

# The kinetic study of photoreduction of tetrachloroaurate acid by methanol in acidic media



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## ABSTRACT

The aim of this study was the spectroscopic investigation of the mechanism of the reduction of gold(III) chloride complex ions in an aqueous methanol solution, illuminated at 405 nm. It has been shown that the gold(III) chlorate complex ions are reduced mainly to the gold(I) chloride complex ions with methanol only in the presence of light. The illumination must be within the range of the  $\text{AuCl}_4^-$  absorption. Kinetic studies have indicated that the reduction is first order with respect to both methanol initial concentration and light intensity, whereas the influence of gold(III) chloride complex ions initial concentration is more complicated. It has also been shown that the precipitation of a solid phase occurs mainly via the disproportionation of the  $\text{AuCl}_2^-$  ions. Moreover, illumination at 405 nm during the disproportionation process, results in the oscillation of the gold(III) chloride complex ions concentration.

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## 1. Introduction

There are several known methods of gold(III) chloride complex ions removal from aqueous solutions that are of industrial importance. Namely, adsorption on activated carbon [1,2], chemical reduction [3], ion exchange [4] and photoreduction using a semiconductor, usually titanium dioxide, as a photocatalyst [5–7]. There is also plenty of known photochemical processes of  $\text{AuCl}_4^-$  reduction [8–20] that are usually applied in order to obtain gold nanoparticles.

It is also well known that molecules in their excited states undergo reduction or oxidation much easier than in their ground states [21]. Therefore, there is a possibility of gold(III) chloride complex ions photoreduction using a reductant that is not able to reduce  $\text{AuCl}_4^-$  in the absence of light, or where the reaction rate is very slow, for instance ethylene glycol [12]. The condition that must be fulfilled is illumination within the range where gold(III) chloride complex ions absorb light according to Grotthuss–Draper law. Although Eustis et al. [12] thoroughly studied the mechanism of gold nanoparticles formation obtained during photoreduction with ethylene glycol via the disproportionation of gold(I) chloride complex ions, the mechanism of gold(III) chloride complex ions photoreduction has not been analyzed.

Quinn and Mills [22] investigated  $\text{AuCl}_4^-$  ions reduction in a basic solution of methanol. They found that at a sufficiently high pH,

in  $\text{CH}_3\text{OH}$  solution, ligand exchange reaction occurs, and one chloride ion is displaced by a methanol molecule which is subsequently oxidized by the metal center. Malone et al. in turn, studied the kinetics of gold crystallites formation in photoresponsive polymer gels, in the presence of methanol, and indicated that the reduction mechanism involves a hydroxymethyl radical as an intermediate [13]. Therefore, to the best knowledge of the authors, the kinetic study of the gold(III) chloride complex ions photoreduction with methanol in acidic solution has not been performed yet.

The photoreduction may open a possibility of the selective reduction of for instance  $\text{AuCl}_4^-$  from a solution containing a mixture of various metal ions by illumination within appropriate wavelength range. Detailed knowledge about the mechanisms of photoreduction and precipitation of solid phase, should be very useful in terms of a future attempt to separate and recover metals from dilute solutions e.g. from wastewater.

The aim of this work was the detailed investigation of the mechanism of gold(III) chloride complex ions photoreduction, i.e. the determination of the influence of light intensity as well as initial concentrations of both  $\text{AuCl}_4^-$  and  $\text{CH}_3\text{OH}$  on the kinetics of the process. In addition, the disproportionation reaction in the dark and under illumination was also examined.

## 2. Experimental

Gold(III) chloride complex ions used in all the experiments were obtained by the dissolution of metallic gold in aqua regia as was described in the authors previous work [23]. All other reagents were of analytical grade, obtained from the POCH S.A., Poland. The

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stock solution composed of  $\text{AuCl}_4^-$  and HCl at concentrations of  $10^{-3}$  M and 0.02 M, respectively, was prepared. Pure methanol was applied as the reducing agent. An absorption coefficient of  $\text{AuCl}_4^-$  at pH=2 and  $[\text{Cl}^-]=0.01$  M was determined using the well-known Lambert-Beer law (1). Absorbance was measured in 1 or 0.1 cm quartz cuvettes using a Shimadzu U-2501 PC UV-Vis spectrophotometer at 314 and 226 nm for  $\text{AuCl}_4^-$  concentrations equal to  $10^{-3}$ ,  $5 \times 10^{-4}$ ,  $10^{-4}$ ,  $5 \times 10^{-5}$  and  $10^{-5}$  M.

Photoreduction experiments were conducted as follows. The stock solution containing  $\text{AuCl}_4^-$  was mixed with methanol in 4 ml quartz cuvette, placed in a box, which was made of mirrors, illuminated with a LED illuminator (Instytut Fotonowy Sp. z o.o., Poland) and vigorously stirred. Every photoreduction experiment was repeated three times. Decrease of  $\text{AuCl}_4^-$  concentration with time was measured spectrophotometrically. The inner surface of the box was made of the mirrors in order to ensure a uniform irradiation of the reaction vessel and thus reproducible experiments.

In all the photoreduction experiments illuminate of 405 nm, where  $\text{AuCl}_4^-$  ions absorb light was applied. In order to clarify, if the  $\text{AuCl}_4^-$  excited state is really involved in the investigated process, the additional experiment at 630 nm, where there is no absorption, was also performed at the same concentrations of the reagents and radiant flux density.

In order to determine the mechanism of photoreduction of gold(III) chloride complex ions with methanol, the influence of the initial concentration of reagents and light intensity on the reaction rate was investigated. Firstly, photoreduction was performed for different methanol initial concentrations (i.e. 25, 18.75, 12.5, 6.25 and 0% v/v) at constant  $\text{AuCl}_4^-$  initial concentration (equal to 50% v/v which is equivalent to  $5 \times 10^{-4}$  M), secondly, for different  $\text{AuCl}_4^-$  initial concentrations (i.e. 15.625, 25, 37.5 and 50%, v/v) at the constant methanol initial concentration (25%, v/v). Radiant flux density was equal to 414 mW/cm<sup>2</sup>, pH and  $\text{Cl}^-$  concentration were set at the level of 2 and 0.01 M respectively by addition of appropriate amount of 0.02 M HCl. Deionized water was added to obtain a total volume of 4 ml. The influence of light intensity was investigated for methanol initial concentration equal to 25% (v/v) and  $\text{AuCl}_4^-$  50% (v/v). All concentrations are further expressed in terms of molar concentrations. The light intensity was varied from 414 down to 51.5 mW/cm<sup>2</sup>.

The kinetic curves of the decrease of  $\text{AuCl}_4^-$  concentration with time were recorded by a UV-Vis Agilent 8453 spectrophotometer. A simple exponential decay curve (5) was fitted to the data points using TableCurve software and the observed rate constant  $k_{\text{obs}}$  was obtained from each kinetic curve. Error bars presented on the graphs correspond to the standard deviation of the mean of three data points. The initial rate method was also applied to determine the reaction order in respect to  $\text{AuCl}_4^-$  initial concentration. A tangent was drawn to each kinetic curve at time  $t=0$  point and, from the slope, the initial rate  $V_0$  was obtained. The reaction order with respect to gold(III) chloride complex ions initial concentration was found as a slope of the straight line in the logarithmic plot (logarithm of the initial reaction rate vs. logarithm of the initial  $\text{AuCl}_4^-$  concentration).

Concurrently to  $\text{AuCl}_4^-$  reduction, methanol was oxidized to formaldehyde which was identified using chromotropic acid disodium salt (POCH P.A.), corresponding to E. Fagnani [24] method with some modifications. In the procedure of formaldehyde determination, 1 mL of analyzed sample was mixed with 1 mL of 5% (m/v) water solution of freshly prepared chromotropic acid and 4 mL of concentrated sulphuric acid. The concentration of formaldehyde in this system is proportional to the absorbance at the wavelength 576 nm. Absorption coefficient of chromogen arising from the reaction of chromotropic acid and formaldehyde was determined using 1 cm quartz cuvette. As the reference, the sulfuric (96%) acid was used.

Formaldehyde formed during the photoreduction as a product of methanol oxidation, may also reduce gold(III) chloride complex ions. Thus, the kinetics of reduction of  $\text{AuCl}_4^-$  with formaldehyde was investigated both in the dark and under illumination at 405 nm. During these experiments, initial concentrations of  $\text{AuCl}_4^-$  and formaldehyde were equal to  $5 \times 10^{-4}$  M and 0.05 M, respectively. Chloride ions concentration and pH were at the same level as previously.

Since disproportionation may be responsible for precipitation of Au solid phase, absorption spectra of the solution after photoreduction were also recorded both in the dark and under illumination at 405 nm with radiant flux density equal to 414 mW/cm<sup>2</sup>. Moreover, a test for the presence of a free radical during photoreduction was performed by addition of 20% (w/v) acrylamide (purity  $\geq 98\%$ , purchased from Fluka) aqueous solution to the irradiated reaction [25].

### 3. Results

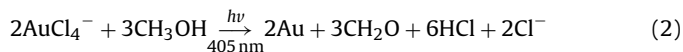
Thermodynamic calculations performed using data taken from Mironov and Makotchenko [26] confirm that under experimental conditions (the pH=2,  $[\text{Cl}^-]=0.01$  M) only  $\text{AuCl}_4^-$  is present in solution and no hydrolysis occur.

In order to determine the gold(III) chloride complex ions concentration spectrophotometrically, the molar absorption coefficient  $\epsilon$  for given conditions was calculated from the Lambert-Beer law (1):

$$A = [\text{AuCl}_4^-] \cdot l \cdot \epsilon \quad (1)$$

where  $l$  is the path length and  $A$  the absorbance measured for the given concentrations of absorbing species  $[\text{AuCl}_4^-]$ . The molar absorption coefficient was determined as equal to  $5932 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$  and  $43,585 \pm 204 \text{ M}^{-1} \text{ cm}^{-1}$  for 314 nm and 226 nm, respectively. Obtained values are in good agreement to the literature [23]. It should be emphasized, that studied system should be treated as semi aqueous, due to relatively high concentration of methanol up to 25% (v/v). The values of absorption coefficient for non-aqueous media, are also comparable to the obtained one [27,28].

The reaction mixture containing gold(III) chloride complex ions and methanol was illuminated at 405 nm and a decrease in the  $\text{AuCl}_4^-$  concentration with time was observed. This effect was measured spectrophotometrically as a exponentially decreasing intensity of  $\text{AuCl}_4^-$  absorption peak at 314 nm (Fig. 1A and B). It is possible to see that at 405 nm  $\text{AuCl}_4^-$  molecules still absorb light, whereas at 630 nm there is essentially no absorption, and illumination at 630 nm does not result in decrease of  $\text{AuCl}_4^-$  concentration. Therefore,  $\text{AuCl}_4^-$  excited state must be involved in the reduction mechanism. Based on this observation, the following description of the reaction occurring in the system was proposed:



When practically no  $\text{AuCl}_4^-$  species were present in the solution, light was switched off and slow precipitation of solid phase was observed. Therefore, at first step, under illumination at 405 nm, gold(III) chloride complex ions must be reduced with methanol to gold(II) or gold(I) chloride complex ions. Methanol in turn is oxidized presumably to formaldehyde. Disproportionation in the dark may be responsible for solid phase precipitation.

The general equation, describing the reaction rate  $V$  of the studied process, may be formulated as follows (3):

$$V = -\frac{d[\text{AuCl}_4^-]}{dt} = k[\text{CH}_3\text{OH}]^\alpha \cdot [\text{AuCl}_4^-]^\beta \cdot \Phi^\gamma \quad (3)$$

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