The "Peroxo Perrhenic Acid" $H_4Re_2O_{13}$: An Oxygen-Rich Metal Peroxide and Oxidation Catalyst**

Wolfgang A. Herrmann,* João D. G. Correia, Fritz E. Kühn, Georg R. J. Artus, and Carlos C. Romão

Dedicated to Professor Herbert Roesky on the occasion of his 60th birthday

Abstract: The rhenium oxides Re_2O_7 and ReO_3 react with hydrogen peroxide solutions yielding peroxo complexes that efficiently catalyze the oxidation of olefins, aromatics, and certain organometallic compounds. In contrast, related oxides of molybdenum (MoO_3) and vanadium (V_2O_5) do not activate H_2O_2 under comparable conditions. The active rhenium peroxo complex was isolated from the system Re_2O_7/H_2O_2: the crystalline red-orange, *explosive* compound of formula $H_4Re_2O_{13}$ is the most oxygen rich rhenium compound isolated to date. Its structure resembles a "peroxo perrhenic acid". The binuclear compound could be isolated in the form of a diglyme adduct, structurally defined as two corner-sharing pentagonal bipyramids with apical oxo and aquo ligands; the equatorial positions are occupied by the bridging oxygen and by η^2-peroxo groups (two $[O_2]^{2-}$ ligands per rhenium). In contrast to the known complex $[CH_3ReO(O_2)_2]\cdot H_2O$, the new peroxo species $[O\{ReO(O_2)_2\cdot H_2O\}_2]$ decomposes hydrolytically during the catalytic cycle and can thus not compete in terms of catalytic activity in oxidation reactions involving H_2O_2. Hydrolysis yields "perrhenic acid" $Re_2O_7\cdot 2H_2O$, the diglyme adduct of which compound was also characterized by means of an X-ray diffraction analysis.

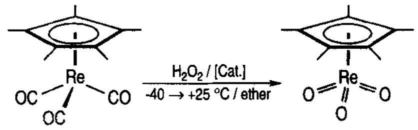
Keywords
catalysis · crystal structure · oxidations · rhenium peroxo complexes

Introduction

The peroxorhenium(VII) complex $[CH_3ReO(O_2)_2]\cdot H_2O$ (**1**) has been isolated in pure form and structurally characterized.[1] This unusual organometallic peroxide is the active catalyst of the $H_2O_2/[CH_3ReO_3]$ system in the epoxidation of olefins,[2] the Baeyer–Villiger oxidation,[3] aromatic oxidation,[4] and in the oxidation of aniline derivatives.[5] Stoichiometric reactions have demonstrated that **1** is responsible for oxygen transfer, and kinetic studies have shown that only one of the two peroxo groups is active in olefin epoxidation.[6a] The present study presents new peroxometal oxidants that derive from both organic and inorganic oxorhenium precursor compounds.

Results and Discussion

1. Catalytic oxidation of $[(\eta^5\text{-}C_5Me_5)Re(CO)_3]$ (Re^I) to $[(\eta^5\text{-}C_5Me_5)ReO_3]$ (Re^{VII}) with hydrogen peroxide: Contrary to previous predictions,[7] simple inorganic rhenium oxides become catalytical active upon treatment with H_2O_2: the π complex **2** (Re^I) underwent smooth oxidation to the oxo complex **3** (Re^{VII}) (Scheme 1, Table 1) with an anhydrous solution of H_2O_2 in ether and Re_2O_7 (4 mol%) as catalyst (81% yield). Under the same conditions and with the same amount of catalyst, ReO_3 gave **3** in 72% yield, while catalytic amounts of $[CH_3ReO_3]$ afforded **3** in excess of 90% yield.[6b] Surprisingly, other organorhenium(VII) oxides of the type $[R\text{-}ReO_3]$ ($R = C_2H_5$, $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4Me$) can also activate H_2O_2. Yellow-orange solutions are obtained in organic solvents (THF, diethyl ether) when these organorhenium(VII) oxides are treated with H_2O_2. However, the formation and lifetime of the catalytic species



Scheme 1. **2** **3**

Table 1. Catalytic oxidation of $[(\eta^5\text{-}C_5Me_5)Re(CO)_3]$ (**2**) to $[(\eta^5\text{-}C_5Me_5)ReO_3]$ (**3**) with H_2O_2 and different rhenium oxides as catalysts.

Catalyst	Yield (%)	Catalyst	Yield (%)
$[CH_3ReO_3]$ [6b]	90	$ClReO_3$ (in situ)	69
$[CH_3CH_2ReO_3]$	78	Re_2O_7	81
$[(\eta^5\text{-}C_5H_5)ReO_3]$	75	ReO_3	72
$[(\eta^5\text{-}C_5H_4Me)ReO_3]$	73		

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[*] Prof. Dr. W. A. Herrmann, J. D. G. Correia, Dr. F. E. Kühn,
G. R. J. Artus, Prof. Dr. C. C. Romão[+]
Anorganisch-chemisches Institut der Technischen Universität
Lichtenbergstrasse 4, D-85747 Garching (Germany)
Telefax: Int. code +(89)3209-3473

[+] Permanent address: Instituto de Tecnologia Química e Biológica
R. da Quinta Grande 6, 2780 Oeiras (Portugal)

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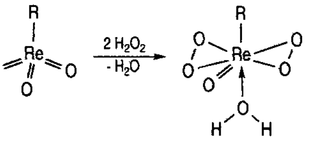
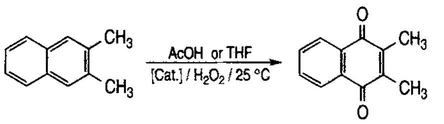
obtained depends on the water content of the H_2O_2 solutions used. In fact, when a 30% (w/w) H_2O_2/water solution is used, no catalytic active species is formed. Formation of these species is only achieved by using an aqueous 85% (w/w) H_2O_2 solution or an anhydrous H_2O_2 solution (e.g., 10% H_2O_2 in 1,4-dioxane, 10%in diethyl ether). The nature of the catalytic active species is under investigation, but is expected to be similar to **1** (Scheme 2) in the case of [$C_2H_5ReO_3$] and to the ReO_3/H_2O_2 system (see below) in the case of [(η^5-C_5H_5)ReO_3] and [(η^5-C_5H_4Me)ReO_3]. The latter rhenium(VII) oxides are expected to lose their organic ligands under the strong oxidizing conditions used. The active species of the $ClReO_3/H_2O_2$ system is also expected to be similar to that of the ReO_3/H_2O_2 system, owing to the lability of the chlorine ligand under the given reaction conditions.



Scheme 2. R = CH_3, C_2H_5, C_3H_5.

2. Oxidation of aromatic compounds: Aromatic compounds are also oxidized by an aqueous 85% (w/w) H_2O_2 solution in the presence of catalytical amounts of Re_2O_7 in acetic acid as solvent.[4a] The oxidation of 2,3-dimethylnaphthalene to the 1,4-quinone (Scheme 3) is catalyzed by a number of different rhenium-containing catalysts (Fig. 1). Though [CH_3ReO_3] is the most efficient catalyst affording the highest product yields, not only in the reaction described above but also in the previously reported synthesis of 2-methyl-1,4-naphthoquinone (vitamine K_3),[4a] the base-stabilized Re_2O_7 (no. 3) shows an activity close to that of methyltrioxorhenium. In contrast, ionic perrhenates such as K[ReO_4] (no. 7) exhibit no catalytic activity. ReO_3 (no. 4) and the ionic Re^{VII} complex [$O_3Re\{(CH_3)_2NC_2H_4\}_2NCH_3$][$ReO_4$] (no. 6) occupy an intermediate position in terms of activity. The activity of catalyst no. 6 is attributed to the cationic part of the molecule (base-stabilized [ReO_3]$^+$). [CH_3ReO_3·tpy] (no. 5) shows a low catalytic activity compared to the analogous derivative [CH_3ReO_3·bipy] (no. 2). However, this difference is easily understood if one recalls that 2,2'-bipyridine, as a bidentate ligand, saturates the rhenium coordination sphere while *tert*-butylpyridine leaves an empty site facilitating attack of water molecules[8] which induces decomposition (see below).



Scheme 3.

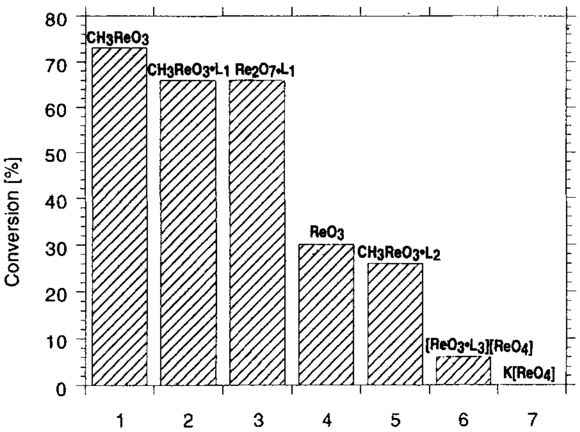


Fig. 1. Catalytic activity of rhenium oxides in the oxidation of 2,3-dimethylnaphthalene to 2,3-dimethyl-1,4-naphthoquinone with H_2O_2 under acidic conditions (acetic acid), 4 h (L_1 = 2,2'-bipyridine (bipy), L_2 = 4-*tert*-butylpyridine (tpy), L_3 = *N,N,N',N'',N''*-pentamethyldiethyltriamine).

Some organorhenium(VII) oxides are not stable enough under the previously described acidic conditions. Therefore, acid-free conditions were chosen (Scheme 3), employing 85% (w/w) H_2O_2 in water as oxidizing agent. As can be seen from Figure 2, [CH_3ReO_3] is again the most efficient catalyst, closely followed by ReO_3 and the base-stabilized Re_2O_7. The organorhenium(VII) oxides tested ([R-ReO_3]; R = C_3H_5, η^5-C_5H_5, η^5-C_5H_4Me) show a moderate catalytic activity. The activity of the system $C_3H_5ReO_3/H_2O_2$ can again be ascribed to peroxorhenium(VII) complexes of the type [R-$ReO(O_2)_2$]·H_2O (Scheme 2).

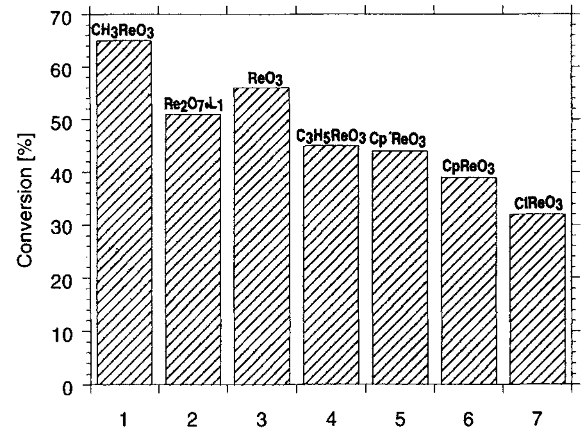
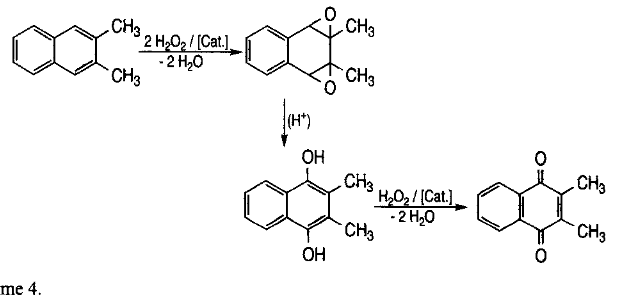


Fig. 2. Catalytic activity of rhenium oxides in the oxidation of 2,3-dimethylnaphthalene to 2,3-dimethyl-1,4-naphthoquinone with H_2O_2 under nonacidic conditions (THF), 24 h (L_1 = 2,2'-bipyridine, Cp' = η^5-C_5H_4Me, Cp = η^5-C_5H_5).

For the sake of comparison, MoO_3 and V_2O_5 were used as catalysts under both conditions: MoO_3 does not dissolve even upon addition of H_2O_2, while V_2O_5 promotes violent *decomposition* of H_2O_2, making it unsuitable as an oxidation catalyst.

Comparing the catalytic activity of [CH_3ReO_3] and Re_2O_7 under acidic (Fig. 1) and nonacidic conditions (Fig. 2), we see higher conversion rates with shorter reaction times in the former case, that is, with acetic acid as the solvent. This behavior can be explained if we bear in mind that acidic conditions favor the mechanism which is likely to yield quinones. By analogy with the dioxirane oxidation under acidic conditions, where arene–epoxide intermediates are postulated,[9] a similar mechanism is proposed for the [CH_3ReO_3]/H_2O_2 and Re_2O_7/H_2O_2 systems (Scheme 4). Since both systems are powerful epoxidizing



Scheme 4.

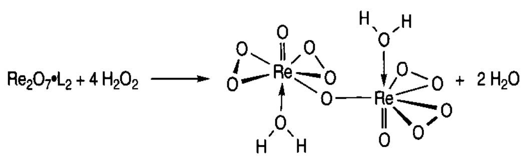
reagents for olefins, we believe that an epoxide is formed in an intermediate step. Epoxides are known to be sensitive to acid or base yielding the corresponding hydroquinones, which are rapidly oxidized to quinones.

Control experiments have shown that [CH_3ReO_3] and Re_2O_7 can catalyze the formation of peroxyacetic acid from acetic acid in the presence of H_2O_2 ($KMnO_4$ titration of H_2O_2 followed by iodometry of the peroxyacetic acid in the same sample[10]). However, under the applied reaction conditions, the resulting amount of peroxyacetic acid is only responsible for around 5% of conversion in the case of [CH_3ReO_3] and around 12% in the case of Re_2O_7.

3. The oxidation system ReO_3/H_2O_2: When a 3.5 M H_2O_2 solution in ether was added to a suspension of ReO_3 in THF, the red-purple solid started to dissolve yielding a red-orange solution (λ_{max} = 350 nm, ε_λ(THF) = 624 L mol^{-1}cm^{-1}). The red-orange product is believed to be responsible for the catalytic activity of ReO_3. The decomposition of this complex follows a first-order reaction leading to the formation of perrhenic acid (UV/Vis). Its half-life ($t_{1/2}$) at 25 °C is approximately 5820 s. If excess water is added to a solution of the same concentration, the stability is much lower ($t_{1/2} \approx 250$ s); this demonstrates the pronounced water sensitivity of the catalytically active species. The colorless solutions obtained after decomposition of the peroxo complex do not show any catalytic activity.

The ^{17}O NMR spectrum of a solution of ^{17}O enriched Re^*O_3 treated with H_2O_2 exhibits only one peak ($\delta(^{17}O)$ = 1157) assigned to a terminal oxo ligand.[8,11] No bridging oxygen ligands are seen.

Treatment of a suspension of ReO_3 in diethyl ether with an anhydrous solution of H_2O_2 (3.5 M) in the same solvent produced a deep red-orange solution. Further addition of HMPT (hexamethylphosphorus triamide) to this solution, previously dried with $MgSO_4$, and evaporation of the solvent at −60 °C gave an oily compound. When this oil was dissolved in a mixture of methylene chloride and *n*-hexane and the solution cooled down to −78 °C, a red-orange *highly explosive* solid was obtained, with a Re:O ratio of 1:7 as determined by elemental analysis. Considering these data we tentatively propose the "peroxo perrhenium acid" [$ReO(O_2)_2OH$]·H_2O as the active species of the ReO_3/H_2O_2 system. It can formally be derived from the known complex [$ReO(O_2)_2CH_3$]·H_2O by replacing CH_3 with OH; the first step of its formation is clearly the oxidation of ReO_3 to the (solvated) ionic species [ReO_3]$^+$ (cf. ref. [15]).



4a

Scheme 5. L = diethyl ether

When Re_2O_7 was suspended in diethyl ether and an etheral solution of H_2O_2 was then added (Scheme 5), a clear red-orange solution was immediately obtained. Careful evaporation of the solvent at −60 °C afforded a red-orange, *explosive* solid. ^{17}O NMR experiments show that the peroxo complex **4a** contains metal-coordinated water, reflecting the Lewis acidity of the heptavalent rhenium. If ^{17}O-labeled $Re_2^*O_7$ is used to prepare [^{17}O]-**4a**, not only are terminal oxo ligands observed ($\delta(^{17}O)$ = 816), but also a bridging oxygen group ($\delta(^{17}O)$ = 184). The coordinated water molecules undergo a fast exchange process on the NMR timescale, as we have also shown for **1**.[11] The formation of **4a** can be followed in situ by UV/Vis spectroscopy (λ_{max} at 350 nm, ε_λ(THF) = 1314 L mol^{-1}cm^{-1}) (Fig. 3).

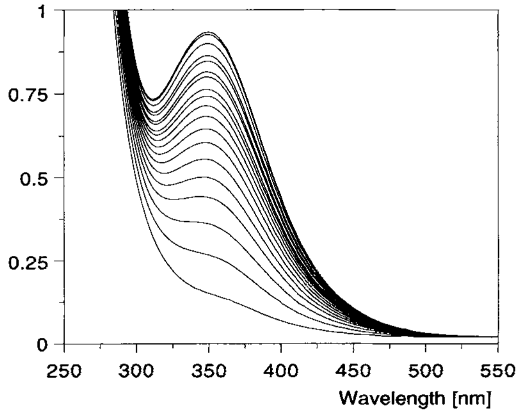


Fig. 3. Time-dependent UV/Vis spectra (λ = 250–550 nm) of $H_4Re_2O_{13}$ (**4a**) generated in situ in THF; $c(Re_2O_7) = 0.73 \times 10^{-3}$ M, $c(H_2O_2) = 5.32 \times 10^{-3}$ M, T = 25 °C.

Complex **4a** is of pronounced lability: even in dry organic solvents (containing around 12 ppm of water), it decomposes rapidly yielding perrhenic acid (Fig. 4 left, $k = 0.51 \times 10^{-3}$ s^{-1}). Addition of excess water leads to a faster decomposition process (Fig. 4 right, $k = 4.07 \times 10^{-3}$ s^{-1}).

4. The active species in the system Re_2O_7/H_2O_2: Apart from the above-mentioned catalytic reactions, this system catalyzes Baeyer–Villiger[3] and olefin oxidations. In spite of being water-sensitive (UV/Vis evidence), the active species **4a** (Scheme 5) of the Re_2O_7/H_2O_2 system was isolated in pure form. As far as we are aware, this compound is the most oxygen rich rhenium compound isolated to date.

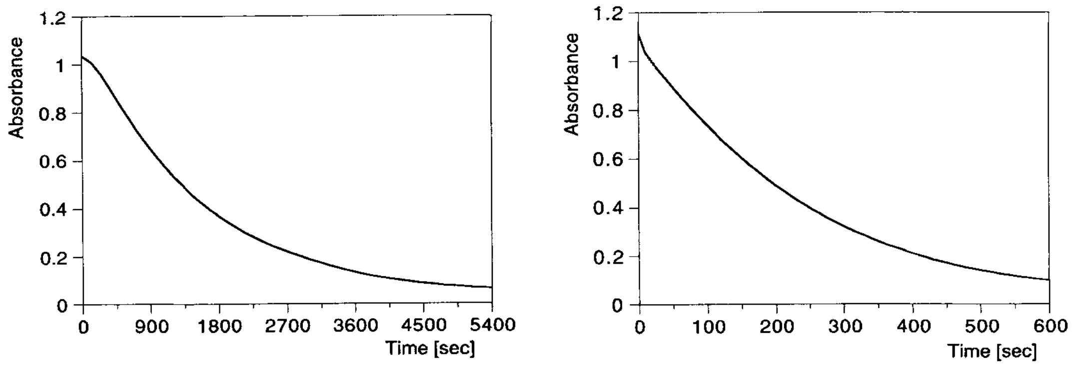
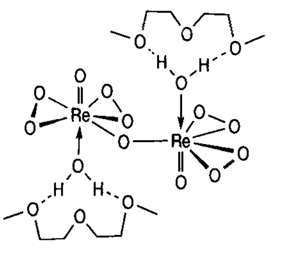


Fig. 4. Kinetics of decomposition of $H_4Re_2O_{13}$ (**4a**) generated in situ in THF, monitored by UV/Vis spectroscopy at λ_{max} = 350 nm. Left: in dry organic solvent; $c(Re_2O_7) = 0.73 \times 10^{-3}$ M, $c(H_2O_2) = 5.32 \times 10^{-3}$ M, $k = 0.51 \times 10^{-3}$ s^{-1} (calculation based on a pseudo-unimolecular reaction), T = 25 °C. Right: decomposition accelerated by addition of water; $c(Re_2O_7) = 0.73 \times 10^{-3}$ M, $c(H_2O_2) = 5.32 \times 10^{-3}$ M, $k = 4.07 \times 10^{-3}$ s^{-1} (calculation based on a pseudo-unimolecular reaction), $c(H_2O) \approx 0.09$ M, T = 25 °C.



4b

Single crystals of **4b** were obtained by adding diglyme (2-methoxyethyl ether) to a solution in diethyl ether and cooling to −35 °C. These crystals correspond to the solvent adduct of formula $[H_4Re_2O_{13}]\cdot(diglyme)_2$ (**4b**). The solid-state structure of this peroxide complex is shown in Figure 5. Each rhenium atom in the binuclear molecule is coordinated by *seven* oxygen atoms. If one considers a peroxo ligand as one structural unit, the coordination geometry can be described as a distorted trigonal bipyramid. The two η^2-peroxo groups and the bridging oxygen occupy equatorial positions, while terminal oxo ligands and water molecules are axial. The bridged structure of this compound is different from all other known solvent adducts of the general formula $Re_2O_7\cdot L_2$[12a, b, c, d, e] (L = H_2O, CH_3CN, THF), since both metal centers exhibit equivalent environments (O7−Re1,2 1.86(1), 1.90(1) Å; Re1-O7-Re2 150.6(5)°). Other Re^{VI} and Re^{VII} oxygen-bridged dimers with symmetrical coordination of both metals are known, for example, $[\{(CH_3)_3ReO\}_2O]$ and $[(ReO_2py)_2O]$ (R = methyl, neopentyl).[12f]

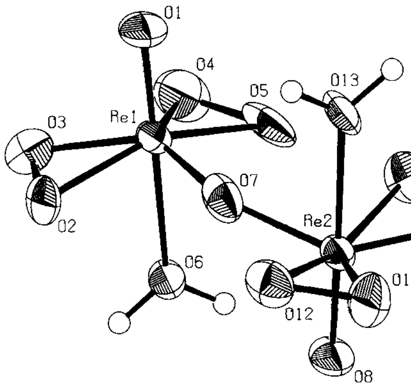


Fig. 5. PLATON representation [23a] of the "peroxo perrhenic acid" $H_4Re_2O_{13}$ as the diglyme adduct **4b** in the solid state. Thermal ellipsoids are at the 50% probability level. The hydrogen-bonded diglyme molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Re1−O1 1.674(9), Re1−O2 1.912(9), Re1−O3 1.87(1), Re1−O4 1.87(1), Re1−O6 2.217(9), Re1−O7 1.86(1), Re2−O7 1.90(1), O2−O3 1.45(1), O4−O5 1.48(1); O2-Re1-O1 100.3(5), O3-Re1-O1 98.7(5), O3-Re1-O2 45.0(4), O4-Re1-O1 99.2(6), O4-Re1-O3 86.4(5), O6-Re1-O1 179.4(5), O6-Re1-O2 79.3(4), O6-Re1-O3 81.3(4), O7-Re1-O1 97.2(5), O7-Re1-O6 82.4(4), O8-Re2-O7 97.6(4), O13-Re2-O7 80.2(4), Re2-O7-Re1 150.6(5).

Hydrolysis of **4a,b** afforded "perrhenic acid" $Re_2O_7\cdot(H_2O)_2$ (**5**). The bisdiglyme adduct of **5** was crystallographically characterized (Fig. 6). The diglyme adduct of "perrhenic acid" was obtained in the form of yellow crystals as a decomposition product of **4b**. The structure reveals the typical *asymmetric* [4+6] coordination. All bond lenghts and angles are as expected. The water molecules are stabilized by hydrogen bonds to diglyme molecules. The Re-O-Re angle is 138.9(3)°. The related Re^{VII} compound $Re_2O_7\cdot(H_2O)_2$[12a] shows a linear bridge, and the water molecules are stabilized by intermolecular hydrogen bonds.

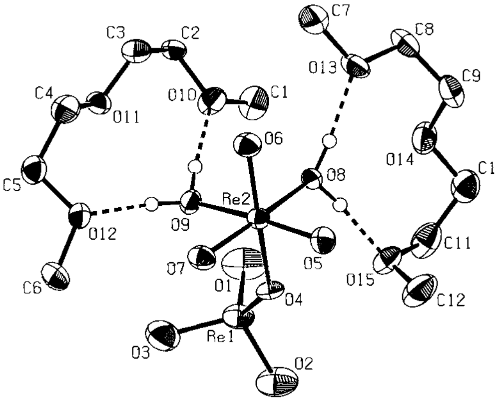


Fig. 6. PLATON representation [23a] of the dirhenium heptoxide aquo complex $H_4Re_2O_9$ ($\equiv Re_2O_7\cdot(H_2O)_2$) as diglyme adduct **5**. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms of diglyme are omitted for clarity. Selected bond lengths (Å) and angles (°): Re1−O1 1.693(5), Re1−O4 1.783(5), Re2−O4 2.086(4), Re2−O8 2.160(4), Re2−O9 2.211(4); O9-Re2-O8 76.2(2), Re2-O4-Re1 138.9(3).

Table 2. Bond lengths (Å) of structurally characterized dinuclear peroxo complexes of rhenium(VII), molybdenum(VI), tungsten(VI), and vanadium(V) [a].

Complex	O–O	$M-O_{peroxo}$	M=O	Ref.
$[Re_2O_3(O_2)_4]\cdot(H_2O)_2\cdot(diglyme)_2$	1.46	1.88	1.67	this paper
$K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot(H_2O)_2$	1.52	1.96	1.66	[13a]
$K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot(H_2O)_2$	1.48	1.96	1.66	[13b]
$(C_3H_5N_2)_2[Mo_2O_3(O_2)_4]\cdot(H_2O)_2$	1.46	1.95	1.68	[13c]
$(Hpy)_2[Mo_2O_3(O_2)_4]\cdot(H_2O)_2$	1.48	1.96	1.67	[13d]
$(NH_4)_4[O(VO(O_2)_2)_2]$	1.46	1.89	1.60	[13e]

[a] Average bond lengths; Hpy = pyridinium.

In spite of being isostructural (Table 2) with some binuclear complexes of molybdenum, tungsten, and vanadium,[13] $H_4Re_2O_{13}$ presents some advantages as a catalyst over the other binuclear peroxo complexes: 1) broad scope of application (different types of substrates can be oxidized) and 2) higher catalytic activity than $[PhCH_2PPh_3]_2[W_2O_3(O_2)_4(H_2O)_2]$ in the oxidation of *cis*-cyclooctene. $H_4Re_2O_{13}$ is a better catalyst in the epoxidation of alkenes, at least when an anhydrous H_2O_2/1,4-dioxane solution is used as the primary oxidant (Fig. 7). Owing to its extreme water sensitivity, $H_4Re_2O_{13}$, the active species of the Re_2O_7/H_2O_2 system, obviously cannot compete with the tungstate anion $[WO_4]^{2-}$, which shows a remarkable activity towards olefin epoxidation in aqueous solutions.[13g] Under the oxidation conditions tested, **1** is the most catalytically active of the complexes examined (cf. Fig. 7). The "peroxo perrhenic acid" described above reacts stoichiometrically with the substrates of Schemes 1 and 3 to give results comparable to those obtained when catalyst **4a** is generated in situ.

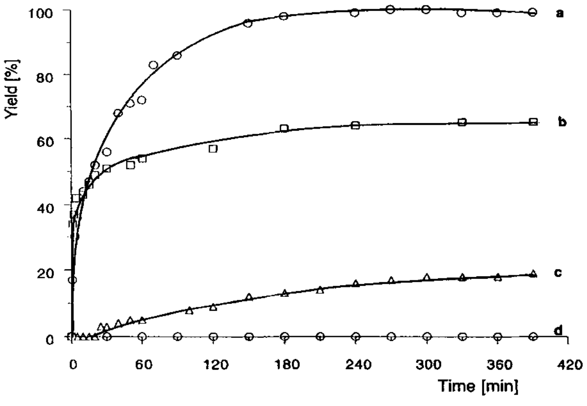


Fig. 7. Catalytic activity of CH_3ReO_3 (**a**), Re_2O_7 (**b**), and $[PhCH_2PPh_3]_2[W_2O_3(O_2)_4(H_2O)_2]$ (**c**) in the oxidation of *cis*-cyclooctene to cyclooctene oxide with H_2O_2. Curve **d**: no catalyst. *cis*-cyclootene:H_2O_2:[cat.] = 1:1.1:0.02; *T* = 25 °C.

Conclusion

A major advantage of the catalyst $[CH_3ReO(O_2)_2]\cdot H_2O$ (**1**) is that the hydrolysis products $[CH_3ReO_3]$ and $[CH_3ReO_2(O_2)]\cdot H_2O$ regenerate the active species **1** on reaction with H_2O_2. In contrast, the hydrolysis product of $H_4Re_2O_{13}$ is perrhenic acid $H[ReO_4]$, which does *not* react with H_2O_2. This explains why the Re_2O_7/H_2O_2 system must be used under anhydrous conditions, to avoid early deactivation by hydrolysis.[14] However, water is continuously formed when H_2O_2 acts as an oxidant ($H_2O_2 \rightarrow H_2O + \langle O \rangle$). The ready hydrolysis of $H_4Re_2O_{13}$ is thus the intrinsic weakness of this species in oxidations by H_2O_2.

Experimental Procedure

All reactions were performed using standard Schlenk techniques in an oxygen-free, dry nitrogen atmosphere. Solvents were dried by using standard methods and distilled under N_2. Infrared spectra were recorded on KBr pellets or CH_2Cl_2 solutions, on a Perkin-Elmer 1600 series FT-IR instrument (resolution 4 cm^{-1}). ^1H and ^{17}O NMR spectra were measured at 399.78 and 54.21 MHz, respectively, on a FT-JEOL GX instrument. All NMR solvents were degassed in a "freeze–pump–thaw" cycle and stored over molecular sieves before use. Elemental analyses were performed at the microanalytical laboratory of our institute. The kinetics investigations were carried out on a Hewlett-Packard 8542-A instrument. In all the cases freshly prepared solutions or suspensions were used. The calculation of the rate constants is based on the absorbance decrease or increase at $\lambda_{max} = 350$ nm. GC/MS data were obtained on a Hewlett Packard 5890 (GC) apparatus equipped with a fused-silica column HP-1 (No. 19091Z-102, $l = 50$ m, $d = 0.2$ mm, thickness of film = 0.33 mm) and a mass-selective detector HP 5970B and a FI detector. Re_2O_7 (Degussa) was used as received. For the preparation of ^{17}O-labeled $Re_2^*O_7$ see ref. [8,11]. ReO_3 was prepared from $Re_2O_7(DME)_2$ [15] according to ref. [8a], and ^{17}O-labeled ReO_3 was prepared from ^{17}O-labeled $Re_2^*O_7(DME)_2$.

1. Procedure related to Scheme 1, Table 1: A solution of **2** [16] (1.00 g, 2.47 mmol) in a H_2O_2/diethyl ether mixture (20 mL, $c(H_2O_2) = 3.5$ M) was cooled down to −45 °C. Catalyst (0.1 mmol) ($[C_2H_5ReO_3]$ [17], $[(\eta 5\text{-}C_5H_5)ReO_3]$ [18], $[(\eta 5\text{-}C_5H_4Me)ReO_3]$ [18], $ClReO_3$ [19], ReO_3, or Re_2O_7), dissolved (ReO_3 and R_2O_7 were added as solids) in diethyl ether (1 mL) was then added. The solution immediately turned yellow-orange. The reaction was allowed to warm up to room temperature overnight, and stirred for an additional 6 h. Diethyl ether (20 mL), $MgSO_4$ (2 g), and a catalytical amount of MnO_2 were added to the light yellow solution and stirred until no more oxygen was liberated (ca. 10 h). After filtration, the residue was washed (2 × 20 mL) with diethyl ether, and the yellow solution obtained was cooled down to −30 °C after partial evaporation of the solvent in order to precipitate **3**. The solution was then filtered and the remaining solid dried in vacuo. The yields are shown in Table 1. The analytical data of **3** are identical with those of authentic pure samples.

2. Procedure related to Scheme 3—acidic conditions: Catalyst (0.1 mmol) ($[CH_3ReO_3]$ [1], $[CH_3ReO_3]\cdot$bipy [20], $Re_2O_7\cdot$bipy [19], ReO_3, $[CH_3ReO_3]\cdot$tpy [21], $[ReO_3\cdot L]^+[ReO_4]^-$ [15], $K[ReO_4]$) and 2,3-dimethylnaphthalene (0.78 g, 5 mmol) were dissolved in glacial acetic acid (5 mL) and dry THF (2 mL). An 85% (w/w) aqueous hydrogen peroxide solution (75 mmol) was added and the reaction was allowed to stir for 4 h at room temperature under nitrogen. The solution was diluted with water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water (2 × 20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The crude material obtained was analyzed by GC/MS and by ^1H NMR. The analytical data correspond to those of authentic pure 2,3-dimethyl-1,4-naphthoquinone samples. Conversions are shown in Figure 1.

3. Procedure related to Scheme 3—nonacidic conditions: The same procedure was followed as in procedure 2, but pure THF was used as solvent and reaction times were longer (24 h). $C_3H_5ReO_3$ was generated in situ according to ref. [22]. Conversions are shown in Figure 2.

4. UV/Vis spectroscopic studies: a) *ReO_3/H_2O_2*: Data for formation and decomposition studies were obtained from freshly prepared solutions of ReO_3 (0.025 g, 0.10 mmol) in THF (50 mL) and a 3.5 M solution of H_2O_2 in ether (420 µL, 1.47 mmol). To achieve the desired concentrations ($c(ReO_3) = 1.45 \times 10^{-3}$ M, $c(H_2O_2) = 19.60 \times 10^{-3}$ M), the red-orange solution (2 mL) was added to THF (1 mL), directly in the spectrometer cell ($l = 1$ cm, slit $s = 2$ nm). For the accelerated decomposition studies, 10 µL of H_2O ($c(H_2O) = 0.18$ M) was also added to the cell. The calculation of the rate constants (k) and $t_{1/2}$ are based on the absorbance decrease at $\lambda_{max} = 350$ nm.
b) *Re_2O_7/H_2O_2*: Data for formation and decomposition studies were obtained from freshly prepared solutions of Re_2O_7 (0.13 g, 0.27 mmol) in THF (30 mL, solution **A**) and a solution of H_2O_2 in ether (0.17 M, solution **B**). For the formation kinetics of **4a**, solution A (250 µL) was diluted with THF (2.75 mL) directly in the spectrometer cell and solution **B** (97 µL) was added ($c(Re_2O_7) = 0.73 \times 10^{-3}$ M, $c(H_2O_2) = 5.32 \times 10^{-3}$ M). For the accelerated decomposition studies, H_2O was added to the cell (5 µL, $c(H_2O) \approx 0.09$ M). The calculation of rate constants (k) are based on the absorbance decrease at $\lambda_{max} = 350$ nm.

5. Preparation of the µ-oxo-bis[aquo(oxo)diperoxorhenium(VII)] (4a) and of the bis(aquo)heptaoxodirhenium(VII) (5) as bis(diglyme) adducts: A dry 3.5 M solution of H_2O_2 in ether (1.3 mL) was added dropwise to a suspension of Re_2O_7 (1.02 g, 2.10 mmol) in scrupulously dried diethyl ether (14 mL) at room temperature and under nitrogen. Re_2O_7 immediately started disolving yielding a deep red-orange solution. The reaction mixture was allowed to stir until a completely clear solution was obtained (ca. 15 min), and then dry diglyme was added (0.5 mL). The solution was cooled down to −60 °C, and the ether was then evaporated. After about 2 h a white solid started to precipitate. The solution was then filtered, and the remaining white residue washed with diethyl ether at −60 °C. The solvent was further evaporated to a volume of around 10 mL (when white solid precipitated, the procedure was repeated), and a small amount of *n*-pentane was then added. The solution was maintained at −35 °C for 18 h. Deep red-orange cystals were obtained in 60% yield (1.05 g): ^{17}O NMR (54.21 MHz, $CDCl_3$, −20° C, H_2O): $\delta = 184$ (Re-O-Re), 816 (Re=O); IR (CH_2Cl_2): $\tilde{\nu} = 1145$ (Re-OH), 1108 (Re=O), 860 cm^{-1} (O_2); UV/Vis (THF): λ_{max} (ε) = 350 (1315) nm; $C_{12}H_{32}O_{19}Re_2$ (852.7): calcd C 16.90, H 3.78, O 35.64, Re 43.67; found C 17.18, H 3.83, O 36.26, Re 43.66; decomposition point: 45 °C.
Yellow crystals of **5** were also obtained in a small amount as a decomposition product of **4b**: ^{17}O NMR (400 MHz, $CDCl_3$, −20 °C, H_2O): $\delta = 184$ (Re-O-Re), 800 (Re=O); IR (CH_2Cl_2): $\tilde{\nu} = 1141$ (Re-OH), 932 (Re=O). $C_{12}H_{32}O_{15}Re_2$ (788.7): calcd C 18.25, H 4.05, O 30.42, Re 47.21; found C 18.36, H 3.74, 32.46 O, Re 46.94.

6. X-ray structure determinations: a) *µ-Oxo-bis[aquo(oxo)diperoxorhenium(VII)] as a bis(diglyme) adduct (**4b**)*: Orange crystals of the compound $C_{12}H_{32}O_{19}Re_2$ (852.79 $g\,mol^{-1}$) were obtained at −35 °C from a mixture of ether and pentane. A crystal with an approximate size of 0.15 × 0.31 mm was transferred into a Lindemann capillary under an inert gas atmosphere (dry box). Crystal system triclinic, space group $P\bar{1}$, int. table no. 2. Cell constants by least-squares refinement of 25 well-centered reflections in the range $22.5 < 2\theta < 33.2°$, $\lambda = 0.70930$ Å, Mo($K_{\alpha 1}$), with programs SET4, CELDIM [23b]: $a = 9.232(2)$, $b = 9.344(2)$, $c = 14.755(4)$ Å, $\alpha = 84.37(2)$, $\beta = 88.80(2)$, $\gamma = 73.37(4)°$, $V = 1213.6$ Å^3, $Z = 2$, $\rho_{calcd} = 2.33$ $g\,cm^{-3}$, $F_{000} = 812$. Data collection with CAD4 diffractometer with graphite monochromator, $\lambda = 0.71073$ Å, Mo(K_{α}), −80(±4) °C, data collected in the range $1.0° < \theta < 25.0°$; $h(-11/0)$, $k(-12/12)$, $l(-18/18)$; ω scan, max. 60 s; every 3600 s, three intensity-monitoring reflections; every 100 reflections three orientation-monitoring reflections, scan width $(2.0 + 0.2\cdot\tan\theta)°$. Data were corrected for Lorentz and polarization terms with the program BEGIN [23c], 10.7% loss of intensity during 73 h of exposure corrected, absorption effects corrected with ψ-scan data (min/max correction: 0.8235/0.9999). 4550 data measured, 397 with negative intensity ($I/\sigma(I) < 0.01$), 445 data merged, $R(I) = 0.025$, $R(F) = 0.022$, 3902 independent reflections, 3471 data with $I > 2.0\sigma(I)$ used for refinement. Structure solution by Patterson methods [23d] and refinement by standard difference-Fourier techniques [23e]. 298 parameters refined, 11.6 data per parameter. All hydrogens calculated and not refined. $w = 1/\sigma^2(F_0)$, shift/error < 0.0001 in the last cycle of refinement, residual electron density max. 2.4 e Å^{-3} at 1.03 Å from Re1, min. −4.4 e Å^{-3}, $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.049$, $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2} = 0.032$.

b) *Bis(aquo)heptaoxodirhenium(VII) (**5**) as a bis(diglyme) adduct*: Yellow crystals of the compound $C_{12}H_{32}O_{15}Re_2$ (788.79 $g\,mol^{-1}$) can be obtained at −35 °C from a mixture of ether and pentane. A crystal with an approximate size of 0.18 × 0.18 × 0.18 mm was transferred into a Lindemann capillary under an inert gas atmosphere (dry box). Crystal system monoclinic, space group $P2_1/n$, int. table no. 14. Cell constants by least-squares refinement of 25 well-centered reflections in the range $30.1 < 2\theta < 39.1°$, $\lambda = 0.70930$ Å, Mo($K_{\alpha 1}$), with programs SET4, CELDIM [23b]: $a = 9.254(2)$, $b = 18.702(2)$, $c = 13.398(3)$ Å, $\beta = 90.14(2)°$, $V = 2318.7$ Å^3, $Z = 4$, $\rho_{calcd} = 2.26$ $g\,cm^{-3}$, $F_{000} = 1496$. Data collection with CAD4 diffractometer with graphite monochromator, $\lambda = 0.71073$ Å, Mo(K_{α}), −80(±4) °C, data collected in the range $1.0 < \theta < 25.0°$; $h(0/12)$, $k(0/23)$, $l(-16/16)$, ω scan, max. 60 s; every 3600 s, three intensity-monitoring reflections; every 100 reflections, three orientation-monitoring reflections; scan width $(0.9 + 0.2\tan\theta)°$. Data were corrected for Lorentz and polarization terms with the program BEGIN [23c], 4.8% loss of intensity during 74.9 h of exposure corrected, absorption effects corrected with ψ-scan data (min/max correction: 0.9105/0.9994). 4474 data measured, 435 with negative intensity ($I/\sigma(I) < 0.01$), 402 data merged, $R(I) = 0.03$, $R(F) = 0.03$, 3652 independent reflections, 3438 data with $I > 1.0\sigma(I)$ used for refinement. Structure solution by Patterson methods [23d] and refinement by standard difference-Fourier techniques [23e]. 263 parameters refined, 13.1 data per parameter. All hydrogens calculated and not refined. $w = 1/\sigma^2(F_0)$, shift/error < 0.0001 in the last cycle of refinement, residual electron density max. 0.96 e Å^{-3} at 1.43 Å from H25, min. −0.91 e Å^{-3}, $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.032$, $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2} = 0.023$.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59169.

7. Procedure related to Figure 7: a) *Preparation of oxidation solution* (10% H_2O_2 in 1,4-dioxane): 1,4-Dioxane (1 L) was maintained at 25–30 °C and mixed with 0.1 L of 85% (w/w) H_2O_2 in H_2O. The solution was stirred with anhydrous $MgSO_4$ (ca. 100 g) for 3 h and then filtered, $c(H_2O_2) = 3.5\,\text{M}$.

b) *General procedure for catalytic oxidation*: The catalyst (0.28 mmol) was dissolved or suspended in the oxidation solution (5.2 mL, 15.6 mmol). Dibutyl ether (1.633 g, internal standard) was added to the catalytic solution. The temperature was maintained at 25 ± 1 °C. *cis*-Cyclooctene (2 mL, 94%) was then added. The reaction was monitered by GC. The results are presented in Figure 7. $[PhCH_2PPh_3]_2[W_2O_3(O_2)_4(H_2O)_2]$ was prepared according to ref. [13f].

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