



## A comparative study on photosensitized oxidation of *trans*-2-vinylthiophenes with *trans*-3-vinylthiophenes

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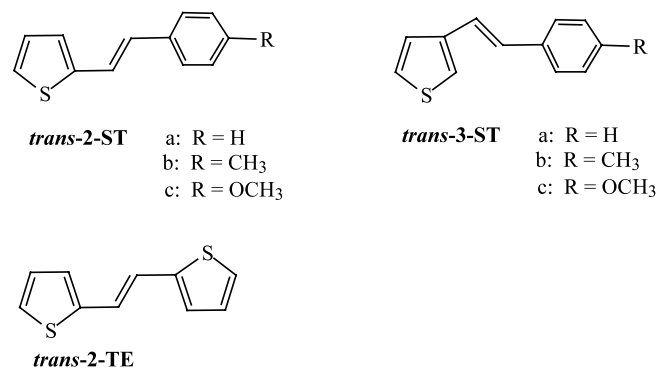
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Received 10 September 2001; revised 15 May 2002; accepted 12 July 2002

**Abstract**—The photosensitized oxidation of *trans*-2-styrylthiophenes (*trans*-2-ST), *trans*-3-styrylthiophenes (*trans*-3-ST) and *trans*-1,2-di(2-thienyl)ethylene (*trans*-2-TE) were investigated using the sensitizers tetraphenylporphyrin (TPP) in a non-polar solvent and 9,10-dicyanoanthracene (DCA) in a polar solvent. The oxidation pathway is dependent on the position of the vinyl substituent in the thiophene ring. While *trans*-2-ST and *trans*-2-TE only undergo photooxidation via the singlet oxygen pathway to yield [4+2] and [2+2] products, the photosensitized oxidation of *trans*-3-ST proceeds exclusively via the superoxide anion pathway to produce the thiophenecarboxaldehyde and benzaldehydes. All of the above substrates may undergo auto-photooxidation via a charge-transfer complex of the substrate and oxygen. © 2002 Published by Elsevier Science Ltd.

Photosensitized oxidation of alkenes is one of the current challenges in the manufacture of organic building blocks and industrial intermediates.<sup>1</sup> There are two well-established types of dye-sensitized photooxidation: energy-transfer pathway and electron-transfer pathway.<sup>2</sup> The energy-transfer pathway involves the energy transfer from the triplet sensitizer to the ground-state oxygen to generate singlet oxygen (<sup>1</sup>O<sub>2</sub>), then the generated <sup>1</sup>O<sub>2</sub> reacts with the substrate. In the electron-transfer pathway, electron-deficient sensitizers are generally used. Electron transfer from an alkene to the excited state sensitizer results in an alkene radical cation and sensitizer radical anion, which subsequently reduces O<sub>2</sub> to give a superoxide radical anion (O<sub>2</sub><sup>•-</sup>). The generated O<sub>2</sub><sup>•-</sup> reacts with the alkene radical cation to yield the oxidation products. Most alkenes can undergo both the energy-transfer and the electron-transfer photosensitized oxidation, depending on the sensitizer and the reaction conditions used.<sup>3</sup> Recently, we examined the photosensitized oxidation of thiophene derivatives with an extra-annular double bond (Scheme 1) in order to understand their behavior as monomers for production of desirable conductive polymers. Our results revealed that the mechanism for the photooxidation of these compounds is remarkably dependent on the substituted position of the thiophene ring. The photosensitized oxidation of 2-vinylthiophenes proceeds exclusively via the energy-transfer pathway, while 3-vinylthiophenes only undergo the electron-transfer sensitized oxidation.

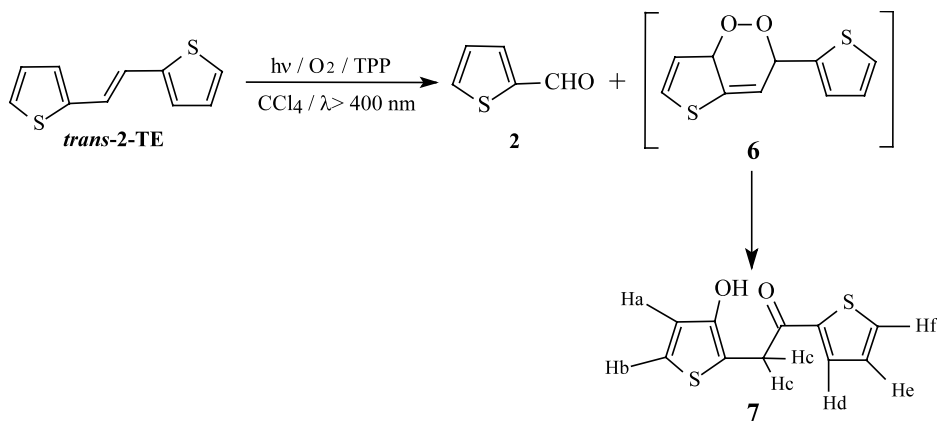
In the photosensitized oxidation via the energy-transfer pathway, we used tetraphenylporphyrin (TPP, triplet energy = ca. 38 kcal/mol) as the sensitizer, since it is known that photoirradiation of TPP in a non-polar solvent generates singlet oxygen in high quantum yield.<sup>4</sup> A solution of the substrate (ca. 5 × 10<sup>-3</sup> M) in carbon tetrachloride containing 1 × 10<sup>-4</sup> M TPP was saturated with oxygen by bubbling the gas and irradiated by a 450 W Hanovia medium pressure Hg arc lamp at room temperature. A combination of Corning O-52 and 7-60 glass filters was used to isolate the light with wavelength greater than 400 nm, which only the sensitizer absorbs. After irradiation, the products were isolated by column chromatography on silica and identified by their <sup>1</sup>H NMR and mass spectra. Generally, the yield of the products was 100% based on the consumption of



Scheme 1.

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Scheme 3.

triplet energy = ca. 43 kcal/mol) as the sensitizer. Since the solubility of this sensitizer is very limited in carbon tetrachloride, we carried out the reaction in acetonitrile. Furthermore, the more polar acetonitrile would favor electron transfer from the alkene to the excited state of DCA. Irradiation was performed with an oxygen-saturated solution of the substrate (ca.  $5 \times 10^{-3}$  M) containing  $1 \times 10^{-4}$  M DCA. In contrast to the case of the energy-transfer pathway, the 2-vinylthiophenes (*trans*-2-STa-c and *trans*-2-TE) did not undergo photooxidation at all, while the photosensitized oxidation of the 3-vinylthiophenes (*trans*-3-STa-c) gave 3-thiophenecarboxaldehydes **8** and the corresponding benzaldehydes **1a–c** in quantitative yields (Scheme 4). Evidently, these two aldehyde products are derived from the intermediate dioxetanes, the cycloaddition products of the alkene radical cations, *trans*-3-ST<sup>+</sup>, and superoxide radical anion.<sup>14,15</sup> Theoretically, the molar ratio of **8** to **1** should be 1:1. However, since **8** can undergo further oxidation, its yield was slightly lower (5–10%) than that of **1**. Substitution by an electron-donating group (-CH<sub>3</sub>, -OCH<sub>3</sub>) at the *para*-position of the phenyl in *trans*-3-ST favors the electron transfer to the excited states of DCA and thus enhances the quantum yield for the photooxidation. For example, photoirradiation of *trans*-3-STa for 5 h resulted in 80% conversion, while under identical conditions photoirradiation of *trans*-3-STc for 2 h led to 100% conversion.

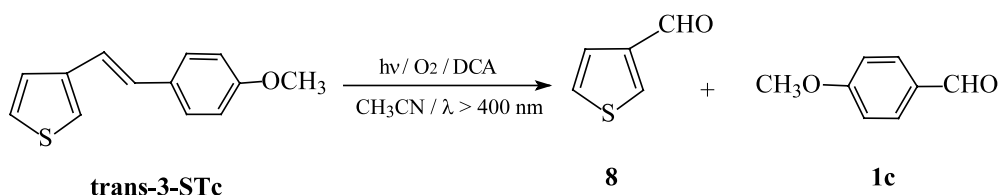
A fluorescence quenching study showed that the fluorescence of DCA could be quenched both by *trans*-2-ST and *trans*-3-ST. For example, the quenching rate constants were ca.  $3.0 \times 10^{10}$  and  $2.7 \times 10^{10}$  M<sup>-1</sup>S<sup>-1</sup> for *trans*-2-STc and *trans*-3-STc, respectively, both are the diffusion-controlled rate constant in acetonitrile. The free energy change ( $\Delta G$ ) involved in the electron-trans-

fer process from the substrate to the singlet excited state DCA was estimated using the Rehm–Weller equation (Eq. (1)).<sup>16,17</sup>

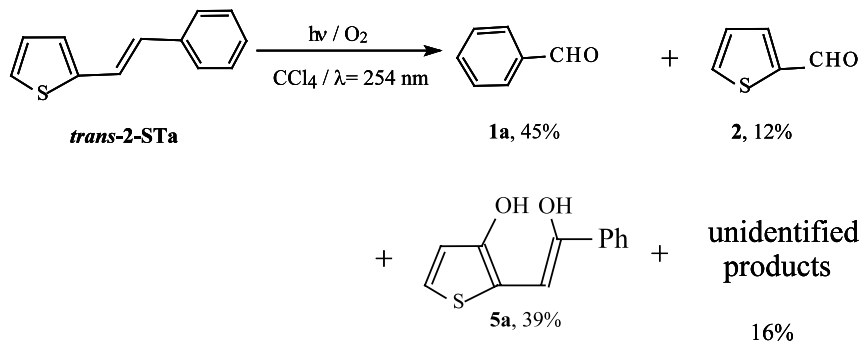
$$\Delta G = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - \Delta E_{00} - e^2/\epsilon R \quad (1)$$

where  $\Delta E_{00}$  is the singlet excited state energy of DCA (ca. 2.89 V),<sup>14</sup>  $E_{\text{ox}}(\text{D})$  is the oxidation potential of *trans*-2-STc (1.16 V versus SCE)<sup>18</sup> or *trans*-3-STc (1.17 V versus SCE),<sup>18</sup> and  $E_{\text{red}}(\text{A})$  is the reduction potential of DCA (-0.89 V versus SCE)<sup>14</sup> determined in acetonitrile solution.  $e^2/\epsilon R$  is the coulombic interaction in the ion pair state and has a value of 0.06 V in acetonitrile.<sup>19</sup> The calculation according to Eq. (1) reveals that electron transfer from *trans*-2-STc and *trans*-3-STc to DCA singlet excited state in acetonitrile is exothermic by ca. 18.7 and 18.4 kcal/mol, respectively. Thus, the electron transfer from *trans*-2-ST to DCA in the singlet excited state does occur. The reason for the absence of photooxidation of *trans*-2-ST is under investigation.

Both 2-vinylthiophenes and 3-vinylthiophenes can undergo auto-photooxidation in the absence of a sensitizer. In previous work,<sup>14</sup> we showed that photoirradiation of an oxygen-saturated solution of 3-STa in acetonitrile with 254 nm light resulted in the ring closure product (naphtha-[1,2-*b*]thiophene) as well as the oxidation products **8** and **1**. This photooxidation was proposed to proceed via the charge-transfer complex between the substrate and oxygen. In the present work we found that photoirradiation of an oxygen-saturated solution of *trans*-2-STa in carbon tetrachloride gave the [2+2] products **1a** and **2**, and the [4+2] derivative **5a** (Scheme 5). Furthermore, a significant quantity of unidentified products were formed. It was reported that the quantum yield of intersystem crossing from the singlet to triplet excited state for this compound is very



Scheme 4.



Scheme 5.

low (less than 0.01).<sup>16</sup> Thus, the singlet oxygen (generated by energy-transfer from the triplet state of *trans*-2-STa to oxygen) pathway is excluded. We proposed that this auto-photooxidation also proceeds via a charge-transfer complex between the substrate and oxygen. In the singlet excited state of the charge transfer complex, the oxygen perturbation enhances the intersystem crossing to generate singlet oxygen which subsequently reacts with the substrate to give the products.

In summary, 2-vinylthiophenes and 3-vinylthiophenes undergo photosensitized oxidation via different pathways. While 2-vinylthiophenes only undergo the energy-transfer photosensitized oxidation, the photosensitized oxidation of 3-vinylthiophenes proceeds exclusively via the electron-transfer pathway. Both 2- and 3-vinylthiophenes only undergo auto-photooxidation through the charge-transfer complex of the substrate and oxygen.

### Acknowledgements

Financial support from the Ministry of Science and Technology of China (Grant Nos. G2000078100 and G2000077502) and the National Science Foundation of China is gratefully acknowledged. We also thank Professor X. T. Liang from the Institute of Materia Medica of the Chinese Academy of Medical Sciences and Professor J. S. Ma from the Institute of Chemistry of the Chinese Academy of Sciences for their help in assigning the structure of **5** and **7**.

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- 7**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 4.24 (s, 2H, H<sub>c</sub>), 6.74 (d, 1H, H<sub>a</sub>, J<sub>ab</sub>=5.4 Hz), 6.99 (d, 1H, H<sub>b</sub>, J<sub>ab</sub>=5.4 Hz), 7.21 (2dd, 1H H<sub>e</sub>, J<sub>de</sub>=4.9 Hz, J<sub>ef</sub>=3.9 Hz), 7.78 (2dd, 1H H<sub>d</sub>, J<sub>de</sub>=4.9 Hz, J<sub>df</sub>=1.1 Hz), 7.90 (2dd, 1H, H<sub>f</sub>, J<sub>ef</sub>=3.9 Hz, J<sub>df</sub>=1.1 Hz), 7.92 (s, 1H, -OH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 36.6, 96.0, 116.0, 121.46, 121.96, 128.61, 134.27, 134.80, 136.30, 152.82 ppm. MS *m/z* (%) 224 (M<sup>+</sup>, 82), 111 (100), 113 (70), 85 (15), 59 (12), 45 (18), 39 (30).
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