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Photochemical Oxidation of 2-Imidazolidinethione by Uranyl Acetate

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Photochemical oxidation of 2-imidazolidinethione by uranyl acetate in presence of perchloric acid has been studied at pH 2.0. 2-Imidazolidone, sulphur, sulphur dioxide and sulphuric acid have been characterized as the photoproducts. The presence of uranium(V) as an intermediate has been proved spectrophotometrically. A probable mechanism has been proposed involving excited state charge transfer complex (exciplex) formation.

INTRODUCTION

The photochemistry provides an effective way of understanding the interaction of light with atoms and molecules and measuring devices of extremely high sensitivity and accuracy are now available. The applications of photochemistry, ranging from photography to photomedicine, are of great importance to us[1]. Many heterocyclic compounds, including drugs, are responsible for phototoxic or photoallergic behaviour[2]. Recent investigation of photo-sensitized oxidation have led to better understandng of chemical processes and the results are now finding applications in the biological field[3]. During the recent past, a lot of work has been initiated in the area of organo-sulphur chemistry primarily due to presence of sulphur atoms, which offer reactive sites for environmental degradation and matabolic pathways[4–6]. Uranyl acetate photochemical oxidation of 2-imidazolidinethione has not been studied so far[7]. The uranyl carbonato complexes are believed to be present in natural waters and their photoexcitation is due to sunlight[8]. It is therefore proposed to study the photochemistry of 2-imidazolidinethione to throw some more light on photochemical behaviour of uranium.

EXPERIMENTAL

2-Imidazolidinethione (Fluka, recrystallized, m.p. 198°C), uranyl acetate (BDH), perchloric acid (BDH) and methanol (BDH) were used to prepare all the solutions. Acetone (BDH) was used after drying over anhydrous calcium chloride. Photochemical oxidations were carried out in Borosil glasswares and all the reactions were performed using dried equipments. Oxygen was continuously purged with the help of an aerator. TLC was run on glass plates (7.5 × 2.5 cm) coated with silica gel G (Merck) using freshly distilled solvents. Silica gel G (100–200 mesh) was used as adsorbent and iodine (Merck) resublimed was used as spot developer. All melting points were recorded on a Reichert-Kofler apparatus. pH measurements were done on a Systronics-335 digital pH meter. Spectrophotometric studies were performed on a Systronics-106 (Mk-II) spectro-

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photometer. IR spectra (ν_{max} cm^{-1}) were scanned on a Perkin-Elmer Grating-377 spectrophotometer. Elemental analyses were carried out using Carlo-Erba-1106 automatic analyzer. 2-Imidoxolidinethione (1.8 g) was dissolved in methanol, solutions of uranyl acetate (20 mL, 0.01 M) and perchloric acid (6 mL, 0.1 M) were added to it and the total volume was made 100 mL. The concentration of different ingredients in the reaction mixture was 2-imidazolidinethione 0.2 M, uranyl acetate 0.002 M and perchloric acid 0.006 M. The pH of the reaction mixture was 2.0. The reaction mixture was irradiated with light source (Tungsten lamp, 3 × 200 W, Sylvania) maintaining a distance of 30 cm between the light source and reaction vessel to eliminate heat radiation. Oxygen gas (2.01 min^{-1}) was continuously bubbled through the reaction mixture. This served two purposes[9]:

(i) Continuous stirring of the reaction mixture.
(ii) Maintenance of steady state concentration of uranyl ions by conversion of UO^{2+} to UO$_2^{2+}$.

The progress of the reaction was followed by TLC using *n*-butanol : acetic acid : water 4 : 1 : 5 (v/v) as solvent system at every 2 h intervals. The spots were developed by placing the TLC plate in iodine chamber. Only one spot, corresponding to the parent compound, has been shown in the initial stages of the reaction. The evolved gas was passed through an acidified potassium dichromate solution. Chromium(III) was formed, which confirms the presence of sulphur dioxide in the gas. Sulphuric acid was confirmed as a photoproduct, giving a white precipitate with barium chloride. It may form due to some SO_2 dissolved in the reaction mixture in presence of water and uranyl ions. After 7 h of irradiation an amorphous solid started to appear in the reaction vessel (recrystallized, m.p. 118°C) which was characterized as sulphur. It was treated with aqueous NaOH and a drop of $KMnO_4$, which rapidly decolourized indicating that thiosulphate is present in the solution[10]. 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 hence sulphur[11]. It was observed that the TLC plate of solution gave two spots, one corresponding to the original 2-imidazolidinethione ($R_f = 0.82$) and another corresponding to the photoproduct ($R_f = 0.72$). The reaction was allowed to go for completion (15 h) and the reaction mixture was filtered to separate the precipitated sulphur. The photoproduct was separated as 2,4-dinitrophenyl hydrazone derivative[12]. 2-Imidazolidone was identified as the

TABLE-1
ABSORPTION SPECTRAL CHARACTERISTICS OF 2-IMIDAZOLIDINETHIONE AND 2-IMIDAZOLIDONE

2-Imidazolidinethione $(cm^{-1})^{13-15}$	2-Imidazolidone $(cm^{-1})^{13-15}$	Assignment
2960	2960	—CH_2
—	1660	>C=O
1538	1508	N—H
1459, 1368, 980	1488, 1449, 980	—CH_2
1273, 1042	1270, 1103	Ring
1208	—	>C=S

photoproduct and the spectral analyses were also performed to confirm. The spectral data are discussed in Table-1.

The structure was further confirmed by quantitative elemental analysis of the photoproduct 2-imidazolidone; the results are as follows:

Found : C = 41.72%, H = 6.90%, N = 32.60%

For $C_3H_6N_2O$ Calculated : C = 41.86%, H = 6.97%, N = 32.56%

RESULTS AND DISCUSSION

2-Imidazolidone was detected as the major photoproduct together with sulphur, sulphur dioxide and sulphuric acid, which were confirmed by their usual tests. 2-Imidazolidone was confirmed by physical, chemical and spectral analysis. The IR analysis shows absorption peak at 1660 cm^{-1}, indicating the presence of (>C═O) group and no absorption peak at 1208 cm^{-1}, which confirms the absence of (>C═S) group in the photoproduct. After separation of sulphur the filtrate (2 mL) was evaporated to dryness in a test tube and a drop of phenyl hydrazine was added. This mixture was then kept at 195°C for 5 minutes in an oven and after cooling, 5 drops of 1 : 1 ammonia and 10% nickel sulphate solution were added. This solution was shaken with chloroform. A red violet colour indicates the presence of substituted amide[11]. The irradiated solution was treated with sodium nitroprusside and sodium hydroxide solution. A dark colour appeared indicating the presence of ketonic group (>C═O). 2-4-Dinitrophenyl hydrazone derivative (recrystallized, m.p. 196°C) also confirms the photoproduct to contain ketonic group (>C═O)[12].

The control experiments were performed; the reaction was carried out in presence of:

(i) Uranyl ions and oxygen (no exposure to light).

(ii) Light and oxygen (no uranyl ions added).

(iii) Uranyl ions and light (no oxygen was bubbled).

It was found that no photoproduct had formed in the first two cases, and the yield was very low in the third case, indicating that uranyl ions and light are necessary for the reaction and oxygen increases the yield of the photoproduct. The U(V) species is short-lived in acidic solution and disproportionates to U(IV) and U(VI). The U(IV) reacts with oxygen in presence of light to give U(VI), hence maintaining a steady state concentration of uranyl ions and hence increasing the yield of the photoproduct[16].

When solutions containing uranyl ions and 2-imidazolidinethione 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 2-imidazolidinethione to uranyl ions and that the subsequent thermal disproportionation of intermediate uranium(V) to uranium(IV) and uranium(VI) occurs. Further, the formation of uranium(V) was established using electron absorption studies in the photochemical reduction of uranyl ions by 2-imidazolidinethione in dry acetone medium. Uranium(V) is not detected in aqueous acidic medium during the photochemical reduction of the uranyl ions with 2-imidazolidinethione due to its rapid disproportionation to uranium(VI) and uranium(IV). The formation of uranium(V) complexed with 2-imidazolidinethione by the addition of perchloric acid to the irradiated solution shows characteristic peaks of uranium(V) in ionic medium appear at 660 nm. However, on addition of perchloric acid the absorbance peaks of uranium(IV) appear at 500 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 band appears in 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 2-imidazolidinethione yielding an exciplex with the uranyl ion and thus resulting in the formation and stabilization of uranium(V). The formation of sulphur-centered radical in the photo-reduction of uranyl ions with sulphur compounds 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 2-imidazolidinethione in aqueous acidic medium is the secondary reaction of disproportionation 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[16–18].

All observations taken together in consideration suggest the probable mechanism for the sensitized photo-oxidation of 2-imidazolidinethione by uranyl ions as given in Fig. 1.

$$\text{Sub} + UO_2^{2+} \overset{h\nu}{\rightleftarrows} [\text{Sub} \ldots UO_2^{2+}]$$

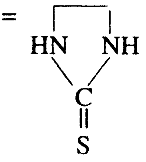
$$[\text{Sub}^{+} \ldots UO_2^{+}] \xrightarrow{H^{+}} P + S + UO^{2+}$$

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

$$SO_2 + H_2O + UO_2^{2+} \xrightarrow{h\nu} H_2SO_4 + UO^{2+}$$

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

where, Sub =



and P =

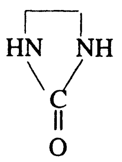


Fig. 1 Mechanism of photochemical oxidation of 2-imidazolidinethione by uranyl acetate.

Firstly, the substrate 2-imidazolidinethione (Sub) forms exciplex $[\text{Sub} \ldots UO_2^{2+}]$[16, 18] with excited uranyl ions, this exciplex has a short life time under the acid medium and decomposes into 2-imidazolidone (P), sulphur (S) and UO^{2+}. Some sulphur (S) is converted to sulphur dioxide (SO_2) which gets dissolved in the reaction mixture to give sulphuric acid (H_2SO_4) in the presence of water and UO_2^{2+}. UO^{2+} so produced reacts with oxygen to yield UO_2^{2+}.[19]

The mechanism (Fig. 1) is in agreement with the work reported by Crank & Mursyidi[6] and Chaudhary[9].

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