

# Photokinetic study on the photochromic reaction of Aberchrome 540<sup>TM</sup>: a further comment about the use of Aberchrome 540<sup>TM</sup> in chemical actinometry

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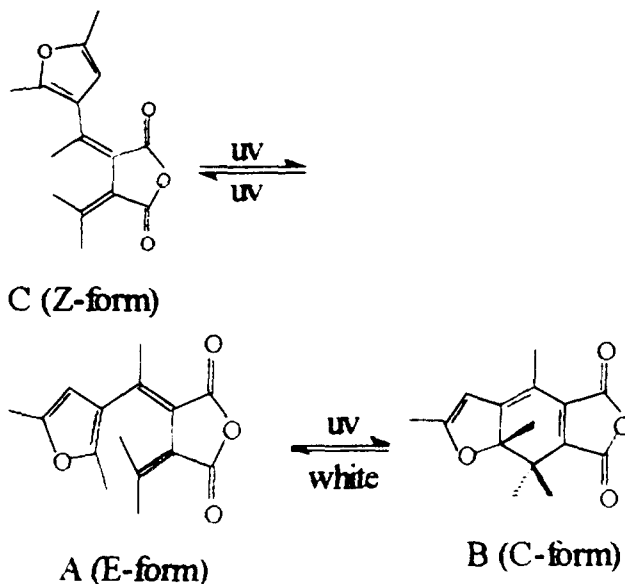
## Abstract

The photochromic reaction of Aberchrome 540<sup>TM</sup> is studied using a photokinetic method. It is found that the photocyclization is accompanied by E ↔ Z isomerization. An equation is derived from photokinetic equations to describe the proportion of the light absorbed by the Z isomer to that absorbed by the E isomer. The value is 0.56 when the fulgide is irradiated after one cycle, which is the very reason why the irradiated solution should not be reused after bleaching.

**Keywords:** Photochromic reaction; Photokinetics; Aberchrome 540<sup>TM</sup>; Chemical actinometry

## 1. Introduction

The pale yellow fulgide (*E*)-2-[1-(2,5-dimethyl-3-furyl)-ethylidene]-3-isopropylidene succinic anhydride (formula A), whose commercial name is Aberchrome 540<sup>TM</sup>, was first synthesized by Darcy et al. [1] and is widely used as a convenient actinometer in the near-UV and visible regions because of its reversible photocyclization into the deep red cyclized valence isomer 7,7a-dihydro-2,4,7,7a-pentamethylbenzo(*b*)furan-5,6-dicarboxylic anhydride (formula B) [2,3]. According to Heller and Langan [2], one of the main advantages of the fulgide is its chemical stability and the reversibility of its photocyclization, so it can be repeatedly used for many cycles. Recently Boule and Pilichowski [4] stated that the irradiated solution should not be reused after bleaching because there was a drop in the apparent quantum yield value of the photocyclization after one cycle due to E ↔ Z isomerization, but Heller [5] immediately refuted this claim, saying there was no detectable change in the quantum yield of the fulgide in toluene when it was reused 10 times. In order to clear up this argument, a detailed photokinetic study on the photochromic reaction of the named compound is desirable.



## 2. Experimental details

The fulgide was synthesized according to Ref. [1] ( $\epsilon_A^{342} = 6035 \text{ mol}^{-1} \text{ l cm}^{-1}$ ,  $\epsilon_B^{494} = 7760 \text{ mol}^{-1} \text{ l cm}^{-1}$ ). The reaction cell was modified (Fig. 1) and fitted in a diode array spectrophotometer (HP8452A, Hewlett-Packard) so that the photoreaction could be followed spectroscopically during irradiation. The irra-

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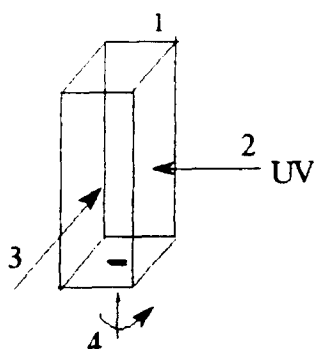


Fig. 1. Modified reaction cell: 1, cell; 2, irradiation beam of 366 nm; 3, observation beam; 4, magnetic stirrer.

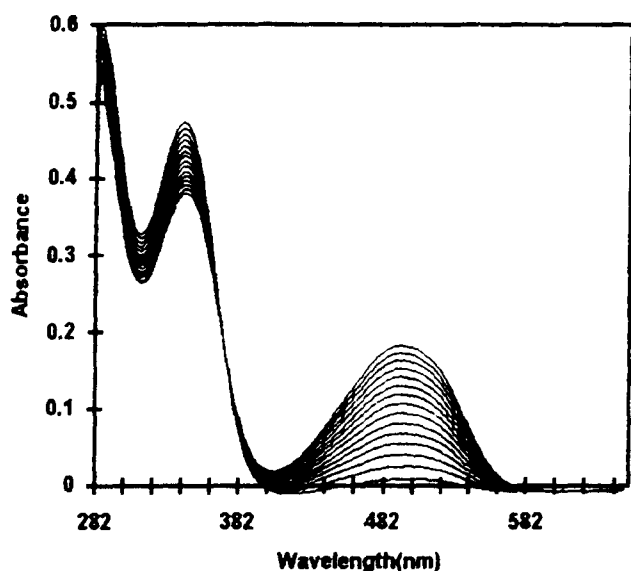


Fig. 2. Reaction spectrum for the photocyclization of compound A in toluene.

irradiation light was perpendicular to the optical pathway of measurement so that the irradiation did not disturb the absorbance measurement; 366 nm light from a 250 W high pressure Hg lamp was used as the excitation source in the photocoloration process; 492 nm light from a 150 W Xe lamp was used as the bleaching source in the photodecoloration process. Toluene was purified by redistillation. The concentration of the toluene solution of the fulgide is about  $1.0 \times 10^4$  mol  $l^{-1}$ .

### 3. Results and discussion

The reaction spectrum is given in Fig. 2, which shows the absorbance vs. wavelength at various reaction times. The absorbance data at wavelengths of 330, 342, 354 and 360 nm plotted vs. the absorbance at 494 nm at all reaction times are shown in Fig. 3 (absorbance ( $E$ ) diagram). From the linear relationship it can be reasonably assumed that the photochromic reaction may

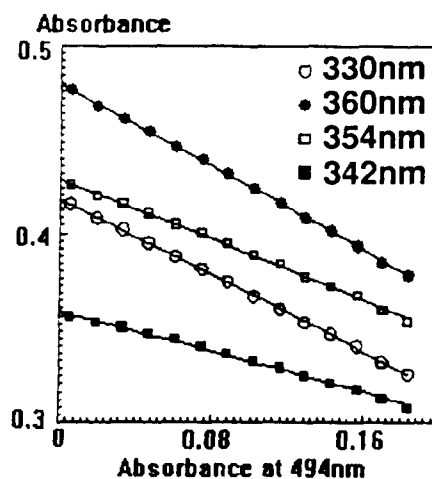


Fig. 3. Absorbance plots for compound A in toluene. Straight lines are observed for combinations of absorbances at two wavelengths.

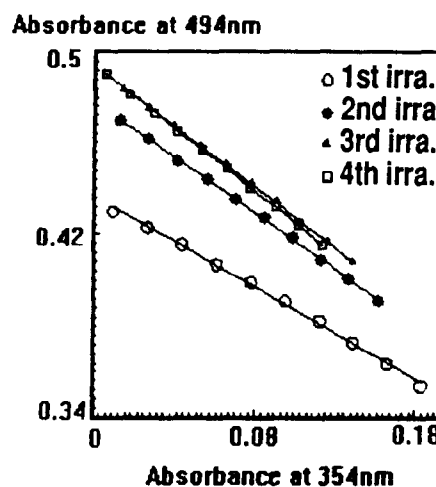


Fig. 4. Absorbance plots for compound A in toluene. Straight lines are observed for combinations of the absorbance at 354 nm vs. 494 nm for one, two, three and four cycles.

be treated as a uniform one; the overall reaction can be considered to follow the mechanism proposed in Ref. [6].

We also obtained the absorbance data at 354 nm vs. 494 nm for the fulgide after one, two, three and four cycles of 492 nm light bleaching (Fig. 4).

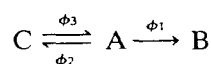
If only considering the reaction  $A \rightarrow B$ , we can obtain

$$E^\lambda(t) = \frac{-\epsilon_A^\lambda + \epsilon_B^\lambda}{\epsilon_B^{494}} [E_B^{494}(t) - E_B^{494}(0)] + E_A^\lambda(0) \quad (1)$$

where  $\epsilon_A^\lambda$  and  $\epsilon_B^\lambda$  are the molar decadic absorption coefficients of compounds A and B respectively at wavelength  $\lambda$ ,  $\epsilon_B^{494}$  is the molar decadic absorption coefficient of compound B at 494 nm,  $E^\lambda(t)$  is the absorbance of the reaction mixture at wavelength  $\lambda$  at time  $t$ ,  $E_B^{494}(t)$  is the absorbance of the coloured form at 494 nm at time  $t$ , and  $E^\lambda(0)$  and  $E_B^{494}(0)$  are the corresponding absorbances at time zero. From this equation the lines in Fig. 4 should have the same slope

value, but the real slope values of Fig. 4 are not the same. This implies that the photoisomerization  $C \leftrightarrow A$  is non-negligible in this case.

The rate law for the reaction



is given by

$$\frac{da}{dt} = -(\phi_1 + \phi_2)1000I_0\epsilon_A'F(E')a(t) + \phi_31000I_0\epsilon_C'F(E')c(t) \quad (2)$$

$$\frac{db}{dt} = \phi_11000\epsilon_A'F(E')a(t) \quad (3)$$

$$\frac{dc}{dt} = -\phi_31000\epsilon_C'F(E')c(t) + \phi_21000\epsilon_A'F(E')a(t) \quad (4)$$

where  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  are the differential photochemical quantum yields of photoreactions  $A \rightarrow B$ ,  $A \rightarrow C$  and  $C \rightarrow A$  respectively,  $\epsilon_A'$  and  $\epsilon_C'$  are the molar decadic absorption coefficients of compounds A and C respectively at the irradiation wavelength,  $F(E') = (1 - 10^{-E'})/E'$  is the photokinetic factor with absorbance  $E'(t)$  at the irradiation wavelength at time  $t$ , and  $a(t)$ ,  $b(t)$  and  $c(t)$  are the concentrations of compounds A, B and C respectively at time  $t$ .

The following equations can also be derived:

$$E_A^\lambda(t) - E_A^\lambda(0) = -(\phi_1 + \phi_2)1000I_0\epsilon_A^\lambda\epsilon_A' \times \int_0^t F(E')a(t) dt + \phi_31000I_0\epsilon_A^\lambda\epsilon_C' \int_0^t F(E')c(t) dt \quad (5)$$

$$E_B^\lambda(t) - E_B^\lambda(0) = \phi_11000I_0\epsilon_B^\lambda\epsilon_A' \int_0^t F(E')a(t) dt \quad (6)$$

$$E_C^\lambda(t) - E_C^\lambda(0) = -\phi_31000I_0\epsilon_C^\lambda\epsilon_C' \times \int_0^t F(E')c(t) dt + \phi_21000I_0\epsilon_C^\lambda\epsilon_A' \int_0^t F(E')a(t) dt \quad (7)$$

where  $\epsilon_C^\lambda$  is the molar decadic absorption coefficient of compound C at wavelength  $\lambda$ ,  $E_C^\lambda(t)$  is the absorbance of compound C at wavelength  $\lambda$  at time  $t$ , and  $E_C^\lambda(0)$  is the absorbance of compound C at time zero.

For the whole reaction mixture we have

$$E^\lambda(t) = E_A^\lambda(t) + E_B^\lambda(t) + E_C^\lambda(t)$$

$$E^\lambda(0) = E_A^\lambda(0) + E_B^\lambda(0) + E_C^\lambda(0) \quad (8)$$

and

$$E^{494}(t) = E_B^{494}(t) \quad (8')$$

From Eqs. (5), (7) and (8) we have

$$E^\lambda(t) = [-\epsilon_A^\lambda(\phi_1 + \phi_2) + \epsilon_C^\lambda\phi_2] \times 1000I_0\epsilon_A' \int_0^t F(E')a(t) dt + (\epsilon_A^\lambda\phi_3 - \epsilon_C^\lambda\phi_3)1000I_0\epsilon_C' \int_0^t F(E')c(t) dt + E_A^\lambda(0) + E_C^\lambda(0) \quad (9)$$

or

$$E^\lambda(t) - E^\lambda(0) = -[(\epsilon_A^\lambda - \epsilon_B^\lambda) - (\epsilon_A^\lambda - \epsilon_C^\lambda)] \times 1000I_0\epsilon_A' \int_0^t F(E')a(t) dt + (\epsilon_A^\lambda - \epsilon_C^\lambda)\phi_31000I_0\epsilon_C' \int_0^t F(E')c(t) dt \quad (10)$$

and

$$E_B^{494}(t) - E_B^{494}(0) = \phi_11000I_0\epsilon_B^{494}\epsilon_A' \int_0^t F(E')a(t) dt \quad (11)$$

Let

$$M = \frac{I_C}{I_A} = \frac{1000I_0\epsilon_A' \int_0^t F(E')a(t) dt}{1000I_0\epsilon_C' \int_0^t F(E')c(t) dt}$$

which represents the proportion of the light absorbed by the Z isomer to that absorbed by the E isomer.

From Eqs. (10) and (11) we can obtain

$$\frac{E^\lambda(t) - E^\lambda(0)}{E^{494}(t) - E^{494}(0)} = -\frac{(\epsilon_A^\lambda - \epsilon_B^\lambda)\phi_1 + (\epsilon_A^\lambda - \epsilon_C^\lambda)\phi_2}{\phi_1\epsilon_B^{494}} + \frac{(\epsilon_A^\lambda - \epsilon_C^\lambda)\phi_3}{\phi_1\epsilon_B^{494}} M \quad (12)$$

Letting

$$K = \frac{E^\lambda(t) - E^\lambda(0)}{E^{494}(t) - E^{494}(0)}$$

which represents the slope of the lines in the absorbance (E) diagram, Eq. (12) can be rewritten as

$$K = - \frac{(\epsilon_A^\lambda - \epsilon_B^\lambda)\phi_1 + (\epsilon_A^\lambda - \epsilon_C^\lambda)\phi_2}{\phi_1 \epsilon_B^{494}} + \frac{\phi_3(\epsilon_A^\lambda - \epsilon_C^\lambda)}{\phi_1 \epsilon_B^{494}} M \quad (13)$$

Considering that when compound A is irradiated by UV light at the earliest time, the light absorbed by compound C can be neglected, then  $M_1 = 0$  and

$$K_1 = \frac{(\epsilon_A^\lambda - \epsilon_B^\lambda)\phi_1 + (\epsilon_A^\lambda - \epsilon_C^\lambda)\phi_2}{\phi_1 \epsilon_B^{494}} \quad (14)$$

Thus Eq. (13) can be rewritten as

$$K_n = K_1 - \frac{\phi_3(\epsilon_A^\lambda - \epsilon_C^\lambda)}{\phi_1 \epsilon_B^{494}} M_n \quad (15)$$

From this equation we can estimate the  $M_n$  values by using experimental data. As we know,  $\epsilon_C^{354} = 7762 \text{ mol}^{-1} \text{ l cm}^{-1}$  [1],  $\phi_1 = 0.20$  [2] and  $\phi_3 = 0.11$  [7]. The calculated  $M_n$  values are listed in Table 1. It can be seen from Table 1 that after one cycle about 30% of

Table 1  
Calculated  $M_n$  values at 354 nm

	Irradiation cycle			
	1st	2nd	3rd	4th
$K_n$	-0.3987	-0.4944	-0.5328	-0.5568
$M_n$	0	0.56	0.79	0.93

the irradiated light is absorbed by the Z isomer produced in the first irradiation of the fulgide, which is the very reason why the apparent quantum yield of photocyclization of Aberchrome™ 540 is lower when it is reused.

#### 4. Conclusions

$E \leftrightarrow Z$  isomerization cannot be neglected in the photochromic reaction of the fulgide. About 30% of the total light is absorbed by the Z isomer when the fulgide used in this work is irradiated for one cycle. It can be suggested that Aberchrome™ 540 should not be reused as a chemical actinometer.

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