

Molecular oxygen reactions catalyzed by an oxorhenium(V) compound

Ruili Huang, James H. Espenson*

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011, USA

Received 23 August 2000; received in revised form 12 September 2000; accepted 30 October 2000

Abstract

The new binuclear oxothiolatorhenium(V) compound, $\text{Re}_2\text{O}_2(\text{mtp})_3$, D_1 , $\text{mtpH}_2 = 2$ -(mercaptomethyl)thiophenol, was found to activate molecular oxygen, which has no precedent in oxorhenium catalysis. The kinetics and mechanism of the oxidation of triaryl phosphines and methyl phenyl phosphines by O_2 were investigated. The reaction pathway inferred from the kinetic data involves two Re(VII) intermediates, a peroxo and a μ -oxo species. The rate constants were determined for both steps in this reaction. The μ -oxo Re(VII) intermediate further reacts with a second phosphine forming more phosphine oxide as D_1 is recovered. This step is very rapid, and does not affect the kinetics. Other substrates, taken alone, such as sulfides and dienes, which coordinate to D_1 weakly, or do not coordinate, were not oxidized by molecular oxygen. However, in the presence of a small amount of phosphine to open up the sulfur bridge in D_1 , then sulfides and dienes were also oxidized to sulfoxides and epoxides accordingly. The relative reactivities of the substrates fall in the order: phosphines > sulfides > dienes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; Rhenium; Oxygen; Phosphine

1. Introduction

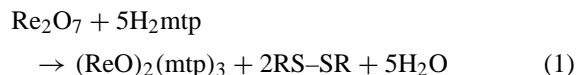
Many rhenium compounds as catalysts for selective oxidation reactions, has not been able to activate molecular oxygen. Many of them catalyze reactions of hydrogen peroxide, as recently reviewed [1–3], and oxygen-atom transfer between a donor and acceptor [4–6]. The compounds referred to are MeReO_3 , $\text{MeReO}(\text{mtp})\text{PPh}_3$ [7], $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ [8], and $\text{Re}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2$ [8]. These compounds are themselves stable towards O_2 ; in general, their catalytic reactions proceed as well under oxygen (air) as under argon.

We prepared a new Re(V) compound D_1 [9]¹ and found that it is air-sensitive, a significant departure from the properties of the others, which are mostly air-stable. On that basis it appeared reasonable to suggest that D_1 might form an intermediate with oxygen that could carry out other chemistry. If the original compound could be recovered, then a catalytic cycle could be established. The new compound has the formula $\text{Re}_2\text{O}_2(\text{mtp})_3$, where $\text{mtpH}_2 =$

¹ ^1H NMR/ CDCl_3 : δ (ppm): 7.50–7.35 (m, 8H, arom), 7.30–7.15 (m, 4H, arom), 5.67 (d, 1H, CH_2 , $J = 11.2$), 5.21 (d, 1H, CH_2 , $J = 11.2$), 5.06 (d, 1H, CH_2 , $J = 12.4$), 4.30 (d, 1H, CH_2 , $J = 11.6$), 3.75 (d, 1H, CH_2 , $J = 12.4$), 3.62 (d, 1H, CH_2 , $J = 11.2$); ¹³C NMR/ CDCl_3 : δ (ppm): 140.92, 140.36, 139.71, 139.02, 135.70, 135.47, 131.07, 130.94, 130.90, 130.58, 130.56, 130.38, 129.22, 128.97, 128.85, 128.70, 128.54, 128.42, 42.29, 40.92, 38.90.

* Corresponding author. Tel.: +1-515-294-5730;
fax: +1-515-294-5233.
E-mail address: espenson@ameslab.gov (J.H. Espenson).

2-(mercaptomethyl)thiophenol (chart 1). It was prepared according to this reaction



where RS-SR is the cyclic disulfide from mtp. Unlike many of its relatives, D₁ has no Me-Re group, which may be extraneous in any event. Here we report studies of autoxidation reactions catalyzed by D₁. They are principally phosphine oxidations, but certain other substrates are considered in less detail.

2. Experimental

Except for D₁, all materials were obtained commercially and used as received. The reaction progress was monitored by ¹H NMR spectroscopy; products and intermediates were studied with ¹H and ³¹P NMR spectroscopy using a Bruker DRX-400 spectrometer. The ¹H NMR chemical shifts were measured relative to the residual resonance of the solvents, C₆D₅H at 7.15 ppm and C₆D₅CD₂H at 2.09 ppm. The ¹H signals were integrated relative to *tert*-butanol, an internal standard. ³¹P chemical shifts were referenced to 85% phosphoric acid. The temperature was maintained at 25°C, except as noted.

For kinetics, the oxygen concentrations were 9.1 mM (oxygen-saturated) and 1.9 mM (air-saturated) [10]. For a few experiments, data taken over the full time course were analyzed. Mostly, however, the method of initial rates was used for the kinetics because it provided the most latitude in the selection of the concentrations. First, NMR intensities were converted to concentrations by means of the internal standard. Then the concentration-time data were fitted to a polynomial function [11]; for phosphine oxide, for example, $C_t = m_1t + m_2t^2 + m_3t^3 + \dots$. The coefficient of the leading term, m_1 , is the initial rate value in units mol l⁻¹ s⁻¹.

3. Results and interpretation

3.1. General observations

Control experiments on uncatalyzed reactions of selected phosphines by molecular oxygen were carried

out. In all of these cases, <5% oxidation had occurred in 24 h. For P(*p*-Tol)₃, no oxidation occurred in 8 h. NMR studies at -23°C were carried out in toluene-d₈. Of course, without oxygen the phosphines are stable.

In the reactions of PAr₃ and oxygen with D₁ as a catalyst, the reactions proceed to 100% conversion. The major product is Ar₃P=O (>90%), accompanied by a small amount of phosphine sulfide, Ar₃P=S, evidently from side reactions between PR₃ and the thiolate ligands of D₁.

In the absence of oxygen there is an initial interaction between PAr₃ and D₁, leading in <0.5 s to a quantitative yield of a 1:1 adduct, which we abbreviate as PD₁, also shown in chart 1. Under such solutions, and throughout all the catalysis experiments, PD₁ is the only form of the catalyst that could be detected in the NMR spectra.² PD₁ is evidently the resting state of the catalyst. Subsequent steps in catalysis occur over many hours, such that PD₁ is always restored by this equilibrium. Other reactive species in the reaction scheme never attain a concentration where they can be detected by NMR or UV-VIS.

The smaller phosphines, PMePh₂ and PMe₂Ph, engage in more complicated interactions. The distribution of species was determined at 50 mM total phosphine and 6 mM total D₁. These species were seen: two forms of PD₁, in which coordination occurred at either Re atom, and the bis(phosphine) compound P₂D₁, in which both Re atoms are coordinated. Refer to the structural formulas in chart 1. These conclusions are based on the ¹H and ³¹P NMR spectra, given in Table 1. In the kinetics experiments to be presented subsequently, where the phosphine was always used in large excess (>50-fold), most (PMePh₂) or all (PMe₂Ph) of the catalyst remains in the form P₂D₁.

3.2. Oxidation of P(*p*-Tol)₃

The typical concentrations ranges for kinetics experiments were 1–30 mM P(Tol)₃, 0.1–9.1 mM O₂, and 5–500 μM D₁. Under air, when [O₂] < 2 mM and [P(Tol)₃] > 4 mM, the reactions were completed

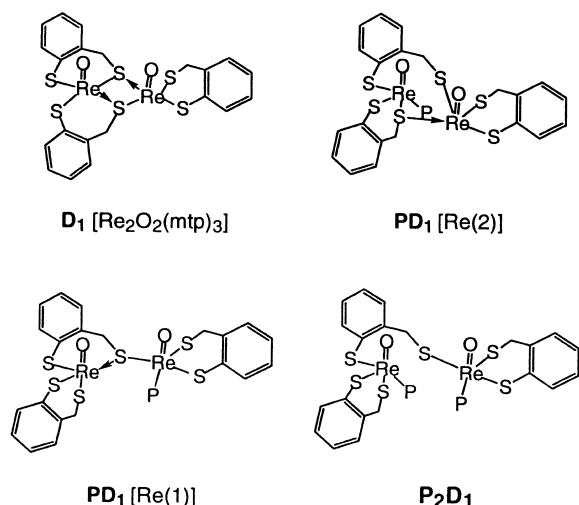
² ¹H and ³¹P spectra for *p*-Tol₃P-D₁: ¹H/CDCl₃ δ (ppm): 7.80–6.70 (m, 24H, arom), 4.98 (d, 1H, *J* = 11.6), 4.93 (d, 1H, *J* = 12.4), 4.58 (d, 1H, *J* = 12.4), 4.57 (d, 1H, *J* = 11.6), 3.45 (d, 1H, *J* = 11.6), 3 (d, 31H, *J* = 11.6), 2.35 (s, 9H, CH₃); ³¹P/CDCl₃ δ (ppm): -6.55.

Table 1

^1H and ^{31}P chemical shifts and relative intensities (%) for the 1:1 (PD_1), 2:1 (P_2D_1) adducts of methylphenylphosphines and D_1 , and the free phosphines (P) in C_6D_6 ($[\text{P}]_{\text{T}} = 50 \text{ mM}$, $[\text{D}_1]_{\text{T}} = 6.0 \text{ mM}$)

P	$\text{P}^{\text{Re}(1)}\text{D}_1$	$\text{P}^{\text{Re}(2)}\text{D}_1$	P_2D_1
Part I: ^1H NMR, δ (ppm)			
MePh ₂ P	8.0–6.5 (m, 22H, arom), 5.32 (d, 1H, $J = 11.2$), 4.94 (d, 1H, $J = 12.4$), 4.59 (d, 1H, $J = 11.6$), 4.16 (d, 1H, $J = 12.8$), 3.48 (d, 1H, $J = 11.6$), 3.24 (d, 1H, $J = 11.6$), 2.20 (d, 3H, $^2J_{\text{P-H}} = 10.0$)	8.0–6.5 (m, 22H, arom), 5.02 (d, 1H, $J = 11.6$), 4.96 (d, 1H, $J = 11.6$), 4.33 (d, 1H, $J = 12.0$), 4.17 (d, 1H, $J = 11.6$), 3.69 (d, 1H, $J = 11.6$), 3.30 (d, 1H, $J = 12.0$), 2.19 (d, 3H, $^2J_{\text{P-H}} = 10.0$)	8.0–6.5 (m, 32H, arom), 5.36 (d, 2H, $J = 12.8$), 4.94 (d, 2H, $J = 12.8$), 4.16 (d, 2H, $J = 12.4$), 2.26 (d, 3H, $^2J_{\text{P-H}} = 10.4$), 2.07 (d, 3H, $^2J_{\text{P-H}} = 10.4$)
Me ₂ PhP	1.67 (d, 6H, $^2J_{\text{P-H}} = 10.8$, Me). Complex pattern convoluted with that of $\text{P}^{\text{Re}(2)}\text{D}_1$	1.73 (d, 6H, $^2J_{\text{P-H}} = 10.8$, Me). Complex pattern convoluted with that of $\text{P}^{\text{Re}(1)}\text{D}_1$	8.0–6.5 (m, 22H, arom), 5.37 (d, 1H, $J = 12.0$), 5.02 (d, 1H, $J = 12.4$), 4.90 (d, 1H, $J = 11.6$), 4.75 (d, 1H, $J = 11.6$), 3.70 (d, 1H, $J = 12.0$), 3.40 (d, 1H, $J = 11.6$), 2.08 (d, 6H, $^2J_{\text{P-H}} = 10.8$), 1.97 (d, 6H, $^2J_{\text{P-H}} = 10.8$)
Part II: ^{31}P NMR, δ (ppm) ^a			
MePh ₂ P	−26.29 −19.21 (62)	−24.15 (7)	7.25 (3.6), 6.00 (31)
Me ₂ PhP	−45.54 −34.92 (0)	−31.14 (0)	−3.96 (14.7), −4.66 (100)

^a Values in percentage are indicated in parentheses.



by diffusion of atmospheric oxygen into the solution. With fixed P(Tol)₃, 13.5 mM, and O₂, 1.9 mM, PD₁ was varied in the range 0.09–0.16 mM; the initial rates, v_i ($10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$) varied in the range 3.30–6.20, establishing a first-order dependence on catalyst concentration.

In other experiments, with 13.5 mM P(Tol)₃ and 0.16 mM PD₁, [O₂] was varied 0.1–10 mM. The variation of v_i with [O₂]₀ takes the form of a rectangular hyperbola, Fig. 1. In another series, with 1.9 mM O₂ and 0.16 mM PD₁, [P(Tol)₃] was varied 1–25 mM. Again, Fig. 2, v_i attains a plateau at high concentration. These

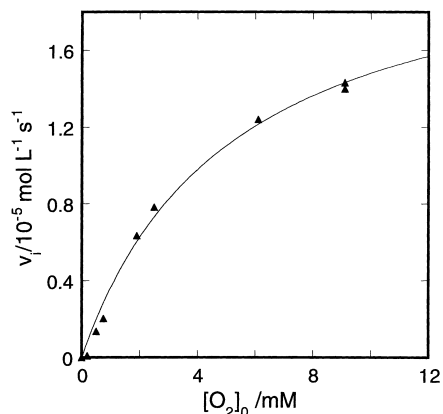


Fig. 1. Kinetic data for the oxidation of P(*p*-Tol)₃ by oxygen with D₁ as a catalyst. Conditions: constant phosphine (13.5 mM) and catalyst (0.16 mM), with variable oxygen concentrations in deuterobenzene at 25°C.

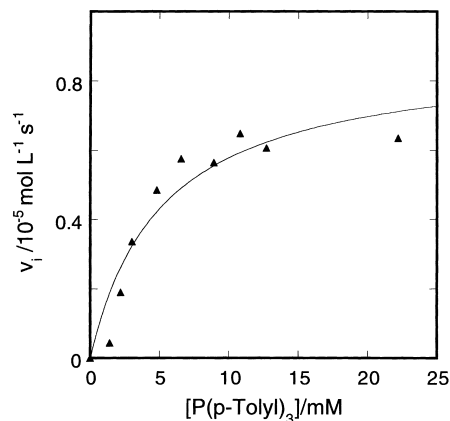


Fig. 2. Kinetic data for the oxidation of P(*p*-Tol)₃ by oxygen with D₁ as a catalyst. Conditions: constant O₂ (1.9 mM) and D₁ (0.16 mM), with variable phosphine concentrations in deuterobenzene at 25°C.

dependences correspond to Michaelis–Menten kinetics. On the basis of these results, with constants to be defined subsequently, the empirical rate equation is

$$v_i = \frac{k_1 k_2 [\text{PD}_1][\text{O}_2][\text{P}(\text{Tol})_3]}{k_{-1} + k_1[\text{O}_2] + k_2[\text{P}(\text{Tol})_3]} \quad (2)$$

According to this equation, rate saturation will occur at sufficiently high concentrations of P(Tol)₃ or O₂. With either concentration much higher than the other, the limiting forms of v_i will be obtained; they are $k_1[\text{PD}_1][\text{O}_2]$ and $k_2[\text{PD}_1][\text{P}(\text{Tol})_3]$. This point was checked as well, leading to approximate values of these constants that were then refined. To cover all the concentration ranges, we used a least-squares program, SCIENTIST, to fit all the initial rate values to Eq. (2). The result is: $k_1 = 21.2 \pm 1.71 \text{ mol}^{-1} \text{ s}^{-1}$, $k_2 = 13.6 \pm 1.81 \text{ mol}^{-1} \text{ s}^{-1}$. The value of k_{-1} was too small to be determined. To show the extent to which this model fits the data, the experimental values of v_i were plotted against values of v_i calculated from the best-fit values of the rate constants from Eq. (2). One expects a linear relation of unit slope. Fig. 3 shows that the agreement between data and model is quite reasonable.

3.3. Oxidation of other phosphines

Other tri(aryl)phosphines were studied in the same way, except that fewer concentration variations were

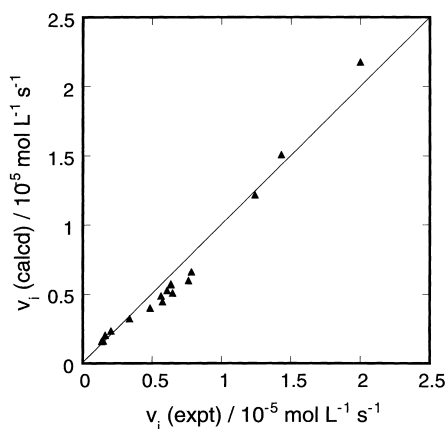


Fig. 3. The data for the multi-variable rate equation that represents the oxidation of $P(p\text{-Tol})_3$ by oxygen with D_1 as a catalyst, after least-squares fitting to Eq. (2), are displayed as the correlation of observed against calculated values, and a line of unit slope.

made. These reactions were studied under 1 atm O_2 , such that a limiting form of the rate was attained. (Since this limit was shown to be realized for $P(p\text{-Tol})_3$, the compound with the second highest value of k_2 , it would hold for all). This approach gave k_2 directly (see Table 2), according to this form

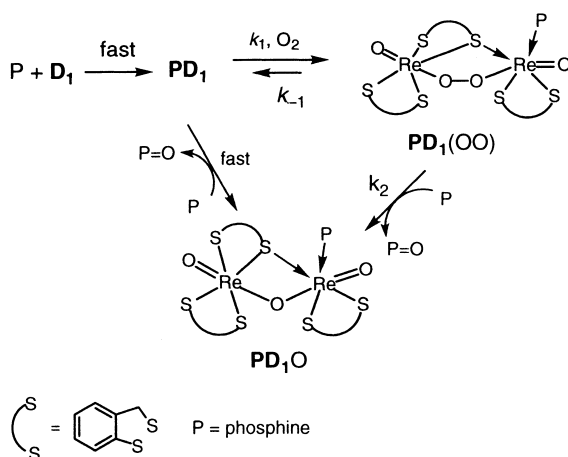
$$v_i = k_2[PD_1][PAR_3] \quad (3)$$

Similar determinations were carried out for $PMePh_2$ and PMe_2Ph . The results are also given in Table 2. The sterically encumbered phosphine $P(o\text{-Tol})_3$ reacts much more slowly than $P(p\text{-Tol})_3$ with O_2 . D_1 was ineffective in this case. Starting with 25 mM $P(o\text{-Tol})_3$, 5% D_1 , under air, 10% of the $(o\text{-Tol})_3P=O$ was formed

Table 2

Kinetic data for the D_1 -catalyzed oxidation of para-substituted triarylphosphines ($p\text{-Y}C_6H_4$) $_3P$ and methylphenylphosphines $Me_nPh_{3-n}P$ ($n = 1\text{--}2$) by molecular oxygen in benzene at 25°C

Phosphine	k_2 ($l\text{ mol}^{-1}\text{ s}^{-1}$)
$P(C_6H_4\text{-}p\text{-OMe})_3$	20.0
$P(C_6H_4\text{-}p\text{-Me})_3$	13.6
$P(C_6H_4\text{-}p\text{-CF}_3)_3$	7.46
$P(C_6H_4\text{-}p\text{-Cl})_3$	3.44
$P(C_6H_5)_3$	1.85
PMe_2Ph	3.29
$PMePh_2$	2.18



Scheme 1.

after 16 h. However, $P(p\text{-Tol})_3$ promotes the oxidation of $P(o\text{-Tol})_3$, probably by helping to break the Re–S bond and allowing O_2 to coordinate, since $P(o\text{-Tol})_3$ itself does not coordinate to D_1 . Under the same conditions, but with 1.0 mM of $P(p\text{-Tol})_3$ added in the beginning, 6.3 mM (25%) of $P(o\text{-Tol})_3=O$ along with 1 mM (4%, i.e. all) $P(p\text{-Tol})_3=O$ were detected after 17 h. Oxidation of the ortho isomer stops once all the essential para isomer has been consumed.

3.4. Low-temperature NMR spectroscopy

During the ambient-temperature kinetics with 1H NMR spectroscopy, no form of the catalyst could be detected except for PD_1 . From the rate constants, it can be shown that the postulated intermediate would have a lifetime of a few seconds, too short for this technique, since about 1 min is needed to obtain the first 1H spectrum.

To detect the intermediate, 1H NMR studies were carried out at 250 K in toluene- d_8 solution. The concentrations were: 2.0 mM PD_1 , 5.0 mM O_2 , and 25.5 mM $P(p\text{-Tol})_3$. A new rhenium species was found; it reached maximum intensity in about 30 min and disappeared after 5–6 h. The proton chemical shifts are consistent with $PD_1(OO)$ in Scheme 1.³

³ 1H NMR (CH_2 shifts only): δ (ppm): 4.98 (d, 1H), 4.71 (d, 1H), 4.45 (d, 1H), 4.22 (d, 1H), 3.98 (d, 1H), 3.78 (d, 1H).

3.5. Oxidation of other substrates by O₂, catalyzed by D₁

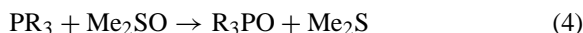
Phosphines are the substrates most likely to succeed in oxidation reactions, since the P=O bond is much stronger than other element-oxygen bonds. Experiments were also carried out with a few substrates X leading to products having weaker X=O bonds. This includes sulfides: (*p*-Tol)SMe and MeSEt; dienes: 2-methyl-1,3-pentadiene, *trans*-1,3-pentadiene and 1,3-cyclohexadiene; and one alkene, cyclohexene. Like P(*o*-Tol)₃, none of these was oxidized by O₂ with D₁ added until a low concentration of P(*p*-Tol)₃, equivalent to D₁, was also added.

Even then, the results were marginal: 0.5–3.4% yield of sulfoxides obtained, and 1–14% of the monoepoxides of each diene. Epoxidation occurred preferentially at the less-substituted double bond, opposite to the results for MTO–H₂O₂ [12]. No cyclohexene oxide was found. Over the reaction time (*p*-Tol)₃PO was formed quantitatively. Clearly, the problem was that the phosphine, essential for catalysis, was concurrently oxidized, bringing the main reaction to a halt.

The conditions and yields are summarized in Table 3. In this system the phosphine is only a catalyst, and it was taken in relatively small amount. The phosphine is, however, oxidized concurrently, and the reaction stopped when all the phosphine had been oxidized.

3.6. Other oxygen transfer reactions

In the absence of O₂, D₁ catalyzes the oxidation of phosphines with Me₂SO. These reactions were carried out in C₆D₆ using Me₂SO at 5–10-fold excess over phosphine, and a higher concentration of D₁ (5% of phosphine). Phosphine oxide and dimethyl sulfide were formed. The reaction stoichiometry is



In 60–90 min, high conversions to the products were realized: PMePh₂, 90%, P(*p*-Tol)₃, 70%, and PPh₃, 65%.









4. Discussion

4.1. Mechanism of phosphine oxidation

A set of chemical reactions by which the catalytic cycle can be accomplished is proposed in Scheme 1. The first reaction, conversion of D₁ to PD₁, was verified directly by spectroscopy. This rapid (<0.5 s) reaction was detected by the stopped-flow method with spectrophotometric detection. In addition, the NMR data show a new resonance for PD₁.

The second reaction has been formulated as occurring between PD₁ and molecular oxygen, leading to a key reactive intermediate. (The rate law suggests that the second step occurs between PD₁ and either O₂ or

Table 3
Reactions conditions and yields^a for the oxidation of sulfides, dienes, and cyclohexene by O₂ catalyzed by D₁ and co-catalyzed by *p*-Tol₃P

X (100%)	(<i>p</i> -Tol) ₃ P (%)	D ₁ (%)	XO (%)	(<i>p</i> -Tol) ₃ P = O (%)
(<i>p</i> -Tol)SMe	0.2	0.2	(<i>p</i> -Tol)MeSO (3.4)	0.2
EtSMe	0.25	0.34	EtMeS(O) (0.53)	0.75
	0.6	1.5		0.6
	0.22	0.22		0.22
	1.2	1.7		1.2
	0.4	0.3		0.4

^a The yields given are based on sulfides and dienes.

PR₃, but the choice of phosphine seems less plausible. It would lead to a bis(phosphine) compound, observed only for the smaller phosphines, which is in any event then likely to find its required reaction with oxygen blocked). Given, then, that such an oxygen adduct is formed, what is its likely role in the reaction cycle?

We speculate that the resultant species contains a chelated peroxide ligand, and that it is a mixed-valent, Re(VII)–Re(V) species. See PD₁OO in Scheme 1. These assignments represent our hypotheses, based on certain precedents in the literature [1,13,14]. The ¹H NMR spectrum of the reaction intermediate does show chemical shifts that are not broadened or greatly shifted; the intermediate is therefore, not likely to be a free radical. As suggested by a referee, it may be that the PD₁OO contains a μ-peroxo group, offering an explanation as to the uniqueness of D₁ in activating O₂. The structure of this highly reactive intermediate has not been determined.

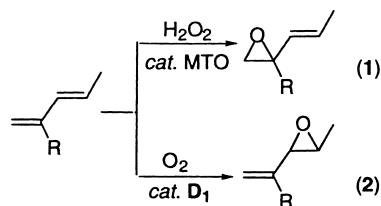
In the next stage of reaction the intermediate PD₁OO reacts with phosphine, yielding the first mole of the phosphine oxide product. This reaction has wide precedent for chelated peroxorhenium compounds [1,15]. This still leaves a single extra oxygen in the catalyst, as shown in the suggested structural formula of PD₁O. We have chosen to represent its formula as containing Re₂(μ-O), because of the final reaction in the scheme. In that step, which from the kinetics occurs much more rapidly than the two that precede it, a second phosphine is oxidized. Literature precedents suggest that the alternative, with PD₁O containing a terminal Re=O bond, would be too slow to match the kinetic data [16–18]. Whether PD₁O is a mixed-valent compound, Re(VII)–Re(V), or a Re(VI)–O₂–Re(VI) compound cannot be assessed from the data; we would note, however, that in the now-extensive body of compounds with these ligands, no Re(VI) compound has been found.

4.2. Oxidation of other substrates

Both organic sulfides and conjugated dienes were effectively oxidized by O₂ with D₁ as catalyst. Both required PD₁ not D₁, however; that is a catalytic quantity of P(*p*-Tol)₃ is needed as an activator. The reactions stopped well short of completion, but only because the requisite phosphine was itself lost to slow concurrent oxidation. A reaction scheme similar to that presented

for phosphines can accommodate these data. This affords at least circumstantial verification that PD₁O does not contain three terminal Re=O groups. The depicted formulation of PD₁O, although not proved, seems more likely to meet the reactivity requirement, because the same intermediate must engage in the oxidation of these substrates as well.

The phosphine is needed to initiate and sustain the catalytic cycle. It must “open” the D₁ structure to allow for entry of oxygen. Sulfides and dienes cannot do that, without which the cycle fails because O₂ cannot bind. The epoxides formed from these dienes are different than those resulting from MTO-peroxide, Eq. (5), probably for steric reasons in the PD₁O-diene reaction.

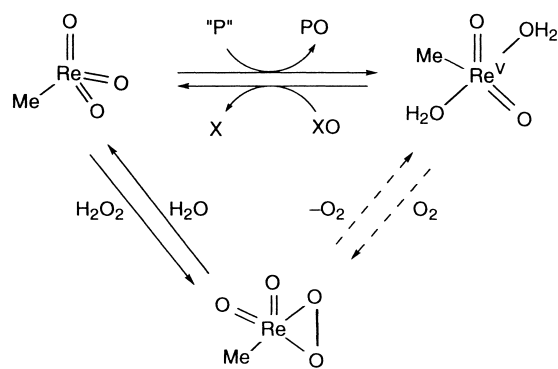


$$1: 2 = 100:0, R = \text{Me}; \quad 1: 2 = 63:37, R = \text{H} \quad (5)$$

Attempts to use a ligand other than a phosphine as co-catalyst were not successful. Neither THF nor acetonitrile is a sufficiently strong Lewis base to open a Re–S bridge bond. Thus, they are without effect. Addition of a pyridine *N*-oxide causes the irreversible oxidation of the catalyst to rhenium oxides and the organic disulfide, thus, deactivating it. Pyridine decomposes the catalyst very quickly. The steric bulk of the phosphine ligand thus, appears important in preserving the dinuclear structure and activity of D₁.

4.3. Reactivity trends

The values of k_2 for the compounds P(C₆H₅-*p*-Y)₃ lie in this order: Y = MeO > Me > CF₃ > Cl > H. In the sense of an inductive effect, this ordering is highly irregular. It must be recognized, however, that not only does Y change along the series, but also the phosphine present in the catalytic intermediate. That is, the identity and presumably the reactivity of PD₁OO varies with the choice of phosphine. The kinetic data therefore, contain dual effects of Y. When the coordinated phosphine has an electron donating substituent, it also donated electron density to the other



"P" = PR_3 , H_3PO_2 ; XO = Me_2SO , PyO , ClO_4^- , etc.

Scheme 2.

rhenium, making the oxygen more electron rich and thus, less reactive. An electron-donating substituent, on the other hand, provides a phosphine more reactive towards the peroxo group. The conflict between the two can account the trends noted.

5. Conclusion

In summary, a dinuclear compound D_1 , which contains two inequivalent rhenium atoms, was found to catalyze the oxidation of phosphines by molecular oxygen. Here, D_1 serves as a dioxygenase: both O atoms are transferred in accord with this chemical equation: $2\text{R}_3\text{P} + \text{O}_2 \rightarrow 2\text{R}_2\text{PO}$. These reactions were studied in benzene (usually) or toluene. The reactions proceed quantitatively, provided O_2 is supplied or replenished as needed, giving 100% conversion of R_3P to R_3PO . Reaction times were 2–20 h, depending on the concentrations used.

We are aware of no other oxorhenium compound that catalyzes oxidations with molecular oxygen. To a minor extent, MeReO_2 can do so, but its instability and sluggish reactions make it ineffective [13]. The principle advanced earlier, however, appears to remain valid, as illustrated in the set of reactions presented in Scheme 2. $\text{MeRe}^{\text{V}}\text{O}_2$ is shown as a diaqua complex

[14,16], but phosphine ligation has also been found [19]. The important difference here is that oxygen uptake occurs quite well, whereas it is a marginal reaction of MeReO_2 .

Acknowledgements

This research was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-7405-Eng-82. We are grateful to a reviewer for help in revising the structures suggested for intermediates that could not be detected.

References

- [1] J.H. Espenson, Chem. Commun. (1999) 479–488.
- [2] K.P. Gable, E.C. Brown, Organometallics 19 (2000) 944.
- [3] W.A. Herrmann, F.E. Kühn, Acc. Chem. Res. 30 (1997) 169–180.
- [4] J.B. Arterburn, S.L. Nelson, J. Org. Chem. 61 (1996) 2260–2261.
- [5] J.B. Arterburn, Tetrahedron Lett. 44 (1996) 7941–7944.
- [6] J.B. Arterburn, M.C. Perry, S.L. Nelson, B.R. Dible, M.S. Holguin, J. Am. Chem. Soc. 119 (1997) 9309–9310.
- [7] Y. Wang, J.H. Espenson, Org. Lett. 2 (2000) 3525–3526.
- [8] M.M. Abu-Omar, S.I. Kahn, Inorg. Chem. 37 (1998) 4979–4985.
- [9] R. Huang, J.H. Espenson, submitted for publication.
- [10] R. Battino (Ed.), Solubility Data Series, Vol. 7, Oxygen and Ozone, American Chemical Society, Washington, DC, 1981 pp. 519.
- [11] K.J. Hall, T.I. Quickenden, D.W. Watts, J. Chem. Educ. 53 (1976) 493.
- [12] H. Tan, J.H. Espenson, Inorg. Chem. 37 (1998) 467–472.
- [13] M.D. Eager, J.H. Espenson, Inorg. Chem. 38 (1999) 2533–2535.
- [14] J.H. Espenson, D.T.Y. Yiu, Inorg. Chem. 39 (2000) 4113–4118.
- [15] M.M. Abu-Omar, J.H. Espenson, J. Am. Chem. Soc. 117 (1995) 272.
- [16] M.M. Abu-Omar, E.H. Appleman, J.H. Espenson, Inorg. Chem. 35 (1996) 7751–7757.
- [17] R.R. Conry, J.M. Mayer, Inorg. Chem. 29 (1990) 4862–4867.
- [18] K.P. Gable, T.N. Phan, J. Am. Chem. Soc. 115 (1993) 3036–3037.
- [19] W.A. Herrmann, P.W. Roesky, M. Wang, W. Scherer, Organometallics 13 (1994) 4531–4535.