

## REDUCTION OF N<sub>2</sub> TO NH<sub>3</sub> BY Ti<sup>3+</sup> IN AQUEOUS MEDIA AND ITS PHOTOENHANCEMENT

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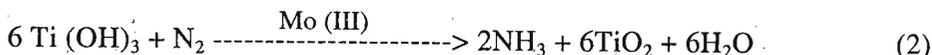
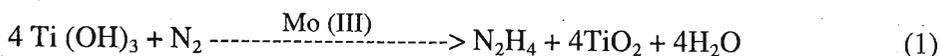
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**Abstract:** Aqueous solutions of Ti<sup>3+</sup> and Ti(OH)<sub>3</sub> suspensions reduce N<sub>2</sub> to NH<sub>3</sub>. The yields are enhanced upon the addition of Mg<sup>2+</sup> and also on irradiation for the heterogeneous suspensions while such efforts are minimal for reactions in homogeneous solution.

### 1. Introduction

Reduction of N<sub>2</sub> to NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> in protic media by the hydroxides of Ti(III), Cr(II) and V(II) with Mo(III) participation has been studied by Shilov<sup>14, 15</sup> and Schrauzer<sup>8, 12, 13</sup> (Reactions 1 & 2).



These workers have observed that Ti(OH)<sub>3</sub> and Cr(OH)<sub>2</sub> are practically inactive toward dinitrogen reduction without Mo(III) participation under the experimental conditions used (P<sub>N<sub>2</sub></sub> = 100 atm). Subsequently the reduction of N<sub>2</sub> by V(OH)<sub>2</sub>/Mg(OH)<sub>2</sub> was reported to give hydrazine and ammonia.<sup>2, 13</sup> However, the reduction of acetylene to ethylene and ethane takes place without the addition of Mg<sup>2+</sup> in these systems. As part of our investigation on the photoreduction of N<sub>2</sub> on irradiated semiconductor suspensions, we have studied the reduction of N<sub>2</sub> with Ti<sup>3+</sup> in both homogeneous solution and as Ti(OH)<sub>3</sub>. Formation of NH<sub>3</sub> on Ti(OH)<sub>3</sub> without added Mg(II) or Mo(III) was observed in contrast to the earlier observations.<sup>8</sup> Aqueous solutions of Ti(III) also showed considerable activity while the addition of Mg(II) or irradiation by visible light also enhanced the production of NH<sub>3</sub>. The role of Ti(III) centers in the photoreduction of N<sub>2</sub> on irradiated rutile surfaces has been suggested by Schrauzer.<sup>4</sup> Indeed the formation and the estimation of Ti(III) centers on such surfaces have been reported by several workers.<sup>5, 6</sup>

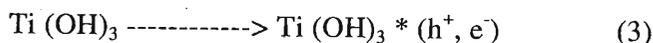
## 2. Experimental

AR grade chemicals were employed for all preparations. These were carefully purified to remove all traces of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . Titanium metal (99.99%, BDH) was dissolved in concentrated HCl by warming in a water bath under argon. For each run 0.020 g of titanium metal was used. For irradiations in homogeneous solution, the dark blue solutions obtained containing 420  $\mu$  moles of  $\text{Ti}^{3+}$  were used either alone or after the addition of  $\text{Mg}^{2+}$  so that the  $\text{Ti}^{3+} : \text{Mg}^{2+}$  ratio was 1:20. The same molar ratio was always used for experiments with the mixed  $\text{Ti}(\text{OH})_3/\text{Mg}(\text{OH})_2$ . The total volume of solution used for irradiation was 100ml. The  $[\text{H}^+]$  in these solutions were Ca.  $5 \text{ mol l}^{-1}$ . Titanium (III) hydroxide was obtained as a dark blue solid by the addition of excess NaOH to Ti(III) solutions prepared above followed by repeated washing with deionized water previously degassed by passing purified argon. The precipitate of  $\text{Ti}(\text{OH})_3$  (420  $\mu$  moles calculated on the basis of the amount titanium metal used) was suspended in 100 ml of degassed double distilled water and irradiated in a slow stream of  $\text{N}_2$  (30ml/min). The  $\text{N}_2$  used was purified by passing through a hot copper pellet column, chromic acid solution, NaOH solution and water. The lamp used was a 125 W medium pressure mercury lamp which produces Ca.  $7 \times 10^{18}$  photons/s inside the flask. The reaction mixture was mechanically stirred throughout the reaction. After passage of  $\text{N}_2$  in the dark or with irradiation, the contents were distilled into a receiving flask containing 10 ml of 0.1 M HCl after the addition of 50 ml of 0.10 M NaOH. The ammonia content in the distillate was determined colorimetrically by the indophenol blue method.<sup>1</sup> Controls were run under argon and also in the absence of metal species. The exit gases during irradiation did not show the presence of any detectable amounts of  $\text{NH}_3$ . Tests were also carried out for the presence of hydrazine on centrifuged samples where heterogeneous mixtures were employed before the addition of NaOH.

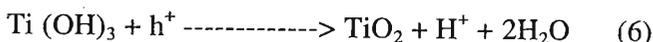
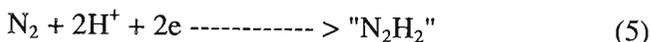
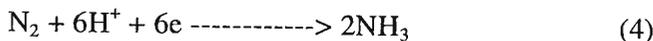
## 3. Results and Discussion

Figures 1 and 2 give the variation of  $\text{NH}_3$  yields with time obtained for the  $\text{Ti}^{3+}$  and  $\text{Ti}^{3+}/\text{Mg}^{2+}$  systems both in homogeneous solution and as their respective hydroxides in the dark and under irradiation from the 125 W Hg arc lamp. In contrast to previous observations, we note the reduction of  $\text{N}_2$  to  $\text{NH}_3$  with  $\text{Ti}^{3+}$  alone. The yields of  $\text{NH}_3$  are enhanced both upon the addition of  $\text{Mg}^{2+}$  and under irradiation for heterogeneous suspensions (figure 2). For homogeneous solutions, there is only a weak enhancement (figure 1). Although the **absolute**  $\text{NH}_3$  yields are higher for homogeneous solutions, the **relative** enhancement effects are more pronounced in heterogeneous media. Thus the  $\text{NH}_3$  yield for the heterogeneous  $\text{Ti}(\text{OH})_3/\text{Mg}(\text{OH})_2$  system in the dark represents an increase of about 140% compared to  $\text{Ti}(\text{OH})_3$  alone. For irradiated samples the corresponding increases are 115%, ( $\text{Ti}(\text{OH})_3$ ) and 83% ( $\text{Ti}(\text{OH})_3/\text{Mg}(\text{OH})_2$ ) for homogeneous solutions, the increase in ammonia yield upon addition of  $\text{Mg}^{2+}$  is Ca. 10% while irradiation results in an increase of Ca. 22% of the  $\text{NH}_3$  yield

for  $Ti(OH)_3$ . Furthermore, in heterogeneous media, the  $NH_3$  yields quickly reach a maximum after Ca. 3h irradiation and records no further increase thereafter. Such levelling effects are commonly observed with heterogeneous suspensions of semiconductors in the photoreduction of  $N_2$ . However, in solution, the  $NH_3$  yields increase regularly and after about 24h of irradiation, nearly 40% of the theoretically expected yield of  $NH_3$  (equation 2) was obtained. The  $NH_3$  yields observed here for the  $Ti(OH)_3/Mg(OH)_2$  system after 3h of passing  $N_2$  is  $14.26 \mu\text{mol l}^{-1}$  which is considerably higher compared to Schrauzer's results<sup>8</sup> for  $Ti(OH)_3/Mo(OH)_3$  under heterogeneous conditions. Photoenhancement of  $NH_3$  yields for heterogeneous suspensions may be attributed to the reported semiconductivity exhibited by  $Ti(OH)_3$ .<sup>15</sup> Thus excitation of  $Ti(OH)_3$  produces electron-hole pairs where the photogenerated electrons are capable of reducing absorbed  $N_2$  on the  $Ti(OH)_3$  surface (reaction 3).



The photogenerated charge carriers bring about the following reactions.



The observed photoenhancement for the  $Ti(OH)_3/Mg(OH)_2$  system (82%) is smaller than the relative enhancement observed for  $Ti(OH)_3$  irradiated alone (112%), while the combined effect of the addition of  $Mg^{2+}$  and irradiation on the  $NH_3$  yield of  $Ti(OH)_3$  is about 333%.  $Mg(OH)_2$  does not exhibit any activity both in the dark as well as upon irradiation. Control experiments carried out under argon did not show any  $NH_3$  formation either in the dark or upon irradiation. In the absence of the  $Ti^{3+}$  metal ions, no  $NH_3$  was detected. Tests for hydrazine with all the systems studied also showed negative results within the experimental levels of detection ( $< 0.1 \mu\text{mol l}^{-1}$ ).

The role of  $Mg(OH)_2$  in the reduction of  $N_2$  with these systems is a subject of much controversy. Shilov has proposed<sup>3</sup> the involvement of four  $V^{2+}$  ions in an active centre mediated via a  $Mg^{2+}$  ion where the  $N_2$  molecule undergoes a 4-electron reduction giving hydrazine. With the related  $V(OH)_2/Mg(OH)_2$  system on the other hand, Schrauzer<sup>10</sup> has postulated that  $V^{2+}$  acts as a 2-electron reductant reducing  $N_2$  to  $N_2H_2$  which then, disproportionates to  $N_2H_4$ . In the latter case, the  $Mg(OH)_2$  lattice is presumed to exert a "diazene protecting effect". Interestingly, magnesium doping also enhances both the photocatalytic water splitting on  $TiO_2$  catalysts<sup>7</sup> and also the reduction of  $N_2$  to  $NH_3$ .<sup>4</sup>

In homogeneous media, the four curves (Figure 1) are quite similar and there appear to be no significant enhancements due to either  $Mg^{2+}$  or irradiation. In the absence of the effects of the  $Mg(OH)_2$  gel discussed above and also the absence of any solid state catalyst poisoning effects, the reaction appears to follow a simple thermochemical pathway in homogeneous media.

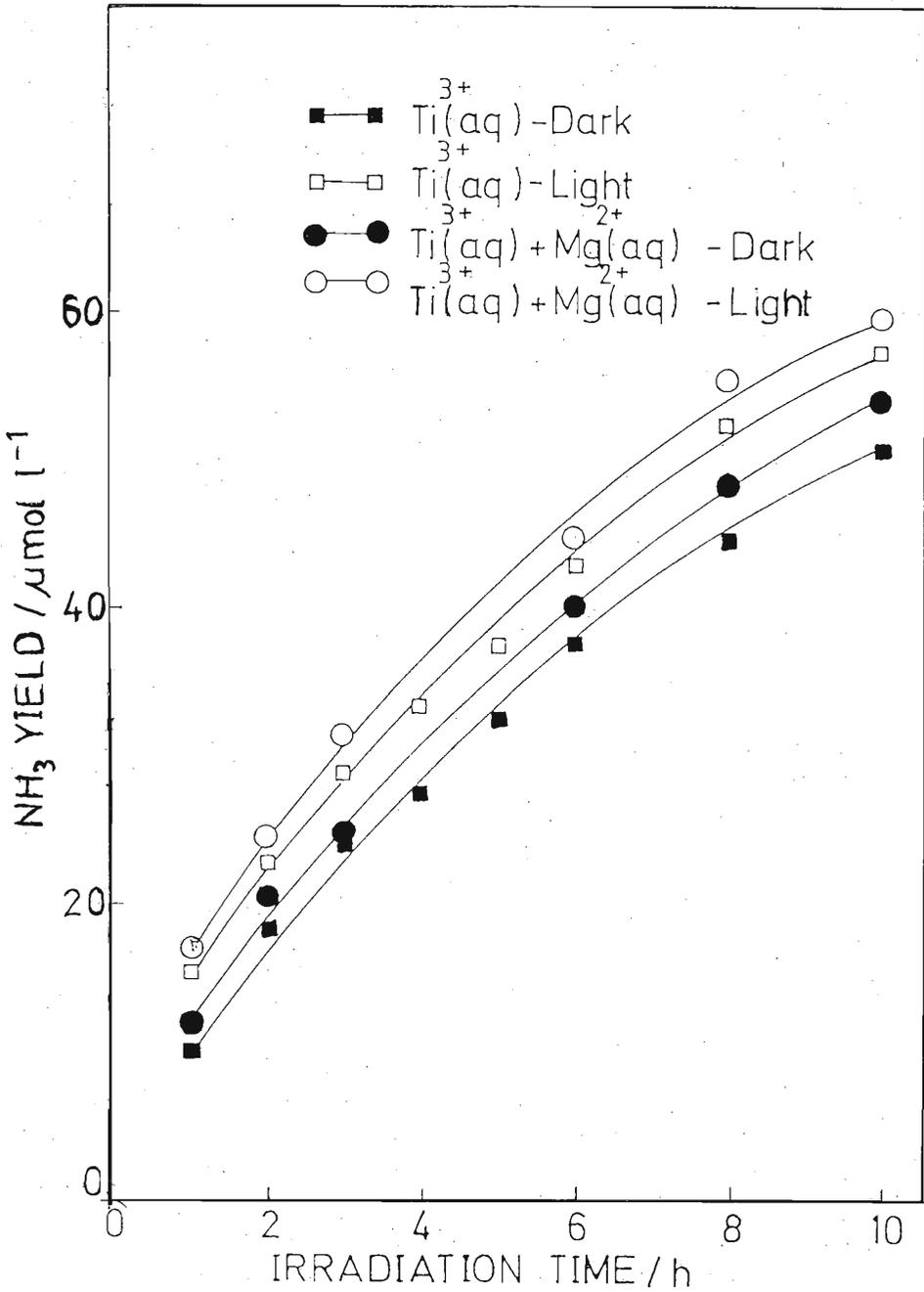


Figure 1: Variation of  $\text{NH}_3$  yields with time for homogeneous solutions.  
 The average standard deviations were as follows : irradiation time  $\pm 0.08$  h,  $\text{NH}_3$  yield  $\pm 5\%$  below  $20 \mu\text{M}$  and  $\pm 2\%$  above  $20 \mu\text{M}$ .

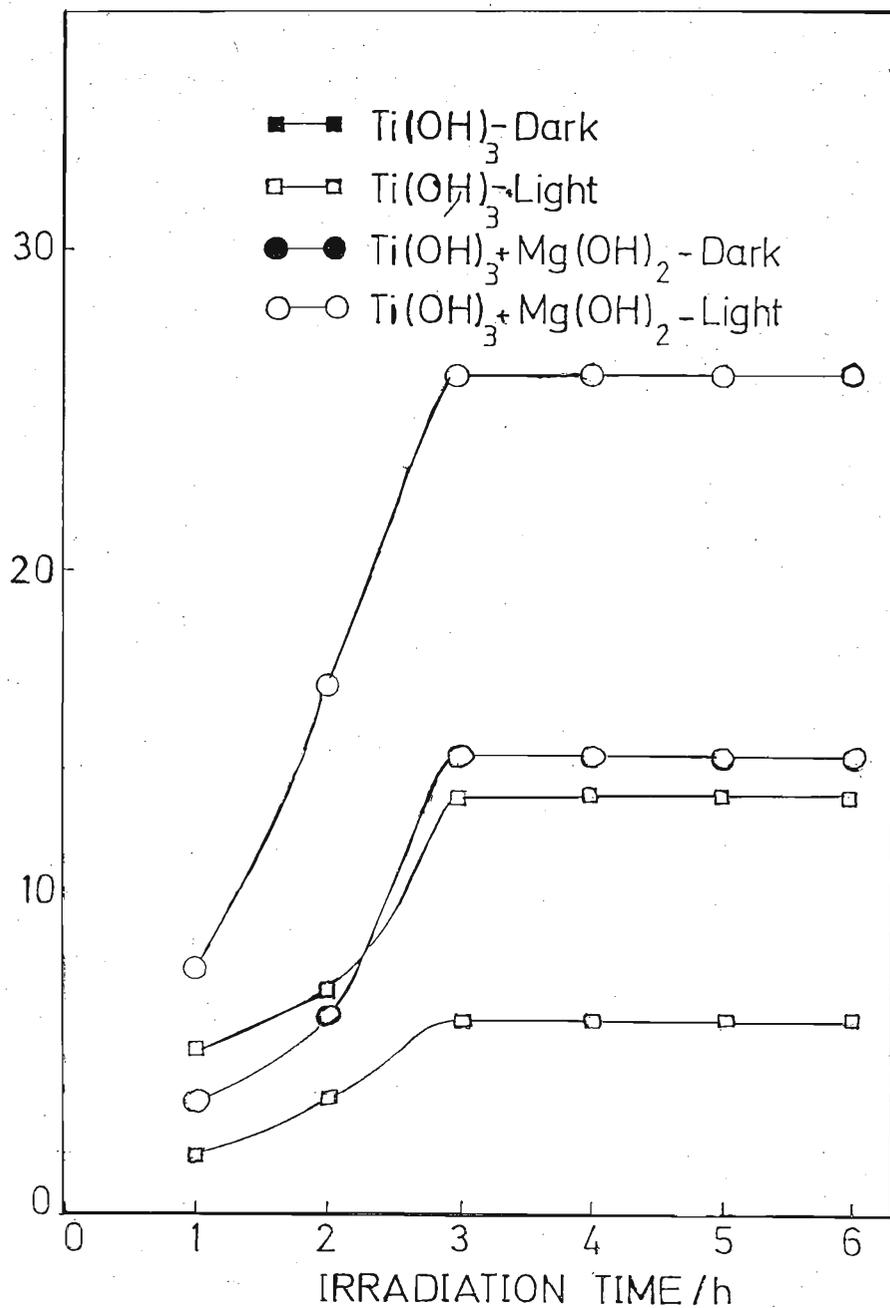


Figure 2: Variation of  $NH_3$  yields with time for aqueous suspensions.

The average standard deviations were as follows :

irradiation time  $\pm 0.08$  h,  $NH_3$  yield  $\pm 8\%$  below  $8 \mu M$  and  $\pm 6\%$  above  $8 \mu M$ .

Studies on the photoreduction of  $N_2$  by  $Ti^{3+}$  also have some relevance to the well known photocatalysts based on  $TiO_2$  and its metal doped modifications.<sup>10</sup> There is now well established evidence<sup>6</sup> for the formation of  $Ti^{3+}$  on irradiated rutile surfaces. Reduced titanium centres are apparently the reactive centres in the photoreduction of substrates such as  $N_2$  and  $C_2H_2$ .<sup>4</sup> Our results give direct evidence for the reduction of  $N_2$  to  $NH_3$  by  $Ti^{3+}$  in both homogeneous and heterogeneous media.

## References

1. BOLTZ, D. F. & HOWELL, J. A. (1978) Colorimetric determination of Nonmetals, John Wiley and Sons, New York.
2. DENISOV, N. T., EFIMOV, O. N., SHUVALOVA, N. I., SHILOV, A. E., & ZHUR, FIZ. KHIM. (1970) **44**, 2694.
3. DENISOV, N. T., SHUVALOVA, N. I., SHILOV, A. E. & KINET, KATAL (1974) **14**, 1325.
4. DISSANAYAKE, W.D.D.P., TENNAKONE, K. & ILEPERUMA, O.A. (1990) *Applied Catalysis* **62**, L1.
5. FERRAR, S. & SOMORJAI, G. A. (1980) *Surf. Sci.* **94**, 41.
6. KIWI, J. (1986) *J. Phys. Chem.*, **90** 1493.
7. KIWI, J. & GRAETZEL, M. (1986) *J. Phys. Chem.* **90**, 637.
8. LIU, N. H., STRAMPACH, N., PALMER, J. G. & SCHRAUZER, G. N. (1984) *Inorg. Chem.*, **23**, 2772.
9. SCHRAUZER, G. N. (1980) New Trends in the Chemistry of Nitrogen Fixation, Chatt, J., Camana Pina, G.L.M., Richards, R.L., Eds. Academic Press, New York, p. 103.
10. SCHRAUZER, G. N. & GUTH, T. D. (1977) *J. Amer. Chem. Soc.*, **99**, 7189.
11. SCHRAUZER, G.N., GUTH, T.D., SALEHI, J., STRAMPACH, N., HUI, L. N. & PALMER, M. R. (1986) Homogeneous and Heterogeneous Photocatalysis, Pelizzetti E., and Serpone N., Eds., Riedel publishing Co., New York, p. 509.
12. SCHRAUZER, G. N. & PALMER, M. R. (1981) *J. Amer. Chem. Soc.*, **103**, 2659.
13. SCHRAUZER, G. N. STRAMPACH, N., & HUGHES, L.A. (1982) *Inorg. Chem.*, **21**, 2184.
14. SHILOV, A.E. (1977) Biological Aspects of Inorganic Chemistry, Dolphin, D., Ed. Wiley, New York, p. 197.
15. SHILOV, A.E. (1980) New Trends in the Chemistry of Nitrogen Fixation, Chatt, J., Camana Pina, G.L.M., Richards, R.L., Eds. Academic Press, New York, p. 121.
16. WATT, G. W., CRISP, J.D. (1952) *Anal. Chem.* **24**, 2006.