Photo-assisted reactions of thiourea with H$_2$O$_2$, Fenton and other related reagents

S K Sharma, Rekha Vaidya & V K Vaidya*
Department of Chemistry, M L V Government P G College, Bhilwara 311 001, India
Received 31 July 2002; revised 3 September 2003

Photo-assisted reaction of thiourea with H$_2$O$_2$, Fenton reagent (H$_2$O$_2$ + FeSO$_4$) and other related reagents (H$_2$O$_2$ + U(VI)/methylene blue) have been studied. The rate of photochemical reaction increases with increase in [substrate], [H$_2$O$_2$], [H$^+$] and increases with increase in polarity of solvents. The rate of oxidation of thiourea shows marked increase with other related reagents. Involvement of free radicals have been confirmed. A probable mechanism has been proposed.

Investigation of photochemical reaction of H$_2$O$_2$ contributes to the development of theoretical knowledge of mechanism of photoinitiated and photocatalytic reactions$^1$. Fenton’s reagent [H$_2$O$_2$ + FeSO$_4$] is used to treat a variety of industrial wastes to convert toxic and bio-resistant organic and inorganic compounds in aqueous solution to harmless species$^{2-6}$. Thiourea and its derivatives are carcinogenic compounds. Contaminants coming from industries, agriculture, domestic use and environment also possess sulphur compounds$^{7-10}$. It is difficult to decompose them by biodegradation through bacteria$^9$. Photo-oxidation of organo-sulphur compounds have been studied$^{11-14}$, but photo-assisted reactions with H$_2$O$_2$, Fenton’s and other related reagents is not known so far. Hence title investigation was undertaken.

Experimental
Thiourea (E Merck), H$_2$O$_2$ (E Merck), ferrous sulphate (E Merck), uranyl acetate (BDH England), methylene blue (MB, Aldrich CI 52015), sulphuric acid (BDH AR) and doubly distilled water and distilled methanol were used. The concentration of various ingredients in the reaction mixture were [Thiourea] = 10.0x10^-2 mol dm$^{-3}$, [H$^+$]=5.0x10^-2 mol dm$^{-3}$, [H$_2$O$_2$] = 6.0x10^-3 mol dm$^{-3}$, [FeSO$_4$] = 4.0x10^-4 mol dm$^{-3}$, [U(VI)] = 4.0x10^-4 mol dm$^{-3}$, [MB] = 4.0x10^-4 mol dm$^{-3}$. H$_2$O$_2$ was added at last in the reaction mixture. The reaction mixture was irradiated with visible light (2x200 W tungsten lamp) and kept at a distance of 30 cm from reaction vessel. A water filter was placed between light source and reaction vessel to avoid heating effect. Air was continuously bubbled through the reaction mixture for stirring purpose and for availability of oxygen. The progress of reaction was studied by regular TLC analysis (butanol:acetic acid (9:1) solvent system) and chemical tests. After 5 h of irradiation, an amorphous solid appeared which consisted of substrate (rf 0.81), and the photoproduct (rf 0.62). The reaction was stopped after 720 min and reaction mixture filtered. The solid residue was confirmed as sulphur by its usual tests (recrystallized m.p. 118°C). In the filtrate, the photoproduct was identified as urea (m.p. 132°C). Control experiments were performed and concluded that H$_2$O$_2$, light and H$_2$SO$_4$ are necessary for photo-assisted reaction of thiourea.

Results and discussion
The rate of reaction depended upon the concentration of various reagents like substrate, H$_2$O$_2$, [H$^+$] and solvents under the conditions, [H$_2$O$_2$] (6%) = 6.0x10^-3 mol dm$^{-3}$ and [H$^+$] = 5.0x10^-2 mol dm$^{-3}$, in methanol the reaction went to completion in 1440, 1080, 720, 600, and 480 min where 10$^2$ [thiourea] was 5, 7.5, 10.0, 12.5 and 15.0 mol dm$^{-3}$ respectively. The rate of reaction increased as the concentration of substrate increased. In methanol under the conditions, [Thiourea]=10.0x10^-2 mol dm$^{-3}$ and [H$^+$]=5.0x10^-2 mol dm$^{-3}$, reaction completion time decreases from 900 to 300 min when 10$^2$ [H$_2$O$_2$] was increased from 3.0 to 15.0 mol dm$^{-3}$. Under the conditions, [Thiourea]= 10.0x10^-2 mol dm$^{-3}$ and [H$_2$O$_2$] (6%) = 6x10^-3 mol dm$^{-3}$ in methanol, reaction completion time decreased from 1200 to 690 min when 10$^2$[H$^+$] was increased from 1.25 to 6.25 mol dm$^{-3}$.

With increase in solvent polarity, the rate of reaction increased. Photo-oxidation of thiourea with H$_2$O$_2$ was affected by presence of metal ions Fe$^{2+}$, which was added in the form of ferrous sulphate$^9$. Thus using Fenton reagent (H$_2$O$_2$ + FeSO$_4$) the photo-oxidation occurred fast. The Fe$^{2+}$ ions had been replaced by various homogeneous catalysts like U(VI) and methylene blue. The results showed that under the conditions, [Thiourea]=10.0x10^-2 mol dm$^{-3}$, [H$^+$]=5.0x10^-2 mol dm$^{-3}$, [H$_2$O$_2$] (6%)=6.0x10^-3 mol
sulphur dioxide. The presence of free radicals was also confirmed by adding acrylamide where a resinous TU = thiourea U = urea conversion into nitrate derivative (m.p. 163°C) and TU turned green, indicating that the liberated gas was observed by Messenger’s method 15. It has been observed that some gas evolved during photochemical process. This evolved gas was passed in an acidified potassium dichromate solution which turned green, indicating that thiosulphate is present. This solution gave black precipitate with lead acetate confirming >C=S group in photoproduct. Urea was also identified as sulphur (m.p. 118°C) . The solid residue in the reaction mixture was identified as sulphur dioxide as observed earlier from dm-3, the reaction went to completion in 720 min while with added [FeSO4] = 4.0x10⁻⁴ mol dm⁻³, it took 450 min. Addition of 4.0x10⁻⁴ mol dm⁻³ of UO₂²⁺ reduced it to 390 min while addition of same amount of MB brought in down to 420 min.

On the basis of physical, chemical and spectral data the photo product was characterized as urea. The IR spectrum shows a peak at 1660 cm⁻¹ confirming >C=O group in the product, whereas absence of absorption band in the region 1130-1140 cm⁻¹ shows absence of >C=S group in photoproduct. Urea was also identified by the usual biuret test and its mass was obtained. The product was also confirmed by elemental analysis as: calc. (%): C, 20.00; H, 6.66; N, 46.66; and obs. (%): C, 20.10; H, 6.86; N, 46.36.

Quantitatively 66.5% conversion of thiourea to urea has been observed by Messenger’s method. The tentative mechanism of the reaction may be proposed as:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \xrightarrow{k_1} \text{Fe}^{3+} + \text{OH}^- + \text{H}_2\text{O}$$

$$\text{TU} + 2\text{OH}^- \xrightarrow{k_2} \text{U} + \text{S} + \text{H}_2\text{O}$$

TU = thiourea U = urea

The sulphur obtained is further oxidized to sulphur dioxide as observed earlier. The rate expression derived is

$$\frac{d[U]}{dt} = k'[\text{Fe}^{2+}]^{1/2}[\text{H}_2\text{O}_2]^{1/2}[\text{H}^+]^{1/2}[\text{TU}]^{1/2}$$

where $$k' = \sqrt{k_1k_2}$$

It explains fractional order each with respect to substrate, H⁺, H₂O₂ as well as ferrous ions.

Fe²⁺ in Fenton reagent is not the best donor of electrons, therefore a search is made for other related reagents which can replace Fe²⁺ ions in Fenton reagent in homogeneous photocatalytic system. So the effect of methylene blue and UO₂²⁺ with H₂O₂ were studied which showed marked increase in the photoxidation activity of thiourea.

The reaction rate is enhanced in the presence of methylene blue instead of Fe²⁺ ions as it generates one hydroxyl radical as well as one singlet oxygen molecule per molecule of methylene blue. Now there are two oxidizing species in this case (i) OH− radical and (ii) ¹O₂ molecule and as a consequence, the reaction rate is enhanced.

$$\text{MB} \rightarrow h\nu \rightarrow \text{MB}^* \xrightarrow{\text{Is}} \text{³MB}^*$$

$$\text{³MB}^* \rightarrow \text{¹O}_2 + \text{MB}^*$$

$$\text{H}^+ + \text{MB}^* + \text{H}_2\text{O}_2 \rightarrow \text{MB} + \text{H}_2\text{O} + \text{OH}^-$$

On the other hand, two hydroxyl radicals are formed from H₂O₂ per uranyl ion. The higher rate of reaction is clearly supports the generation of large concentration of hydroxyl radicals.

$$2 \text{UO}_2^{2+} + 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{UO}_2^{4+} + 4 \text{OH}^- + \text{O}_2$$

$$2 \text{UO}_2^{2+} + \text{O}_2 \rightarrow 2 \text{UO}_2^{4+}$$

References