

Tetrahedron Letters 43 (2002) 6633-6636

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

Kai Song, Ming-Li Peng, Ming Xu, Li-Zhu Wu,\* Li-Ping Zhang and Chen-Ho Tung\*

Technical Institute of Physics and Chemistry, The Chinese Academy of Sciences, Beijing 100101, China

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  $({}^{1}O_{2})$ , then the generated  ${}^{1}O_{2}$  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  $(O_2^{-\bullet})$ . The generated  $O_2^{-\bullet}$  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.  $5 \times 10^{-3}$  M) in carbon tetrachloride containing  $1 \times 10^{-4}$  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



b:  $R = CH_3$ c:  $R = OCH_3$ 



*trans*-3-ST a: R = H b: R = CH<sub>3</sub> c: R = OCH<sub>3</sub>



trans-2-TE



<sup>0040-4039/02/</sup>\$ - see front matter © 2002 Published by Elsevier Science Ltd. PII: S0040-4039(02)01445-4

<sup>\*</sup> Corresponding authors.

the starting materials. All of the trans-2-vinylthiophenes undergo such photooxidation (Scheme 2). In these compounds, an intra-annular double bond in the thiophene ring conjugates with the extra-annular double bond to form a diene system. Thus, it is expected that these compounds are capable of undergoing both [4+2] and [2+2] cycloaddition with singlet oxygen.<sup>5-9</sup> Indeed, the photosensitized oxidation of *trans*-2-STa gave benzaldehyde 1a, 2-thiophenecarboxaldehyde 2, epoxide 3a, and an enol 5a (Scheme 2). The product distribution is shown in Table 1. Obviously, the main product is 5a. We proposed that 5a is derived by the rearrangement of endoperoxide (4a), which is a product of 1,4-cycloaddition of  ${}^{1}O_{2}$  to the diene system. This 1,4-cycloaddition occurred exclusively on the  $\beta$ -carbon of the vinyl and the 3-position of the thiophene ring.<sup>10</sup> The assignment of this product as the enol is mainly based on its mass spectrum and <sup>1</sup>H NMR spectrum.<sup>11</sup> Compounds 1a and 2 are most likely derived from an intermediate dioxetane, a [2+2] cycloaddition product of  ${}^{1}O_{2}$  with the extra-annular vinyl, which would decompose under the reaction conditions. 3a Could be formed by the Bartlett reaction.<sup>12</sup> Similarly, trans-2-STb and *trans*-2-STc undergo both [2+2] and [4+2] cycloaddition with  ${}^{1}O_{2}$  to give the aldehydes 1 and 2, epoxides 3 and enols 5 (Scheme 2). The product distributions are listed in Table 1. For each substrate, the main product is the one derived from [4+2] cycloaddition. It is worth noting that the electron-donating group (-CH<sub>3</sub> and -OCH<sub>3</sub>) at the para-position of the phenyl in *trans*-2-ST enhanced the quantum yield of the photosensitized oxidation. For example, photoirradiation of a  $5 \times 10^{-3}$  M trans-2-STa solution in CCl<sub>4</sub> containing  $1 \times 10^{-4}$  M TPP for 5 h led to a 67% conversion to the products, while under identical conditions photoirradiation of trans-2-STc for 2 h resulted in 90% conversion. This observation is attributed to the fact that the electrophilic reagent <sup>1</sup>O<sub>2</sub> would react favorably with more electron-rich alkenes.

In the photosensitized oxidation of *trans*-2-TE in carbon tetrachloride using TPP as the sensitizer, we isolated the aldehyde **2** and a ketone **7** in quantitative yield (Scheme 3). The product distribution is given in Table 1. As in the case of *trans*-2-ST, **2** is derived from the [2+2] cycloaddition of  ${}^{1}O_{2}$  with the extra-annular vinyl. We believe that **7** is produced from **6**, a [4+2] cycloaddition product which undergoes rearrangement to **7** under the reaction conditions. The assignment of **7** is based on its mass spectrum, and  ${}^{1}H$  and  ${}^{13}C$  NMR spectra.<sup>13</sup>

In contrast with the 2-vinylthiophenes, 3-vinylthiophenes do not react with  ${}^{1}O_{2}$ . For example, photoirradiation of *trans*-3-STa-c solutions in CCl<sub>4</sub> in the presence of TPP with light of  $\lambda$ >400 nm for 10 h resulted in no reaction. The starting materials were recovered in 100% yield. Possibly, the 1,4-cycloaddition products of 3-vinylthiophenes with  ${}^{1}O_{2}$  (endoperoxides) could be produced, but these endoperoxides involve a -C=C-S-C(-C=C-)-O-O- structure, and would be unstable. Thus, they undergo a reversible reaction to regenerate the starting materials and oxygen under the reaction condition.

In the photosensitized oxidation via the electron-transfer pathway, we used 9,10-dicyanoanthracene (DCA,

**Table 1.** Product distribution in the oxidation of *trans*-2-ST and *trans*-2-TE photosensitized by TPP in  $CCl_4$ 

Substrate	Product		
	1 (or 2)	3	5 (or 7)
trans-2-STa	7	11	82
trans-2-STb	11	7	82
trans-2-STc	39	0	61
trans-2-TE	7	0	93





## 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 exited 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+•, 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  $(5 \sim 10\%)$  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>

$$\Delta G = E_{\rm ox}(\mathbf{D}) - E_{\rm red}(\mathbf{A}) - \Delta E_{00} - e^2 / \varepsilon R \tag{1}$$

where  $\Delta E_{00}$  is the singlet exited state energy of DCA (ca. 2.89 V),<sup>14</sup>  $E_{ox}(D)$  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  $E_{red}(A)$  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 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 chargetransfer 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 2and 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 G 2000077502) 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**.

#### References

- 1. Dartt, C. B.; Davis, M. E. Ind. Eng. Chem. Res. 1994, 33, 2887.
- 2. Foote, C. S. Photochem. Photobiol. 1991, 54, 659.
- Tung, C.-H.; Song, K.; Wu, L.-Z.; Li, H.-R.; Zhang, L.-P. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V.; Schanze, K. S., Eds. Microreactor-Controlled Product Selectivity in Organic Photochemical

Reactions; Marcel Dekker: New York, 2001; Vol. 8, Chapter 5.

- Rossbroich, G.; Garcia, N. A.; Braslavsky, S. E. J. Photochem. 1985, 31, 37.
- 5. Sevin, F.; McKee, M. L. J. Am. Chem. Soc. 2001, 123, 4591.
- Maranzana, A.; Ghigo, G.; Tonachini, G. J. Am. Chem. Soc. 2000, 122, 1414.
- Bobrowski, M.; Liwo, A.; Oldziej, S.; Jeziorek, D.; Ossowski, T. J. Am. Chem. Soc. 2000, 122, 8112.
- 8. Adam, W.; Prein, M. Acc. Chem. Res. 1996, 29, 275.
- 9. Clennan, E. L. Tetrahedron 2000, 56, 9151.
- Matsumoto, M.; Dobashi, S.; Kondo, K. *Tetrahedron Lett.* 1975, 4471.
- 11. **5a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 5.78 (s, 1H, H<sub>c</sub>), 6.66 (d, 1H, H<sub>a</sub>,  $J_{ab}$ =5.4 Hz), 6.94 (d, 1H, H<sub>b</sub>,  $J_{ab}$ =5.4 Hz), 7.45 (2dd, 2H H<sub>e</sub>,  $J_{de}$ =7.3 Hz,  $J_{ef}$ =7.5 Hz), 7.57 (d, 1H, H<sub>f</sub>,  $J_{ef}$ =7.5 Hz), 8.05 (d, 2H, H<sub>d</sub>,  $J_{de}$ =7.3 Hz) ppm. MS m/z (%): 218 (M<sup>+</sup>, 49), 113 (24), 105 (100), 85 (16), 77 (66), 59 (9), 51 (15), 45 (8).
- 12. Erikson, J.; Foote, C. S. J. Am. Chem. Soc. 1980, 102, 6083.
- 13. 7: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 4.24 (s, 2H, H<sub>c</sub>), 6.74 (d, 1H, H<sub>a</sub>,  $J_{ab} = 5.4$  Hz), 6.99 (d, 1H, H<sub>b</sub>  $J_{ab} = 5.4$  Hz), 7.21 (2dd, 1H H<sub>c</sub>  $J_{de} = 4.9$  Hz,  $J_{ef} = 3.9$  Hz), 7.78 (2dd, 1H Hd,  $J_{de} = 4.9$ Hz,  $J_{df} = 1.1$  Hz), 7.90 (2dd, 1H, H<sub>f</sub>,  $J_{ef} = 3.9$  Hz  $J_{df} = 1.1$ Hz), 7.92 (s, 1H, -OH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 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).
- 14. Song, K.; Wu, L.-Z.; Yang, C.-H.; Tung, C.-H. Tetrahedron Lett. 2000, 41, 1951.
- 15. Tung, C.-H.; Wang, H.-W.; Ying, Y.-M. J. Am. Chem. Soc. 1998, 120, 5179.
- Gajdek, P.; Becker, R. S.; Elisei, F.; Mazzucato, U.; Spalletti, A. J. Photochem. Photobiol. A. 1996, 100, 57.
- 17. Rehm, D.; Weller, A. Isr. J. Chem. 1970, 8, 259.
- Redox potentials were measured by cyclic voltammetry in acetonitrile using a glass carbon working electrode and a Hg/Hg<sub>2</sub>Cl<sub>2</sub> reference electrode in the presence of 0.1 M tetrabutylammoniun hexafluorophosphate as the supporting electrolyte.
- Erikson, J.; Foote, C. S.; Park, T. L. J. Phys. Chem. 1978, 82, 2659.