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Hydrogen production by water photolysis using nitrilotriacetic acid as electron donor

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Abstract

Nitrilotriacetic acid was used as sacrificial electron donor for the photochemical production of hydrogen in a system containing $Ru(bipy)_3^{2+}$, methyl viologen, colloidal Pt catalyst and nitrilotriacetic acid. Highest turn-over numbers were approximately 175 for both methyl viologen and $Ru(bipy)_3^{2+}$, and greater than 250 for the Pt catalyst after 4 h irradiation at pH 4.5. After $6\frac{1}{2}$ h irradiation, 49% (8 mmol l^{-1}) of nitrilotriacetic acid was oxidised.

Keywords: Hydrogen production; Water photolysis; Nitrilotriacetic acid; Electron donors

1. Introduction

Photochemical reduction of water (protons) to yield hydrogen has been a matter of interest to scientists for the last two decades. Success has been reported using substances such as ethylenediaminetetraacetic acid (EDTA) as sacrificial electron donor for the reduction [1,2], but an efficient stable system for the photolysis of water to hydrogen and oxygen has so far not been reported. The reason for this is mainly the problems concerning the water oxidation, such as back reactions, sensitizer bleaching and catalyst corrosion [3]. A more feasible method to store solar energy photochemically is offered by the production of hydrogen with concomitant oxidation of appropriate waste compounds instead of the water oxidizing step. Encouraging investigations of systems producing hydrogen have been performed with substances such as triethanolamine [4], hydrogen sulphide [5,6] and ascorbic acid [7,8]. Nitrilotriacetic acid (NTA) is a compound acting as an excellent chelating agent. It is vastly used for complexometry, for sequestering heavy-metal ions and for softening water. In particular, in washing powders and cleaning agents, NTA is used as a replacement for phosphate. Large quantities of NTA acid are being used in industries, e.g. textile, paper and galvanic. In former West Germany, about 8000 t of NTA was produced in 1984. One third of this amount was used in the country itself. As a waste compound, problems arise because it increases the growth of seaweed.

Also in sediment deposits, heavy metals can be remobilized by NTA [9,10].

Under advantageous conditions, up to 95% of NTA could be biologically destroyed [9]. Also photo-oxidation of NTA has been described [11].

In the present paper, another possibility for oxidizing NTA photochemically is investigated, namely with concomitant hydrogen production. Furthermore, the photochemical behaviour of the corresponding di-(iminodiacetic) and mono-(aminoacetic) acids are examined.

2. Experimental details

All the substances, NTA (Riedel-de Haën), iminodiacetic acid (IDA) (Merck), aminoacetic acid (AAA) (Merck), tris(2,2'-bipyridyl) ruthenium(II) chloride hexahydrate $(Ru(bipy)_3^{2+})$ (Janssen Chimica), methyl viologen dichloride hydrate (MV^{2+}) (Aldrich Chemie), indicator buffer tablets (to determine the concentration of Ca^{2+} and Mg^{2+} in water) (Merck), $CaCl_2 \cdot 2H_2O$ (Merck), sodium citrate–acetic acid buffers (Merck), were reagent grade. The colloidal Pt catalyst was prepared according to [12]. Twice distilled water, free of Ca^{2+} and Mg^{2+}, was used.

The hydrogen production experiments were performed using a 250 W tungsten halide lamp with a water jacket enclosing the reaction cell. The light flux ($\lambda > 400$ nm) was 0.13 W cm^{-2}, measured with a Solrad solar radiation measurement system (Recom Electronics). The amounts of pro-

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duced hydrogen were measured with a GC-6000 gas chromatograph (Carlo Erba Instruments) fitted with 2 m packed columns (5 Å molecular sieve) and a HWD-430 with argon (5.0) as carrier gas. The reaction mixture (3.0 ml) was kept in a 1 cm optical cell with a silicon septum. The volume of the gas phase was 2.5 ml. Typical reaction mixture concentrations were as follows: $Ru(bipy)_3^{2+}$, 0.5 mmol l^{-1}; MV^{2+}, 2.0 mmol l^{-1}; NTA, 17 mmol l^{-1}; Pt catalyst, 10 mg l^{-1}; buffer, 0.2 mol l^{-1}. For calculation of turn-over numbers (TONs), the concentration of the substance of investigation was one order of magnitude less than usual.

To determine the consumption of NTA during the irradiation experiments, the following procedure was used. After an irradiation experiment, the reaction solution was diluted with water and 1 ml NH_3 solution (25%) to 50 ml and an indicator buffer tablet was added. This solution was titrated with a $CaCl_2$ solution (0.1 mol l^{-1}) (tests confirmed that 1 mol NTA corresponds to 1 mol Ca^{2+}).

3. Results and discussion

It is reported that NTA is only slightly soluble in water but quite good in hot alcohol [9,13]. However, this claim could not be verified in this paper. On the contrary, it was not possible to dissolve any detectable amounts of NTA at all in a boiling solution of ethanol even after boiling for several hours (at 1 atm). The problem with the insolubility of NTA in water was resolved by dissolving NTA in a dilute NaOH solution. However, the stock solution of the sodium salt of NTA (0.1 mol l^{-1}) prepared for the present work was stable for only a short time; after a few weeks, precipitation occurs and the ability of solutions to reduce $Ru(bipy)_3^{3+}$ is strongly diminished. Therefore only fresh prepared solutions of NTA were used in the present work.

Besides NTA, the possibility of oxidizing IDA and AAA was also investigated. With AAA instead of NTA, no hydrogen was produced. Furthermore, both AAA and IDA do not form complexes with Ca^{2+}. However, with IDA, small amounts of hydrogen are produced, 1% or less than the amounts produced with NTA under the same conditions (see also [14]). This means that a small number of the electrons necessary for the production of hydrogen came from IDA, originating from oxidized NTA [11].

A typical hydrogen production curve is presented in Fig. 1. In this case, 49% (about 8 mmol l^{-1}) of the NTA was oxidized after 6.5 h irradiation. For comparison, about 13 days were needed to oxidize 50% of NTA, without yielding any hydrogen, in a methanol:water (1:1) solution containing 60 mmol NTA l^{-1} and with rose bengal as sensitizer [11]. The decrease in the hydrogen production rate is partly due to reduced NTA concentration. Deactivation of the heterogeneous catalyst might also be responsible for the decreased hydrogen production rate. It has been reported that activity of noble metal catalysts decreases in the presence of IDA

[15]. The decline in the concentration of NTA is presented in Fig. 1.

The amount of hydrogen produced is dependent on pH as shown in Fig. 2 and on catalyst concentration as presented in Fig. 3. At higher catalyst concentrations, precipitation is enhanced, causing a decrease in catalytic activity and con-
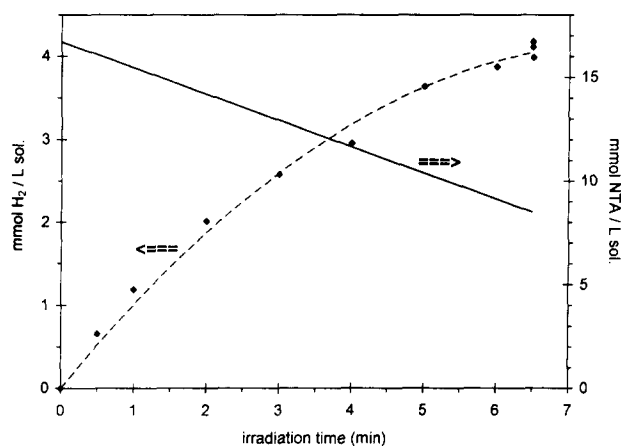

Fig. 1. Hydrogen production ($\blacklozenge$, - - -) as well as NTA concentration (—) upon irradiation. The hydrogen production rate for the first 120 min is 18 μmol min^{-1} (l solution)$^{-1}$.
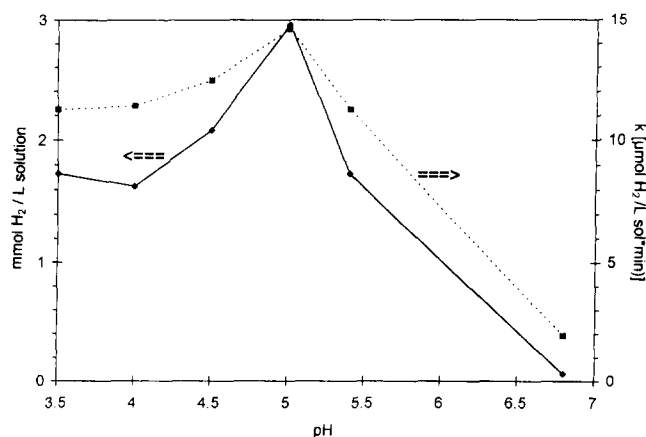

Fig. 2. Amount of hydrogen produced after 4 h irradiation (-$\blacklozenge$-) and hydrogen production rate (0–240 min), (-$\blacksquare$-) as functions of pH.
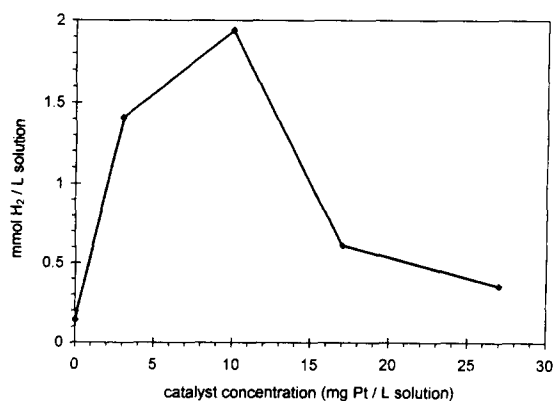

Fig. 3. Amount of hydrogen produced after 4 h irradiation as a function of catalyst concentration at pH 4.5.

sequently lower hydrogen production rates. The consumption of NTA during irradiation corresponds stoichiometrically to the quantity of hydrogen produced.

The pH dependence of methyl viologen upon irradiation is the same as with EDTA as sacrificial electron donor, i.e. at higher pH more methyl viologen is present in its reduced (blue) form [16]. From Figs. 2 and 3 and this information, it is concluded that mechanism of reduction is the same as with EDTA, i.e. via an intramolecular electron transfer within a methyl viologen radical-proton complex (CT protonation) [16].

The stability of the sensitizer was very high. After 4 h irradiation, only an insignificant decrease in the absorption of the sensitizer (less than 2%) could be observed.

4. Conclusion

After $6\frac{1}{2}$ h, almost 50% of the NTA could be photochemically oxidized with visible light with simultaneous stoichiometric hydrogen production. The investigation presented in the current work could offer a principal novel way to remove NTA from polluted waters.

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