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Short Communication

Quantum yields in the photolysis of *cis*-cyclooctene at 185 nm

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In the photolysis of *cis*-cyclooctene in the liquid phase *cis* → *trans* isomerization is by far the major process [1]. In the gas phase other processes gain in importance [2]. Using the conversion of oxygen into ozone as a reference, the sum of the quantum yields of *cis* → *trans* ($\Phi_{c\rightarrow t}$) and *trans* → *cis* ($\Phi_{t\rightarrow c}$) isomerization has been estimated [1] to be 2. This result, which is unique for a *cis* ⇄ *trans* isomerization [3] has recently [4] been adduced to support theoretical considerations as to the dynamics of such isomerizations. As it is an important question whether or not there is an exception to the rule that the sum of $\Phi_{c\rightarrow t}$ and $\Phi_{t\rightarrow c}$ never exceeds unity, we reinvestigated this system using the ethanol actinometer. This actinometer (5 M ethanol in water, $\Phi(H_2) = 0.4$) has proved its usefulness in the past [5]. It has the advantage that actinometry and sample irradiation are carried out in the same vessel, thus avoiding a possible systematic error of the earlier quantum yield determination.

Samples of an *n*-pentane solution of fractionated (gas chromatography purity, better than 99.95%) *cis*-cyclooctene ($(2.0 \pm 0.1) \times 10^{-2}$ M) were placed in a Suprasil QS cell and were deaerated by purging with argon while the sample was kept cold to minimize solvent evaporation. The samples (2 ml) were irradiated with the unfiltered light of a low pressure mercury arc (Gräntzel), of which the 185 nm portion is totally absorbed, at an absorbed light intensity of $(4.5 \pm 0.3) \times 10^{17}$ quanta (185 nm) $\min^{-1}$. The presence of 254 nm light had no effect; this was shown in a separate experiment using a Vycor quartz filter to eliminate the 185 nm line. Products were identified by means of gas chromatography—mass spectrometry and/or reference material, and were measured by gas chromatography employing an internal standard. The sample preparation, the irradiation and the analysis procedures were similar to those already described [6, 7]. The spectra of the *cis* and *trans* isomers in cyclohexane solution were measured on a Cary model 17 spectro-

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photometer (Fig. 1). The *trans*-cyclooctene was isolated via its silver complex [8] from pentane solutions of *cis*-cyclooctene irradiated on a preparative scale (Gräntzel 185 nm photoreactor). The purity of the *trans*-cyclooctene (boiling point 56 °C at a pressure of 30 Torr) so obtained was 98.2%, the rest being mostly *cis*-cyclooctene (1.5%).

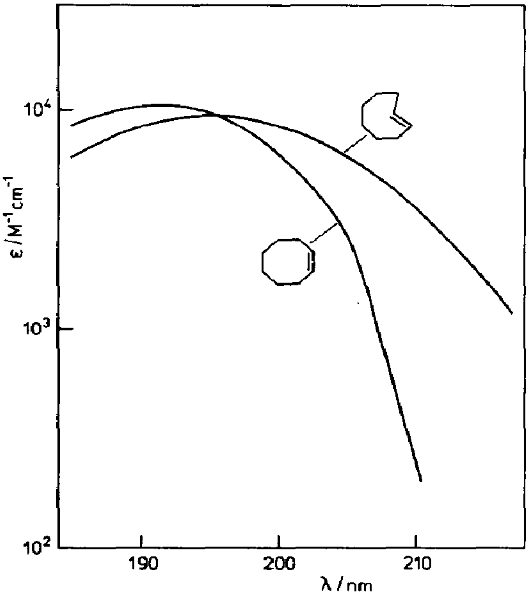


Fig. 1. Molar extinction coefficients of *cis*- and *trans*-cyclooctene in cyclohexane solution at wavelengths above 185 nm.

The photolysis products and their quantum yields are given in Table 1. There are traces of unidentified products, some of which have a molecular weight above that of cyclooctene as judged by their gas chromatographic behaviour, but collectively they do not amount to more than 3% of the *cis*-cyclooctene consumed. We find no evidence for the formation of bicyclo-[4.2.0]-octane. This product has been reported in the triplet-sensitized decomposition of cyclooctene, along with bicyclo-[5.1.0]-octane, bicyclo-[3.3.0]-octane and 1,7-octadiene [9, 10].

The kinetics of photochemical *cis*–*trans* rearrangements (see ref. 11) in the absence of side reactions are described by expressions (1) and (2) (where I is the absorbed light intensity, N_L is the Avogadro number, V is the sample volume, ϵ is the molar extinction coefficient, the subscript 0 indicates zero conversion and the subscript ∞ indicates the photostationary state).

$$\frac{d[cis]}{dt} = \frac{I(-\epsilon_{cis}[cis]\,\Phi_{c\rightarrow t} + \epsilon_{trans}[trans]\,\Phi_{t\rightarrow c})}{N_L V(\epsilon_{cis}[cis] + \epsilon_{trans}[trans])} \qquad (1)$$

$$[cis] + [trans] = [cis]_0 \qquad (2)$$

For the photostationary state eqn. (3) defines a further relationship between $\Phi_{c\rightarrow t}$ and $\Phi_{t\rightarrow c}$:

TABLE 1

Products of the photolysis (185 nm) of *cis*-cyclooctene (2.0×10^{-2} M in *n*-pentane)[a]

Product	Φ
trans-Cyclooctene	0.34[b] 0.32 ± 0.02[c]
Bicyclo-[5.1.0]-octane	0.008 ± 0.002
Methylenecycloheptane	0.007 ± 0.002
Bicyclo-[3.3.0]-octane	0.004 ± 0.001
1-Methylcycloheptene	0.003 ± 0.001
1,7-Octadiene	≈ 0.001
Vinylcyclohexane	Trace (≈0.0001)

[a] Except for the determination of Φ(*trans*-cyclooctene), conversions of the starting material did not exceed 5%.
[b] Value calculated using eqns. (3) and (4); see text.
[c] Value obtained by extrapolation to zero conversion.

$$\Phi_{c\to t}\epsilon_{cis}[cis]_\infty = \Phi_{t\to c}\epsilon_{trans}[trans]_\infty \tag{3}$$

When eqn. (1) is integrated, expression (4) is obtained:

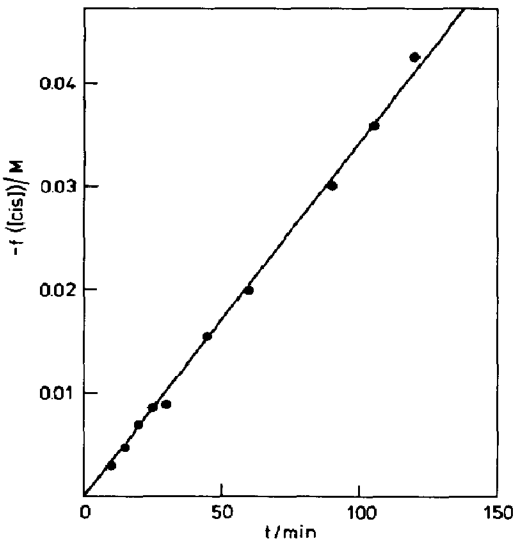
$$f([cis]) = -\frac{I[cis]_0}{N_L[cis]_\infty}\Phi_{t\to c}t \tag{4}$$

where $f([cis])$ is given by

$$\frac{\epsilon_{cis} - \epsilon_{trans}}{\epsilon_{trans}}([cis] - [cis]_0) + $$
$$+ \left([cis]_0 + \frac{\epsilon_{cis} - \epsilon_{trans}}{\epsilon_{trans}}[cis]_\infty\right)\ln\frac{[cis] - [cis]_\infty}{[cis]_0 - [cis]_\infty}$$

In the present system $[trans]_\infty/[cis]_\infty = 52/48$ (49/51 [9]). In order to calculate both $\Phi_{c\to t}$ and $\Phi_{t\to c}$, ϵ_{cis} and ϵ_{trans} are needed. They are reported [9] to be of similar size. A redetermination yields $\epsilon_{cis} = 8500\ \text{M}^{-1}\ \text{cm}^{-1}$ and $\epsilon_{trans} = 6000\ \text{M}^{-1}\ \text{cm}^{-1}$ at 185 nm (Fig. 1). Equations (3) and (4) strictly apply only to systems with two components which photoreversibly transform into each other. This requirement is nearly met in the present case as there are only a few minor side reactions occurring (see Table 1), some of which are photoreversible [12]. In Fig. 2 the left-hand side of eqn. (4) is plotted against the irradiation time. From the slope $\Phi_{t\to c} = 0.44$ is calculated which, using eqn. (3), leads to $\Phi_{c\to t} = 0.34$. Alternatively, and in good agreement, $\Phi_{c\to t} = 0.32$ is given by the intercept when the apparent quantum yield Φ(*trans*) is plotted against the irradiation time (Fig. 3).

The redetermination of $\Phi_{c\to t}$ and $\Phi_{t\to c}$ in the cyclooctene system thus yields a value for $\Phi_{c\to t} + \Phi_{t\to c}$ of 0.78, *i.e.* the cyclooctene system also obeys the rule [3] that the sum of $\Phi_{c\to t}$ and $\Phi_{t\to c}$ does not exceed unity.



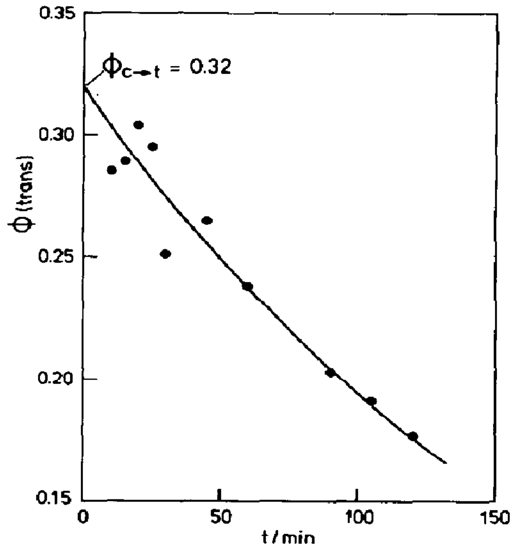


Fig. 2. The *cis–trans* photoisomerization of cyclooctene at 185 nm: a plot of $-f([cis])$ *vs.* time, with $f([cis])$ as defined in the text.

Fig. 3. Photolysis of *cis*-cyclooctene at 185 nm: a plot of the apparent quantum yield $\Phi(trans)$ *vs.* time; $\Phi_{c \to t}$ is obtained by extrapolation of $\Phi(trans)$ to zero conversion.

This rule must of necessity hold if a common intermediate is reached from the *cis* and the *trans* sides. The present result conforms to this requirement and a common intermediate in the photoisomerization of cyclooctene is no longer excluded.

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