

## Photoreduction of CO to Methanol. The Photolysis of Aqueous Solutions of $[\text{Os}(\text{NH}_3)_5(\text{CO})]^{2+}$

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The carbonyl complex  $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{CO})]^{2+}$  undergoes a photolysis in aqueous solution which yields  $[\text{Os}^{\text{VI}}(\text{NH}_3)_4\text{N}]^{3+}$  ( $\Phi = 10^{-3}$  at  $\lambda_{\text{irr}} = 255 \text{ nm}$ ) and methanol. This photoreduction of CO to  $\text{CH}_3\text{OH}$  represents a novel type of photoreactivity of metal carbonyl complexes and could be utilized for an artificial photosynthesis.

**Key words:** Photochemistry, Osmium Complexes, Metal Carbonyl Complexes, CO Reduction, Artificial Photosynthesis

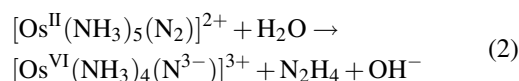
### Introduction

The reduction of CO to methanol may be a significant step towards a “methanol economy” [1]. This reaction can be accomplished by the catalytic conversion of synthesis gas (Eq. 1) as an important modification of the Fischer-Tropsch process [2, 3].

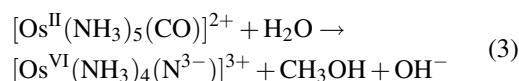


If the reduction of CO could be achieved photochemically it would represent a rather new type of artificial photosynthesis since in distinction to  $\text{H}_2$  as a result of photochemical water splitting, methanol is well suited for storage and transportation. As an energy-rich liquid it offers many benefits [1]. Metal carbonyl complexes should be attractive candidates for this purpose. Unfortunately, methanol has not yet been observed as a photoproduct of metal carbonyls [4, 5]. Generally, the photolysis of such compounds leads simply to the release of a CO ligand originating from LF excited states. In order to reduce the CO ligand, a MLCT state should be populated [6, 7]. However, a reduction to methanol will be only facilitated if the MLCT ( $\text{M} \rightarrow \pi^*\text{CO}$ ) transition as a one-electron process is followed by a multi-electron transfer from the central metal to CO. We now examined this possibility and selected the complex  $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{CO})]^{2+}$  [8] for this purpose. This

choice was based on the close relationship between  $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{CO})]^{2+}$  and  $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ . The latter complex has been shown to react according to Eq. 2 following ( $\text{Os}^{\text{II}} \rightarrow \pi^*\text{N}_2$ ) MLCT excitation [9].



For this photoreduction of  $\text{N}_2$  to  $\text{N}_2\text{H}_4$  four electrons are supplied by  $\text{Os}(\text{II})$ . In addition, four protons are required which are provided by an ammonia ligand and water as the solvent. Accordingly, in the present study we anticipated the occurrence of the photolysis according to Eq. 3:



The expected analogy was also based on the similarity of CO and  $\text{N}_2$  which are both characterized by a very stable triple bond and  $\pi^*$  orbitals at comparable energies.

### Results and Discussion

Solution of  $[\text{Os}(\text{NH}_3)_5(\text{CO})]^{2+}$  are light sensitive. The photolysis of aqueous solutions with white

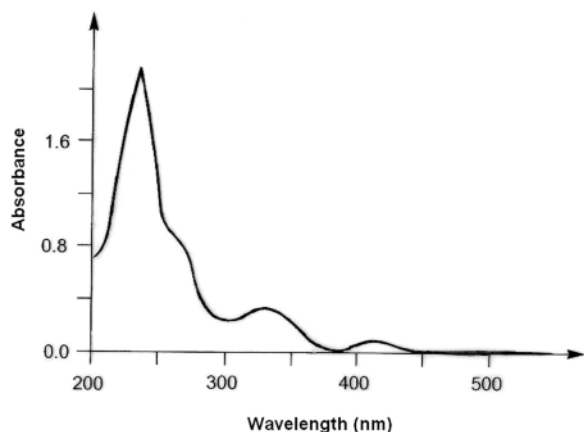


Fig. 1. Absorption spectrum of the photolyzed solution of aqueous  $2.3 \times 10^{-3}$  M  $[\text{Os}(\text{NH}_3)_5(\text{CO})]\text{Cl}_2$ ; photolysis with  $\lambda_{\text{irr}} = 255$  nm, 1-cm cell, for 2 h and 40 min.

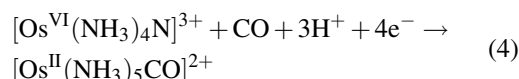
light or UV light ( $\lambda_{\text{irr}} = 255$  nm) is accompanied by spectral variations which indicate the formation of  $[\text{Os}(\text{NH}_3)_4\text{N}]^{3+}$ . The photolysis can be driven to completion. In this case the final spectrum (Fig. 1) shows only the presence of  $[\text{Os}(\text{NH}_3)_4\text{N}]^{3+}$  which is characterized by absorption features at 236, 265, 325, and 410 nm [10]. Since the longest-wavelength maximum at 410 nm ( $\epsilon = 30$ ) does not overlap with bands of different origin it can be used to monitor the formation of  $[\text{Os}(\text{NH}_3)_4\text{N}]^{3+}$ . Its formation is corroborated by the appearance of the luminescence of this nitride complex with  $\lambda_{\text{max}} = 570$  nm [10–13]. It grows with the evolution of the corresponding absorption spectrum (Fig. 1).

The quantum yield of the formation of the nitride complex amounts to approximately  $\Phi = 10^{-3}$  at  $\lambda_{\text{irr}} = 255$  nm. The photolysis leads also to the formation of methanol. It was detected and determined by an enzyme-based method (alcohol dehydrogenase or alcohol oxidase) as a UV test ( $\lambda_{\text{max}} = 340$  nm) from Roche and Sanelco. The reliability of this analysis in our system was confirmed by control experiments with the photolyzed and non-photolyzed solution containing additional amounts of methanol. According to Eq. 3  $[\text{Os}(\text{NH}_3)_4\text{N}]^{3+}$  and methanol should be formed in a stoichiometric ratio of 1 : 1, but only 70% (10%) of the expected amount of methanol were analytically confirmed. Moreover, a pH increase accompanied the photolysis (see Eq. 3).

The photoreduction of CO to  $\text{CH}_3\text{OH}$  seems to be indeed an unique photoredox reaction of a metal carbonyl complex. The success of this photolysis

(Eq. 3) is based on the availability of a reactive MLCT ( $\text{M} \rightarrow \pi^*\text{CO}$ ) state and the capability of the metal center ( $\text{Os}^{\text{II}}$ ) to donate  $4e^-$  yielding the stable oxidized complex with  $\text{Os}^{\text{VI}}$ . Our choice of  $[\text{Os}(\text{NH}_3)_5\text{CO}]^{2+}$  was also guided by the anticipated analogy to  $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$ . In both cases (Eqs. 2 and 3) the ligands in question (CO and  $\text{N}_2$ ) are very similar with regard to their bonding properties and photochemical reduction to  $\text{CH}_3\text{OH}$  and  $\text{N}_2\text{H}_4$ , respectively, which requires 4 electrons and 4 protons. The detection of  $[\text{Os}^{\text{VI}}(\text{NH}_3)_4\text{N}]^{3+}$  as photooxidation product is facilitated by its photoluminescence which appears in solution at ambient conditions [10–13]. It is very likely that some less important side and/or secondary reactions suppress the yield of methanol. For example, the interference of small residual amounts of oxygen may decrease this yield. Such an oxygen effect has been observed for the photolysis of  $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  [14]. In the context of our present observations it must be kept in mind that in the past the photoreduction of coordinated CO was not considered to be a reasonable possibility for the photolysis of metal carbonyls. In some cases, a photoreduction of CO may have been simply overlooked. Among other aspects, the presence of different excited states (*e.g.* LF states which initiate CO substitutions) [4, 5] below a potentially reactive ( $\text{M} \rightarrow \pi^*\text{CO}$ ) MLCT state needs to be avoided in order to favor CO photoreduction.

A further point of interest concerns the possibility for  $[\text{Os}^{\text{VI}}(\text{NH}_3)_4\text{N}]^{3+}$  to undergo a facile reduction back to the  $[\text{Os}^{\text{II}}(\text{NH}_3)_5]^{2+}$  complex fragment which should be able to add CO as a sixth ligand in order to regenerate  $[\text{Os}(\text{NH}_3)_5\text{CO}]^{2+}$  (Eq. 4)



While solving of this problem was not within the scope of the present study, some relevant observations should be mentioned here. Previous reports indicate the possibility to put Eq. 4 into reality [11–13, 15, 16]. When  $[\text{Os}(\text{NH}_3)_4\text{N}]^{3+}$  is reduced by dithionite in the presence of 4-phenylpyridine, the complex  $[\text{Os}^{\text{II}}(\text{NH}_3)_5(4\text{-phenylpyridine})]^{2+}$  is formed. This blue cation is characterized by an intense MLCT absorption near 660 nm [17] (Fig. 2). In principle, other  $\pi$ -accepting ligands including CO should also trap the reduced fragment  $[\text{Os}(\text{NH}_3)_5]^{2+}$ . However, when the concentration of this ligand is too low, the re-

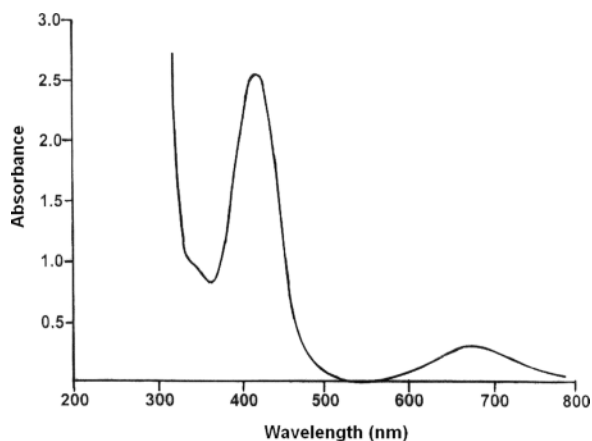


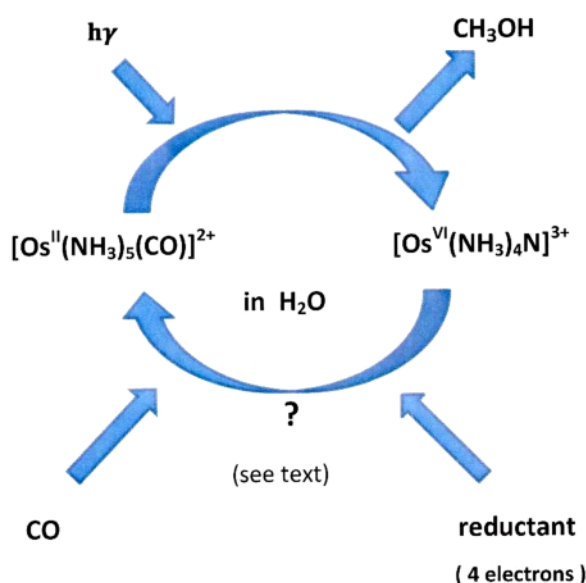
Fig. 2. Absorption spectrum of aqueous  $4.2 \times 10^{-3}$  M  $[\text{Os}(\text{NH}_3)_5(4\text{-phenylpyridine})]^{2+}$ .

duction of water by  $[\text{Os}(\text{NH}_3)_5]^{2+}$  [18–20] interferes with the formation of a stable  $[\text{Os}^{\text{II}}(\text{NH}_3)_5\text{L}]^{2+}$  complex. This apparently applies to  $\text{L} = \text{CO}$  under ambient conditions [8]. Nevertheless, under suitable reaction conditions such as higher CO pressures or replacing water by other solvents, Eq. 4 may proceed as expected.

### Conclusion and Perspective

It follows from these consideration that a cyclic system could be designed (Scheme 1) which represents a photocatalytic reduction of CO to methanol. However, while the present study led to the realization of Eq. 3, Eq. 4 is certainly feasible but its investigation represents a separate project for the future.

Our results may also stimulate further attempts to search for photoreductions of CO in metal carbonyl complexes. In particular, reductions to formaldehyde are conceivable since  $2e^-$  reductions are easier to achieve compared to the  $4e^-$  reductions which yield methanol. The oxidation of a metal center and the concomitant reduction of CO to  $\text{H}_2\text{CO}$  by  $\pm 2e^-$  may be viewed as a special type of reductive elimination which might be facilitated at  $d^{10}$  or  $d^8$  metal centers such as  $\text{Au}^{\text{I}}$  or  $\text{Ir}^{\text{I}}$ , respectively.



Scheme 1. (color online).

### Experimental Section

$[\text{Os}(\text{NH}_3)_5\text{CO}]\text{Cl}_2$  and  $[\text{Os}(\text{NH}_3)_4\text{N}]\text{Cl}_3$  were prepared according to published procedures [8] and [13], respectively. Absorption spectra were measured with a Varian Cary 50 spectrophotometer and emission spectra with a Hitachi 850 spectrofluorometer. The light sources used for irradiation were a low-pressure mercury lamp (Hanau, 6W) or a high-pressure mercury lamp (Osram HBO 200 W/2). Monochromatic light was obtained using Schott PIL/IL interference filters and Schott cutoff filters to avoid short-wavelength and second-order irradiation. The light beam was focused on a photolysis cell (1-cm spectrophotometer quartz cell) by a quartz lens. The photolyses were performed at room temperature. The quantitative analysis of methanol was carried out by the enzymatic procedures provided by Roche (product No 10176290035) and Sanelco (quick saliva test) calibrated by methanol aliquots in water.

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