

# Photocatalytic reduction of hydrazine to ammonia catalysed by $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$ complex in a Pt/TiO<sub>2</sub> semiconductor particulate system

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## Abstract

Illumination of aqueous suspensions of Pt/TiO<sub>2</sub> semiconductor photocatalyst in the presence of  $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$  resulted in the reduction of hydrazine to ammonia. A working mechanism involving the formation of a  $[\text{Ru}^{\text{III}}(\text{edta})(\text{N}_2\text{H}_5)]$  species (adsorbed onto TiO<sub>2</sub> surface) which undergoes two-electron transfer reduction followed by cleavage of the N–N bond of coordinated hydrazine has been suggested. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Photocatalysis; Hydrazine reduction; Platinum/titania; Ru–edta complex; Ammonia

## 1. Introduction

Interest in ammonia photoproduction by a TiO<sub>2</sub> semiconductor particulate system was initiated by Scrauzer and Guth [1]. The results were followed by several reports on photo-reduction of N<sub>2</sub> to NH<sub>3</sub> [2–5]. However, the mechanism of the photoprocess, which involves several intermediates, is not well documented. Hydrazine is reported to be one of the intermediate which undergo two-electron reduction followed by N–N bond cleavage to yield ammonia in the dinitrogen reduction process. Catalytic ability of  $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$  in electrochemical reduction of hydrazines was reported

earlier [6,7]. The idea of introducing  $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$  in TiO<sub>2</sub> semiconductor particulate system was to examine that how the system behaves in presence of the complex that can essentially provide a coordination site (through rapid aquo-substitution) for hydrazine to undergo reduction (thus lowering the activation barrier) and can form a surface complex with TiO<sub>2</sub> semiconductor particle through the pedant carboxylate group. The present paper reports the results of photocatalytic reduction of hydrazine to ammonia in presence of  $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$  complex.

## 2. Experimental

The complex  $\text{K}[\text{Ru}^{\text{III}}(\text{HEDTA})\text{Cl}]$  was prepared and characterized by following the proce-

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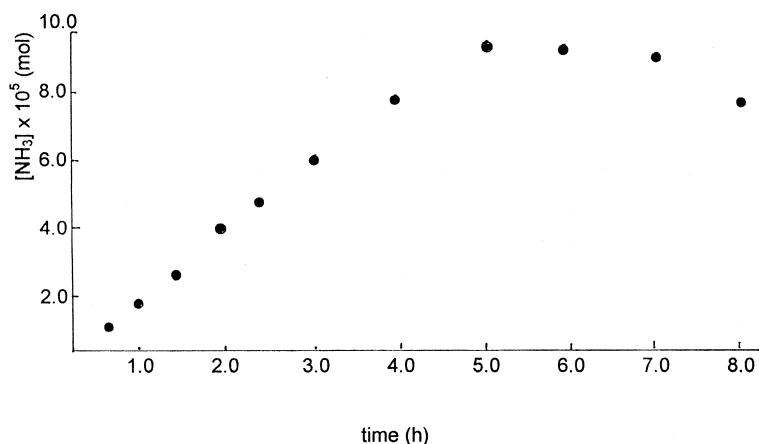


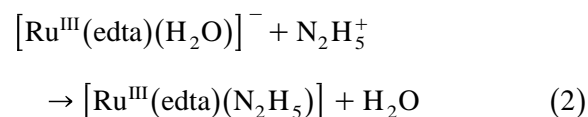
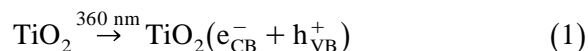
Fig. 1. Formation of NH<sub>3</sub> with irradiation time (see Section 2 for reaction conditions).

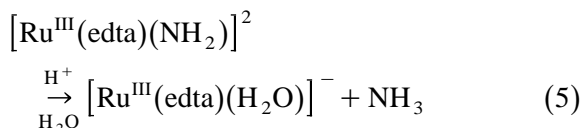
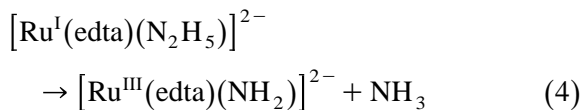
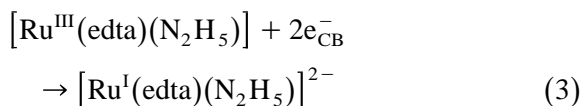
dure reported earlier [8]. K[Ru<sup>III</sup>(HEDTA)Cl] rapidly gets aquated when dissolved in water and predominantly exists in its most labile form [Ru<sup>III</sup>(edta)(H<sub>2</sub>O)]<sup>-</sup> (complex **1**) in the pH range 3–6 [9]. Semiconductor grade TiO<sub>2</sub> (Degussa p25) was loaded with platinum (4%) by following the procedure reported by Erbs et al. [10]. All other chemicals used were of A.R. grade. Double-distilled water used throughout the studies. In a typical photocatalytic experiment a reaction mixture (100 ml) containing 300 mg of Pt/TiO<sub>2</sub> photocatalyst, 25 mg of complex **1** (0.25 mmol) and 1.0 mmol of hydrazine (N<sub>2</sub>H<sub>5</sub><sup>+</sup>HSO<sub>4</sub><sup>-</sup>) was irradiated at 390 nm with a 250 W Xe lamp. The pH of the reaction mixture was kept at 3.1. Aliquots of the reaction mixture were withdrawn at a chosen intervals of time and subjected to spectrophotometric analysis (indophenol blue method) for NH<sub>3</sub>. Spectral measurements were carried out with a GBC Cintra 10 spectrophotometer.

### 3. Results and discussion

The N<sub>2</sub>H<sub>5</sub><sup>+</sup> reacts with [Ru<sup>III</sup>(edta)(H<sub>2</sub>O)]<sup>-</sup> (complex **1**) to produce [Ru<sup>III</sup>(edta)(N<sub>2</sub>H<sub>5</sub>)] (complex **2**) in a stopped-flow scale ( $k = 0.48$

M<sup>-1</sup> s<sup>-1</sup> at 25°C, pH = 3.1) [6]. A series of control experiments were performed in order to examine the catalytic ability of complex **1** towards reduction of hydrazine to ammonia. The yield of ammonia (1.98 × 10<sup>-5</sup> mol h<sup>-1</sup>) is shown in Fig. 1. No ammonia was detected in the absence of any one of the following: UV-light, hydrazine or Pt/TiO<sub>2</sub>. Rate of formation of ammonia was found to be low in absence of complex **1**. The decline in yield was observed after 5 h. This may be due to deactivation of TiO<sub>2</sub> powder caused by the physico-chemical change during the course of irradiation. A recovery of the activity was achieved by heating the TiO<sub>2</sub> photocatalyst (obtained by filtration) at 550°C in presence of air. Based on the above experimental results the following working mechanism is developed (reminiscent of the complex **1** catalysed electrochemical reduction of hydrazine) for the photoreduction of hydrazine to ammonia.





Upon illumination (at 390 nm) the electrons are generated in the conduction band of the  $\text{TiO}_2$  semiconductor photocatalyst which are channelled through the pre-deposited platinum to the surface adsorbed (chemisorbed through uncoordinated carboxylate group)  $[\text{Ru}^{\text{III}}(\text{edta})(\text{N}_2\text{H}_5)]$  (formed in the reaction between  $[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$  complex and hydrazine) to produce  $[\text{Ru}^{\text{I}}(\text{edta})(\text{N}_2\text{H}_5)]^{2-}$  intermediate which subsequently undergoes N–N bond cleavage coupled with intramolecular electron transfer (two-electron transfer) process to produce one molecule of ammonia and  $[\text{Ru}^{\text{III}}(\text{edta})(\text{NH}_2)]^{2-}$  species. The  $[\text{Ru}^{\text{III}}(\text{edta})(\text{NH}_2)]^{2-}$  species further hydrolyses to give another molecule of ammonia and complex **1** back in the system. The basis of the proposed  $[\text{Ru}^{\text{I}}(\text{edta})(\text{N}_2\text{H}_5)]^{2-}$  intermediate is our earlier observation on the complex **1** catalysed electrochemical reduction of hydrazine to ammonia. The lower reactivity of the catalytic in absence of complex **1** may be explicable from thermodynamic consideration. Reduction of coordinated hydrazine is facile as the complex **2** is more oxidising agent ( $E_{1/2}(\text{Ru}^{3+}/\text{Ru}^{2+}) = 0.035$  V vs.  $\text{Ag}/\text{AgCl}$ ) for the conduction band electrons than  $\text{N}_2\text{H}_5^+$  alone (redox potential for  $\text{N}_2\text{H}_4 - 2\text{NH}_3$  transformation is approximately is  $-1.3$  V). The rate controlling step of photocatalytic process is most likely a surface chemical step (electron transfer) probably coupled with ad-

sorption of reactants and desorption of ammonia molecule.

#### 4. Conclusion

In conclusion, the salient indication of the present study is that complex **1** acts as an efficient catalyst to effect the photoreduction of hydrazine to ammonia. Coordination of hydrazine to complex **1** lowers the energy barrier substantially for the reduction of hydrazine. The possible significance of the results of the present work with respect to the use of a water-soluble metal complex that can bind dinitrogen or its reduced intermediate(s) in a kinetically preferred pathway is implied.

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