

## SELF-SENSITIZED PHOTO-OXIDATION OF AROMATIC COMPOUNDS AND PHOTOCYCLOREVERSION OF ENDOPEROXIDES: APPLICATIONS IN CHEMICAL ACTINOMETRY<sup>†‡</sup>

R. SCHMIDT and H.-D. BRAUER

*Institute for Physical and Theoretical Chemistry, University of Frankfurt, Robert Mayer Strasse 11, D-6000 Frankfurt am Main (F.R.G.)*

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### Summary

The self-sensitized photo-oxidation of *meso*-diphenylhelianthrene is recommended for actinometric application in the 475 - 610 nm range. The photoreversible photocycloreversion of the endoperoxide of heterococerdianthrene is excellently suited for reusable actinometry in the 248 - 334 nm range. Both photochemical systems represent reliable, convenient and sensitive actinometric systems.

### 1. Introduction

Chemical actinometry is a common method for determining the quantum flux  $I_\lambda$  of a given monochromatic radiation source. Chemical actinometry is used in cases of complex irradiation geometries, where  $I_\lambda$  can be determined easily, exactly and inexpensively by this method, while, in contrast, actinometry by physical methods is difficult. In laboratories which are not equipped with high standard calibrated radiometers, chemical actinometry is even the only method to determine accurately the quantum flux of a radiation source.

Up to this day a considerable number of photochemical systems have been proposed for actinometric application [1], but only a few of them are commonly used. The most popular is the famous ferrioxalate actinometer, developed by Hatchard and Parker [2], which is suggested for use in the 253 - 546 nm spectral range. However, in a recent study, Demas *et al.* [3] pointed out severe irreproducibility problems in the UV region, which presumably result from the complex chemistry involved in the actinometric

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procedure. As the sources of irreproducibility are still unknown, the reliability of this actinometer in the far-UV region seems to be questionable.

Reinecke's salt actinometer, proposed by Wegner and Adamson [4], covers the visible range. However, similar to the ferrioxalate actinometer, its handling is rather inconvenient, since irradiated solutions have to be mixed in the dark with developing reagents to determine the absorbed quanta spectrophotometrically. In addition, Reinecke's salt actinometer suffers from the thermal instability of its actinometric solutions, which therefore have to be prepared immediately before use.

Despite these disadvantages both actinometers are frequently used, as they represent valuable approximations to an ideal actinometer.

In the following are listed the most important requirements that photochemical systems have to meet to be suitable for actinometry.

(1) The photochemical system should be simple and well known. Its photoreaction has to be reproducible under well-defined and easily controllable experimental conditions.

(2) The chemical components have to be thermally stable to exclude complications by dark reactions.

(3) For convenience the photoreaction should be followed directly by spectrophotometric analysis.

(4) Actinometric factors should be accurately known for a large number of wavelengths. A wide useful spectral range and wavelength-independent actinometric factors are desired.

(5) The system should be very sensitive in actinometry.

(6) The handling of the photochemical system and the evaluation of the number of the absorbed quanta should be simple and straightforward.

(7) The actinometric material should be easy to synthesize and purify. Preferably it should be commercially available.

The requirements mentioned above are severe and only a restricted number of photochemical systems appear to fulfil most of them. Among those, surprisingly, there are two systems, one based on the self-sensitized photo-oxidation of aromatic compounds and the other based on the photochemical cleavage of endoperoxides.

This is surprising because self-sensitized photo-oxidation is a reaction with quantum yields depending on the hydrocarbon and on the oxygen concentrations and because endoperoxides are known to be thermally unstable and to exhibit a complex photochemistry [5 - 7].

However, as will be demonstrated, the self-sensitized photo-oxidation of *meso*-diphenylhelianthrene (MDH) and the photocycloreversion of heterocoerdianthrene endoperoxide (HCDPO) avoid these disadvantages, thus making both reactions well suited for actinometry.

## 2. Experimental section

MDH and heterocoerdianthrene (HCD) were prepared following literature procedures [8, 9]. HCDPO was obtained by the self-sensitized photo-

oxidation of HCD in sunlight behind a cut-off filter (450 nm) and subsequent purification by column chromatography (silica gel;  $\text{CH}_2\text{Cl}_2$ ). Toluene, hexane and  $\text{CH}_2\text{Cl}_2$  from the Uvasol series of Merck were used as solvents without further purification.

Monochromatic light was selected using a Schoeffel GM 250 grating monochromator from the output spectra of XBO 150 or HBO 100 lamps from Osram. A current-stabilized power supply from Oriel reduced the intensity fluctuations of the radiation below 0.5%. Sample solutions were stirred during irradiation by spin bars. For the determination of the quantum flux of the irradiation beam a UV 100 photodiode from UDT was used, which had been calibrated before by the Physikalisch Technische Bundesanstalt, Braunschweig. The homogeneity of the sensitive area of the diode was proved before calibration. Maximum deviations of  $\pm 0.4\%$  from homogeneity were observed. The uncertainties in the calibration values are given together with the actinometric factors in the respective tables. A high precision operational amplifier from Teledyne Philbrick model 1023 was used for current-voltage conversion. Photochemical measurements were done at 23 and 0 °C. The photodiode was always kept at 23 °C, the temperature at which the calibration was performed.

Sample volumes were determined by difference weighing. The conversion of the hydrocarbons was measured on a Perkin-Elmer 555 spectrophotometer.

### 3. Results and discussion

#### 3.1. Photo-oxidation of meso-diphenylhelianthrene

##### 3.1.1. Photoreaction

On irradiation with visible light MDH is readily photo-oxidized with quantum yield  $Q_2$ :

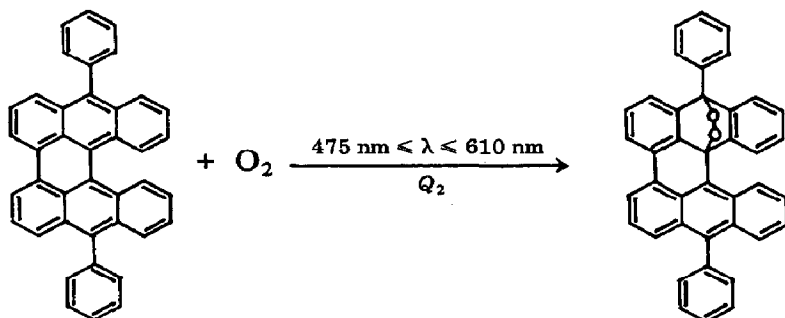


Figure 1 shows a reaction spectrum which has been recorded during the photo-oxidation of a diluted MDH solution in hexane. The spectrum shows several isosbestic points. This fact and also linear absorbance diagrams prove that the photo-oxidation MDH reaction is a simple and uniform reaction [10]. Since the decrease in MDH equals the increase in MDHPO, the progress of

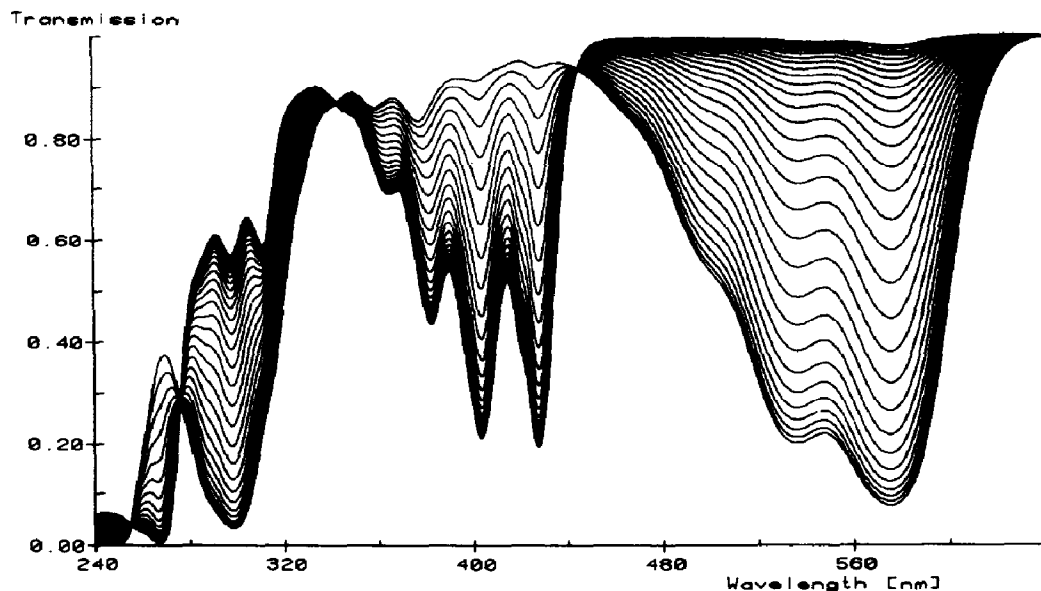


Fig. 1. Reaction spectrum of the self-sensitized photo-oxidation of MDH in hexane ( $\lambda_{irr} = 546$  nm).

the photoreaction can be monitored easily at the maxima of absorption of MDH and of MDHPO.

### 3.1.2. [MDH] dependence of $Q_2$

The quantum yield  $Q_2$  of the self-sensitized photo-oxidation is as usual dependent on hydrocarbon and oxygen concentrations. In the medium MDH concentration range (i.e.  $10^{-6}$  M  $\leq$  [MDH]  $\leq$   $5 \times 10^{-4}$  M)  $Q_2$  can be described by

$$Q_2 = \frac{[\text{MDH}]}{[\text{MDH}] + k_{\text{dea}}/k_r} Q_{\Delta} \quad (1)$$

where  $k_{\text{dea}}$  and  $k_r$  are the rate constants of the deactivation of  $^1\text{O}_2$  and of the reaction of ground state MDH and  $^1\text{O}_2$  respectively.  $Q_{\Delta}$  represents the  $[\text{O}_2]$ -dependent quantum yield of  $^1\text{O}_2$  formation by MDH.

From the [MDH] dependence of  $Q_2$  at constant  $[\text{O}_2]$  in toluene the ratio  $k_{\text{dea}}/k_r = 5.5 \times 10^{-6}$  M is obtained [11]. Therefore the reaction between  $^1\text{O}_2$  and MDH is diffusion controlled with  $k_r = 10^{10}$  M $^{-1}$  s $^{-1}$ . Hence, for [MDH]  $\geq$   $5 \times 10^{-4}$  M  $Q_2$  is no longer dependent on [MDH].

### 3.1.3. $[\text{O}_2]$ dependence of $Q_2$

The  $[\text{O}_2]$  dependence of  $Q_{\Delta}$  is usually expressed by

$$Q_{\Delta} = A + B \frac{K[\text{O}_2]}{1 + K[\text{O}_2]} \quad (2)$$

where  $A$  and  $B$  represent two constants, and  $K$  is the Stern-Volmer constant for the oxygen quenching of the hydrocarbon fluorescence [5, 12]. As is

shown by Fig. 2 the self-sensitized photo-oxidation of MDH also follows the linear relationship of eqn. (2). Since the ratio  $B/A = 0.84$  is remarkably small and the quenching constant amounts to only  $K = 89 \text{ M}^{-1}$ , it follows that moderate variations in  $[\text{O}_2]$  have almost negligible influence on  $Q_\Delta$ . For air-saturated MDH solutions in toluene, for example, from Fig. 2  $Q_\Delta$  values of 0.218 at an atmospheric pressure of 760 Torr (corresponding to sea-level) and of 0.214 at 590 Torr (corresponding to an altitude of 2000 m) are calculated.

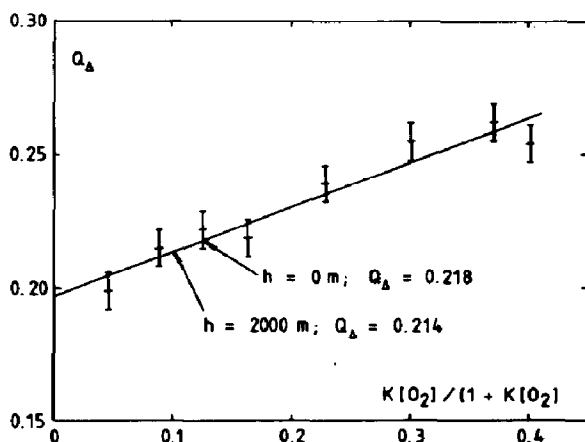


Fig. 2.  $[\text{O}_2]$  dependence of  $Q_\Delta$  in toluene. For further information see text.

Because of this weak  $[\text{O}_2]$  dependence of  $Q_\Delta$ , quantum yield determinations of the photo-oxidation of air-saturated MDH solutions in toluene will result in only slightly altitude-dependent  $Q_2$  values.

#### 3.1.4. Actinometric factors

$10^{-3} \text{ M}$  solutions of MDH in toluene totally absorb incident irradiation in the 472 - 613 nm range. For this MDH concentration  $Q_2$  is independent of  $[\text{MDH}]$  and the photo-oxidation reaction can be followed photometrically at 429 nm, where only MDHPO absorbs considerably. At irradiation wavelengths  $475 \text{ nm} \leq \lambda \leq 610 \text{ nm}$  the quantum yield  $Q_2(\lambda)$  can be calculated by

$$Q_2(\lambda) = \frac{\Delta A_{429} V}{\Delta \epsilon_{429} d \times 0.96 I_\lambda \Delta t} \quad (3)$$

where  $\Delta A_{429}$  is the difference in absorbance at 429 nm during the irradiation time interval  $\Delta t$  (s).  $V$  (l) is the sample volume,  $\Delta \epsilon_{429}$  ( $\text{M}^{-1} \text{ cm}^{-1}$ ) is the difference between the extinction coefficients of MDH and MDHPO at 429 nm,  $d$  (cm) is the optical path length and  $I_\lambda$  (einsteins  $\text{s}^{-1}$ ) is the quantum flux of the monochromatic irradiation beam.

However, the actinometric factor  $f(\lambda) = \Delta \epsilon_{429} Q_2(\lambda)$  can be determined with higher precision than  $Q_2(\lambda)$ . Therefore in Table 1  $f(\lambda)$  rather than  $Q_2(\lambda)$  values are listed for different irradiation wavelengths. The  $f(\lambda)$  values clearly reveal the wavelength independence of the self-sensitized photo-oxidation of

TABLE 1

Actinometric factors  $f(\lambda) = \Delta\epsilon_{429} Q_2(\lambda)$  for *meso*-diphenylhelianthrene

$\lambda$ (nm)	$\lambda_{1/2}$ (nm)	$f(\lambda)^a$ ( $M^{-1} cm^{-1}$ )	$\pm\sigma_c^b$ (%)	$\pm\sigma_f^{ib}$ (%)
475	5	4000	0.3	2.0
500	5	4260	0.3	2.0
525	5	4000	0.2	2.0
546	1	4040	0.2	2.0
560	5	4100	0.3	2.0
578	1	4020	0.3	2.0
600	5	4100	0.2	2.0

Solvent, toluene;  $[MDH] = 10^{-3} M$ ; wavelength-independent mean value of  $f$  at sea-level,  $4070 \pm 90 M^{-1} cm^{-1}$  (at altitudes of 1000 m, 2000 m and 3000 m  $f$  amounts to  $4030 M^{-1} cm^{-1}$ ,  $4000 M^{-1} cm^{-1}$  and  $3970 M^{-1} cm^{-1}$  respectively).

<sup>a</sup>Mean values of three experiments.

<sup>b</sup> $\sigma_c$ ,  $\sigma_f$ , uncertainties in the photodiode calibration and the actinometric factors respectively.

MDH in the 475 - 610 nm range. A wavelength-independent mean value of  $f = 4070 \pm 90 M^{-1} cm^{-1}$  can be calculated for the actinometric factor at sea-level, indicating that MDH may be used as a high accuracy photon counter for polychromatic light in this wavelength range. The calculated altitude dependence of  $f$  is also given in Table 1. As can be seen,  $f$  decreases only by 2.5% in the altitude range from 0 to 3000 m.

For the evaluation of the quantum flux

$$I_\lambda = \frac{\Delta A_{429} V}{fd \times 0.96 \Delta t} \quad (\text{einsteins s}^{-1}) \quad (4)$$

has to be used. In the following the most prominent features of the MDH photo-oxidation with respect to the actinometric requirements are pointed out.

(1) The overall photochemical reaction is quite simple and reproducible under well-defined and easily controllable experimental conditions.  $Q_2$  is independent of  $[MDH]$  and for air-saturated solutions only slightly dependent on altitude. The correction for reduced atmospheric pressure is well known and given in Table 1.

(2) No dark reaction competes with photoreaction.

(3) The photoreaction can be easily followed spectrophotometrically.

(4) The useful wavelength range for actinometry extends from 475 to 610 nm. The actinometric factors are known with high accuracy and are independent of wavelength. Therefore MDH may be used as a quantum counter even for polychromatic light.

(5) The value of  $f$  determines the sensitivity. With  $f = 4070 M^{-1} cm^{-1}$  the photo-oxidation of MDH is by a factor of 8 more sensitive than Reinecke's salt actinometer, when the dilution of Reinecke's salt by the addition of developing reagents is taken into account.

(6) The actinometric procedure is very simple. No reagents have to be added to the irradiated solution. Total absorption simplifies the application. The evaluation is straightforward and several actinometric measurements can be done with one sample.

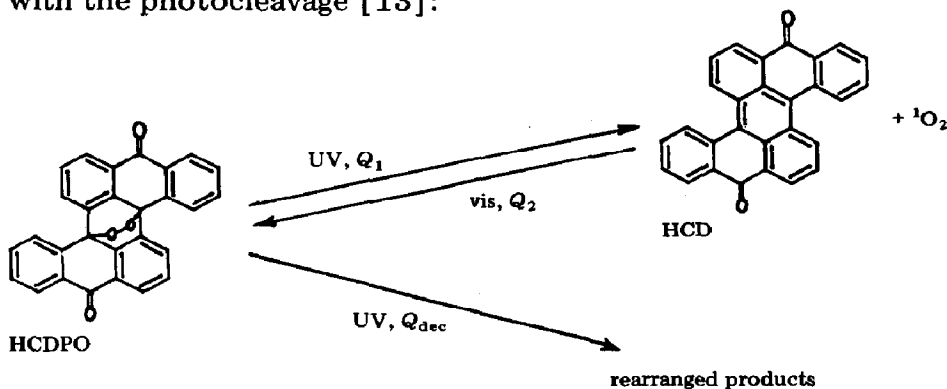
(7) The synthesis of MDH requires some experience. However, solutions are commercially available for actinometry from Amko G.m.b.H., D2082 Tornesch, F.R.G., under the designation Actinochrome N(475/610).

From this it follows that the self-sensitized photo-oxidation reaction of MDH is excellently suitable for actinometric application [10].

### 3.2. Photocleavage of heterocoerdianthrone endoperoxide

#### 3.2.1. Photoreversibility of the photo-oxidation

Photo-oxidation reactions are in principle photoreversible processes. The reverse reaction is the photocleavage of the endoperoxide reproducing the parent hydrocarbon and  $^1\text{O}_2$  with a quantum yield  $Q_1$ . Irreversible photochemical rearrangement reactions with a quantum yield  $Q_{\text{dec}}$  compete with the photocleavage [13]:



However, some endoperoxides exhibit a remarkably clean photochemistry. Particularly for HCDPO the ratio  $Q_1/Q_{\text{dec}}$  is very high with a value of 60 [14], *i.e.* photocycloreversion dominates over the rearrangement. As can be seen from the reaction spectrum of Fig. 3 the photocycloreversion of HCDPO produces a large absorption shift. From the evaluation of the reaction spectra it follows that the photocleavage of HCDPO and the self-sensitized photo-oxidation of HCD are simple and uniform reactions.

Because of this and its high photoreversibility the system HCDPO-(HCD +  $\text{O}_2$ ) is a very promising candidate for reusable actinometry [15].

#### 3.2.2. Actinometric factors

Since the photoproduct HCD absorbs stronger than HCDPO at all wavelengths, we took care that the conversion of HCDPO never exceeded 0.35% during our measurements, to avoid internal filter effects. For the determination of the quantum yield  $Q_1$  of photocleavage the formation of HCD was observed spectrophotometrically at 572 nm. For  $[\text{HCDPO}] = 2 \times 10^{-3}$  M the solutions absorb incident radiation completely between 248 and 334 nm. Therefore

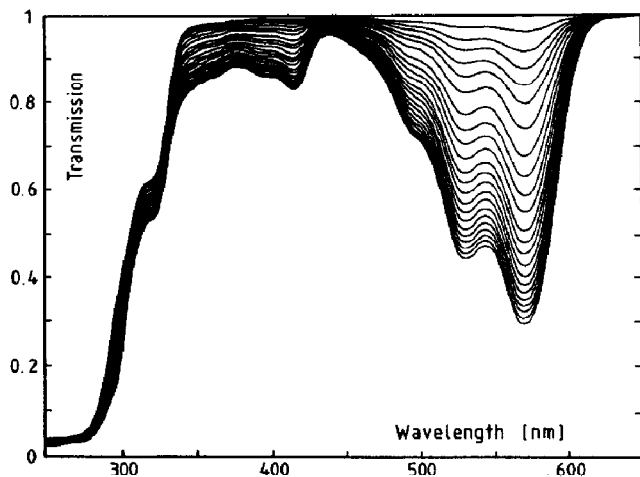


Fig. 3. Reaction spectrum of the photocycloreversion of HCDPO in  $\text{CH}_2\text{Cl}_2$  ( $\lambda_{\text{irr}} = 280 \text{ nm}$ ).

$$Q_1(\lambda) = \frac{\Delta A_{572} V}{\epsilon_{572} d \times 0.96 l_{\lambda} \Delta t} \quad (5)$$

where  $\epsilon_{572}$  is the extinction coefficient of HCD at 572 nm, was used for the evaluation of  $Q_1(\lambda)$ .

$Q_1(\lambda)$  proved to be independent of  $[\text{O}_2]$ ,  $[\text{HCDPO}]$  and the irradiation intensity, provided that the solutions were kept homogeneous by stirring.

In Table 2 the actinometric factors  $f(\lambda) = \epsilon_{572} Q_1(\lambda)$  are listed as a function of wavelength. The small uncertainty in the  $f(\lambda)$  values is noteworthy. It results from the high reproducibility of the photochemical system and from the high accuracy of the calibration of the photodiode used for the radiation measurements. Interestingly  $f(\lambda)$  is only slightly wavelength depen-

TABLE 2

Actinometric factors  $f(\lambda) = \epsilon_{572} Q_1(\lambda)$  for heterocoerdianthrone endoperoxide

$\lambda$ (nm)	$\lambda_{1/2}$ (nm)	$f(\lambda)^a$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\pm \sigma_c^b$ (%)	$\pm \sigma_f^b$ (%)
248	1	7050	0.8	1.3
253	1	7460	0.8	2.0
265	3	7850	0.5	1.2
280	1.5	7770	0.6	1.4
302	1	7900	0.5	1.4
313	1	6740 <sup>c</sup>	0.5	1.1
334	1	4630	0.5	1.0

Solvent,  $\text{CH}_2\text{Cl}_2$ ;  $[\text{HCDPO}] = 2 \times 10^{-3} \text{ M}$ .

<sup>a</sup> Mean values of five experiments.

<sup>b</sup>  $\sigma_c$ ,  $\sigma_f$ , uncertainties in the photodiode calibration and the actinometric factors respectively.

<sup>c</sup> Mean value of 30 experiments.



dent between 253 and 302 nm, making this system suitable as a photon counter in this range. The temperature coefficient of  $f(\lambda)$  has been investigated at 313 nm. At this wavelength it amounts to  $\Delta f(313)/(f(313) \Delta T) = 0.2\% \text{ K}^{-1}$ .

### 3.2.3. Reusability

During UV irradiation the originally colourless HCDPO solution turns red owing to the formation of HCD. Since the self-sensitized photo-oxidation of HCD can be readily accomplished without the occurrence of side reactions, the actinometric solution may be re-formed simply by using a cut-off filter (cut-off, below 450 nm) and sunlight.

Therefore, HCDPO is in principle a reusable actinometer. To investigate the influence of the number  $n$  of repeated applications on the actinometric accuracy, we irradiated a solution of HCDPO (concentration,  $2 \times 10^{-3} \text{ M}$ ) at 313 nm until 0.35% of HCDPO was converted. Subsequently the solution was decolourized by sunlight using a cut-off filter and then irradiated again. This procedure was repeated more than 80 times and afterwards the actinometric factors were determined for this solution at different wavelengths.

Table 3 lists the mean values obtained after 82, 85 and 88 applications. A comparison with the mean values, which were determined under identical conditions and with the recommended actinometric factors, reveals no significant deviation. Hence about 100 repeated actinometric applications of one sample are possible without loss in accuracy.

This is by far the largest number of repeated actinometric applications verified experimentally for a reusable chemical actinometer.

The photochemical features of HCDPO concerning its possible application as a reusable actinometric system are the following.

(1) The photocycloreversion of HCDPO and the photo-oxidation of HCD have been studied in detail. These are uniform reactions reproducible under easily controllable experimental conditions.

TABLE 3

Actinometric factors  $f(\lambda)$  as a function of the number  $n$  of repeated actinometric applications

$\lambda$ (nm)	$n$	$f(\lambda) (\text{M}^{-1} \text{ cm}^{-1})$		
		After $n$ applications <sup>a</sup>	With fresh samples <sup>a</sup>	Recommended
313	82	$6780 \pm 50$	$6740 \pm 20$	$6740 \pm 70$
302	85	$7820 \pm 70$	$7860 \pm 80$	$7900 \pm 100$
253	88	$7400 \pm 80$	$7560 \pm 70$	$7460 \pm 150$

[HCDPO] =  $2 \times 10^{-3} \text{ M}$ ; 0.35% conversion of HCDPO per cycle;  $\Delta A_{572} \approx 0.2$ .

<sup>a</sup>Mean values of three subsequent experiments.

(2) No dark reaction competes with photoreaction.

(3) The photoreaction can easily be followed spectrophotometrically.

(4) Actinometric factors have been determined for seven wavelengths with high accuracy. HCDPO has an interesting wavelength range, which extends from 248 to 334 nm. Between 253 and 302 nm almost wavelength-independent actinometric factors are observed.

(5) With actinometric factors of about  $7000 \text{ M}^{-1} \text{ cm}^{-1}$ , HCDPO is particularly sensitive. It exceeds the sensitivity of the ferrioxalate actinometer by a factor of 3 when the dilution of the ferrioxalate by the addition of developing reagents is taken into account.

(6) The handling of the photochemical system is very simple. No reagents have to be added to the solution. The evaluation is straightforward.

(7) The photochemical system is highly photoreversible. About 100 repeated actinometric applications of one actinometric sample are possible without loss in accuracy. To prepare for the next usage nothing more is required than merely exposure of the actinometric sample to sunlight behind a cut-off filter until complete decolourization occurs.

(8) The synthesis and purification of HCDPO require some experience. However, solutions are commercially available for actinometry from Amko G.m.b.H., D2082 Tornesch, F.R.G., under the designation Actinochrome R(248/334).

Both photochemical systems discussed here meet the essential requirements for an actinometric application. Although they are limited in their respective wavelength ranges they represent accurate and uncomplicated radiation measurement systems. As we are pursuing our systematic studies on photoreversible photo-oxidation, we hope to find more photochemical systems suited for actinometry in the near future.

## Acknowledgments

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