



PHOTOLYSIS OF FLUORENE AND 9-FLUORENONE A TOXIC ENVIRONMENTAL CONTAMINANT: STUDIES IN THE EFFECT OF SOLVENT AND INTENSITY OF THE SOURCE

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Abstract:

Polycyclic aromatic hydrocarbons (PAHs) are a class of genotoxic environmental contaminants and are always exposed to solar radiations. Fluorenes are important PAHs widely distributed in nature and hence the studies in the effect of light on them are of utmost significance. Therefore in this paper, we have studied the photo irradiations of fluorene (1) and 9-fluorenone (2) with UV light in different solvents, which results in the formation of different products.

Keywords: *Photolysis; 9-Fluorenone; Acetonitrile; Benzene; Acetone.*

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1. Introduction

A considerable amount of PAHs are being used which are mutagenic or carcinogenic (or both) in nature and produce a hazardous impact upon the environment. Prolonged light irradiation originated either by sunlight or by other light sources is known to induce photochemical transformations within such substances. This also further enhances the dangerous impact of such materials on natural resources and food.

Chain related industries. Fluorene is an important, naturally occurring polycyclic aromatic hydrocarbon. It is biodegraded readily (aerobically) in the presence of microbes present in soil or water. Human exposure to fluorene occurs primarily through the smoking of tobacco, inhalation of polluted air and by ingestion of food and water contaminated by combustion effluents. It is used in manufacturing anti-malarial drugs and other pharmaceuticals. It plays an important role in metallocene catalysis as ligand. It is used in the formation of polyradicals for resins. Fluorene family compounds are base materials for dyes and optical brightening agents. They have useful functions such as light and temperature sensitivity, heat resistance, conductivity, emitability, corrosion resistance and detection of amino group.

They are used in the application of thermo and light sensitizer, liquid crystal chemistry, luminescence chemistry, spectrophoto complexes and in biochemophology industry. The Photochemistry of polycyclic aromatic hydrocarbons (PAH) has been widely studied and reviewed¹⁻¹⁶. Some work on the photochemistry of fluorenes and fluorenones¹⁷⁻²⁶ has also been done, but looking into its wide applications, we have studied the photochemistry of fluorene and 9-fluorenone in different solvents and have drawn some conclusions regarding the solvents effect on the course of photolysis.

2. Aims and Objectives

The purpose of this work is to study the effect of polarity of solvents and intensity of light source on the photochemical reaction of fluorene and fluorenone and propose the mechanism of the reaction.

3. Material and Methods

Photochemical reaction of fluorene and 9-fluorenone: The substrate (1g) was dissolved in the solvent (100 ml) in a beaker and 0.01 g of benzophenone was added as a sensitizer (in case of fluorene). Then the solution was transferred into the Immersion well photo reactor (SAIC make) and was irradiated under 125 W or 250 W mercury vapour lamp which had been placed inside the immersion well. The temperature of the reaction was kept constant by continuous water circulation. The progress of the reaction was monitored by TLC using benzene: hexane (9:1) solvent system. When the spot of the substrate disappeared, the irradiation was stopped and the solution was concentrated on water bath under reduced pressure and kept overnight. The products obtained were recrystallized from benzene.

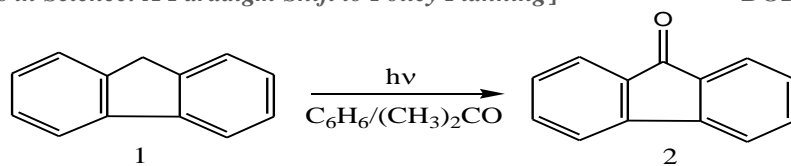
Elemental analysis (Product 3): Found C 85.71 %, H 5.49 % and Calculated for C₁₃H₁₀O: C 85.69 %, H 5.45 %.

4. Results and Discussion

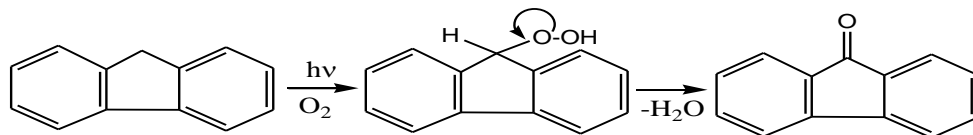
When fluorene (1) was irradiated by UV light in different solvents using benzophenone as sensitizer, it undergoes photo oxidation with aerial oxygen to give 9-fluorenone in benzene and acetone whereas in acetonitrile no reaction takes place (Scheme-1). The formation of 9-fluorenone has been confirmed by its co-tlc with the authentic sample and mixed M.P.

9-Fluorenone shows no reaction in benzene and acetone but in acetonitrile it underwent photo reduction by H-abstraction from CH₃CN giving fluorene-9-ol and succinonitrile (Scheme-2).

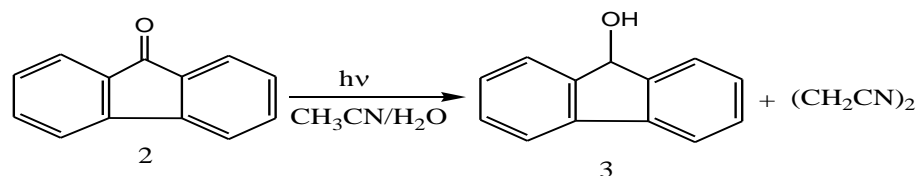
Similar products are obtained with 125w and 250w mercury vapour lamp but yields of the products are increased with high pressure mercury vapour lamp and time required for the completion of photoreaction is also decreased. It may be due to increase no of photons in high pressure mercury vapour lamp (250 W) which irradiates more no of reactant molecules.



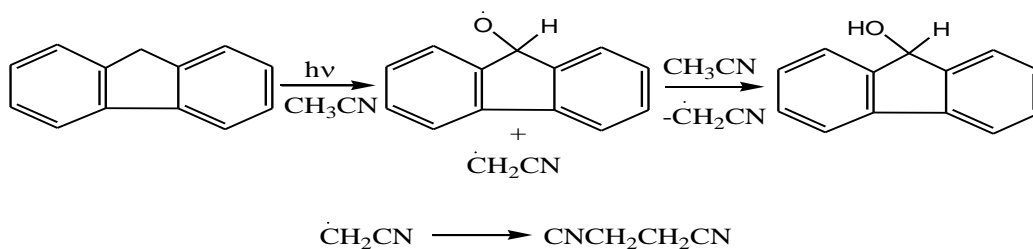
Mechanism:



Scheme-1



Mechanism:



Scheme-2

The identity of 9-fluorenol was established by its spectral and elemental analyses. Its IR spectrum shows important peaks at 3061.12 (arom. C-H stretch.) And 3418.25 (OH stretch.) along with other peaks. The ¹H NMR spectrum of the product shows peaks at δ 7-8.16 (arom. protons); δ 3.85 (OH proton). And δ 2.85 (C-H proton). The ¹³C NMR spectrum of the product shows peaks at δ 120-130 (arom. carbons) and δ 64.5 (CHOH carbon atom). The mass spectrum of the product shows molecular ion peak at m/z 182 corresponding to the molecular weight of fluorenol and other peaks at m/z 181, 165, 164, 152, 76, 51 etc. The results of elemental analyses are given in experimental section and are in accordance with the calculated values. The formation of succinonitrile was confirmed by its M.P., which is 55-56°C (Lit. M.P. 57 °C).

5. Conclusion

The results show that as the polarity of the solvent is increased, the overall rate of reaction is increased in case of fluorene, i.e. time of irradiation decreases and the yields of the products formed increase, whereas in case of fluorenone it is not reactive in low polarity solvents, this shows that increase in the polarity of the solvent, increases its photoreactivity. (Table-1)

Table 1

Substrate	Solvents taken	Intensity of UV Source	Time of Irradiation	Product	Yield(in g)
Fluorene	Benzene	125 W, 250 W	58 hrs., 48 hrs resp.	9-Fluorenone	0.73 & 0.90 resp.
Fluorene	Acetone	125 W, 250 W	55 hrs, 40 hrs resp.	9-Fluorenone	0.73 & 0.90 resp.
Fluorene	Acetonitrile	125 W, 250 W	No reaction	-	-
9-Fluorenone	Benzene	125 W, 250 W	No reaction	-	-
9-Fluorenone	Acetone	125 W, 250 W	No reaction	-	-
9-Fluorenone	Acetonitrile	125 W, 250 W	64 hrs, 56 hrs resp.	Fluoren-9-ol & Succinonitrile	0.70 & 0.25 resp.

In the present work, effect of intensity of light source and polarity of solvent is studied. Polarity and intensity both factor favours the photoreaction in case of fluorene and fluorenone i.e. Time required for completion of photoreaction decreased and yields of the products formed increased with increasing polarity of solvents and intensity of light sources.

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