HETEROCOERDIANTHRONE: A NEW ACTINOMETER FOR THE VISIBLE (400 - 580 nm) RANGE

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Summary

The photochromic system of heterocoerdianthrone and its endoperoxide is used for a simple, reliable and convenient chemical actinometer in the visible wavelength range. Without analytical expenditure the photoreaction can be evaluated using UV–visible spectroscopy and a simple graphical method.

1. Introduction

Heterocoerdianthrone (HCD; dibenzo[*aj*]perylen-1,16-dione) is a photochromic system [1]. Its photo-oxidation in toluene to an endoperoxide (EPO) by irradiation at 546 nm has been extensively investigated [2, 3]:
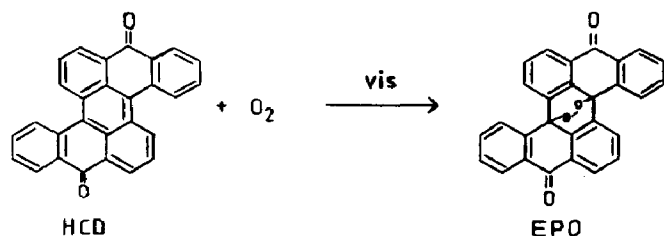

This reaction can be used for actinometric purposes in wavelength regions where Parker's solution does not totally absorb [4] and there are no suitable alternatives [5]. Excited singlet and triplet HCD both activate oxygen to $^1O_2$ via a self-sensitized photoreaction. Therefore the mechanism is very

complex. A detailed kinetic analysis [2] shows that the minimum number of reaction steps that has to be considered is as follows.
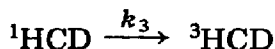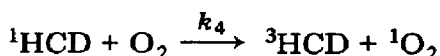
(1) Excitation of HCD:

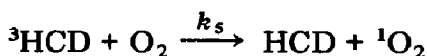$$HCD \xrightarrow{I_{abs}\,(h\nu)} {}^1HCD$$

(2) Fluorescence:

$$^1HCD \xrightarrow{k_2} HCD + h\nu'$$
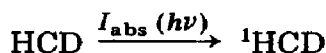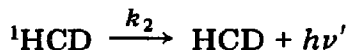
(3) Intersystem crossing:

$$^1HCD \xrightarrow{k_3} {}^3HCD$$

(4) Sensitization of O_2 by ^1HCD:

$$^1HCD + O_2 \xrightarrow{k_4} {}^3HCD + {}^1O_2$$

(5) Sensitization of O_2 by ^3HCD:

$$^3HCD + O_2 \xrightarrow{k_5} HCD + {}^1O_2$$

(6) Formation of EPO:

$$HCD + {}^1O_2 \xrightarrow{k_6} EPO$$
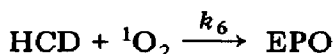
(7) Radiationless decay of $^1O_2$:

$$^1O_2 \xrightarrow{k_7} O_2$$
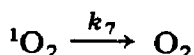
2. Theory

Table 1 gives a formalism [6] which can be used to set up the time–concentration differential equations in a simple way even for this complex mechanism. x_k represents the degree of advancement of the kth partial reaction step. Its dependence on time $\dot{x}_k = dx/dt$ is given in the last column. $\dot{x}_k$ is calculated by multiplying the rate constant of the kth partial reaction step by the concentration of the products taken to the power of the absolute value of the specific stoichiometric coefficient $|\nu_{ik}|$ (only vanishing products are considered and hence ν_{ik} is negative). To determine the overall change in the concentration of one reactant, the products of ν_{ik} and $\dot{x}_k$ are obtained for each step (rows in Table 1) and summed for all steps. An example is given for HCD (Table 1, second column):

$$-\dot{c}_{HCD} = I_{abs} - k_2 c_{^1HCD} - k_5 c_{^1HCD} c_{O_2} + k_6 c_{O_2} c_{HCD} \tag{1}$$

TABLE 1

Description of the partial reaction steps in the photoreaction of heterocoerdianthrone to the endoperoxide according to Mauser's formalism

	HCD	^1HCD	^3HCD	O_2	$^1O_2$	EPO	$\dot{x}_K$
1	−1	+1					I_{abs}
2	+1	−1					$k_2[^1HCD]$
3		−1	+1				$k_3[^1HCD]$
4		−1	+1	−1	+1		$k_4[^1HCD][O_2]$
5	+1		−1	−1	+1		$k_5[^3HCD][O_2]$
6	−1				−1	+1	$k_6[HCD][^1O_2]$
7				+1	−1		$k_7[^1O_2]$

The changes in concentration of $^1O_2$, ^1HCD and ^3HCD can be represented by similar equations. Since these changes are equal to zero according to Bodenstein's assumption, eqn. (1) can be rearranged to

$$-\dot{c}_{HCD} = \underbrace{\frac{k_6 c_{HCD}}{k_6 c_{HCD} + k_7}}_{A}\left(\underbrace{\frac{k_4 c_{O_2}}{k_2 + k_3 + k_4 c_{O_2}}}_{B} + \underbrace{\frac{k_3 + k_4 c_{O_2}}{k_2 + k_3 + k_4 c_{O_2}}}_{C}\right)I_{abs} \qquad (2)$$

$$\underbrace{\hspace{8cm}}_{\varphi^{HCD}}$$

In this equation the partial photochemical quantum yield φ^{HCD} of the photo-oxidation can be expressed in terms of three fractions A, B and C where A is the fraction of $^1O_2$ that reacts with HCD to form EPO, B is the fraction of ^1HCD that is responsible for the formation of $^1O_2$ and C is the fraction of ^1HCD that reacts to form ^3HCD which subsequently produces $^1O_2$ according to step (5) with a 100% yield. The sum of B and C gives the total fraction of ^1HCD causing the formation of $^1O_2$.

The following conditions must be satisfied if a photoreaction is to be used as an actinometer.

(a) The complex mechanism should be reducible to a single linear independent differential equation, *i.e.* the photoreaction should be uniform.

(b) A direct relationship between the concentration of one of the reactants and the measurable absorbance should exist.

(c) When no other products absorb at the irradiation wavelength, the mathematical evaluation should be simple even for complex mechanisms.

3. Experimental results

The reaction spectrum [6] of the photo-oxidation of HCD in toluene, which was recorded using an automatic combined irradiation and measurement device [7], is given in Fig. 1. HCD is the only absorbing product at wavelengths above 400 nm. According to eqn. (2) the photochemical
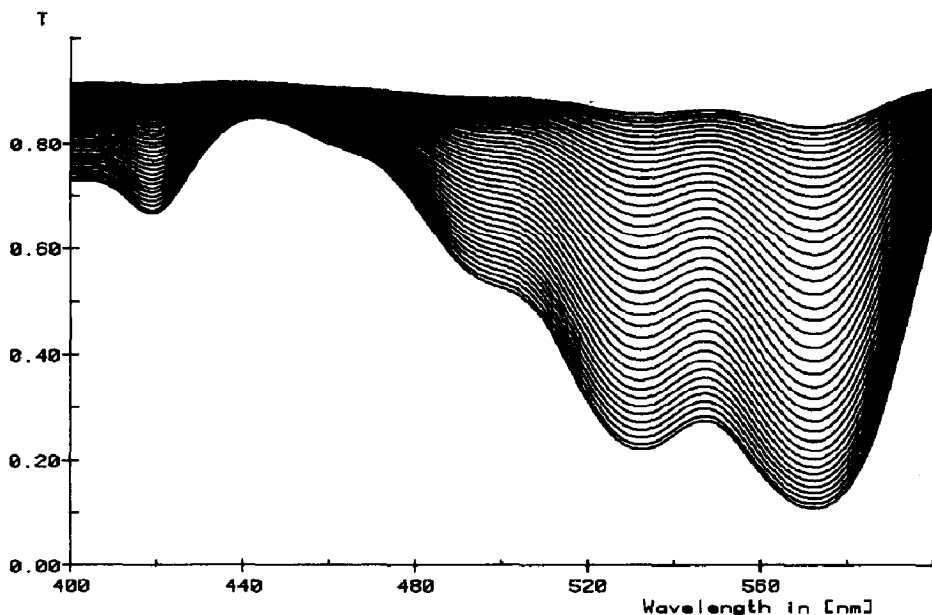
Fig. 1. Reaction spectrum of the photo-oxidation of HCD.

quantum yield depends on the concentrations of oxygen and HCD which explains why aerated solutions react three times more slowly than oxygen-saturated samples. At constant irradiation intensities the rate of the reaction increases non-linearly with increasing HCD concentration.

Various methods of evaluating the measured changes of absorbance during the reaction can be considered.

(a) Since the absorbance diagrams [6, 8] are linear, the photo-oxidation was assumed to be spectroscopically uniform. The differential equation for this mechanism was solved by formal integration [6]. In a subsequent step this value and the differential equations were used to recalculate theoretical absorbances at selected reaction times by "back simulation" [6] employing Runge–Kutta procedures. When the complete reaction time domain was used, a significant deviation between the measured and theoretical absorbances was found. This effect was particularly marked when measurement methods such as derivative spectroscopy, which is very sensitive to small changes in absorbance, were used [9, 10]. However, when the time domain of the evaluation was restricted to the beginning of the reaction (until a yield of about 20% was obtained) the deviation was very small. Therefore the mechanism postulated above is only justified in the early part of the reaction. Since the expenditure required for this type of evaluation is large, other approximations were investigated.

(b) If it is assumed that there is total absorbance $(E' > 4)$ and that the photoproducts are non-absorbing $(\epsilon_B' = 0)$ at irradiation wavelengths during the irradiation time of interest, the following approximation can be used:

$$\frac{\Delta E'}{\Delta t} = \frac{1000 I_0 \varphi^{HCD} \epsilon_{HCD}'}{d} \tag{3}$$

where I_0 is in einsteins per centimetre squared per second and d = 1 cm. Reflectance losses are neglected in this equation. However, the required linearity between the change $\Delta E'$ in the absorbance at the irradiation wavelength and the change Δt in the irradiation time was not found.

(c) If the photoproducts do not absorb at the irradiation wavelength ($\epsilon_B' = 0$), the following equation can be used [11]:

$$\ln(10^{E'} - 1) = \ln(10^{E_0'} - 1) - 2.303 \times 1000 \times I_0 \varphi^{HCD} \epsilon_{HCD}' t \qquad (4)$$

where E_0' is the absorbance at time t = 0. This approximation is valid since a diagram of $\ln(10^{E'} - 1)$ versus the irradiation time t is linear for HCD concentrations of about 3.2×10^{-5} mol l^{-1} as shown in Fig. 2 (E^{546} = 0.5).

Evaluation procedure (c) can be used for chemical actinometry by HCD in the visible region provided that only the beginning of the reaction is examined. If the initial absorbance is E_0^{546} = 0.5 + 0.01(3.2×10^{-5} mol l^{-1}) the error in the calculation of I_0 is less than 1%. The oxygen concentration in air-saturated toluene (about 2×10^{-3} mol l^{-1}) is high compared with the HCD concentration and can be assumed to be constant. Parker's solution does not totally absorb at wavelengths above 480 nm and Reinecke's salt does not fulfil the requirements with respect to exactness and accuracy [7]. Therefore the intensity of a mercury lamp was determined at 365 - 366 and 405 - 408 nm using Parker's solution [4] and a quantum counter (rhodamine B) [12] was used to calculate the intensities of the mercury lines at 546 and 577 - 579 nm. These values were in good agreement with published intensity ratios [13]. A constant photochemical quantum yield was found for the irradiation wavelengths 405 - 408, 546 and 577 - 579 nm: φ^{HCD} = 0.016 ± 0.001.
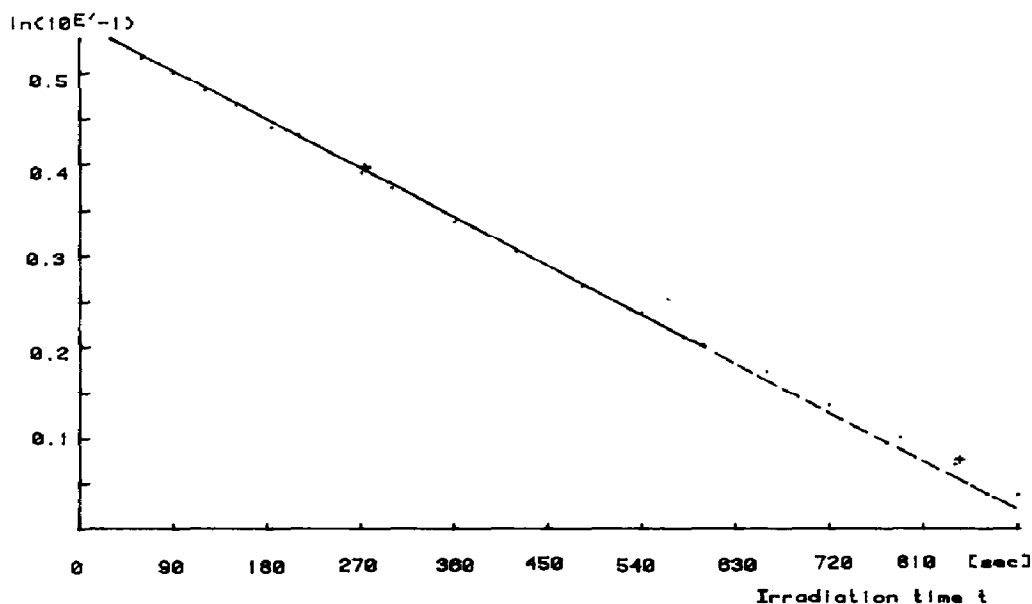

Fig. 2. $\ln(10^{E'} - 1)$ vs. irradiation time t for the determination of the lamp intensity I_0.

4. Recommended actinometric procedure

An air-saturated solution of 3.2×10^{-5} mol HCD 1^{-1} in toluene is produced ($E^{546} = 0.5 \pm 0.01$). The absorbance E' is measured as a function of the irradiation time t. The linearity of the logarithmic plot can be checked and the slope can be used to calculate the intensity of the unknown lamp using the known quantum yields and the known absorptivities (Table 2). Only the linear region of the diagram at the beginning of the reaction is used. The accuracy is increased if the measurement is made using a combined measuring and irradiation device which is also recommended for all types of photokinetic examination.

TABLE 2

Absorptivities at various mercury lines

Irradiation wavelength λ' (nm)	405 - 408	546	577 - 579
Absorptivity ϵ_{HCD}' (1 mol^{-1} cm^{-1}) at λ'	3200	15900	27000

5. Conclusion

The photochromic system HCD $\rightleftharpoons$ EPO is a suitable actinometer for use in the visible range where no other reliable and convenient actinometers exist. Small errors and good reproducibility were obtained using standardized procedure. Each actinometric experiment produces many data points and their linearity can be used to check the lamp stability and to control the reliability of the measurement. The evaluation is simple and no extended analytical procedure is necessary; the advantages of spectroscopic methods of concentration determination are used.

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