Inorganica Chimica Acta, 45 (1980) L69–L71
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Photoinduced Deoxygenation of Peroxotitanium(IV) Porphyrins

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Received March 22, 1980

In two recently published reports, photolysis of a transition metal peroxo complex has been shown to yield dioxygen by photoinduced reductive elimination. Thus, $Ir^{III}(O_2)Cl(CO)(PPh_3)_2$ afforded Vaska's complex $Ir^{I}Cl(CO)(PPh_3)_2$ and molecular oxygen in its triplet ground state [1], while *trans*-bisperoxomolybdenum(VI) tetra(*p*-tolyl)porphyrin yielded the corresponding *cis*-dioxomolybdenum(VI) complex and dioxygen in its presumably triplet state [2]. In this communication, we wish to report that titanium(II) porphyrin intermediates and dioxygen are generated by photolysis of peroxotitanium(IV) tetraphenylporphyrins, and that a peculiar photooxidation behavior observed in this system suggests singlet character of the evolved dioxygen.

Photolysis of benzene solutions of the peroxotitanium(IV) porphyrins $Ti(O_2)$(TPP) and $Ti(O_2)$(TmTP) [3] lead to the corresponding oxotitanium(IV)porphyrins almost quantitatively (*ca.* 95% isolated yields). In a typical experiment, a weighed amount (*ca.* 50 mg) of the more soluble $Ti(O_2)$(TmTP) complex was dissolved in 2 ml of dry benzene under argon; the solution was degassed by four freeze-pump-thaw cycles, then irradiated for 30 minutes with a high-pressure mercury lamp with glass windows under stirring. Vigorous gas evolution was observed. Analysis by mass spectrometry identified the gaseous product as dioxygen, suggesting the overall stoichiometry:

$$2\,Ti(O_2)(TmTP) \xrightarrow{h\nu} 2\,TiO(TmTP) + O_2 \qquad (1)$$

When the starting complex was doubly labelled with ^{18}O, only $^{18}O_2$ and $Ti^{18}O$(TmTP) were obtained, indicating that the evolved dioxygen and the oxo ligand were derived exclusively from the starting peroxo ligand* in agreement with reaction 1. Furthermore, irradiation of a 1:1 mixture of unlabelled and doubly labelled $Ti(O_2)$(TmTP) gave $^{16}O_2$ and $^{18}O_2$ in a 1:1 molar ratio within experimental error, and no $^{16}O^{18}O$ could be detected. The O–O bond of the starting peroxo complex is thus found intact in the

TABLE I. Amounts of O_2 Liberated upon Irradiation of $Ti(O_2)$ (TmTP).[a]

Experiment number	Moles of peroxo complex $\times 10^5$	Volume of O_2 liberated in ml (% of calculated)[b]		Other gases in ml
1	6.74	0.396	(48)	2.5×10^{-3} [c]
2[d]	6.97	0.370	(43)	4.7×10^{-3} [c]
3[d,e]	6.74	0.215	(26)	1.1×10^{-2} [f]
4[g]	7.13	0.468	(54)	1.4×10^{-2} [c,f]

[a] *ca.* 50 mg (6.68×10^{-5} mol) of peroxo-complex dissolved in 2 ml benzene were irradiated with a high-pressure mercury lamp for 30 min in an evacuated Pyrex tube. [b] Based on equation 1, the calculated volume of O_2 liberated is 0.82 ml at 25 °C, 1 atm for 50 mg of peroxo-complex. [c] Mass spectral peak at m/e = 44 corresponding to CO_2. [d] Cyclohexene (0.25 ml) was added to the reaction mixture. [e] ^{18}O-labelled peroxo-complex. [f] Mass spectral peaks at m/e = 48 and 30 only, corresponding to $C^{18}O_2$ and $C^{18}O$. [g] Photolysis of a 1:1 mixture of unlabelled and labelled peroxo-complexes gave 0.231 ml of $^{16}O_2$ and 0.237 ml of $^{18}O_2$, and no $^{16}O^{18}O$ was detected.

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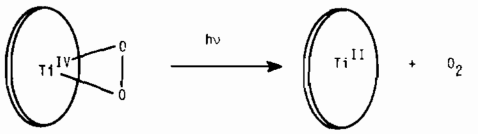
*$Ti(^{18}O_2)$(TmTP) was prepared by stirring TiO(TmTP) with 1,1-dimethylhydrazine in THF solution under $^{18}O_2$ (*ca.* twofold excess) containing more than 99% ^{18}O, and was recrystallized from CH_2Cl_2–CH_3OH to give a 94% yield. IR (KBr pellet): 856 cm^{-1} (ν_{O-O}), *cf.* reference 4. This preparation presumably involves autoxidation of 1,1-dimethylhydrazine producing *in situ* hydrogen peroxide which is scavenged by the oxotitanium(IV) porphyrin, *cf.* reference 5.

TABLE II. Photosensitized Oxidation of Cyclohexene (2 ml) by Peroxotitanium(IV) Porphyrins.

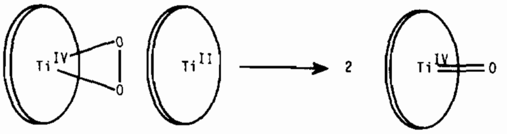
Solvent (ml)	Sensitizer (mol × 10^4)	Conditions	Relative Yields in % of:		
			2-cyclohexen-1-ol	2-cyclohexen-1-one	epoxide
benzene (20)	H_2TPP (4.4)	hν (75 hr)	traces	traces	traces
benzene (30)	$Ti(O_2)$ (TPP) (4.4)	dark (55 hr)	none	none	none
benzene (30)	$Ti(O_2)$ (TPP) (4.4)	hν (28 hr)	15	80 (3 × 10^{-3} mol)[a]	5
CH_3COOEt (20)	$Ti(O_2)$ (TPP) (4.4)	hν (28 hr)	32	45 (2 × 10^{-3} mol)[a]	23

[a] Total yield of oxidation products.

evolved dioxygen, implying a photoinduced reductive elimination and the generation of a formal titanium(II) intermediate in a first step. In a second step, this intermediate undergoes an oxygen-atom transfer from another peroxotitanium(IV) porphyrin – known to be a two-electron oxidant [S] – yielding the corresponding oxotitanium(IV) complex (Scheme I).



(2)



(3)

The volume of released dioxygen, as determined by quantitative mass spectrometric analysis (Table I), was always lower by *ca.* 50% or more than that predicted from eqn. 1. Detection of CO_2 and CO in the evolved gases (Table I) led us to assume that the remaining oxygen, presumably in a singlet state, was lost as solvent oxidation products. Indeed, photoinduced oxidation of benzene is known to give open chain polyenic dialdehydes as well as uncharacterized phenols [6], and there is probably a sliding scale of oxidation products with carbon dioxide being the ultimate stable product. Consistent with this interpretation is the apparent relationship between the amounts of O_2 and CO_2 produced (Table I): the lower the yield of evolved dioxygen, the higher the volume of carbon dioxide detected, *i.e.* the loss of oxygen through solvent oxidation.

Cyclohexene was oxidized to a mixture of 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and cyclohexene oxide upon irradiation in the presence of $Ti(O_2)$(TPP) under 1 atm of dioxygen. It is of interest that the relative yields of epoxide are rather high in these photosensitized oxidations (Table II). In contrast, autoxidation of cyclohexene *via* free radical chain processes catalyzed by iron, cobalt, and manganese porphyrin complexes [7] gives low epoxide selectively (2–13%), while oxygen transfer reactions catalyzed by iron and chromium porphyrins [8] lead to entirely different product distributions. The scope and mechanisms of these photooxidations are under investigation.

Titanium(III) porphyrins are obtained by zinc amalgam reduction of difluorotitanium(IV) porphyrins [9], but access to titanium(II) complexes by chemical reduction seems difficult: reaction of fluorotitanium(III) porphyrins with sodium anthracenide yields unstable products [10]. The probable intermediacy of a titanium(II) tetraphenylporphyrin in the photolysis of $Ti(O_2)$(TPP) raises some hope concerning the stabilization and isolation of this reactive species. This observation, as well as several precedents in the titanocene series [11], suggest that photoreduction [12] in the presence of appropriate ligands might afford an alternative, clean preparative route to titanium(II) porphyrin complexes.

Acknowledgements

We thank Dr. Henry Ledon for communicating us his manuscript cited in reference 2 prior to publication. This work was supported by the Centre National de la Recherche Scientifique through grants ERA 675 (Grenoble) and LA 33 (Dijon) and the attribution of a research fellowship to C.J.B.

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