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Photo-oxidation of Thioacetamide by Uranyl Ions

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Photo-oxidation of thioacetamide by uranyl ions in presence of perchloric acid has been studied, at pH 2.0. Acetamide, sulphur and sulphur dioxide have been characterized as the products. The intermediacy of uranium(V) has been proved spectrophotometrically. A mechanism has been proposed involving excited state charge transfer complex (exciplex) formation.

INTRODUCTION

Organo-sulphur compounds are chiefly employed in pharmaceuticals[1], pesticides[2, 3] and other technically important classes of compounds[4]. The fate of their environmental degradation is mainly photo-oxidation in presence of photocatalysts or photosensitizers present in the atmosphere and water[5, 6]. It is believed that minute quantities of uranyl ions are present in natural waters as uranyl carbonato complexes[7] and its photochemical behaviour can be understood in presence of light. Uranyl compounds are widely used as photosensitizers in the oxidative reactions[8–12]. The literature reveals that no attention has been paid to the uranyl ions sensitized photo-oxidation of thioacetamide, so it is proposed to undertake the title investigation.

EXPERIMENTAL

Thioacetamide (Merck, m.p. 111°C), uranyl acetate (BDH), perchloric acid (Merck, 60%) and methanol (BDH) were used. Thioacetamide was recrystallized before use. Methanol and other solvents were doubly distilled. All other chemicals were used directly without further purification. Silica gel G (Merck), acetone (Merck, freshly distilled) and resublimed iodine were used for thin layer chromatography analysis.

The pH of the solutions was determined by Systronics-335 digital pH meter. Spectrophotometric studies were performed on Systronics 106 (Mk-II) spectrophotometer. Infrared spectra were scanned on Perkin-Elmer Grating-377 spectrophotometer.

The reaction mixture was prepared by dissolving thioacetamide (1.58 g) in methanol and appropriate amounts of prepared solutions of uranyl acetate and perchloric acid were added to it, so that the concentration of different ingredients in the reaction mixture was thioacetamide 0.2 mol L^{-1}, uranyl acetate

0.002 mol L^{-1} and perchloric acid 0.006 mol L^{-1}. The pH of the solution was measured and found to be 2.0. The solution was irradiated with light source (Tungsten lamp, Sylvania, 3 × 200 W). The distance between the lamps and the reaction vessel is 30 cm. Water cells (15 cm) were placed between the light source and reaction vessel to cut off thermal radiations. Oxygen gas was purged in the solution, at the rate of 2.01 min^{-1}. This served two purposes, (i) continuous stirring of the reaction mixture and (ii) regeneration of U(VI) from U(IV).

The outcoming gas was trapped in acidified solution of dichromate, which was reduced to Cr(III) showing that SO_2 has formed. After 3 h an amorphous solid started to separate (recrystallized, m.p. 118°C). The solid was found to be sulphur. It was treated with a drop of aqueous NaOH and a drop of $KMnO_4$, which rapidly decolorized the colour, indicating that thiosulphate is present in the solution. A black precipitate of lead sulphide was obtained, when this solution was treated with lead acetate. This also confirms the presence of sulphide ions and sulphur. The TLC was run using acetone as solvent. Two spots were obtained, one corresponding to the photo product ($R_f = 0.77$) and another to the substrate ($R_f = 0.84$).

After 8 h the reaction was stopped. The product was identified as acetamide (25%) and sulphur (5%). The unreacted thioacetamide (75%) was recovered.

Control experiments were also performed in the presence of:

(i) light and uranyl ions (no oxygen was passed).

(ii) uranyl ions and oxygen (no exposure to light).

(iii) light and oxygen (no uranyl ions added).

No product was obtained in the last two cases, and the yield was very low in the first case. So it may be concluded that uranyl ions and light is necessary for the photo-oxidation of thioacetamide and oxygen is required to regenerate U(VI) from U(IV) and hence increasing the product[13]. The presence of acid assists in decomposition of [Sub . . . UO_2^{2+}] exciplex into the product[11].

RESULTS AND DISCUSSION

In all the experiments sulphur, sulphur dioxide and acetamide were the products. Sulphur and sulphur dioxide were confirmed by the usual tests. The major product acetamide (recrystallized, m.p. 82°C) was characterized by physical, chemical and spectral data.

It was treated with NaOH solution; the smell of ammonia shows that it is a primary amide. When the photo product was heated with aniline, ammonia evolves out and acetanilide (m.p. 114°C) is formed. The picrate (m.p. 107°C) was also prepared[14].

The absorption band at 1670 cm^{-1} in IR spectrum confirms the >C═O group, whereas the absence of absorption in the region 1300–1100 cm^{-1} shows absence of >C═S group.

When solutions containing uranyl ions and thioacetamide were irradiated, the absorbance decreased and uranium(IV) was produced and it was found that the spectrophotometric concentration of uranium(IV) increased over a period of about 30 min after illumination was stopped. This effect was explained assuring that an intermediate uranium(V) species was formed as a consequence of the photochemical electron transfer from the thioacetamide to uranyl ions and that the subsequent thermal disproportionation of intermediate uranium(V) to uranium(IV) and uranium(VI) occur. Further the formation of uranium(V) was estabished using electron absorption studies in the photochemical reduction of uranyl ions by thioacetamide in dry acetone medium. Uranium(V) is not detected in aqueous acidic medium during the photochemical reduction of the uranyl ions with thioacetamide due to its rapid disproportionation to uranium(VI) and uranium(IV). The formation of uranium(V) complexed with thioacetamide shows characteristic peaks of uranium(V) in ionic medium appearing at 660 nm. However, on addition of perchloric acid the absorbance peak of uranium(IV) appear at 550 nm and 642 nm; the uranium(VI) shows peaks at 430, 440, 450 and 472 nm. The uranyl ions absorb strongly at 420 nm and no distinct bands in the region between 500–700 nm and uranium(IV) absorbs weakly at 420 nm. No absorption peaks of uranium(IV) appear after prolonged irradiation. In the reaction mixture the uranium(VI) is only photoexcited by radiation in visible region. From a mechanistic point of view the uranyl ion in the excited state abstracts an electron from the sulphur atom in the thioacetamide yielding an exciplex with the uranyl ion and thus resulting in the formation and stabilization of uranium(V). The formation of sulphur centred radical in the photo-reduction of uranyl ions with sulphur compounds has already been established, and the mechanism of quenching has already been discussed in the fast reversible electron transfer and the intermediacy of exciplex. After addition of perchloric acid a sharp band indicates the formation of uranium(VI) together with uranium(IV). Thus, uranium(IV) formation during the photochemical reduction of uranyl ions by thioacetamide in aqueous acidic medium is the secondary reaction of disproportination of uranium(V) formed in the primary step. Uranium(V) is known to disproportionate in an acid catalysed process, but is moderately stable above pH 2.0[9, 11, 15].

Taking all the observations into consideration a mechanism can be proposed as in Fig. 1.

$$\begin{tikzcd} & {\mathrm{Sub} + \mathrm{UO_2^{2+}}} \arrow[r, shift left, "h\nu"] & {[\mathrm{Sub} \ldots \mathrm{UO_2^{2+}}]} \arrow[l, shift left] \arrow[dl] \\ {[\mathrm{Sub^{+}} \ldots \mathrm{UO_2^{+}}]} \arrow[r] & {\mathrm{P} + \mathrm{S} + \mathrm{UO^{2+}}} & \end{tikzcd}$$

$$\mathrm{S} + 2\mathrm{UO_2^{2+}} \xrightarrow{h\nu} \mathrm{SO_2} + 2\mathrm{UO^{2+}}$$

$$2\mathrm{UO^{2+}} + \mathrm{O_2} \xrightarrow{h\nu} 2\mathrm{UO_2^{2+}}$$

where, $\mathrm{Sub} = \mathrm{CH_3CSNH_2}$ and $\mathrm{P} = \mathrm{CH_3CONH_2}$

Fig. 1 Mechanism of photochemical oxidation of thioacetamide by uranyl ions.

The charge transfer from thioacetamide (Sub) to the excited uranyl ion results into formation of the exciplex $[\mathrm{Sub^{+}} \ldots \mathrm{UO_2^{+}}]$ (excited state charge transfer complex). This exciplex is a short-lived species in acidic medium and decomposes to give acetamide (P), sulphur (S) and uranium(IV). A part of sulphur is oxidized by excited uranyl ions to sulphur dioxide. U(IV) so produced is converted to U(VI) by the action of light and oxygen[16], and hence a steady state concentration of uranyl ion is maintained.

The above mechanism is in conformation with the results reported earlier[7, 11]

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