Electronic Supplementary Information

Continuous Process of the Vacuum Ultraviolet- (VUV-) Photochemical Oxidation of Thiophene in the Gas Phase

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Controlled introduction and analysis of thiophene (TP).

The concentrations of **TP** (c_{TP}) introduced by streams (c) or (c') may be calculated from the mass of the substrate mixing with the carrier gas per unit of time (Q_{TP}, equation (ESI a)).

$$c_{TP} = \frac{Q_{TP}}{f_{N_2} . 10^{-6}} \qquad \text{(ESI a)}$$

where f_{N_2} :   flux of N_2 passing through the diffusion cell [cm^3 s^{-1}]

$$Q_{TP} = \frac{D_{TP,N_2} \, MW_{TP} \, P \, S}{R \, T \, l} \, ln\left(\frac{P}{P - p_{T,TP}}\right) \qquad \text{(ESI b)}$$

where Q_{TP} :   mass of the substrate mixing with the carrier gas per unit of time [g s^{-1}]

D_{TP,N_2} :   vapor diffusion coefficient of **TP** in N_2 [cm^2 s^{-1}], defined by equation (ESI c)

MW_{TP} :   molar mass of **TP** [84.14 g mol^{-1}]

P: pressure at the diffusion cell (1 atm)

S: area of the diffusion capillary (0.2 cm^2)

R: gas constant (82.05 cm^3 atm mol^{-1} K^{-1})

T: temperature of the evaporating system [K]

l: length of the diffusion capillary (8 cm)

$p_{T,TP}$:   partial vapor pressure of the diffusing **TP** at working temperature T to be calculated by Antoine equation (equation (ESI e)) [atm] [e.g. ESI R1]

$$D_{TP,N_2} = \frac{10^{-3}.T^{1,75}.\left(\dfrac{1}{MW_{TP}} + \dfrac{1}{MW_{N_2}}\right)^{0,5}}{P.\left[\left(\displaystyle\sum_{T_{TP}} v_{TP}\right)^{1/3} + \left(\displaystyle\sum_{T_{N_2}} v_{N_2}\right)^{1/3}\right]^2} \qquad \text{(ESI c)}$$

where MW_{N_2}:   molar mass of N_2 (28 g mol^{-1})

$\displaystyle\sum_{T_{TP}} v_{TP}$:   liquid molar volume of **TP** at the boiling temperature [cm^3 mol^{-1} g^{-1}] to be calculated as the sum of the liquid molar volumes $\displaystyle\sum_{T_i} v_i$ of the elementary species [ESI R2] that form the molecule of interest

$$= 4\sum_{T_C} v_C + 4\sum_{T_{H_2}} v_{H_2} + \sum_{T_S} v_S \qquad \text{(ESI d)}$$

$$= 66 + 7.62 + 17 = 90.92 \text{ cm}^3 \text{ mol}^{-1} \text{ g}^{-1}$$

$\displaystyle\sum_{T_{N_2}} v_{N_2}$:   liquid molar volume of N_2 at the boiling temperature = 17.9 cm^3 mol^{-1} g^{-1}

$$p_{T,TP} = exp\left(AntA - \frac{AntB}{T + AntC}\right) \qquad \text{(ESI e)}$$

where $\left.\begin{array}{l} AntA \\ AntB \\ AntC \end{array}\right]$:   Antoine coefficients specific of the substrate for a given temperature range. For **TP**, the values of AntA, AntB, and AntC are 16. 0243, 2869.07 and -51.80, respectively, for a range of 260 to 380 K [ESI R3].

By substitution of Q_{TP} and D_{TP,N_2}, equation (ESI b) may be transformed into equation (ESI f) for a calculation of c_{TP} in function of f_{N_2} and T. Figure ESI 1 shows the characteristics of $c_{TP} = f(T)$ for the diffusion cell used in this work and the good accordance of calculated and experimentally checked values (§2.1.4.) of c_{TP}.

$$c_{TP} = \frac{T^{0,75}}{f_{N_2}} \cdot 0.107 \cdot ln\left(\frac{1}{1-\dfrac{1}{760} \cdot exp\left(6.959-\dfrac{1246.02}{T+221.35}\right)}\right) \qquad \text{(ESI f)}$$
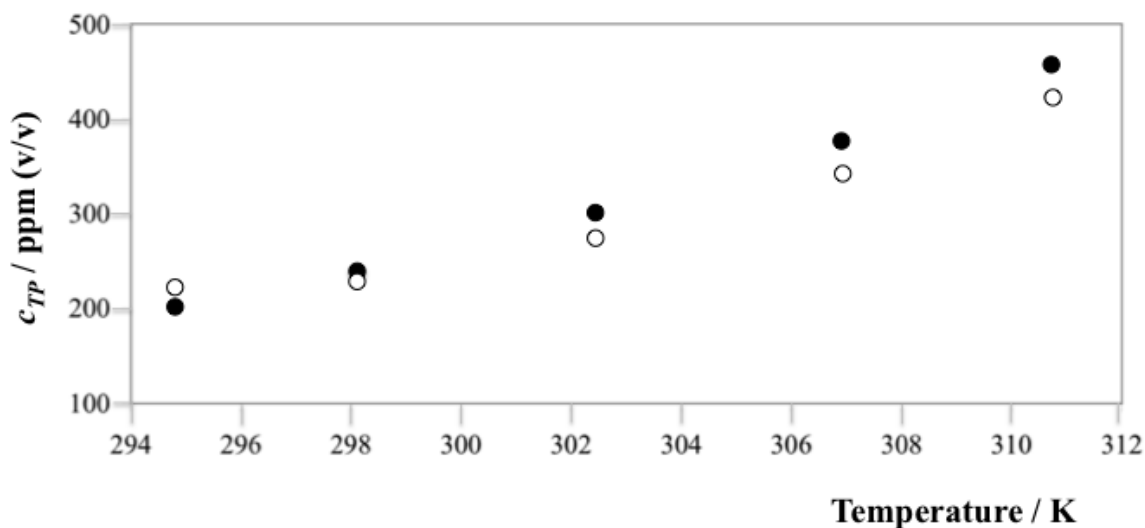
Figure ESI 1. Calculated concentrations of thiophene (**TP**, c_{TP}) in function of the temperature of the diffusion cell (f_{N_2} = 30 cm^3 min^{-1}) and corrected for the total gas flow (f_T = 500 cm^3 min^{-1}, (●)) compared with the results of the GC analysis of the corresponding samples taken at the exit of the dark photochemical reactor (○).

References:

[ESI R1] M. Zaoui-Djelloul-Daouadji, A. Negadi, I. Mokbel, L. Negadi, (Vapor-liquid) equilibria and excess Gibbs free energy functions of (ethanol + glycerol), or (water + glycerol) binary mixtures at several temperatures, *J. Chem. Thermodyn*., 2014, **69**, 165 - 171.

[ESI R2] E. N. Fuller, P. D. Schettler, J. C. Giddings, A new method for prediction of binary gas-phase diffusion coefficients, *Ind. Eng. Chem*., 1966, **58**, 19 - 27.

[ESI R3] J. Bai, B. Guo, S. Xia, Y. Li, P. Ma, Isobaric vapor-liquid equilibrium for four binary systems of thiophene, *Fluid Phase Equilibria,* 2012, **315**, 84 - 90.

Evaluation of photolysis conditions

The photochemical reactor might be adapted in its (radial) optical path length ($r_{ext} - r_{int}$) to the range of concentrations (c_i) for given absorption cross sections ($\sigma_{i,\lambda}$) of components i. The respective values of absorbance of the components i of a given homogeneous gaseous reaction system are evaluated in using a unit-adapted Lambert-Beer law (equation (ESI g)). The volume V_R of the annular photochemical reactor (equation (ESI h)) is then decided by its height or length (h) that in turn must be adapted to the radiation source to be installed. Usually, ($r_{ext} - r_{int}$) is chosen within limits linked to the experimental conditions to the value of total absorption at λ_{exc} [ESI R4], with an upper limit advantageously chosen to be approx. 1.5 times the value of $l_{ta,\lambda_{esc}}$ (equation (ESI i)).

However, due to details of the reactor construction, restricted availability of materials and flux conditions might impose larger or smaller dimensions. Depending on the flux of the reactions system and the design of the photochemical reactor, larger dimensions might favor „short-circuiting", where relative large volume fractions may pass through the photochemical reactor without entering into the irradiated volume. In addition, high concentrations of reactive intermediates localized within the irradiated volume might not be trapped efficiently and might lead to secondary products [ESI R5]. If $r_{ext} < (r_{int} + l_{ta,\lambda_{exc}})$, photonic energy will be wasted and depending on the flux of the gas mixture and on the absorption spectra of intermediates and products, secondary photochemical reactions might be of increasing importance.

For O_2, an absorption cross-section of $\sigma_{O_2,172}$ = 6 x 10^{-19} cm^2 was taken from the absorption spectrum published by Yoshino et al [ESI R6]. Applying equations (ESI g), the absorbance of O_2 ($A_{O_2,172}$) under the given experimental conditions (50 ± 1% dilution by N_2 for all experiments in the presence of O_2, ($r_{ext} - r_{int}$) = 2.3 cm and process temperature: 80°C) is calculated to be approximately 15.

The published value of $\sigma_{H_2O,172}$ = 5 x 10^{-18} cm^2 [ESI R7] was retained for calculating the absorbance of gaseous H_2O ($A_{H_2O,172}$). The saturation concentration of H_2O (mass per volume of gas) in gaseous O_2 was calculated from the partial pressure of water at working temperature (equation (ESI j)). Under conditions of p = 1 atm, T = 353 K, p_{H_2O} = 0.469 atm (s. § 2.1.2), saturation is reached with c_{H_2O} = 291 g m^{-3} or 1.62 x 10^{-5} mol cm^{-3} leading to an approx. value of $A_{H_2O,172}$ of approximately 50.

The evaluation of the contribution of **TP** to the absorbance of the gaseous mixtures was

based on the spectral data shown in Figure 1 [49]. The calculated absorption cross-section ($\sigma_{TP,172}$) of 6.3 x 10^{-17} cm^2 is one order of magnitude higher than those of O$_2$ and H$_2$O. Different c_{TP} in gas streams (c), (c') and (c'') (s. §2.1.2.) were generated in the diffusion cell at constant f_{N_2} but varying T and mixed with gas streams (a) and (b), (a') and (b') or (b'') and checked at the exit of the dark reactor. c_{TP} was systematically analyzed by gas chromatography at the exit of the dark photochemical reactor (Figure ESI 1). For the c_{TP} involved (14 to 200 ppm), the values of $A_{TP,172}$ are within a domain of 15 to 85 and are therefore comparable to the values of O$_2$ and gaseous H$_2$O. For all values of absorption, the optical path length ($r_{ext} - r_{int}$) of the reactor at our disposal was too large (limited availability of Suprasil® tubes) to satisfy the condition of $l_{\lambda,ta}$ (equation ESI i), and important „short-circuiting" as well as inefficient trapping of intermediate radicals might be expected, depending on flux and diffusion.

References:

[ESI R4]   A. M. Braun, M.-T. Maurette, E. Oliveros, *Photochemical Technology*, Wiley, Chichester, 1991

[ESI R5]   G. Heit, A.M. Braun, VUV Photolysis of Aqueous Systems: Spatial Differentiation between Volumes of Primary And Secondary Reactions, *Water Sci.Techn.*, 1997, **35**, 25 - 30.

[ESI R6]   a) K. Yoshino, W.H. Parkinson, K. Ito, T. Matsui, Absolute Absorption Cross Section Measurements of Schumann-Runge Continuum of O2 at 90K and 295K, *J. Mol. Spectr.*, 2005, **229**, 238 - 243.
   b) J. Phys. Chem. A J. B. Nee, P. C. Lee, Detection of O(1D) Produced in the Photodissociation of O$_2$ in the Schumann-Runge Continuum, *J. Phys. Chem. A*, 1997, **101**, 6653 - 6657.

[ESI R7| H. Keller-Rudek, G. K. Moortgat, R. Sander, R. Sörensen, The MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest, www.uv-vis-spectral-atlas-mainz.org
   b) K. Yoshino, J. R. Esmond, W. H. Parkinson, K. Ito, T. Matsu*i,* Absorption cross section measurements of water vapor in the wavelength region 120 to 188 nm, *Chem. Phys.*, 1996, **211**, 387 - 391.

Evaluation of photolysis conditions

$$A_\lambda = \log \frac{1}{T} = l \sum_i (\sigma_{i,\lambda} N_i)$$

(ESI g)

where A_λ: absorbance at λ_{exc}

       T_λ: transmittance at λ_{exc}

       l: optical path length (cm)

       N_i: density of absorbing species i [molecule cm^{-3}]

       $\sigma_{i,\lambda}$:   absorption cross section of species i at λ_{exc} [cm^2 molecule^{-1}]

$$V_R = \pi \left(r_{ext}^2 - r_{int}^2 \right) h$$

(ESI h)

where r_{ext}^2:   radius of the inner wall of the external tube [cm]

       r_{int}^2:   radius of the outer wall of the internal tube [cm]

       h: emitting height or length of the source of radiation [cm]

$$l_{\lambda_{exc}} = \frac{A_{\lambda_{exc}}}{\sum_i (\sigma_{i,\lambda_{exc}} N_i)} \; ; \; l_{ta,\lambda_{exc}} = \frac{2}{\sum_i \sigma_{i,\lambda_{exc}} N_i}$$

(ESI i)

$$\frac{m_{H_2O}}{V} = \frac{p_{H_2O} MW_{H_2O}}{RT}$$

(ESI j)

where m_{H_2O}:   mass of H$_2$O (g)

       V: volume of gas (cm^3)

       p_{H_2O}:   partial pressure of H$_2$O at a given temperature [atm]

       MW_{H_2O}: molecular weight of H$_2$O (18 g mol^{-1})

       R: gas constant (82.06 cm^3 atm mol^{-1} K^{-1})

       T: temperature [K]

GC-Analysis of thiophene (TP)
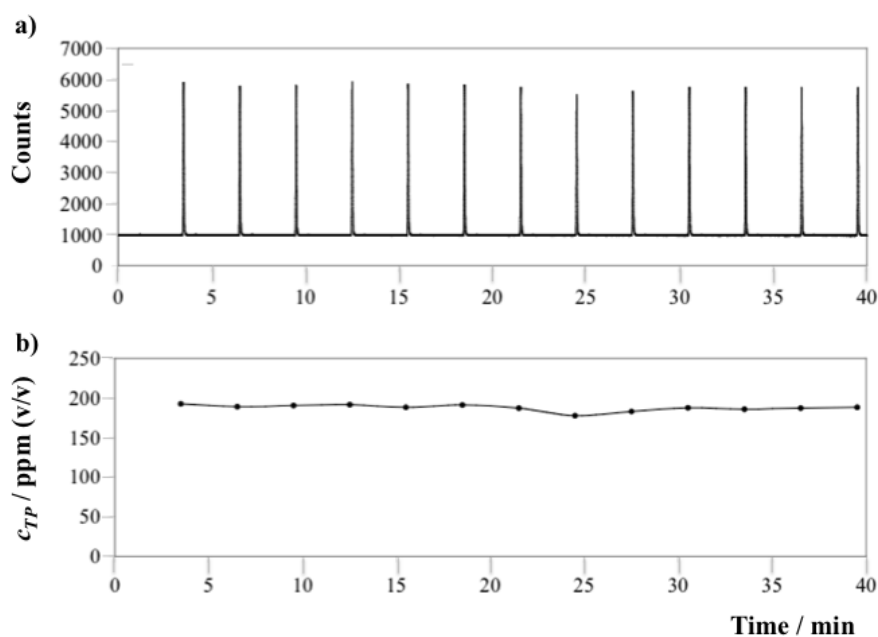
Figure ESI 2. Test of the stability of the concentration of thiophene (**TP**, c_{TP}) exiting the dark photochemical reactor and automatically injected for GC-analysis. a) Counts found by the automatic sampling (3 min interval) and GC-analysis, b) Corresponding **TP** concentrations calculated by means of a calibration curve.
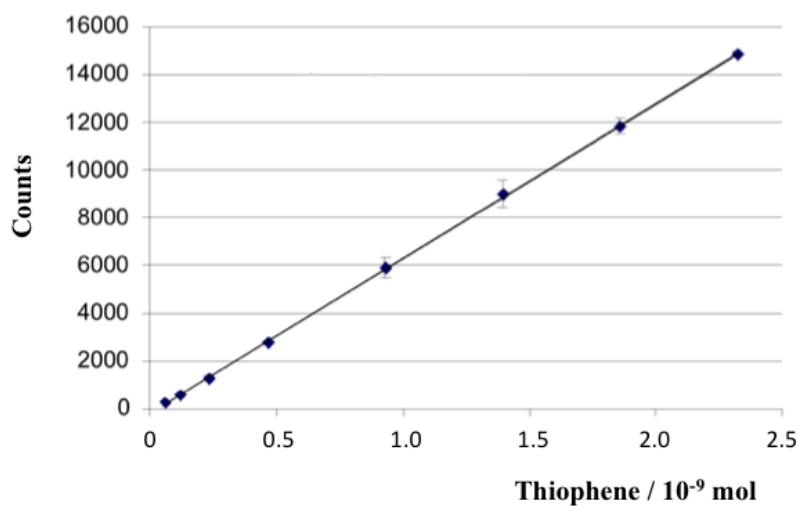
Figure ESI 3. Calibration of the thiophene (**TP**) concentration (c_{TP}) by gas chromatography. Peak surfaces in function of c_{TP} in *n*-hexane. Experimental details, s. $2.1.4.

GC-Analysis of CO₂
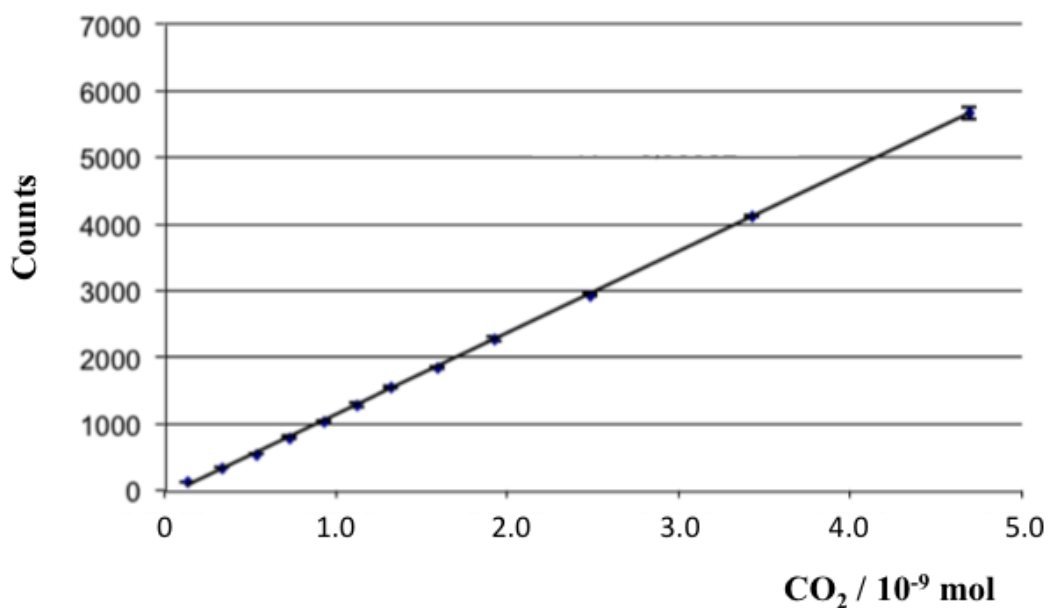
Figure ESI 4. Calibration of the concentration of CO$_2$ (c_{CO_2}) by gas chromatography. Peak surfaces in function of c_{CO_2} contained in the injected samples. The number of moles of CO$_2$ contained in the injected samples was calculated from the known volumes of CO$_2$ (flow control) in using the gas equation (ESI k)

$$pV = nRT \qquad\qquad\qquad \text{(ESI k)}$$

where p: atmospheric pressure (atm)

        V: volume of CO$_2$ in the volume of the sample (0.25 mL) (L)

        n: number of moles

        R = 0,08206 L atm mol^{-1} K^{-1}

        $T = 453,15$K

*Physical data concerning the VUJV-photochemicaly initiated oxidation of thiophene (**TP**)*

Table 1. Absorption cross sections and rate constants of substrates, oxidants and reactions relevant for the present study.

Reaction	Absorption cross section [a]	Rate constant [b]	Symbol	Equations	Ref.
$O_2 + h\nu \longrightarrow 2\,O$	6×10^{-19}		$\sigma_{O_2,172}$	(1)	[ESI R6]
$O + TP \longrightarrow \dots$		1.2×10^{-11}	$k_{O/TP}$	(5), (6), (7)	[36, 37]
$O + H_2O \longrightarrow 2\,HO^\bullet$		2.3×10^{-10}	k_{O/H_2O}	(17)	[61]
$H_2O + h\nu \longrightarrow H^\bullet + HO^\bullet$	5×10^{-18}		$\sigma_{H_2O,172}$	(9)	[ESI R7]
$H^\bullet + O_2 \longrightarrow HO_2^\bullet$		1×10^{10} $M^{-1}\,s^{-1}$ (in H_2O)		(10)	[ESI R8]
$HO^\bullet + TP \longrightarrow HO\text{-}TP^\bullet$		8.2×10^9 $M^{-1}\,s^{-1}$ (in H_2O)	$k_{HO*/TP}$	(13)	[43]
$HO^\bullet + TP \longrightarrow HO\text{-}TP^\bullet$		9.5 to 11×10^{-12}	$k_{HO*/TP}$	(12)	[22a, 26]
$O + O_2 \longrightarrow O_3$		2.8×10^{-12}	k_{O/O_2}	(2)	[62]
$O_3 + TP \longrightarrow \dots$		6×10^{-20}	$k_{O_3/TP}$		[22]
$TP + h\nu \longrightarrow TP*$	6.3×10^{-17}		$\sigma_{TP,172}$	(15)	calc. from [49]

[a] cm^2

[b] cm^3 molecule^{-1} s^{-1}

References:

[ESI R8]   M. G. Gonzalez, E. Oliveros, M. Wörner, A. M. Braun, Vacuum-ultraviolet photolysis of aqueous reactions systems, J. Photochem. Photobiol. C: Photochem. Revs, 2004, **5**, 225-246.