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Photocyclization and photooxidation of 3-styrylthiophene

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Abstract

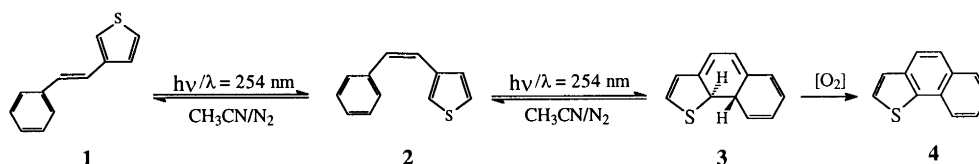
The photocyclization, dye-sensitized photooxidation and auto-photooxidation of 3-styrylthiophene have been examined. *cis*-3-Styrylthiophene undergoes photochemical *cis*–*trans* isomerization and cyclization to dihydronaphtho-[1,2-*b*]thiophene. The quantum efficiency for photocyclization in nonpolar solvents is greater than that in polar solvents. Dye-sensitized photooxidation of 3-styrylthiophene gives benzaldehyde and 3-thiophenecarboxaldehyde. This oxidation proceeds via a superoxide radical anion pathway rather than singlet oxygen pathway. In the presence of oxygen photoirradiation of 3-styrylthiophene solution results in photocyclization, oxidation and dimerization. The mechanism of the latter two reactions was described in terms of formation of a charge transfer complex between oxygen and the substrate. © 2000 Elsevier Science Ltd. All rights reserved.

Thiophene and its derivatives have been shown to be the best monomers for the production of desirable conductive polymers in terms of high conductivity, processibility and ease of manufacture.^{1–3} Although the electrochemical oxidation of a wide variety of thiophene derivatives, leading to the formation of conductive polymers, has been extensively investigated, the photochemical oxidation of these compounds has rarely been reported.^{4–6} It is known that polythiophenes are susceptible to photodegradation in the presence of oxygen. Thus, the study of photochemical reactions of polythiophenes and their monomers is critical for understanding the behavior and for the manufacture of high quality conductive polymers. Here we report the photocyclization and photooxidation of 3-styrylthiophene in the presence and absence of a sensitizer.

3-Styrylthiophene exists as two isomers: *trans*-3-styrylthiophene (**1**) and *cis*-3-styrylthiophene (**2**).⁷ While **1** undergoes only *trans*–*cis* isomerization, **2** may undergo a photochemical ring closure reaction to form dihydronaphtho-[1,2-*b*]thiophene (**3**) in addition to the *cis*–*trans* isomerization (Scheme 1). In the present study, we used a mixture of **1** and **2** as starting materials. Photoirradiation of starting materials (1×10^{-2} M, degassed by purging with nitrogen) in organic solvents was carried out in a quartz reactor with a 450 W Hanovia medium pressure Hg arc lamp at room temperature. The products were isolated by column chromatography on silica and identified from their ¹H NMR and MS spectra. It was found

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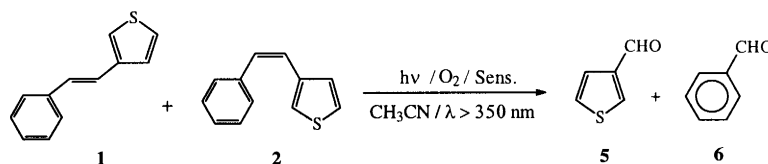
that **3** was oxidized to naphtho-[1,2-*b*]thiophene (**4**, Scheme 1) by air during the isolation.⁸ The yield of this product was 100% based on the consumption of the starting materials **1** and **2**, suggesting that any unidentified product must be minor. The efficiency of the ring closure reaction from **2** to **3** is dependent on the solvent. In acetonitrile, photoirradiation of a 1×10^{-2} M solution of **2** for 20 min leads to a 30% conversion of **2** to **3**. Under identical conditions, photoirradiation of **3** in cyclohexane for the same period results in a 40% conversion. By reference to the photochemical reaction of *cis*-stilbene,⁹ we attributed the high efficiency of the photocyclization of **2** in a nonpolar solvent to the small rate constant of the *cis*-*trans* isomerization compared with that in a polar solvent.



Scheme 1.

Photosensitized oxidation of **1** and **2** was carried out by using several sensitizers in both polar and nonpolar solvents. A combination of Corning 0-52 and 7-60 glass filters were used to isolate the $\lambda > 350$ nm light, which was only absorbed by the sensitizer. Photoirradiation of oxygen-saturated solutions of the mixtures of **1** and **2** in acetonitrile containing 9,10-dicyanoanthracene (DCA) gave 3-thiophenecarboxaldehyde (**5**) and benzaldehyde (**6**) (Scheme 2). The products were isolated by column chromatography and analyzed by GC. The ratio of **5** to **6** was 1:1, and the yield was 100% based on the consumption of the starting material. Generally, after 3 h of irradiation the conversion of the starting material was near 100%. There are two well established types of dye-sensitized photooxidation of alkenes: the energy transfer pathway and the electron transfer pathway.¹⁰ It has been established that DCA can act both as a singlet oxygen sensitizer and as an electron transfer sensitizer.¹¹ To clarify the mechanism of the DCA-photosensitized oxidation of **1** and **2** we examined the fluorescence quenching. The fluorescence of DCA in acetonitrile was quenched by **1** and **2** following the linear Stern-Volmer relationship and the quenching rate constant (k_q) was 9.0×10^9 M/S (assuming the fluorescence lifetime of DCA in acetonitrile in the absence of quencher to be 13.4 ns¹²), close to the diffusion-controlled rate constant. The energy of the singlet excited state of DCA (ca. 66 kcal/mol¹³) is lower than that of **1** and **2** (ca. 96 kcal/mol, as determined from the absorption spectra), suggesting that singlet-singlet energy transfer from the excited DCA to **1** and **2** is impossible. Thus, we examined the possibility of electron transfer from **1** and **2** to the singlet excited state of DCA as the cause of the fluorescence quenching. The free energy change (ΔG) involved in a photostimulated electron transfer process can be estimated by Eq. (1),¹⁴ where ΔE_{00} is the singlet excited state energy of DCA. E_{ox} (D) and E_{red} (A) are the oxidation potential of **1** and **2** (1.48 V vs SCE¹⁵) and the reduction potential of DCA (-0.89 V vs SCE¹³), respectively, determined in acetonitrile solution.

$$\Delta G = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - \Delta E_{00} - e^2 / \epsilon R_{\text{cc}} - e^2 / 2 (1/r_+ + 1/r_-) (1 - 1/\epsilon) \quad (1)$$



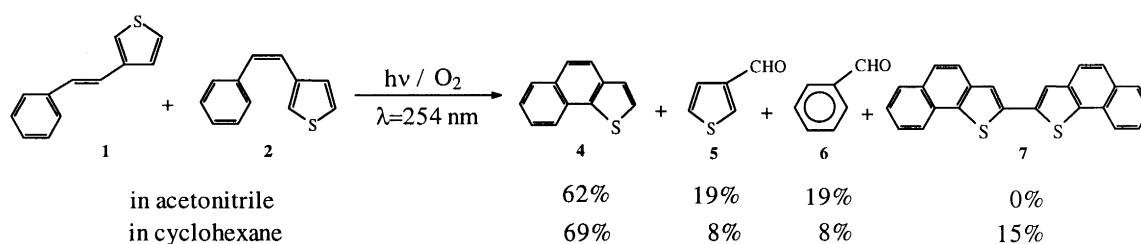
Scheme 2.

$e^2/\epsilon R_{cc}$ is the Coulombic interaction ($R_{cc}=r_++r_-$, ϵ =dielectric constant of the medium) in the ion pair state. The last term in Eq. (1) is the Born Correction to the solvation energy. Assuming both donor and acceptor are spherical, we set r_+ and r_- to equal 3.8 Å and 4.8 Å, respectively. The calculation according to Eq. (1) reveals that electron transfer from **1** or **2** to the DCA singlet excited state in acetonitrile is exothermic by 12.7 kcal/mol. Thus, the fluorescence quenching indeed can occur via the electron transfer process, and the photosensitized oxidation may proceed via the superoxide radical anion pathway.

The proposal of the electron transfer mediated mechanism for the photosensitized oxidation of **1** and **2** was further supported by an *N,N*-dimethylaniline (DMA) quenching experiment. Because DMA has a lower oxidation potential¹⁶ than **1** and **2**, electron transfer from DMA to the excited state of DCA should be more favorable. Thus, one might expect that DMA would intercept the photooxidation of **1** and **2** sensitized by DCA. Experimentation revealed that this is indeed the case. Addition of DMA to the oxygen-saturated solution of **1**, **2** and DCA in acetonitrile led to efficient quenching of the oxidation reaction.

We also studied the photosensitized oxidation of **1** and **2** in cyclohexane by using tetraphenylporphyrin (TPP) as the sensitizer. TPP is a typical sensitizer for the production of singlet oxygen, particularly in nonpolar solvents.¹⁷ Photoirradiation of an oxygen-saturated solution of a mixture of **1** and **2** in cyclohexane containing TPP with visible light for 10 h resulted in no reaction of **1** and **2**. All the above observations suggest that in the dye-sensitized oxidation of **1** and **2** the reaction proceeds via an electron transfer pathway rather than an energy transfer pathway.

Compounds **1** and **2** can also undergo auto-photooxidation in the absence of the sensitizer. Photoirradiation of an oxygen-saturated solution of **1** and **2** in acetonitrile with 254 nm light resulted in the ring closure product **4** as well as the oxidation products **5** and **6** (Scheme 3). The product distribution is given at the bottom of Scheme 3. Material balance was greater than 90%. Photoirradiation of oxygen-saturated solutions of **1** and **2** in cyclohexane gave a dimer of **4** (**7**, Scheme 3) as a precipitate in addition to **4**, **5** and **6**. The dimer **7** was identified by its ¹H NMR and MS spectra.¹⁸ It is possible that the triplet excited state of **1** and/or **2** (generated by intersystem crossing from the singlet excited state) interacts with oxygen to produce singlet oxygen. However, the singlet oxygen does not react with **1** or **2**, Holdcroft and his co-workers reported that molecular oxygen forms reversible charge transfer complexes (CTC) with oligo- and poly(3-alkylthiophenes).⁴ We proposed that **1** and **2** also might form a CTC with oxygen. The complex possesses character of the radical pair formed from superoxide anion radical and the thiophene cation radical, and the products **5** and **6** were produced from the radical pair as in the case of the electron transfer pathway in the dye-sensitized oxidation. The dimer **7** might be formed from the radical cation of **4**.



Scheme 3.

In summary, 3-styrylthiophene may undergo photocyclization to dihydronaphtho-[1,2-*b*]thiophene in the absence of oxygen. In the presence of oxygen photoirradiation of this compound gave the oxidation products, benzaldehyde, 3-thiophenecarboxaldehyde, and the cyclization product **4**. In DCA sensitized

oxidation the reaction proceeds via an electron transfer pathway. We believe that this study may provide the basis for improvement of the photostability of polythiophene conductive polymers.

Acknowledgements

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7. Compound **1 (2)**: mp 121–123°C, ¹H NMR (CDCl₃) δ 6.95–7.47 (m, ethyl-H, 2H and aromatic-H, 8H), MS 186 (M⁺).
8. Compound **4**: ¹H NMR (CD₃COCD₃) δ 7.54–8.14 (m, aromatic-H, 8H), MS 184 (M⁺).
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18. Compound **7**: ¹H NMR (CD₃COCD₃) δ 7.66–7.89 (m, aromatic-H, 14H), MS 366 (M⁺).