Inorganic Chemistry Communications 70 (2016) 175–176

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

Photochemistry of Os(bipy)$_2$(CO$_3$). Photoreduction of carbonate to formaldehyde

Arnd Vogler

Institute of Inorganic Chemistry, University Regensburg, Germany

ARTICLE INFO

Article history:
Received 23 April 2016
Received in revised form 8 June 2016
Accepted 11 June 2016
Available online 14 June 2016

Keywords:
Photochemistry
Photoredox reaction
Carbonate
Carbon dioxide
Osmium

ABSTRACT

The complex Os(II)(bipy)$_2$(CO$_3$) undergoes a photoredox reaction in acetonitrile/H$_2$O yielding [Os(VI)(bipy)$_2$(O)$_2$]$^{2+}$ and formaldehyde. The reactive excited state is suggested to be of the (Os(II) to π* carbonate) MLCT type.

The photochemical reduction of carbon dioxide is of fundamental importance in the field of biochemistry. Accordingly, many efforts have been devoted to understand and to simulate this part of natural photosynthesis. As a key step of an artificial photosynthesis it is considered to be an important contribution to the utilization of solar irradiation as a regenerative energy source provided by chemistry. It has been shown that transition metal complexes can facilitate this photoreduction by sensitizing and catalyzing this process [1–4]. In order to avoid an undesired interference, in particular by the intermediate formation of radicals, the reduction should proceed by a transfer of an even number of electrons. For example, the reduction of CO$_2$ by two electrons may yield CO. In a few cases this has been accomplished [3,4]. The photoreduction of CO$_2$ with 4 or 6 electrons should give formaldehyde or methanol, respectively. We explored this possibility and selected the complex Os(II)(bipy)$_2$(CO$_3$) [5] (bipy = 2,2′-bipyridyl) for the present study. The oxidation of Os(II) complexes of this type tends to yield Os(VI) as stable product [6,7]. Moreover, carbonate as a ligand is better accessible than CO$_2$. In both cases the 4-electron reduction should lead to the generation of formaldehyde. Finally, there is an opportunity to photoreduce Os(VI) back to Os(II) in order to provide a cyclic process, which could be considered as a photocatalysis.

The complex Os(bipy)$_2$(CO$_3$) was prepared by a literature procedure [5].

Emission spectra were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were recorded for monochromator and photomultiplier efficiency variations. Solutions were irradiated in 1-cm quartz cells at r.t. The photolyses were performed by irradiation with a high-pressure mercury lamp Osram HBO 100 W/2. Formaldehyde was identified by the Merckoquant test stripes.

The complex Os(bipy)$_2$(CO$_3$) is soluble in CH$_2$Cl$_2$ and polar solvents such as acetonitrile (AN). In our case most experiments were performed in mixtures of acetonitrile and water (1:1 vol%). Upon irradiation of Os(bipy)$_2$(CO$_3$) in AN/water spectral changes are observed (Fig. 1), which suggest that Os(bipy)$_2$(CO$_3$) is converted to [Os(bipy)$_2$(O)$_2$]$^{2+}$ [6]. The spectrum of the dioxo complex is characterized by an absorption maximum near 400 nm, in addition to the much more intense band at $\lambda_{max} = 300$ nm [6].

The photolyzed solution shows a weak, but distinct luminescence (Fig. 2) with $\lambda_{max} = 638$ nm. Moreover, formaldehyde was identified as a further photolysis product. A gas evolution which should take place when the carbonate ligand would undergo a two-electron reduction to CO was not observed.

When the solution of Os(bipy)$_2$(CO$_3$) was treated with increasing amounts of Ce(NO$_3$)$_4$, the spectral variations (Fig. 3) were nearly identical to those of the photolysis (Fig. 1). In this case it is well known that the oxidation by Ce(IV) leads to the formation of [Os(VI)(bipy)$_2$(O)$_2$]$^{2+}$ [6].

The absorption spectrum of Os(II)(bipy)$_2$(CO$_3$) in the visible region displays bands which are of the (Os(II) to π* bipy) MLCT type [5]. MLCT excitation with $\lambda_{irr} > 380$ nm is essentially not effective, but shorter-wavelength irradiation (with white light) leads to an efficient photolysis which proceeds according to the Eq. (1).

$$\mathrm{Os(II)(bipy)_2(CO_3) + 2\,H_2O \rightarrow [Os(VI)(bipy)_2(O)_2]^{2+} + H_2CO + 2\,OH^-} \qquad (1)$$

http://dx.doi.org/10.1016/j.inoche.2016.06.011
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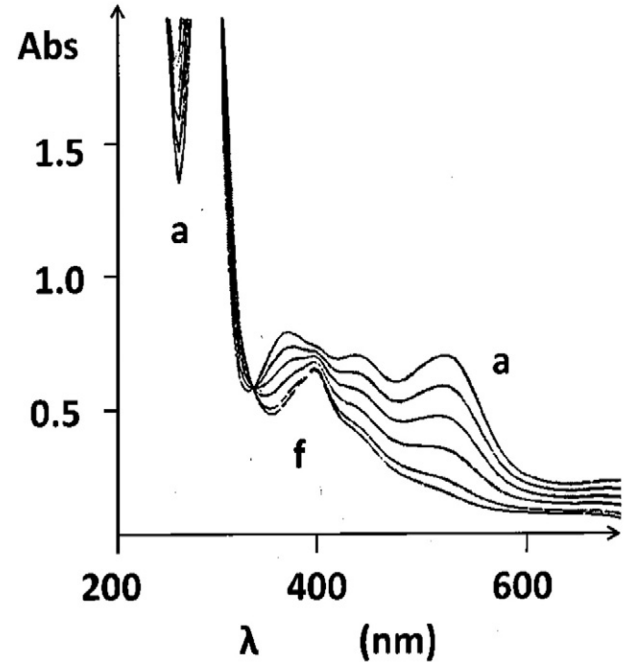

Fig. 1. Spectral changes during the irradiation of 7×10^{-3} M $Os(bipy)_2(CO_3)$ in acetonitrile/H_2O under argon with white light; irradiation times: a (0 min), b, c, d, e, f (5, 10, 15, 20, 30 min, respectively).

Although the π* orbital of carbonate is certainly located at very high energies [8], Os(II) to π* CO_3^{2-} MLCT excitation may take place by irradiation with white light which includes short-wavelength UV-light. The photolysis proceeds by a 4-electron redox process which is facilitated by the stability of Os(VI). This product is apparently photostable and does not undergo a secondary photolysis although it is anticipated that it should take place according to Eq. (2).

$$\textit{cis}-\left[\mathrm{Os(VI)(bipy)_2(O)_2}\right]^{2+} + 2\,\mathrm{H_2O} \rightarrow \left[\mathrm{Os(II)(bipy)_2(H_2O)_2}\right]^{2+} + \mathrm{O_2} \quad (2)$$

However, it has been shown that the cis complex undergoes easily ligand loss of bipy and isomerization to the trans complex [6]. Indeed, such a cis to trans isomerization takes place, at least partially, as indicated by the appearance of the red luminescence of the photolyzed solution. Complexes of the type *trans*-$Os(VI)(O)_2L_4$ are d^2 complexes which are well known to exhibit a long-wavelength emission in solution at r.t. which originates from a LF excited state [7,9]. Its low energy is determined by both oxo ligands in a trans position. So it is not surprising that a facile ejection of O_2 which requires an adjacent position of both oxide ligands does not occur.

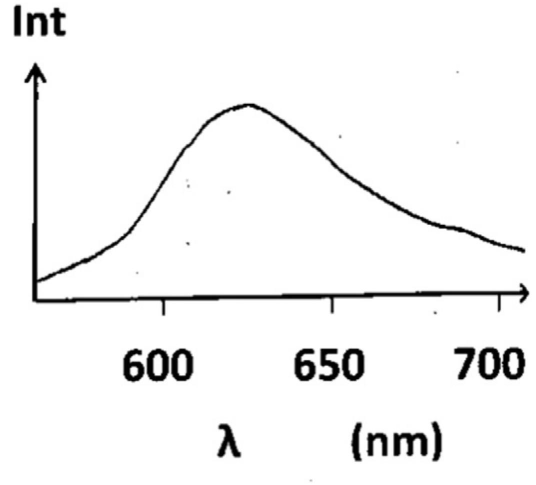

Fig. 2. Emission spectrum of the photolyzed solution of $Os(bipy)_2(CO_3)$ in acetonitrile/H_2O; intensity in arbitrary units, $\lambda_{exc} = 420$ nm.

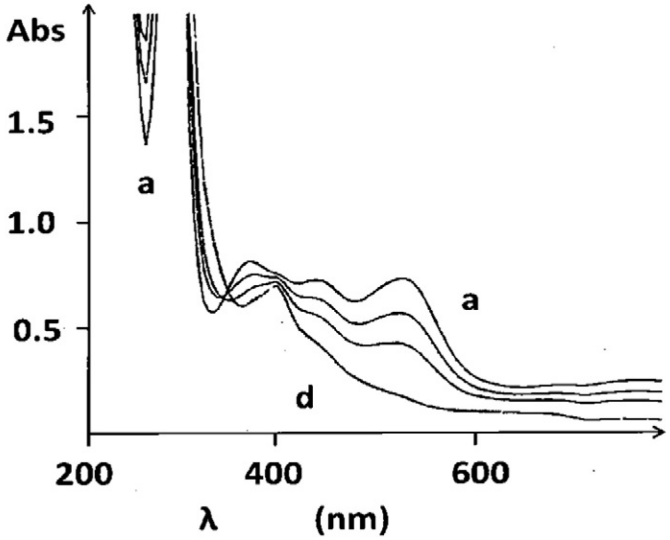

Fig. 3. Spectral variations upon addition of increasing amounts of $Ce(NO_3)_4$ to a solution of 7×10^{-3} M $Os(bipy)_2(CO_3)$; a (0 M), b, c, d (10^{-2} M) $Ce(NO_3)_4$.

This is quite unfortunate because otherwise a closed circle might exist which would represent a photocatalysis according to Eq. (3).

$$CO_3^{2-} + 2\,H^+ \rightarrow H_2CO + O_2 \quad (3)$$

In conclusion, it is anticipated that a suitable complex may be designed which could realize Eq. (3) representing an attractive model for an artificial photosynthesis. A key step might be the replacement of bipy by a related tridentate ligand which prevents a cis to trans isomerization of both oxide ligands as well as the loss of the tridentate ligand. It should be also emphasized that formaldehyde as product of the photoreduction offers a much better possibility for a storage as energy-rich compounds compared to gases such as CO or H_2 as products of an artificial photosynthesis.

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