

New aspects in the photokinetics of Aberchrome 540¹

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Abstract

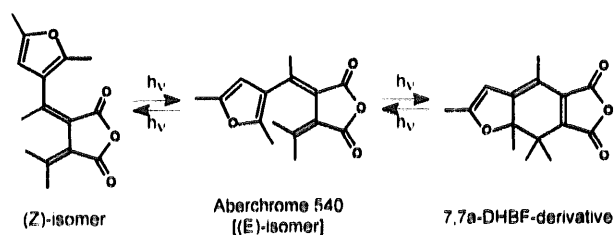
The photokinetics of the furylfulgide Aberchrome 540 were investigated in the solvents *n*-hexane, toluene and ethylacetate. A wavelength of 365 nm for the colouring process and a wavelength of 436 nm for the bleaching process were used for irradiation. The reactions were monitored by UV–visible absorption spectroscopy. The reaction spectra were used to calculate by means of multicomponent analysis the concentration–time curves of the reactants. From these the partial photochemical quantum yields were determined by numerical integration of the photokinetic equations. These examinations and thin layer chromatography demonstrated that after irradiation at 365 nm in the photostationary state, besides the 7,7a-dihydrobenzofuran (DHBF) derivative, further compounds exist. This is in contrast with earlier investigations by other workers who stated quantitative conversion in the colouring process and set the UV–visible spectroscopy data of the photostationary state equal to those of the 7,7a-DHBF derivative. Our differing results affect the usage of Aberchrome 540 as a chemical actinometer.

Keywords: Photokinetics; Aberchrome 540; Bleaching; Irradiation

1. Introduction

The furylfulgide Aberchrome 540 is a widely used photochromic compound being investigated in solution [1–7], in polymers [6–9] and in the solid state [10]. Aberchrome 540 is also known as a chemical actinometer in the UV range [11]. On irradiation at 365 nm the electrocyclic ring closure reaction of the (*E*)-isomer to the red 7,7a-dihydrobenzofuran (DHBF) derivative is the desired photoreaction, but in addition a reversible photochemical *E*–*Z* isomerization to the (*Z*)-isomer occurs (Scheme 1). The *E*–*Z* isomerization with respect to the influence of the (*Z*)-isomer on the usage of Aberchrome 540 as chemical actinometer has been discussed for a long time. However, up to now the photostationary state (PSS) has been considered as a pure 7,7a-DHBF derivative and the UV–visible spectroscopy data obtained have been interpreted as those of this compound. In consequence in the literature [2–5] a quantitative conversion of the (*E*)-isomer to the 7,7a-DHBF derivative is postulated which implies that the quantum yield ϕ_{CE} of the ring opening reaction equals zero.

However, according to our experiments by irradiation at 365 nm the 7,7a-DHBF derivative is in equilibrium with the



Scheme 1. Reaction scheme of the furylfulgide Aberchrome 540.

(*E*)-isomer. If this photostationary state is irradiated at 436 nm, the 7,7a-DHBF derivative will be reconverted to the (*E*)-isomer. As both the (*E*)- and the (*Z*)-isomer do not absorb light at this wavelength of irradiation, the ring-opening reaction occurs without any side reactions. Furthermore, the thermal stability of all the reactants allows their isolation and the measurement of their spectroscopic properties (the UV–visible absorption spectra). These spectra can be used to evaluate a reaction spectrum by means of multilinear regression. Thus the concentration–time curves can be calculated to obtain the photochemical quantum yields. In addition the spectra of the pure compounds can be used to control whether the photostationary state is pure 7,7a-DHBF derivative, which is a prerequisite for kinetic treatment found in literature.

¹ Dedicated to Professor Scharf on the occasion of his 65th birthday.

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2. Experimental details

2.1. Synthesis

The (*E*)- and the (*Z*)-isomer were synthesised according to the literature [1]. Their purity was checked by thin layer chromatography (7:1 *n*-hexane:ethylacetate as eluent on silica gel). The 7,7*a*-DHBF derivative was obtained by irradiation of a solution of the (*E*)-isomer in ethylacetate at 365 nm. The crude product was purified by flash column chromatography on silica gel (0.063–0.2 mesh) with a mixture of 7:1 *n*-hexane:ethylacetate as eluent, followed by recrystallization from 4:1 *n*-hexane:chloroform. The product was pure 7,7*a*-DHBF derivative according to thin layer chromatography [12].

2.2. Spectroscopic measurements

Several air-saturated solutions of both the (*E*)- and the (*Z*)-isomer and the 7,7*a*-DHBF derivative were prepared in *n*-hexane, toluene and ethylacetate by weighing in (two or three times per compound and solvent) and diluting (three to four times). The concentrations of the obtained solutions were about 10^{-4} mol L⁻¹. A Zeiss DMR10 spectrophotometer and a Zeiss Specord M500 spectrophotometer respectively were used to determine the absorption coefficients and to follow the photoreactions at a temperature of 293 K.

2.3. Irradiation

Monochromic light of wavelength 365 or 436 nm was supplied by a high pressure mercury lamp ST75 (Heraeus) in combination with adequate interference filters (UV PII.; bandwidth, 10 nm). The irradiation intensity was determined using the trioxalatoferrate(III) chemical actinometer (Parker) [13,14].

The photoreactions were carried out until the photostationary states were reached. Irradiation intensities of about $(2-3) \times 10^{-9}$ Einsteins cm² s⁻¹ lead to exposure times of 60–90 min for both irradiation wavelengths. On irradiation at 365 nm, excessive exposure of the probe caused a decomposition of about 4% within 14 h.

3. Results and discussion

3.1. UV-visible absorption spectra

Fig. 1 shows the UV-visible absorption spectra of all reactants measured in *n*-hexane. The absorption coefficients at the wavelength of maximum absorbance are given in Table 1 for several solvents. The comparison to the values determined by Heller and coworkers [1,15] and Kurita and coworkers [7] demonstrates significant differences in the obtained values of the 7,7*a*-DHBF derivative.

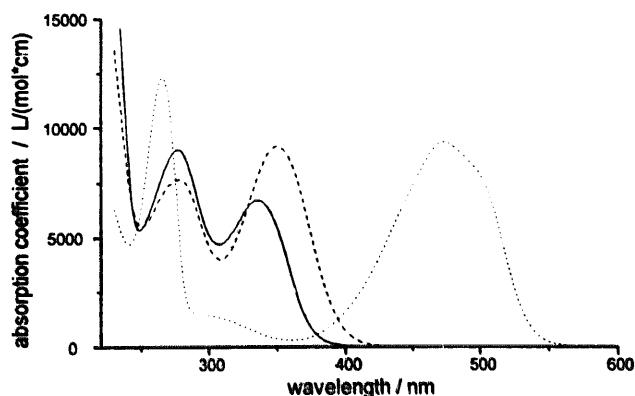


Fig. 1. UV-visible absorption spectra of Aberchrome 540 and its isomers in *n*-hexane: —, Aberchrome 540, (*E*)-isomer; - - -, Aberchrome 540, (*Z*)-isomer; ·····, 7,7*a*-DHBF derivative.

3.2. Photostationary state

The reason for the strongly differing absorption coefficients of the 7,7*a*-DHBF derivative becomes obvious by comparing the spectrum of this compound with the spectrum of the photostationary state after irradiation at 365 nm (Fig. 2). In the photostationary state the remaining (*E*)- and (*Z*)-isomers contribute to the absorbance below 400 nm, which causes in this wavelength range a higher absorbance than in the spectrum of the 7,7*a*-DHBF derivative, if the maximum absorbance at 473 nm is set to be equivalent. This proves that there is no quantitative conversion to the 7,7*a*-DHBF derivative, which is in agreement to examinations of other furylfulgides [16] which exhibit an equilibrium between 7,7*a*-DHBF derivative and (*E*)-isomer also.

The composition of the photostationary state after irradiation at 365 nm was determined by means of multicomponent analysis using the method of multilinear regression (see Appendix). The relative amount of the reactant is given in Table 2. The content of the 7,7*a*-DHBF derivative does not exceed 96% in any solvent, and in *n*-hexane it is less than 90%. The fact that the absorbance in the photostationary state has been considered by Heller and others to belong to 100% conversion instead of 90–95% might explain most of the difference between the absorption coefficients of the 7,7*a*-DHBF derivative determined by the different research groups.

The generation of two different photostationary states according to Scheme 2 makes it possible to verify the consistency of calibration of the reactants among one another. The concentration of solution of (*Z*)-isomer is compared with the total concentration of the photostationary state after irradiation at 365 nm respectively 436 nm (Fig. 3). In *n*-hexane we obtained a deviation of less than 2% from the mean of the three solutions whereas the absorption coefficients determined by Heller and coworkers lead to a difference of approximately 14% if they are used to calculate the concentrations of the various isomers. In toluene and ethylacetate the results are quite similar.

Table 1
Absorption coefficient ϵ_{\max} of the isomers at the wavelength λ_{\max} of maximum absorbance where the data are taken from the studies of Heller and coworkers [1,15] and Kurita and coworkers [7]; experimental values are the absorption coefficients determined after purification via chromatography and recrystallization

	Solvent, <i>n</i> -hexane			Solvent, toluene			Solvent, ethylacetate		
	λ_{\max} (nm)	ϵ_{\max} (l mol ⁻¹ cm ⁻¹)	Heller and coworkers	λ_{\max} (nm)	ϵ_{\max} (l mol ⁻¹ cm ⁻¹)	Heller and coworkers	λ_{\max} (nm)	ϵ_{\max} (l mol ⁻¹ cm ⁻¹)	Heller and coworkers
(<i>E</i>)-isomer	335	6710	6612	343	6290	6077	340	6270	5940
(<i>Z</i>)-isomer	350	9170	—	354	8520	—	349	8650	—
7,7 <i>a</i> -DHBF derivative	473	9360	8200	493	8840	8200	492	8850	7874
									Kurita and coworkers
									6200
									8500
									8500

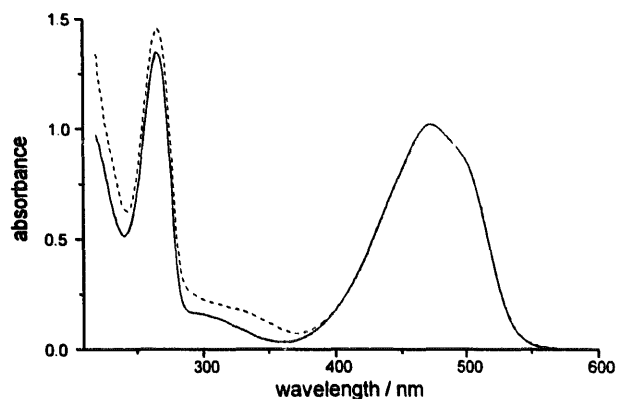
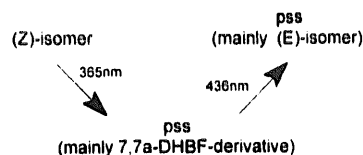


Fig. 2. UV-visible absorption spectra of the 7,7*a*-DHBF derivative (—) and of the photostationary state after irradiation at 365 nm (---) in *n*-hexane.

Table 2
Relative amounts of the isomers in the photostationary state after irradiation at 365 nm

	Relative amount (%) in following solvents		
	<i>n</i> -Hexane	Toluene	Ethylacetate
(<i>E</i>)-isomer	9.1	4.1	2.7
(<i>Z</i>)-isomer	1.5	0.9	1.3
7,7 <i>a</i> -DHBF derivative	89.4	95.0	96.0



Scheme 2. Verification of calibration using two different photostationary states.

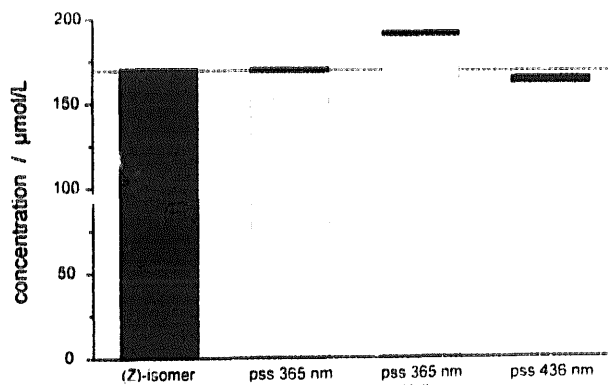


Fig. 3. Composition of the solutions obtained according to Scheme 2 using *n*-hexane as solvent: □, (*E*)-isomer; ■, (*Z*)-isomer; ▣, 7,7*a*-DHBF derivative.

3.3. Photokinetics

The experimental concentration–time curves in Fig. 4 were calculated by multicomponent analysis of the reaction spectra. The rate equations describing the photoreaction at 365

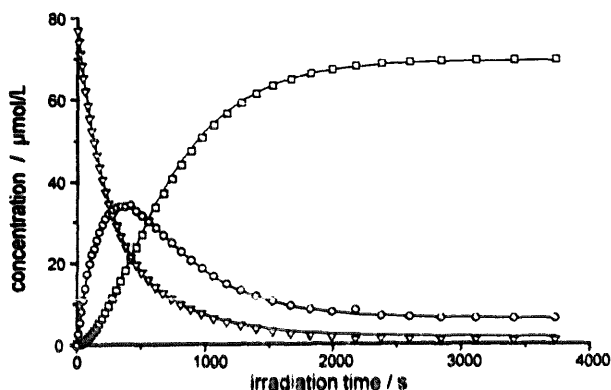


Fig. 4. Calculated values (by multilinear regression) of the concentration-time curves of the photoreaction of the (Z)-isomer in *n*-hexane at an irradiation wavelength of 365 nm: O, (E)-isomer; ∇ , (Z)-isomer; \square , 7,7a-DHBF derivative; —, results from the Runge-Kutta-Fehlberg back simulation calculated with the quantum yields given in Table 3.

Table 3
Partial photochemical quantum yields for irradiation at 365 and 436 nm for the four possible partial reaction steps

Solvent	λ' (nm)	ϕ_{ZE}	ϕ_{EZ}	ϕ_{EC}	ϕ_{CE}	ϕ_{CE}'
<i>n</i> -Hexane	365	0.11	0.12	0.20	0.12	
Toluene	365	0.12	0.13	0.18	0.07	
Ethylacetate	365	0.12	0.12	0.18	0.05	
<i>n</i> -Hexane	436					0.11
Toluene	436					0.09
Ethylacetate	436					0.06

E, (E)-isomer; Z, (Z)-isomer; C, 7,7a-DHBF derivative. For example ϕ_{EC}

Table 4
Calculated values for the expression $\phi_{EC}\epsilon_{C,\lambda_{max}}$ which is necessary in chemical actinometry using Aberchrome 540 where experimental values are calculated from our own experiments and the values from Heller and coworkers and Kurita and coworkers are calculated from data in literature

Solvent	$\phi_{EC}\epsilon_{C,\lambda_{max}} (\times 10^3 \text{ cm}^2 \text{ Einstein}^{-1})$		
	Experimental	Heller and coworkers	Kurita and coworkers
<i>n</i> -Hexane	1870	1720	—
Toluene	1590	1640	1660
Ethylacetate	1590	1570	1700

nm and 436 nm respectively were numerically integrated (see Appendix). The resulting partial photochemical quantum yields of all the reaction steps are given in Table 3. On irradiation at 365 nm the ring-opening reaction of the 7,7a-DHBF derivative to the (E)-isomer takes place in all the solvents used, which is in contradiction to investigations by Heller and coworkers [1] and Kurita and coworkers [7] and is not taken into account in a recent report by Guo et al. [5]. The values of ϕ_{CE} at 365 nm are of the same magnitude as of ϕ_{CE}' at 436 nm. This implies that the ring-opening reaction occurs in both cases from the same excited state.

If Aberchrome 540 is used as a chemical actinometer in the UV range, the product $\phi_{EC}\epsilon_{C,\lambda_{max}}$ is essential to calculate the irradiation intensity. The values for this expression obtained from the experimental results of various research groups are given in Table 4. There is not sufficient correspondence between these results. The large differences in the absorption coefficients of the 7,7a-DHBF derivative are obviously one reason for that.

4. Conclusions

The photoreaction of Aberchrome 540 was investigated for the first time using the UV-visible absorption spectrum of the pure 7,7a-DHBF derivative (obtained by preparative chromatography followed by recrystallization) instead of the spectroscopic data of the photostationary state. Therefore it was possible to elucidate that the photochemical ring-opening reaction from the 7,7a-DHBF derivative to the (E)-isomer occurs by irradiation not only in the visible range but also in the UV range. This causes an equilibrium reaction rather than a pure electrocyclic ring closure. Furthermore, the corresponding quantum yields of the ring opening reaction show the same magnitude.

The problem of Aberchrome 540 in chemical actinometry is not the occurrence of the (Z)-isomer [4] as the high concentration of Aberchrome 540 used for this purpose leads only to a low conversion and a negligible concentration of the (Z)-isomer. In fact neglect of the ring opening and the ring-closure reaction, the differing spectroscopic data concerning the 7,7a-DHBF derivative and in consequence the different photokinetic results of various research groups dealing with Aberchrome 540 indicate that a stringent recalibration of this compound is necessary if it is used as a chemical actinometer.

Appendix

A.1. Multilinear regression [17]

$$A = \epsilon cd + e \quad (\text{A1})$$

Eq. (1) has to be solved for the unknown concentration vector c . The vector A represents the measured absorbance spectra of the solution, the matrix ϵ the absorbance spectra of three reactants, and d the path length of the cell. The difference between the measured spectrum A and the result of the multilinear regression is considered in the error vector e . The product of the transposed vector e^T and the vector e results in the sum of squares which has to be minimized (least-squares regression). This condition leads to

$$c = (\epsilon^T \epsilon)^{-1} \epsilon^T A \frac{1}{d} \quad (\text{A2})$$

The exponent -1 means inversion of a matrix.

A.2. Photokinetics [18]

A.2.1. Irradiation at 365 nm. The following rate equations describing the photokinetics of the fulgide system according to Scheme 1 have to be numerically integrated to estimate the quantum yields because of the time-dependent photokinetic factor $F(A')$:

$$\frac{dc_Z}{dt} = -\epsilon_Z' c_Z \phi_{ZE} I_0 F(A') + \epsilon_E' c_E \phi_{EZ} I_0 F(A')$$

$$\frac{dc_E}{dt} = +\epsilon_Z' c_Z \phi_{ZE} I_0 F(A') - \epsilon_E' c_E \phi_{EZ} I_0 F(A') - \epsilon_E' c_E \phi_{EC} I_0 F(A') + \epsilon_C' c_C \phi_{CE} I_0 F(A') \quad (A3)$$

$$\frac{dc_C}{dt} = +\epsilon_E' c_E \phi_{EC} I_0 F(A') - \epsilon_C' c_C \phi_{CE} I_0 F(A')$$

where ϵ_i' is the absorption coefficient of the compound I at the wavelength of irradiation λ' , c_i the molar concentration of the compound I, ϕ_{IJ} the partial photochemical quantum yield of the partial reaction $I \rightarrow J$, I_0 the irradiation intensity, $F(A') = (1 - 10^{-A'})/A'$ the photokinetic factor and A' absorbance at the irradiation wavelength λ' . The numerical integration is done within an interval l starting at the measured point i :

$$c_Z(t_{i+l}) - c_Z(t_i) = -\epsilon_Z' \phi_{ZE} I_0 Z_{i,l} + \epsilon_E' \phi_{EZ} I_0 E_{i,l}$$

$$c_E(t_{i+l}) - c_E(t_i) = +\epsilon_Z' \phi_{ZE} I_0 Z_{i,l} - (\epsilon_E' \phi_{EZ} I_0 E_{i,l} + \epsilon_E' \phi_{EC} I_0) E_{i,l} + \epsilon_C' \phi_{CE} I_0 C_{i,l} \quad (A4)$$

$$c_C(t_{i+l}) - c_C(t_i) = +\epsilon_E' \phi_{EC} I_0 E_{i,l} + \epsilon_C' \phi_{CE} I_0 C_{i,l}$$

where

$$C_{i,l} = \int_i^{i+l} c_C F(A') dt$$

$$E_{i,l} = \int_i^{i+l} c_E F(A') dt$$

$$Z_{i,l} = \int_i^{i+l} c_Z F(A') dt$$

Taking various measured points as starting point of the integration interval leads to a system of linear equations. Its solution supplies the photochemical quantum yields.

A.2.2. Irradiation at 436 nm. As only the 7,7a-DHBF derivative absorbs light at this wavelength, the rate equations (A3) simplify to

$$\frac{dc_C}{dt} = -\phi_{CE}' I_0 \frac{1 - 10^{-A'}}{d}$$

$$\frac{dc_E}{dt} = +\phi_{CE}' I_0 \frac{1 - 10^{-A'}}{d} \quad (A5)$$

The numerical integration executed by analogy to the procedure described above leads to Eq. (A6). The photochemical quantum yield ϕ_{CE}' is part of the slope of a straight line which can be obtained by calculating several integrals.

$$c_C(t_{i+l}) - c_C(t_i) = -\frac{\phi_{CE}' I_0}{d} \int_i^{i+l} (1 - 10^{-A'}) dt$$

$$c_E(t_{i+l}) - c_E(t_i) = +\frac{\phi_{CE}' I_0}{d} \int_i^{i+l} (1 - 10^{-A'}) dt \quad (A6)$$

References

- [1] P.J. Darcy, H.G. Heller, P.J. Strydom and J. Whittall, *J. Chem. Soc., Perkin Trans. I*, (1981) 202.
- [2] R. Bär, *Ph.D. Thesis*, Tübingen, 1987.
- [3] P. Boule and J.F. Pilichowsky, *J. Photochem. Photobiol. A: Chem.*, 71 (1993) 51.
- [4] H.G. Heller, *EPA Newsllett.*, 47 (1993) 44.
- [5] Z. Guo, G. Wang, Y. Tang and X. Song, *J. Photochem. Photobiol. A: Chem.*, 88 (1995) 31.
- [6] V. Deblauwe and G. Smets, *Makromol. Chem.*, 189 (1988) 2503.
- [7] Y. Yokoyama, H. Hayata, H. Ito and Y. Kurita, *Bull. Chem. Soc. Jpn.*, 63 (1990) 1607.
- [8] M. Rappon, A. Chuenarm, A.J. Duggal, H. Gill, O. Bhaovibul and R.T. Syvitski, *Eur. Polym. J.*, 27 (1991) 365.
- [9] M. Rappon, R.T. Syvitski and A. Chuenarm, *Eur. Polym. J.*, 28 (1992) 399.
- [10] K. Ulrich and H. Port, *J. Mol. Struct.*, 218 (1990) 45.
- [11] H.G. Heller and J.R. Langan, *J. Chem. Soc., Perkin Trans. II*, (1981) 341.
- [12] E. Uhlmann, *Ph.D. Thesis*, Tübingen, 1995.
- [13] C.G. Hatchard and C.A. Parker, *Proc. R. Soc. London A*, 235 (1956) 518.
- [14] S. Hubig, *Ph.D. Thesis*, Tübingen, 1980.
- [15] A.P. Glaze, H.G. Heller and J. Whittall, *J. Chem. Soc., Perkin Trans. II*, (1992) 591.
- [16] Y. Yokoyama, T. Iwai, N. Kera, I. Hitomi and Y. Kurita, *Chem. Lett.*, (1990) 263.
- [17] P. Valko and S. Vajda, *Data Handling in Science and Technology*, Elsevier, Amsterdam, 1989.
- [18] H. Mauser, *Formale Kinetik*, Bertelsmann Universitätsverlag, Düsseldorf, 1974.