decay. Absorption corrections were applied using three intense reflections near Chi = 90°, employing the empirical absorption correction method.[14]

Table 1. Crystal data for $[Ru(EDTA\text{-}H)PPh_3]_2 \cdot 3H_2O$

Formula	$Ru_2P_2O_{19}N_4C_{55}H_{62}$
Molecular weight	1359.22
a (Å)	18.572(2)
b (Å)	14.786(2)
c (Å)	22.000(2)
β (°)	110.33(2)
Space group	$P2_1/a$
V (Å^3)	5665.0(9)
Z	4
Density (g cm^{-3})	1.593
(Cu-K_α)	1.54184
F(000)	2784
μ(Cu-k_α) (cm^{-1})	56.230
2θ range (°)	4–130
No. of reflections measured	7103
No. of reflections observed	3207
Data collected	$+h, +k_1, \pm l$
Temperature (K)	293
Transmission factors	Min. 51.67%
	Max. 99.25%
	Av. 75.08
R	0.031
R_w	0.039
(Δ/δ)	0.03

The structure was solved by the heavy atom method and was developed by alternating cycles of isotropic least-squares followed by difference-Fourier syntheses. Three water molecules in addition to two [Ru(EDTA-H)PPh_3] moieties could be located. Hydrogens could be either generated using stereochemical constraints or obtained from difference maps. A mixed mode refinement was adopted in which ruthenium, phosphorus and oxygen were refined anisotropically and carbon and nitrogen isotropically. The hydrogens were fixed employing a weighting scheme with a Dunitz–Seiler factor.[15] This resulted in convergence at an R of 0.031 (Rw = 0.039). Because of the large number of atoms refinement was performed in blocks. At the end of the refinement the largest shift-to-error ratio of refined parameters was 0.03; the difference map had ripples of 0.9 e Å^{-1} around the ruthenium atoms. The scattering factors for ruthenium, phosphorus, carbon, nitrogen and oxygen were from Vol. IV of the International Tables for Crystallography,[16] while those of hydrogens were from Stewart *et al.*[17] All the crystallographic computations were obtained using the SDP set of programs available on the PDP-11/73 system.[18]

RESULTS AND DISCUSSION

Figure 2 shows a PLUTO view of molecule **1**; the structure of molecule **2** is similar. The selected bond lengths and angles along with e.s.d.s are shown in Table 2. The PPh_3 moiety is *trans* with respect to one of the nitrogens of the bound EDTA ligand in both the molecules and the resulting ruthenium(III) octahedra are distorted; the dis-

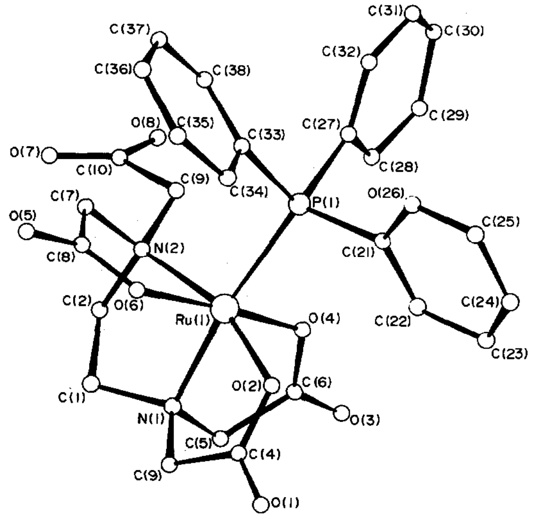


Fig. 2. PLUTO of $Ru^{III}(EDTA\text{-}H)(PPh_3)$ (molecule **1**).

Table 2. Some important bond distances (Å) and angles (°) in structures **1** and **2**

Atoms	**1**	**2**	Atoms	**1**	**2**
Ru—P	2.351(2)	2.376(2)	P—Ru—O(2)	92.6(2)	92.9(2)
Ru—N(1)	2.061(5)	2.079(7)	P—Ru—O(4)	92.9(1)	95.7(2)
Ru—N(2)	2.116(8)	2.136(6)	P—Ru—O(6)	91.4(1)	88.9(2)
Ru—O(2)	1.998(6)	1.995(6)	P—Ru—N(1)	173.2(2)	172.9(2)
Ru—O(4)	1.981(5)	1.984(6)	P—Ru—N(2)	102.2(2)	101.4(2)
Ru—O(6)	2.060(5)	2.041(6)	O(2)—Ru—O(4)	94.1(3)	93.8(2)
C(4)—O(1)	1.20(2)	1.24(2)	O(2)—Ru—O(6)	88.3(3)	90.9(2)
C(6)—O(2)	1.313(8)	1.26(1)	O(2)—Ru—N(1)	82.1(3)	80.2(2)
C(6)—O(3)	1.18(2)	1.24(2)	O(2)—Ru—N(2)	160.6(2)	162.5(3)
C(6)—O(4)	1.332(8)	1.28(1)	O(4)—Ru—O(6)	175.0(2)	173.2(2)
C(8)—O(5)	1.24(2)	1.17(2)	O(4)—Ru—N(1)	83.5(2)	83.3(2)
C(8)—O(6)	1.27(2)	1.32(2)	O(4)—Ru—N(2)	97.7(3)	94.8(2)
C(10)—O(7)	1.21(1)	1.18(2)	O(6)—Ru—N(1)	92.5(2)	92.8(3)
C(10)—O(8)	1.33(1)	1.32(1)	O(6)—Ru—N(2)	78.8(2)	79.4(2)
C(1)—N(1)	1.5(1)	1.500(5)	N(1)—Ru—N(2)	84.1(3)	85.7(3)
C(2)—N(2)	1.518(9)	1.54(2)	O(1)—C(4)—O(2)	127.7(8)	123.3(7)
C(1)—C(2)	1.52(1)	1.53(1)	O(3)—C(6)—O(4)	123.2(7)	124.8(8)
			O(5)—C(8)—O(6)	123.3(8)	124.8(9)
			O(7)—C(10)—O(8)	125.2(9)	127.0(2)

tortion being reflected in the *cis* angles which span from 78.8(2)° to 102.2(2)° in molecule **1** and from 79.4(2)° to 101.4(2)° in molecule **2**. The range from *trans* angles in molecule **1** is 160.6(2)–175.0(20)° and for **2** 162.5(2)–173.2(2)°. The EDTA-aquo complex has a span of 17° in *cis* angles. Part of the increase in the span of *cis* angles in our complex is due to the steric effects produced by the bulky PPh_3 group and part of it comes from the elongated Ru(1)—N(1) distance produced by the *trans* influence of the PPh_3 ligand. The distances involving oxygen atoms coordinating as a pair are smaller [1.998(6), 1.981(5), av. 1.990(6) Å in molecule **1**; 1.999(5), 1.984(6), av. 1.992(6) Å in molecule **2**] than those which coordinate singly [2.060(8) and 2.041(6) Å in molecules **1** and **2**]; a phenomenon found in other metal–EDTA structures[6,19,20] and may have resulted due to the greater coordinating ability of the carboxylate group when both the oxygens are pulled into the coordination sphere of the metal ion. The difference in Ru—O and Ru—N distances involving the coordinated acetato groups and the connecting amino moiety are 0.071(6) and 0.056(6) Å for molecule **1** and 0.087(6) Å for molecule **2**. While part of the difference arises from the difference in the ionic radii of oxygen and nitrogen, the remainder can be attributed to steric factors. Other metal–aminopolycarboxylate derivatives also exhibit the same trend.

The Ru^{III}—O and Ru^{III}—N distances in the structure are within the range reported for [Ru(EDTA-H)(H_2O)],[19] as well as in K[Ru(EDTA-H)Cl]·$2H_2O$.[20] The Ru^{III}—P distances of 2.351(2) Å in the structure compare well with those found for $Ru_2O[O_2(Ph)_2MeCN(PPh_3)_2](ClO_4)\cdot H_2O$,[21] $Ru_2O(O_2C—C_6H_4—P—OMe_4(PPh_3)_2$[22] and $Ru_2Cl_6(DPPM)_2$.[23]

The coordinated C—O lengths (Table 2) in molecule **1** [av. 1.305(1) Å] and molecule **2** [av. 1.287(15) Å] are longer than the uncoordinated C—O bonds (Table 2) [av. 1.21(2) Å] in molecules **1** [av. 1.23(2) Å] and **2**; a situation encountered in other metal complexes of aminopolycarboxylic acids. A difference of 0.07–0.09 Å exists between the C—O lengths, of which the larger value is associated with the oxygen involved in coordination resulting in a stronger metal–oxygen binding. By this complexation the single bond is shortened by 0.03 Å, while the double bond becomes elongated by 0.04 Å.

The O—C—O angle is widened from the value of 120° by 3.3° in **1** and 4° in **2**, which is compensated for by a contraction in the —CCO angles in the coordinated carboxylate groups. In the protonated non-coordinating carboxyl group the difference in C—O lengths is more pronounced; 0.12(1) Å in **1** and 0.14(1) Å in **2**. One of the —CCO angles is widened and the other compressed in molecule **1**, whereas in molecule **2** both the —CCO angles are compressed. The compression of the —CCO angles is due to its involvement in hydrogen bond formation.

The bond lengths and angles in the EDTA moiety lie in the range reported for other structures.[19,20] The torsion angles [N(1)—C(1)—C(2)—N(2)] in **1** and **2** have values of $-56.6(8)^\circ$ and lie in the range (53–63°) reported for similar structures. The ethylenediamine ring adopts an unusual envelope conformation, with the atom C(1) displaced by 0.668(6) Å from the plane of Ru(1)N(1)N(2)C(2) [maximum deviation 0.086(6) Å]. This conformation has been found in other mono-substituted pentadentate EDTA complexes of ruthenium.[19,20] Rings R_1 in **1** and **2** are planar within 0.015(6) and 0.035(6) Å, while rings R_2 and G are more strained and exist as envelopes with N(2) out of the Ru(1)C(7) C(8)O(6) plane by 0.413(6) Å. In ring G N(1) is displaced by $-0.508(6)$ Å from Ru(1)C(3) C(4)O(6) in **1**. The acetate groups are planar within experimental error.

Equilibrium studies for the formation of mixed-ligand $[Ru^{III}(EDTA)(PR_3)]^-$ *complexes*

The formation constants (K_1) of Ru^{III}-EDTA-PR_3 mixed-ligand complexes determined spectrophotometrically[11] at $\lambda_{max} = 481$ nm under nitrogen are summarized in Table 3. The values of the formation constants decrease with a decrease in π-acidity of the PR_3 ligands (Table 3). The stability of the mixed-ligand complex $[Ru^{III}(EDTA)(PR_3)]^-$ decreases in the following order:

$$[Ru^{III}(EDTA)P(C_6H_4{-}F)_3]^- > [Ru^{III}(EDTA)P(C_6H_5)_3]^- > [Ru^{III}(EDTA)P(C_6H_{11})_3]^-.$$

Catalytic oxidation of PR_3 *with oxygen*

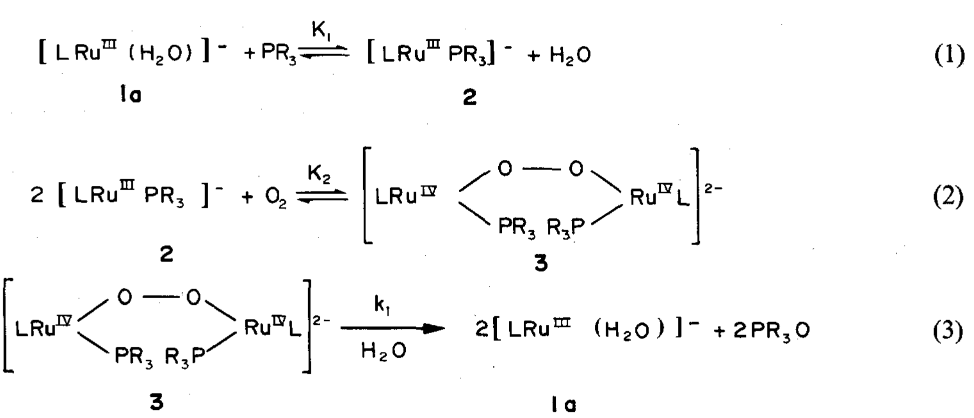
Catalytic oxidations of PR_3 to PR_3O with molecular oxygen were studied in 50% water–dioxane medium. The rate of reaction was found to be first-order with respect to catalyst concentration for each substrate studied. The rate of reaction increases with an increase in PR_3 concentration. At high PR_3 concentration ($[PR_3]/[Cat] > 10^2$) a limit in rate[11] was observed for all the phosphine substrates studied. At constant catalyst (5×10^{-4} M) and PR_3 (5×10^{-3} M) concentrations the rate of reaction was found to be half-order with respect to dissolved oxygen concentration. The kinetic details are similar to those published earlier[11] at 35°C. Based on the above kinetic results a mechanism is proposed, as outlined in Scheme 1, which is similar to that reported earlier.[11]

The catalyst $K[Ru^{III}(EDTA\text{-}H)Cl]$ (**1**) is rapidly aquated when dissolved in water to the corresponding aquo complex (**1a**) at low pH ($\simeq 3$).[23] Complex **1a** reacts with PR_3 to give a mixed-ligand complex (**2**) in a pre-equilibrium step (1) (Scheme 1). The formation of this complex is supported by the successful isolation of (Ru^{III}-EDTA-PR_3) complexes in the present studies. Complex **2** subsequently reacts with dissolved molecular oxygen to form a transient μ-peroxo intermediate (**3**), which undergoes a homolytic cleavage of the O—O bond with one oxygen atom transfer to the substrate in a concerted rate-determining step to give the catalyst (Ru^{III}-EDTA complex) along with the oxidation product (PR_3O). The equilibrium constant (K_2) (determined kinetically)[11] and the rate constant (k) values are summarized in Tables 3 and 4, respec-

Table 3. Values of equilibrium constants (K_1 and K_2) for the oxidation of PR_3 with oxygen catalysed by the Ru^{III}-EDTA complex

System	Temperature (°C)	K^a (M^{-1})	$K_2{}^b$ (M^{-2})
$LRu^{III}/P(C_6H_4F)_3/O_2$	25	87	3.3×10^3
	35	136	3.9×10^3
	45	228	4.3×10^3
$LRu^{III}/P(C_6H_5)_3/O_2$	25	78	3.9×10^3
	35	115	4.7×10^3
	45	172	4.9×10^3
$LRu^{III}/P\text{-}(C_6H_{11})_3/O_2$	25	55	4.3×10^3
	35	68	4.9×10^3
	45	87	5.3×10^3

[a] Determined spectrophotometrically.[11]
[b] Determined kinetically.[11]



Scheme 1.

tively. The reactivity of the phosphines towards oxidation by molecular oxygen decreases in the order $P(C_6H_4F—P)_3$ > $P(C_6H_5)_3$ > $P(C_6H_{11})_3$, which can be explained in terms of the stability of the Ru^{III}-EDTA phosphine and Ru—μ-peroxo bond strengths in the intermediate **3** (Table 3). The fluoro-substituted substrate $P(C_6H_4—F)_3$ has maximum reactivity since it is more π-acidic in nature than $P(C_6H_5)_3$. The electron density at the ruthenium centre is depleted by increasing π-acidity of the PR_3 ligands in the $[Ru^{III}(EDTA)(PR_3)]^-$ mixed-ligand complexes. This is further supported by the positive shift of the redox potentials for Ru^{3+}/Ru^{2+} couples, increasing in the order **3** > **2** > **4**. The stability (K_2) of the μ-peroxo ternary $[Ru^{IV}(EDTA)PR_3]_2O_2$ complexes also increases in the same order.

It is of interest to note that Taqueshi has synthesized Ru^{IV}=O complexes with phosphine coordinated *cis* to the oxo ligand in the complex $[O{=}Ru^{IV}(bipy)(PPh_3)]$.[24] The coordinated phosphine in this complex is not oxidized to $OPPh_3$. The complex nevertheless oxidizes PPh_3 in solution by an outer sphere mechanism, without the "spectator" phosphine coordinating to the metal ion. In our case, however, the presence of the σ-basic EDTA ligand makes the oxo oxygen of the Ru=O intermediate (after cleavage of the O—O bond in **3**) sufficiently labile for oxygen atom transfer to coordinated phosphine. Thus, the oxygen atom transfer in our case occurs through a coordinated phosphine, as supported by the kinetic evidence (first-order dependence on phosphine concentration). The reaction is slowest in the case of the most basic $P(C_6H_{11})_3$, in which the σ-donation of electrons from phosphine to the metal centre strengthens the O—O bond towards homolytic cleavage. Triphenylphosphine falls between the fluoro and the tricyclohexylphosphine in terms of σ-basicity and π-acidity and thus has a reactivity intermediate of the two extremes.

The catalytic oxidation of PR_3 with molecular

Table 4. Rate and activation parameters for the catalytic oxidations of different aryl-phosphines (PR_3) with molecular oxygen; [Cat] = 5×10^{-4} M, O_2 pressure = 1 atm., pH = 3.0

System	Temperature (°C)	k_1 (s^{-1})	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (cal ° mol^{-1})	$\Delta G^\ddagger$ (kcal mol^{-1})
$Ru^{III}(EDTA)(H_2O)^-/P(C_6H_4F)_3/O_2$	25	1.8×10^{-4}			
	35	3.0×10^{-4}	8±1	−48±2	22.5
	45	4.6×10^{-4}			
$Ru^{III}(EDTA)(H_2O)^-/P(C_6H_5)_3/O_2$	25	1.4×10^{-4}			
	35	2.2×10^{-4}	9±1	−46±2	22.6
		3.9×10^{-4}			
$Ru^{III}(EDTA)(H_2O)^-/P(C_6H_{11})_3/O_2$	25	0.5×10^{-4}			
	35	1.0×10^{-4}	13±2	−36±3	23.3
	45	1.9×10^{-4}			

oxygen was studied at three different temperatures and the activation parameters calculated from the temperature dependence of the rate constant are summarized in Table 4. The low value of $\Delta H^{\ddagger}$ and negative value of $\Delta S^{\ddagger}$ are consistent with the concerted oxygen atom transfer process, as shown in Scheme 1.

Stoichiometric oxygen atom transfer from $Ru^V(EDTA)(O)^-$ *to* PR_3

In order to probe into the nature of the oxygen atom transfer step in the catalytic oxidation of PR_3 with oxygen we have studied the stoichiometric oxygen atom transfer reaction from the oxo complex $Ru^V(EDTA)(O)^-$ to the phosphine PR_3 under the pseudo-first-order condition of excess phosphine, where the rate of reaction was found to be first-order with respect to the oxo complex concentration. The rate of reaction increases with an increase in PR_3 concentration (Fig. 3). The above kinetic data suggest the following mechanism [eq. (4)] for the oxo transfer reaction:

$$\underset{\mathbf{4}}{[Ru^V(EDTA)(O)]^-} + PR_3 \xrightarrow{k_2} \underset{\mathbf{5}}{[Ru^{III}(EDTA)(OPR_3)]^-} \xrightarrow[H_2O]{\text{Fast}} [Ru^{III}(EDTA)(H_2O)]^- + OPR_3. \quad (4)$$

In the above mechanism the substrate PR_3 attacks the oxo oxygen in a rate determining redox step to give an $[Ru^{III}(EDTA)(OPR_3)]^-$ intermediate, which undergoes rapid hydrolysis to give the $Ru^{III}(EDTA)(H_2O)^-$ complex and PR_3O as an oxidation product.

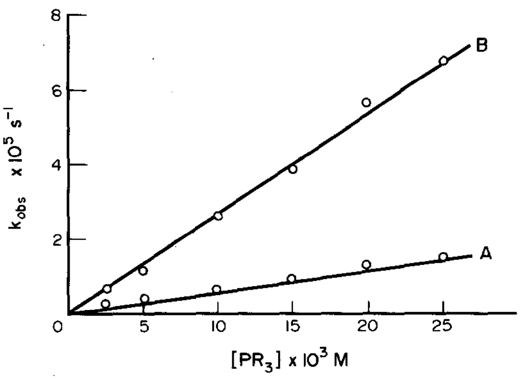


Fig. 3. Effect of $[PR_3]$ on rate constant (k_{obs}) at 30°C: (a) $P(C_6H_5)_3$, (b) $P(C_6H_4{-}F)_3$; $[Ru^{VI}]_T = 5\times10^{-4}$ M, pH = 3.0 and $\mu = 0.2$ M (KCl).

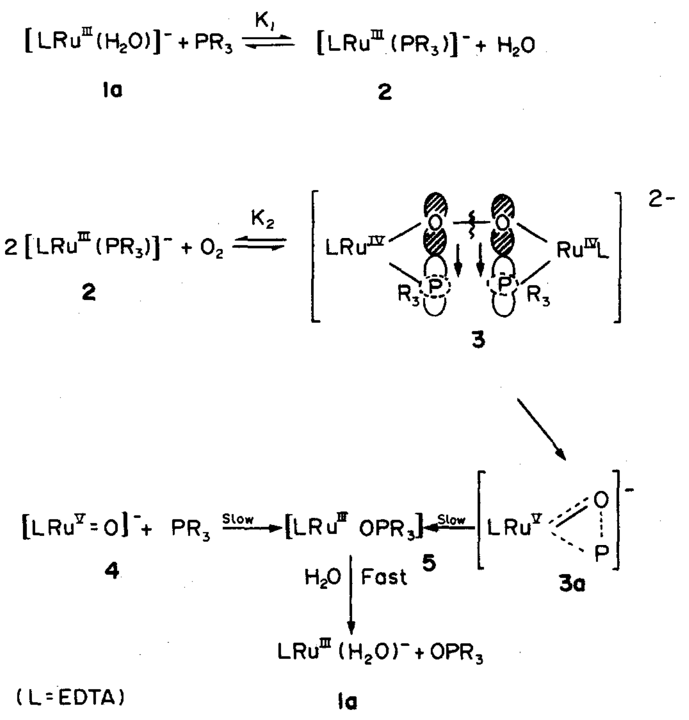
The reactivity order for the oxygen atom transfer reaction in the oxidation of PR_3 by $Ru^V(EDTA)(O)^-$ decreases in the order $P(C_6H_{11})_3 > P(C_6H_5)_3 > P(C_6H_4{-}F)_3$, in accordance with the decrease in nucleophilicity of the phosphines. The rate and the activation parameters are reported in Table 5. The small positive value of $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ values are in good agreement to the proposed mechanism [eq. (4)].

It is of interest to compare the free energy of activation, $\Delta G^{\ddagger}$, for the catalytic oxidation of phosphine by molecular oxygen to those observed for the stoichiometric reaction with the oxo complex **4**. $\Delta G^{\ddagger}_1$ is more positive (2–3 kcal mol^{-1}) for the molecular oxygen reaction compared with $\Delta G^{\ddagger}_2$ for the stoichiometric reaction with complex **4**. The small difference ($\Delta G^{\ddagger}_1 - \Delta G^{\ddagger}_2$), which is significant, reflects on the lowering of the O—O bond dissociation energy in the intermediate μ-peroxo complex **3**.

The interaction of one π^* orbital of the oxygen

Table 5. Rate and activation parameters for the reaction $(EDTA)Ru^V{=}O^- + PR_3 \rightarrow (EDTA)Ru^{III}(H_2O)^- + PR_3O$; $[Ru^V] = 5\times10^{-4}$ M, pH = 3.0

System	Temperature (°C)	k_2 ($M^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}_2$ (kcal mol^{-1})	$\Delta S^{\ddagger}_2$ (cal ° mol^{-1})	$\Delta G^{\ddagger}_2$ (kcal mol^{-1})
$Ru^V(EDTA)(O)^-P(C_6H_4F)_3$	30	0.7×10^{-3}			
	40	1.5×10^{-3}	14±1	−26±1	21.9
	50	3.1×10^{-3}			
$Ru^V(EDTA)(O)^-/P(C_6H_5)$	30	2.7×10^{-3}			
	40	5.0×10^{-3}	12±1	−31±2	21.2
	50	9.8 ± 10^{-3}			
$Ru^V(EDTA)(O)^-/P(C_6H_{11})_3$	30	3.8×10^{-2}			
	40	6.7×10^{-2}	10±1	−34±2	20.5
	50	12.1×10^{-2}			



Scheme 2.

atom of the μ-peroxo group with the substrate has been suggested by Solomon *et al.*[25] as the crucial step in the oxygen atom transfer reaction in tyrosinases. The oxygen atom transfer to phosphine in the molecular oxygen oxidation occurs through a concentrated homolytic cleavage of the μ-peroxo bond, assisted by electron withdrawal by the substrate and transfer of oxo oxygen to phosphine to form Ru^{III}-OPR_3 (**5**) species. This interaction may be triangular **3a** with the association of phosphine either with the metal ion or/and the oxo oxygen. The rate-determination step in this case is the transfer of oxo oxygen to the phosphine to form Ru^{III}-OPR_3 species (Scheme 2).

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