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New catalysts in the photo-oxidation of water

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Abstract

Of the 20 dithiolene complexes investigated, only three were effective in the photo-oxidation of water to O_2 in the visible region and at the same time sufficiently stable: tris-[1-(4-dimethylaminophenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S′]tungsten, tris-[1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S′]tungsten and tris-[1-(4-methoxyphenyl)-1,2-ethylenodithiolenic-S,S′]tungsten. Four more produced oxygen, but were not sufficiently stable for the reaction to be truly catalytic.

The three successful catalysts are non-symmetrical and have phenyl rings with para electron-donating substituents. The metals used were W, Mo, Re and Ni. The dithiolene complexes of the first three are trigonal prismatic and of nickel are square planar. The best results in terms of yield and stability were obtained with tungsten, and specifically with tris-[1-(4-dimethylaminophenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S′]tungsten; the light storage efficiency for this catalyst was estimated to be better than 9%.

As indicated by the oxidation potentials, the excited states of the dithiolenes used were powerful oxidizing agents, sufficient to oxidize water. © 1997 Elsevier Science S.A.

Keywords: Dithiolenes; Photo-oxidation of water; Light storage

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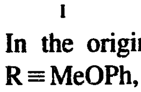
1. Introduction

A prismatic tris-dithiolenic complex, tris-[1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S′]tungsten, has been found [1,2] to catalyse the photodecomposition of water in the visible region

$$2H_2O \xrightarrow[h\nu]{PC-C,\,EA} 2H_2(g)+O_2(g) \qquad (1)$$

where EA is a reversible electron acceptor, notably MV^{2+}, and PC-C is the photocatalyst-catalyst. This reaction is homogeneous (in water–acetone mixed solvent) and requires no sacrificial reagents.

The general formula of the dithiolenes is



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In the original PC-C for reaction (1), M≡W, R′≡Ph, R≡MeOPh, $n=0$ and $m=3$; R and R′ differ in the seventh position from the metal centre. In this paper, we investigate a number of other compounds, with M≡W, Mo, Re ($m=3$ and $n=0$) and M≡Ni ($m=2$, $n=0$) and various combinations of R and R′. A basic requirement is that, in addition to being active, a good photocatalyst must also be stable, both thermally and photochemically.

2. Experimental details

2.1. Synthesis

The symmetrical (R≡R′) and non-symmetrical complexes with R′≡phenyl were synthesized by a method described previously [2,3] based on the reaction of the corresponding benzoin with tetraphosphorus decasulphide [4,5]. The rest of the non-symmetrical complexes (R′≡H) were prepared by adjustment of the method proposed by Mueller-Westerhoff et al. [6] as described in Ref. [3]. All the symmetrical complexes have been reported [7–15] in the literature. The tungsten complexes with R′≡phenyl and R≡p-methylphenyl, p-methoxyphenyl and p-dimethylaminophenyl, as well as the rhenium complexes, were synthesized and their cyclic voltammograms recorded according to the methods described in Ref. [3].

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2.2. *Instruments*

UV–visible spectra were recorded on Hitachi U-2000 and Cary 17D spectrophotometers using 1 cm quartz cells. Illuminations were performed using an Oriel 1000 W xenon lamp and a Varian Eimac 350 W tungsten–halogen lamp. The IR part of the spectrum was cut off with a water filter and the UV part with an appropriate glass filter.

2.3. *Purification*

The purification methods used were standard techniques [16]: distillations, recrystallizations, extractions, ion exchange, etc. The final purification was performed using a column (1.2 m) filled with Merck silica gel 60 (70–230 mesh ASTM) and eluted with toluene–cyclohexane (7 : 3). However, it is important to emphasize that, in the case of the photochemistry of dithiolenes, the factors causing instability are still not fully understood. Dithiolenes exist which are inherently stable, both thermally and photochemically, in the visible and near-IR, and others that are unstable in the presence of water, even without illumination. In several cases, instability was not inherent, but due to the high sensitivity to impurities in the solvent or the initial reagents, or to impurities formed during synthesis. The purity was checked meticulously at every step of the synthesis routinely by thin layer chromatography, but occasionally by gas chromatography-mass spectrometry (GC-MS) or high performance liquid chromatography-mass spectrometry (HPLC-MS) [3] and nuclear magnetic resonance (NMR) methods. In every case, the results reported here correspond to pure complexes.

2.4. *Photochemistry*

The basic photochemistry, including material balance for reaction (1), experimental set-up and mechanism, is given in Refs. [1,2] and [17]. Dioxygen was measured chemically using Cr(II) traps. This is a reliable method provided that air is carefully kept out and that a blank, i.e. non-photochemical, experiment is performed in parallel [2].

3. Results and discussion

The spectra of the complexes investigated are summarized in Table 1 [18–20].

The potentials of the excited states ($E^0(C^*/C^-)$) (Table 2) were estimated on the basis of Eq. (2) [21,22]

$$E^0(C^*/C^-) = E^0(C/C^-) + E_{0-0}(C/C^*) \qquad (2)$$

where $E^0(C/C^-)$ is the one-electron reduction potential of the ground state obtained from Refs. [3] and [14] and $E_{0\text{-}0}(C/C^*)$ is the potential for the 0–0 transition, obtained approximately from the absorption spectrum, since there is no fluorescence.

Table 1

UV–visible spectra of the dithiolene complexes in chloroform and acetone–water (70 : 30) mixed solvent. The active L → M absorptions for some complexes appear as a shoulder and λ_{max} was determined by taking the second derivative

Metal	R′	R	L → M[a]	L → M[a]	L → M[b]	L → M[b]
W	H	*p*-CH_3OPh	670 (18100)[c]	413 (11200)	676 (18800)	414 (11700)
W	H	*p*-CH_3Ph	644 (17800)	410 (10800)	648 (18700)	410 (11300)
W	H	Ph	630 (14400)	405 (8670)	633 (14100)	407 (8730)
W	H	*p*-ClPh	634 (19400)	407 (11700)	635 (18100)	406 (11600)
W	H	*p*-BrPh	634 (20100)	406 (12100)	637 (18500)	405 (12000)
Mo	H	*p*-CH_3OPh	705 (12800)	459 (8460)	711 (12600)	463 (8360)
Mo	H	*p*-CH_3Ph	677 (12000)	449 (9600)	687 (12300)	450 (9700)
Mo	H	Ph	667 (20800)	445 (14800)	670 (20900)	446 (15200)
W	Ph	*p*-CH_3OPh	679 (19100)	415 (10450)	685 (18500)	413 (10250)
W	Ph	*p*-CH_3Ph	668 (15700)	412 (8300)	676 (16000)	411 (8450)
W	Ph	Ph	660 (27900)	417 (23900)	654 (28100)	416 (22500)
W	*p*-CH_3OPh	*p*-CH_3OPh	682 (16300)	407 (7200)	679 (16600)	405 (7000)
W	Ph	*p*-$(CH_3)_2NPh$	793 (23000)	441 (15100)	821 (22600)	446 (15100)
Mo	Ph	*p*-CH_3OPh	720 (10600)	455 (7224)	717 (11500)	455 (7900)
Mo	Ph	Ph	690 (20900)	449 (12200)	695 (21200)	447 (12000)
Re[d]	Ph	Ph	712 (24000)	426 (12300)	709 (23700)	425 (12300)
Re	Ph	*p*-CH_3OPh	732 (19000)	432 (8540)	728 (17000)	427 (7800)
Ni[e]	Ph	*p*-CH_3OPh	894 (29700)	610 (1900)	889 (30000)	602 (2400)
Ni[f]	Ph	*o*-ClPh	837 (34200)	593 (2245)	840 (28000)	593 (2100)
Ni	Ph	Ph	865 (30400)	417 (5100)	882 (32000)	415 (5300)

[a] Values obtained in chloroform; assignments according to Ref. [18].

[b] Values obtained in acetone–water (70 : 30) mixed solvent.

[c] λ_{max} in nanometres (ϵ in $dm^3\ cm^{-1}\ mol^{-1}$).

[d] Ref. [7].

[e] Ref. [19].

[f] Ref. [20].

Table 2
Estimates of E^0 for the one-electron reduction of the excited state. Values[a] were calculated as described in the text

Metal	R'	R	$E_{0-0}(C/C^*)$[b]	$E^0(C/C^-)$	$E^0(C^*/C^-)$
W	H	p-CH_3OPh	2.799	−0.168	2.631
W	H	p-CH_3Ph	2.819	−0.040	2.779
W	H	Ph	2.850	0.030	2.88
W	H	p-ClPh	2.837	0.095	2.932
W	H	p-BrPh	2.844	0.060	2.904
Mo	H	p-CH_3OPh	2.536	−0.030	2.506
Mo	H	p-CH_3Ph	2.469	0.022	2.491
Mo	H	Ph	2.448	0.044	2.492
W	Ph	p-CH_3OPh	2.786	−0.003	2.783
W	Ph	p-CH_3Ph	2.773	0.027[c]	2.800
W	Ph	Ph	2.774	0.045	2.819
W	p-CH_3OPh	p-CH_3OPh	2.835	−0.055	2.775
W	Ph	p-$(CH_3)_2NPh$	2.695	−0.108	2.587
Mo	Ph	p-CH_3OPh	2.562	0.035	2.597
Mo	Ph	Ph	2.586	−0.105	2.481
Re	Ph	Ph	2.719	+0.210	2.989
Re	Ph	p-CH_3OPh	2.683	+0.240	2.923
Ni	Ph	Ph	1.937	−0.125	1.812
Ni	Ph	p-CH_3OPh	1.990	−0.030	1.960
Ni	Ph	o-ClPh	1.433	−0.205	1.228

[a] In volts with respect to the hydrogen electrode; solvent, CH_2Cl_2; reference cell, Ag/AgCl.

[b] Values calculated at $\lambda_{max}+30$ nm; this choice makes the final numbers uncertain to one-tenth of a volt. A similar error is introduced by using electrochemical and spectral data in different solvents.

[c] Values of $E_{1/2}$ for this complex, for the formation of the monoanion and dianion, are 0.127 and −0.355 V respectively [3] vs. Ag/AgCl.

Table 3
Volume of dioxygen produced using visible light (tungsten halide lamp, UV and IR cut-off filters [1,2]). The illumination time was 3 h using light at wavelengths longer than 350 nm. The temperature was kept stable at 25 °C. The solvent was acetone–water (70 : 30), except for the dimethylamino complex where it was acetone–water (85 : 15)

Metal	R'	R	[C] $(M\times10^5)$	$[MV^{2+}]$ $(M\times10^3)$	O_2^a (ml)	Stability
W	H	p-CH_3OPh	0.9	0.9	0.49	Stable
W	H	p-CH_3Ph	1.3	0.9	0.24	Decomposed very slowly
W	H	Ph	1.0	0.9	0.19	Decomposed very slowly
W	Ph	p-CH_3OPh	1.1	1.2	1.00	Stable
W	Ph	p-CH_3Ph	1.4	1.3	0.50	Decomposed
W	Ph	p-$(CH_3)_2NPh$	1.5	1.2	1.30	Stable
Re	Ph	p-CH_3OPh	1.5	1.2	0.3	Decomposed very slowly

[a] Average of five measurements relative to the original photocatalyst-catalyst ($M\equiv W$, $R'\equiv Ph$, $R\equiv p$-CH_3OPh).

The relative efficiencies of the various complexes in producing oxygen, and their stability, are recorded in Table 3.

Of the 20 dithiolene complexes used, only three produced sufficient O_2 and were stable, i.e. those with $R'\equiv H$, $R\equiv p$-CH_3OPh and $M\equiv W$, $R'\equiv Ph$, $R\equiv p$-CH_3OPh and $M\equiv W$ and $R'\equiv Ph$, $R\equiv p$-$(CH_3)_2NPh$ and $M\equiv W$.

Four more, i.e. those with $R'\equiv H$, $R\equiv p$-CH_3Ph and $M\equiv W$, $R'\equiv H$, $R\equiv Ph$ and $M\equiv W$, $R'\equiv Ph$, $R\equiv p$-CH_3Ph and $M\equiv W$ and $R'\equiv Ph$, $R\equiv p$-CH_3OPh and $M\equiv Re$, produced O_2 but were not sufficiently stable. The other complexes used (Tables 1 and 2) did not produce O_2 and were thermally and/or photochemically unstable. Instability leads to destruction of the dithiolene rings and an associated decrease in absorbance or to an accumulation of the monoanion and the $MV^{\cdot +}$ radical. Included in the unstable and inefficient species are the symmetrical species ($R\equiv R'$) and those containing phenyl rings with electron-withdrawing substituents. The non-symmetrical complexes of Mo are also unstable and inefficient, while the non-symmetrical complex of Re is quite effective, but is not sufficiently stable. The square planar complexes of nickel are ineffective and unstable, even thermally towards hydrolysis [19,20].

Also important is the role of the substituent in the para position of the phenyls. A donor substituent increases the yield and stability. This is due to an internal donor effect. External donors, e.g. ethanol added to the solvent, have a similar effect [17]. According to our experiments, both temperature and ethanol increase the yield of oxygen. In a solution of pentanone-2–water–ethanol (50 : 30 : 20) at 20 °C containing tris-[1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S']tungsten (3×10^{-4} M) and MV^{2+} (6×10^{-2} M), the oxygen produced in 4 h is 2.4 times that produced in a similar solution when the ratio of pentanone-2 to water to ethanol is 65 : 30 : 5. Ethanol has a profound effect.

All effective complexes are non-symmetrical ($R \neq R'$). This seems to be a necessary condition, and it is interesting that a similar requirement exists in the photosynthetic system [23].

The maximum light storage efficiency [17] achieved with tris-[1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S′]tungsten in a solvent containing ethanol is approximately 7%. Yields for the dimethylamino derivative are about 30% higher (Table 3); hence the maximum light storage efficiencies for this compound should be better than 9%.

The oxidation of water to O_2 is a difficult four-electron step in the splitting reaction (Eq. (1)). In the oxygen-producing complexes, the values of E^0 for the couple C^*/C^- lie in the 2.6–2.9 V range. These values far exceed the required 1.23 V for the oxidation of water to O_2. It should also be noted that this "oxidizing power" comes essentially from light (Table 2); the ground states $E^0(C/C^-)$ are close to zero. Indeed, C^- is not a sufficiently powerful reducing agent to produce H_2 from water; this is achieved by the mediation of MV^{2+} using some of the available excess potential. It should also be noted that the higher potentials are observed for Re complexes, yet these are not the best catalysts. Electronic and/or mechanistic effects are obviously important.

Two more factors affecting the thermodynamics should also be mentioned: (1) under the conditions of the experiments (purging during illumination), the partial pressures of H_2 and O_2 are not those corresponding to the standard states; (2) the solvent is mixed (water–acetone).

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