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Photochemical Oxidation of Phenyl-3-(2-pyridyl) Thiourea by Singlet Oxygen

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Rose bengal-sensitized oxidation of phenyl-3-(2-pyridyl) thiourea by singlet oxygen has been carried out in methanol. Phenyl-3-(2-pyridyl) urea has been isolated and characterized as the final product. A tentative mechanism for the sensitized oxidation will be proposed involving singlet oxygen as an active oxidising species.

INTRODUCTION

Photooxidation of organo sulphur compounds have been studied in details,[1-8], but still remains many compounds, whose mechanistic details may be used as a model systems in the primary process of the photooxidation.

EXPERIMENTAL

Phenyl-3-(2-pyridyl) thiourea has been synthesized by taking equimolar quantity of 2-amino pyridine and phenyl isothiocyanate. 0.94 Equimol of 2-amino pyridine and 1.35 equimol of isothiocyanate (5 : 5) ratio in 10 ml absolute alcohol was refluxed in a round bottom flask for 3½ hrs. The refluxed mixture was then poured in ice cold water, to obtain cream coloured crystals of phenyl-3-(2-pyridyl) thiourea. These crystals were recrystallized (m. pt. 171°C).

Phenyl-3-(2-pyridyl) thiourea, 1,4-diazabicyclo (2,2,2) octane (DABCO), nickel chloride, cobalt chloride, β-carotene, α-tocopherol (BDH) were used. For generation of singlet oxygen, various sensitizers like methylene blue (CI 52015, Aldrich), eosin-Y (CI 45380, BDH), rose bengal (CI 45440, Aldrich), thionine (CI 52000, Reidel) and riboflavin (LC) were used. Double distilled water and methanol were used to prepare all solutions. Phenyl-3- (2-pyridyl) thiourea (1.0 gm) was dissolved in (100 ml.) methanol. A solution of rose bengal (1 ml; 8×10^{-3} M) was added so that the concentration of rose bengal in the reaction mixture was 8×10^{-5} M. The solution was then irradiated with a light source using 200 W tungsten lamp. A water filter was placed between the light source and the reaction vessel to eliminate heat radiation. Air was continuously

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bubbled through the solution during the experiment. The progress of reaction was followed by TLC using solvent system, n-butanol: acetic acid: water = 4 : 1 : 5 (v/v).

Some turbidity was observed after irradiating the reaction mixture for 12 hrs. It was observed that TLC of the solution gave two spots, one corresponding to the original phenyl-3-(2-pyridyl) thiourea ($R_f = 0.81$) and another one corresponding to the product ($R_f = 0.91$). The reaction was allowed to go to completion and turbidity thus obtained was identified as sulphur by usual tests[9]. The dye was removed from the filtrate using activated charcoal. The filtrate was then treated with a solution of 2,4-dinitrophenyl hydrazine. An orange solid mass was obtained (m. pt. 124°C).

The control experiments were also carried out and it was observed that in absence of any of the three components (light, dye and oxygen), no product was obtained showing the necessity of light, dye and oxygen for photooxidation. The reaction was also carried out in presence of different sensitizers and the results are summarized in Table 1.

TABLE 1
EFFECT OF TRIPLET ENERGIES ON THE YIELD OF PHOTOPRODUCT

[Sensitizer] = 8×10^{-5} M Time of irradiation = 28 hrs.

Sensitizer	Triplet Energy[10-12] KJ/Mol	Yield of Product %
Rose bengal	157.0–176.6	15.0*
Eosin Y	181.3–192.6	10.0
Methylene blue	142.3	8.0
Thionine	200.9	9.0
Riboflavin	242.0	6.0

*In presence of monochromatic light the yield decreases.

The participation of singlet oxygen was confirmed by using different singlet oxygen scavengers in the reaction mixture where the yield was considerably reduced in presence of these scavengers and the results are summarized in Table 2.

RESULTS AND DISCUSSION

The absorption peak at 1650 cm^{-1} indicates the presence of >C=O group in photoproduct while no absorption in the region 1130–1340 cm^{-1} shows the absence of >C=S group in product. For confirmation of >C=O in photoproduct, the irradiated solution was treated with activated charcoal and filtrate was then tested with sodium nitroprusside and sodium hydroxide solution. A dark red colouration showed the presence of >C=O group. The filtered solution was heated with 2,4-dinitrophenyl hydrazine to obtain the product. The product was obtained as 2,4-dinitrophenyl hydrazine derivative, which was recrystallized (m. pt. 124°C).

TABLE 2
EFFECT OF SINGLET OXYGEN SCAVENGERS

[Rose bengal] = 8.0×10^{-5} M; [Scavenger] = 1.0×10^{-6} M
Time of irradiation = 28 hrs.

Scavenger[13–15]	Yield of Product %
—	15.0
Nickel Chloride	Nil
Cobalt Chloride	Nil
β-Carotene	Nil
DABCO	Nil
α-Tocopherol	Nil

The infrared spectral data (cm^{-1}) obtained are summarized in Table 3.

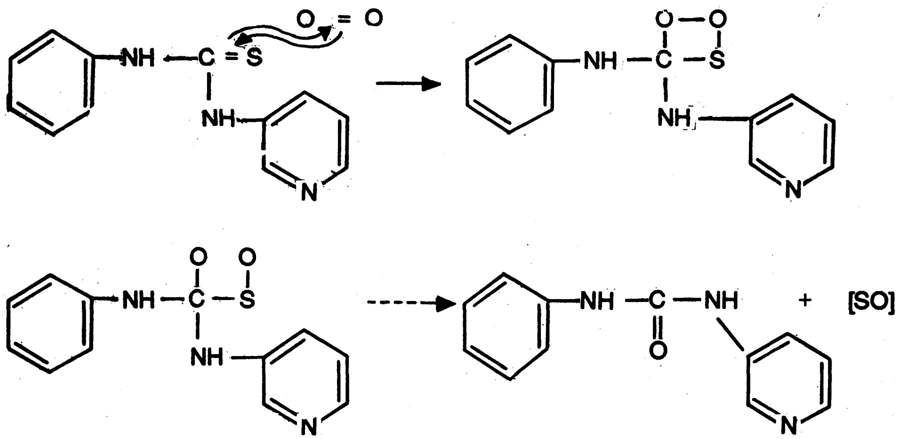
TABLE 3
(A) IR-ABSORPTION BANDS (cm^{-1}) OF PHENYL-3-(2-PYRIDYL) THIOUREA AND PHENYL-3-(2-PYRIDYL)UREA

Phenyl-3-(2-Pyridyl) Thiourea[16,17]	Phenyl-3-(2-Pyridyl) Urea[16,17]	Assignments
3460	3470	N–H Stretching
3400	3420	N–H Stretching
3090	3100	N–H Stretching
3060	3065	C–H Stretching (aryl)
—	1650	C=O Stretching
1595	1600	C=N Pyridyl ring
1505	1520	C=N Pyridyl ring
1490	1500	C=N Pyridyl ring
1460	1470	C=N Pyridyl ring
1390	1410	C–N Stretching
1250	—	C=S Stretching
790	800	C–H Bending (out of plane)

(B) MASS SPECTROSCOPIC DATA

m/e = 213, 136, 135, 121, 120, 93, 92, 78, 77, 58, 43, 28, 15.

The over all photochemical reaction can be divided into primary process and secondary reactions. The primary photochemical process involves a series of events that starts with the absorption of a photon by a molecule and ends with the disappearance of molecule or with its conversion to its ground state back. The secondary reactions are those photochemical process that leads to chemical products *i.e.* (a) absorption of radiation (b) transformation of various electronically excited state to give chemical products. The information gained from the experimental data leads to following probable mechanism, which explains the observed results (Fig. 1).



$$3SO \rightarrow S_2O + SO_2$$
$$2S_2O \rightarrow 3S + SO_2$$
$$SO_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow H_2SO_4$$

Fig. 1. Mechanism of the dye-sensitized photooxidation of phenyl-3-(2-pyridyl) thiourea.

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