

Photolysis of Aqueous $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$. Photoreduction of Coordinated Dinitrogen to Hydrazine as a Model for a New Type of Artificial Photosynthesis?

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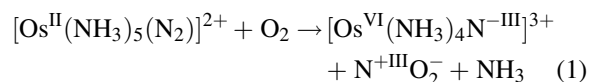
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In the absence of oxygen the photolysis of $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ leads to the reduction of the N_2 ligand according to $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{N}_2)]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Os}^{\text{VI}}(\text{NH}_3)_4\text{N}]^{3+} + \text{N}_2\text{H}_4 + \text{OH}^-$. The photochemical formation of hydrazine from N_2 is discussed with regard to the photochemical conversion and storage of solar energy.

Key words: Osmium Complexes, Dinitrogen Complexes, Photochemistry, Hydrazine, Artificial Photosynthesis

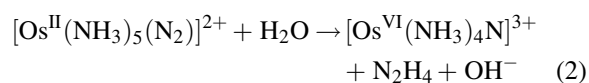
Introduction

Dinitrogen coordinated to Os(II) and as a bridging ligand between Os(II) and Os(III) has been shown to undergo a variety of photochemical transformations [1–3]. Photoreductions to nitride and photooxidations to nitrite and related photoredox processes take place depending on the reaction conditions. The photolysis of $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ in aqueous solution [3] in the presence of oxygen essentially proceeds according to Eq. 1.



When the concentration of oxygen is reduced by saturating the solution with argon, this photodismutation of N_2 is less efficient, and the quantum yield drops from $\Phi = 6 \times 10^{-3}$ to 2×10^{-3} . Recent considerations led to the assumption that in the absence of O_2 another photoreaction comes into play. Since Os(II) provides four

electrons when it is oxidized to Os(VI), we anticipated that the photolysis may proceed according to a very simple stoichiometry (Eq. 2).



We were now able to confirm this expectation and report here our observations. These results are not only interesting in their own right but also potentially important for a new type of artificial photosynthesis.

Results

The spectral variations (Fig. 1) which accompany the photolysis of $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ in argon-saturated water indicate the disappearance of the starting complex. Owing to the intense absorption of $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ in the UV region the irradiation ($\lambda_{\text{irr}} = 254 \text{ nm}$) essentially leads to a bleaching since the photoproducts apparently absorb much less. The absorption of the products are obscured by the residual absorption of remaining $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ and small amounts of potential products such as $[\text{Os}(\text{NH}_3)_5\text{Cl}]^{2+}$ [4]. However, inflections at 325

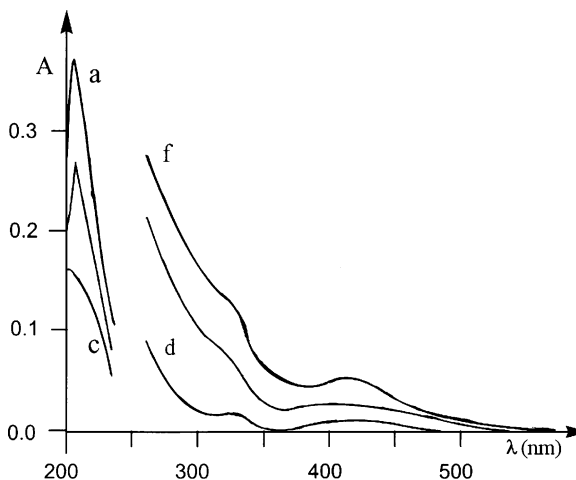


Fig. 1. Spectral changes during the photolysis of $1.4 \times 10^{-5} \text{ M}$ $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ in water under argon at r. t. after 0 min (a), 15 and 30 min (c) and at higher concentration ($1.6 \times 10^{-3} \text{ M}$) after 40 (d), 80 and 140 min (f) irradiation times with a low pressure mercury lamp (Hanau, 6 W).

and 410 nm (Fig. 1) indicate the formation of $[\text{Os}(\text{NH}_3)_4\text{N}]^{3+}$.

This is unambiguously corroborated by the luminescence ($\lambda_{\text{max}} = 570 \text{ nm}$) of the nitride complex [1, 5, 6] which is utilized for the detection and quantitative determination of $[\text{Os}^{\text{VI}}(\text{NH}_3)_4\text{N}]^{3+}$. As expected the formation of hydrazine as reduction product (see Eq. 2) was now confirmed. This analysis was carried out by the spectrophotometric Merck test (art. no. 1.09711.0001) which generates an absorption maximum at 464 nm in the presence of hydrazine. However, a first analysis showed that only about 10% of the amount of hydrazine was recovered in comparison to the amount required by Eq. 2. Of course, the residual oxygen in the argon-saturated solution contributed to the formation of the Os(VI) nitride complex (Eq. 1). Nevertheless, the question arises what happened to the missing 90% of hydrazine?

It is well known that transition metal complexes catalyze the decomposition of hydrazine. We assumed that owing to an open coordination site the photooxidation product $[\text{Os}(\text{NH}_3)_4\text{N}]^{3+}$ might function as a catalyst for such a decay. Indeed, the amount of N_2H_4 strongly depends on the time which elapsed from the end of irradiation until starting the analysis of hydrazine. For example, an immediate analysis led to the recovery of *ca.* 70% while after 0.5 h only traces of hydrazine could be detected. Without an extensive examination which was not within the scope of the present study a quantitative evaluation by extrapolation is not reliable. Nevertheless, on the basis of a rough estimate we suggest that in the absence of oxygen the photolysis of $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ indeed proceeds according to Eq. 2. In this context, it is of interest that the known synthesis of $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ is accomplished by the reaction of complexes of osmium in higher oxidation states with hydrazine [7, 8].

Discussion

The photochemical conversion of N_2 to N_2H_4 is certainly of considerable interest. Of course, the subsequent catalytic decomposition must be avoided by insulating the catalyst. There are various possibilities such as the addition of gelatine which stabilizes N_2H_4 and blocks potential decay catalysts.

An artificial photosynthesis has the aim to convert and store solar energy. Most efforts have been devoted

to split water into hydrogen and oxygen, and to use hydrogen as a fuel [9]. However, H_2 is difficult to store and accordingly, novel storage systems for H_2 are of great demand. Metal compounds, boranes, formic acid and aromatic compounds such as ethyl carbazol have been suggested to act as H_2 carriers [10, 11]. Hydrazine is another attractive candidate. It is a liquid and water soluble, and it can be decomposed catalytically into its components [12] (Eq. 3).



Hydrazine burns with oxygen in a very exothermic process (Eq. 4):



This reaction is utilized to propel rockets.

The hydrogen release according to Eq. 3 is well known and suggests its application in fuel cells. Moreover, N_2H_4 can also directly feed fuel cells [13]. The use of N_2H_4 for energy generation is environmentally friendly because only nitrogen and water are the final products. Dinitrogen as hydrogen carrier is available without limitation.

Unfortunately, the present observations serve only as proof of principle and should encourage further research in this area. What are the challenges? The detrimental properties of our system are obvious and hamper any immediate application. The quantum yield of photoreaction 2 ($\Phi \sim 2 \times 10^{-3}$) is too low, and the necessity of UV light for this photolysis is not acceptable for any practical aspect. However, it is anticipated that light of longer wavelength is effective with inter- or intramolecular sensitization. Last but not least, the oxidation product $[\text{Os}^{\text{VI}}(\text{NH}_3)_4\text{N}]^{3+}$ must be reduced in order to regenerate the starting complex $[\text{Os}^{\text{II}}(\text{NH}_3)_5(\text{N}_2)]^{2+}$. Some previous studies indicate that such a reduction may be achieved thermally [14] or photochemically [5, 6, 15]. For the conversion and chemical storage of solar energy reaction 2 and the reduction of the Os(VI) complex have to be incorporated into a cyclic system which then proceeds photocatalytically.

Acknowledgement

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