

## Oscillations of the lophyl radical concentration during the photo-decomposition of *o*-Cl-hexaarylbisimidazole

M. Schrödner<sup>a,\*</sup>, H. Schache<sup>a</sup>, H. Lindauer<sup>a</sup>, R. Schrödner<sup>b</sup>, A. Konkin<sup>c</sup>

<sup>a</sup> Thüringisches Institut für Textil- und Kunststoff-Forschung (TTK), Breitscheidstr. 97, 07407 Rudolstadt, Germany

<sup>b</sup> Leibniz-Institut für Troposphärenforschung (IfT), Permoserstr. 15, 04318 Leipzig, Germany

<sup>c</sup> TU Ilmenau, PF 100565, 98684 Ilmenau, Germany

### ARTICLE INFO

#### Article history:

Received 19 December 2011

Received in revised form 3 February 2012

Accepted 11 February 2012

Available online 22 February 2012

#### Keywords:

Lophyl radical

Photoreaction

Oscillating reaction

ESR

Hexaarylbisimidazole

### ABSTRACT

Hexaarylbisimidazole (HABI) is a well established photoinitiator in the graphics industry which undergoes in the absence of other reaction partners a fully reversible homolytic bond cleavage into two lophyl radicals  $L^\bullet$ . Surprisingly we now found oscillations of the radical concentration at low temperature in a solution of *o*-Cl-HABI in toluene, which is an indication of a more complex photochemistry of the HABI/lophyl system. Furthermore this reaction is a very simple example of an oscillating chemical system working under non-flow conditions which involves only one initial reactant. A possible reaction mechanism based on kinetic simulations is proposed.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

The history of the photochemistry of hexaarylbisimidazole (HABI) started in 1960 with synthesis of the photochromic dimer by oxidation of 2,4,5-triphenylimidazole [1]. Since this time a wide variety of derivatives has been synthesized and investigated. In combination with co-initiators and sensitizers many photochemical systems of industrial importance were formulated for applications, e.g. in proof paper (Dylux from DuPont), printing plates, holography and others. All this work is extensively reviewed in the book of Dessauer [2].

In the simplest case the HABI photochemistry can be described by the scheme given in Fig. 1 for the *o*-Cl-HABI.

This reaction consists of a fast homolytic photo scission step of the HABI dimer ( $L_2$ ) into two lophyl radicals  $L^\bullet$  and their slow backward reaction in the dark. Because of its slow recombination the lophyl radical can be easily detected by Electron Spin Resonance (ESR) spectroscopy. There are some hints in the literature that the simple reversible reaction given in Fig. 1 is not sufficient to describe the HABI photochemistry correctly.

ESR investigations of HABI solutions at low temperatures by Maeda and Hayashi reveal an anomalous behavior of the radical concentration at temperatures between  $-40^\circ\text{C}$  and  $-120^\circ\text{C}$  where

the lophyl radical completely disappears, even under continuous illumination [3–5]. They explain this effect by a temperature dependent equilibrium between the lophyl radical and two HABI isomers (photochromic and piezochromic dimer). The equilibrium is on the radical side at higher temperatures and shifts to side of the piezo-dimer at temperatures below  $-20^\circ\text{C}$ .

Wilks and Willis found a deviation from the expected second order reaction kinetics for the dark recombination of the lophyl radicals [6,7]. After switching the light off the reaction order is 3/2 and drops to unity after some hundred seconds. This is an indication of a more complex reaction mechanism. The authors could explain this behavior by the inclusion of intermediate ionic species and an adduct (complex) of the lophyl radical with the parent HABI molecule or a solvent molecule. They also found a weak dependence of the 3/2 rate constant on concentration.

These results had been confirmed by Prokhoda and Krongauz [8], who found a second order recombination at low concentrations ( $10^{-5}\text{ M}$ ) and a 3/2 order reaction at higher concentrations ( $>10^{-4}\text{ M}$ ) of the starting HABI in benzene.

Oscillating chemical reactions have first been observed in 1920 by Bray during the decomposition of hydrogen peroxide with iodide and iodide acid [9]. In this reaction intermediates like HIO, HIO<sub>2</sub> and I<sub>2</sub> are involved. In 1952 Belousov and Zhabotinsky found oscillations during the oxidation of citric acid by bromate in the presence of Ce<sup>4+</sup> [10,11]. Also this reaction consists of at least five steps and involves several intermediates. Other known oscillating reactions are the Briggs–Rauscher reaction or the thermal decomposition

\* Corresponding author. Tel.: +49 3672 379553; fax: +49 3672 379379.  
E-mail address: [schroedner@titk.de](mailto:schroedner@titk.de) (M. Schrödner).

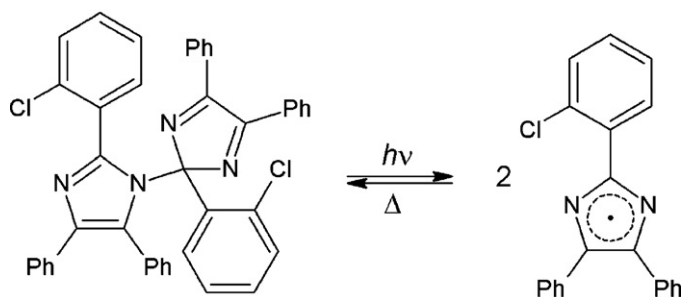


Fig. 1. Standard reaction scheme of the reversible *o*-Cl-HABI photolysis.

of sodium dithionite [12]. Photochemical oscillations occur, e.g. during the photoreduction of benzoquinone or 4-aminophenol in acidic bromate solution [13–15].

According to theory an oscillating chemical reaction system must be far away from equilibrium, involve at least one non-linear autocatalytic or autoinhibitory reaction step which exerts a large enough feedback regulation and show bi-stability. Most of the known oscillating reactions work in a continuous flow reactor where the consumed educts are compensated and products are removed continuously. Depending on the appropriate choice of the kinetic parameters (rate constants, initial concentrations) such a system can show sustained or damped oscillations.

## 2. Materials and methods

The hexaarylbisimidazole derivative (2,2'-di(*ortho*-chlorophenyl)-4,4',5,5'-tetraphenylbisimidazole) was provided by Kodak Polychrome Graphics and used without further purification.

For ESR spectroscopy a 0.5 mM solution of *o*-Cl-HABI in toluene was prepared and filled in a quartz tube of 4 mm inner diameter. The solution was degassed by evaporation during three freeze–thaw cycles. After degassing the samples were sealed and placed in the ESR microwave cavity. The sample was illuminated through the cavity front side by UV light from a 150 W xenon lamp.

ESR spectra were recorded using a Bruker X-band ESR spectrometer ELEXYS E500 equipped with a variable temperature system. The spectrometer was operated in the continuous wave mode with 100 kHz modulation. ESR intensities as a measure of the radical concentration were taken as half peak height of the ESR derivative spectrum.

## 3. Results

### 3.1. ESR measurements

ESR spectra were continuously recorded every 11.2 s during illumination of the samples at  $-50^{\circ}\text{C}$ . The spectrum consists of broad line at  $g=2.003$  with a peak to peak line width of 0.68 mT which shows some poorly resolved hyperfine splitting of about 0.072 mT (insert in Fig. 2). The spectrum is attributed to the lophyl radical  $\text{L}^{\bullet}$ . The hyperfine splitting originates from magnetic interactions of the electron spin with paramagnetic nitrogen nuclei at the imidazole ring and hydrogen nuclei at the phenyl rings [16]. The spectrum can also include adducts of the lophyl radical with diamagnetic species which cannot be separated from the lophyl spectrum under our experimental conditions.

The radical concentration grows during the first 50 s as expected and then tends to saturate. Surprisingly, it does not keep constant but begins to oscillate with a period of about 90 s (Fig. 2). This behaviour was observed not only for the pure *o*-Cl-HABI solution, but also in the presence of, e.g. 5-*tert*-butyl-1,2,4-triazole-3-thiol, which should act as a co-initiator. The concentration of this

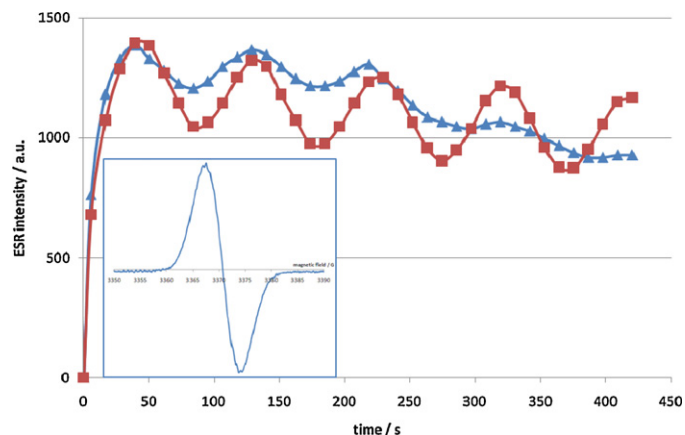


Fig. 2. ESR intensity of radicals produced under continuous illumination of  $0.5 \times 10^{-3}$  M *o*-Cl-HABI solution in toluene at  $-50^{\circ}\text{C}$ ; triangles: pure *o*-Cl-HABI; squares: with  $0.3 \times 10^{-3}$  M 5-*tert*-butyl-1,2,4-triazole-3-thiol; insert: ESR spectrum.

co-initiator up to 0.5 mmol/l had no significant effect on the oscillating patterns.

### 3.2. Kinetic modeling

To generate oscillations the reaction scheme (I) was extended by a reversible formation of an adduct of the lophyl radical with a solvent (toluene) molecule (II) as proposed in [6,7]. This adduct decomposes either by a first order decay (backward reaction of (II)) or by an autocatalytic step involving at least two lophyl radicals (III). The complete reaction scheme is as follows:



Herein **S** denotes the solvent and **SL<sup>•</sup>** the solvent-lophyl adduct. The third or higher order reaction (III) perhaps can be subdivided into further elementary second order reaction steps as proposed by [17]. This model resembles a reduced Walz–Caplan model [18] or a modified Brusselator [19] or Gray–Scott model [20]. Preliminary Monte Carlo simulations using the IBM chemical kinetics simulator [21] were done to check whether the system oscillates and to stake out the range of kinetic parameters where such oscillations exist. Oscillations were found for  $n \geq 2$  only. Moreover it was found that the backward reaction in step (III) is not essential for oscillations and can be omitted ( $k_{-3} = 0$ ).

Subsequently, taking account of these results a set of differential equations for the reaction rates was derived from the reaction schemes (I)–(III) with  $n=2$  and  $k_{-3}=0$ :

$$\frac{d[\text{L}_2]}{dt} = -k_1[\text{L}_2] + k_{-1}[\text{L}]^2 \quad (1)$$

$$\frac{d[\text{L}]}{dt} = 2k_1[\text{L}_2] - 2k_{-1}[\text{L}]^2 + k_3[\text{SL}][\text{L}]^2 - k_2[\text{L}][\text{S}] + k_{-2}[\text{SL}] \quad (2)$$

$$\frac{d[\text{SL}]}{dt} = -k_3[\text{SL}][\text{L}]^2 + k_2[\text{L}][\text{S}] - k_{-2}[\text{SL}] \quad (3)$$

with the initial conditions:  $[\text{L}](0) = [\text{SL}](0) = 0$ ;  $[\text{L}_2](0) = 0.5 \times 10^{-3}$  mol/l;  $[\text{S}](0) = 9.44$  mol/l.

The system of differential equations was solved numerically using the atmospheric box model SPACCIM (Spectral Aerosol Cloud Chemistry Interaction Model) which is normally applied for the description and connection of multiphase chemistry and microphysical processes of clouds [22]. In this model the kinetics of different atmospheric processes are integrated in an

Download English Version:

<https://daneshyari.com/en/article/26332>

Download Persian Version:

<https://daneshyari.com/article/26332>

[Daneshyari.com](https://daneshyari.com)