

FLASH PHOTOLYSIS OF TETRAPHENYLCYCLOBUTANE IN SOLUTION — A CONVENIENT CHEMICAL ACTINOMETER

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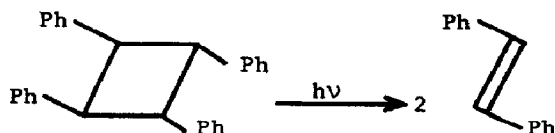
Summary

r-1,c-2,t-3,t-4-Tetraphenylcyclobutane (TPCB) was irradiated in n-butyl chloride at room temperature with 20 ns flashes of 265 nm light and in stationary experiments with 260 nm light. *trans*-Stilbene was found to be formed during the flash with a quantum yield of 0.27. By measuring the optical absorption at 300 nm of the generated *trans*-stilbene at the end of the flash the conversion of TCPB was determined. It is shown that TPCB-n-butyl chloride is useful as an actinometric system at 265 nm.

1. Results and discussion

During flash photolysis investigations the accurate determination of the dose absorbed per flash is often a problem. In principal, classical actinometer systems such as the ferrioxalate actinometer can be used. However, the application of these systems generally yields only an order of magnitude value of the absorbed dose. This is due to the fact that except at very high incident intensities ($\geq 10^{17}$ photons flash⁻¹) the actinometer solution has to be irradiated repeatedly in order to obtain conversions that are sufficiently high for an accurate determination after the irradiation. Frequently such a procedure is strongly hampered by broad variations in the number of photons emitted per flash from the laser.

It therefore appeared to be highly desirable to possess a chemical actinometer which allows the measurement of the dose absorbed per flash by means of the generally used optical absorption detection method. An appropriate system was found in the photolysis of r-1,c-2,t-3,t-4-tetraphenylcyclobutane (TPCB). This compound undergoes a $2\sigma \rightarrow 2\pi$ cleavage upon irradiation with UV light, the essential product being *trans*-stilbene [1 - 3]:



It appears that other photoproducts formed with minor yields are predominantly generated during secondary processes involving the additional absorption of photons by stilbene. The occurrence of such reactions during flash photolysis, *i.e.* during the irradiation of the solution with a single flash, is therefore very improbable.

On irradiating solutions of TPCB in *n*-butyl chloride with a 20 ns flash of 265 nm light, *trans*-stilbene was formed. Figure 1 shows the spectrum obtained at the end of the flash and the inset demonstrates a typical oscilloscope trace. From the optical density measured at 300 nm the concentration of *trans*-stilbene was calculated and plotted against the digital readout of a photodiode which is proportional to the incident intensity of the photolysing laser beam. This diode served as an intensity reference during all experiments. Figure 2 shows that the concentration of *trans*-stilbene formed

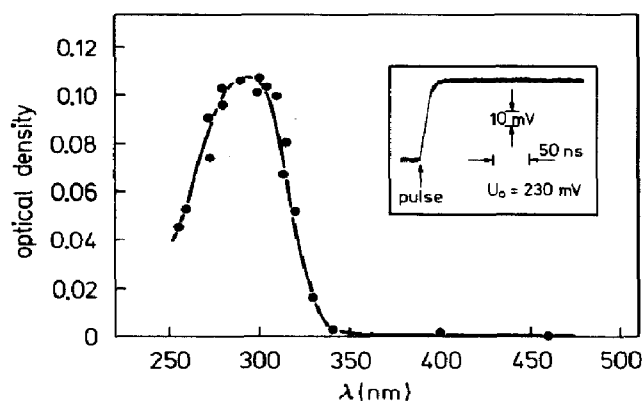


Fig. 1. The optical absorption spectrum measured at the end of a 20 ns flash obtained during the irradiation of a TPCB solution ($1.1 \times 10^{-4} \text{ mol l}^{-1}$) in $n\text{-C}_5\text{H}_{11}\text{Cl}$ at room temperature. Inset: typical oscilloscope trace obtained by monitoring the optical absorption during and after the flash at $\lambda = 300 \text{ nm}$.

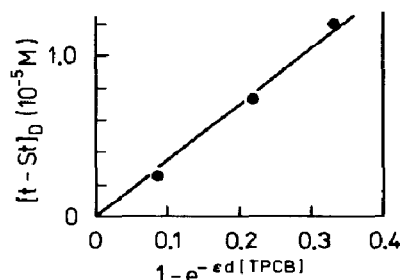
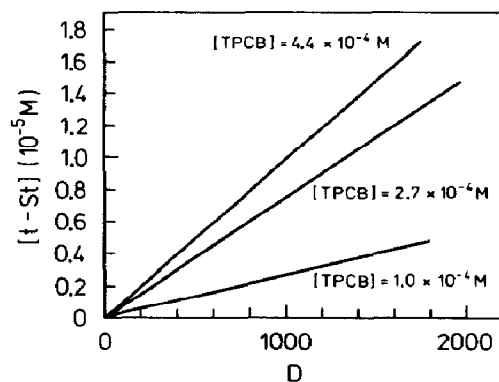


Fig. 2. The *trans*-stilbene concentration *vs.* the digital readout D of the reference photodiode at various TPCB concentrations.

Fig. 3. The *trans*-stilbene concentration measured at $\lambda = 300 \text{ nm}$ at the end of the flash *vs.* the initial concentration of TPCB (intensity of incident light, $8.2 \times 10^{16} \text{ photons flash}^{-1}$).

during the flash depends linearly on the incident intensity. From Fig. 3 it is seen that the concentration of *trans*-stilbene formed at constant incident intensity of the photolysing light depends on the concentration of TPCB as is expected from eqn. (3) (presented later).

Parallel to the flash photolysis experiments stationary irradiations were performed which yielded the quantum yield of the reaction: $\phi(\textit{trans}\text{-stilbene}) = 0.27$. The results show that the system TPCB–n-C₅H₁₁Cl is appropriate for actinometry at $\lambda = 265$ nm. It is suitable for flash photolysis experiments if the laser output is greater than 10^{14} photons flash⁻¹ (corresponding to incident intensities greater than about 4×10^{14} photons cm⁻² flash⁻¹). In this case the incident intensity is obtained upon irradiation of the actinometer solution with a single flash. Manipulation of the irradiated solution is avoided.

The number D_{abs} of photons absorbed per flash is calculated using

$$D_{\text{abs}} = \frac{[t\text{-St}]_{\text{D}} N_{\text{A}} V_{\text{ir}}}{\phi(t\text{-St}) \times 10^3} \quad (1)$$

where $\phi(t\text{-St})$ is the quantum yield for *trans*-stilbene formation, V_{ir} the irradiated volume in cubic centimetres, N_{A} Avogadro's number and $[t\text{-St}]_{\text{D}}$ the concentration (in moles per litre) of *trans*-stilbene formed during the flash.

The number D_{inc} of photons incident on the cuvette is obtained from

$$D_{\text{inc}} = \frac{D_{\text{abs}}}{1 - \exp(-\epsilon d[\text{TPCB}])} \quad (2)$$

where $[\text{TPCB}]$ is the tetraphenylcyclobutane concentration in moles per litre, ϵ the extinction coefficient for TPCB in l mol⁻¹ cm⁻¹ (900 at 265 nm and 1000 at 260 nm [4]) and d is the optical path length of the cuvette in centimetres. *trans*-Stilbene concentrations were calculated using $\epsilon_{300\text{nm}} = 2.8 \times 10^4$ l mol⁻¹ cm⁻¹ [4].

By combining eqns. (1) and (2) we obtain:

$$[t\text{-St}]_{\text{D}} = \frac{\phi(t\text{-St}) D_{\text{inc}} \times 10^3}{N_{\text{A}} V_{\text{ir}}} \{1 - \exp(-\epsilon d[\text{TPCB}])\} \quad (3)$$

2. Experimental

TPCB was prepared by irradiating *trans*-stilbene (0.55 mol l⁻¹) for 48 h in benzene solution with a high pressure mercury lamp [2]. The yield was about 7%. The reported quantum yield at this concentration is 0.33 [5]. The product was recrystallized three times from ethanol solution and dried under high vacuum (m.p. 163.8 - 164.3 °C).

n-Butyl chloride (Riedel de Haën, p.a.) was treated as follows: washed with concentrated H₂SO₄ and water, then dried with CaCl₂, distilled and passed through an Al₂O₃ (Merck, neutral) column. Then it was fractionally distilled over a splitting tube column (Fisher, Bonn). Irradiations were per-

formed in rectangular quartz cells. The solutions were bubbled with argon beforehand. For the flash photolysis an Nd-YAG (yttrium aluminium garnet) laser was used. The laser pulse was produced by a Nd-YAG oscillator (J. K. Lasers Ltd.) delivering an output energy of 100 mJ in 20 ns which was amplified by a Nd-glass amplifier (Korad) to about 1.5 J. The 1060 nm light was frequently quadrupled using a potassium dideuterophosphate crystal and an ammonium dihydrogenphosphate crystal. An S-5 vacuum photodiode (ITT) was used as an intensity reference. For this purpose a small fraction of the light emitted by the laser was guided via a beam splitter after the second doubler and before reaching the cell to the photodiode. The signal of the latter was displayed on a digital readout which was calibrated using a radiometer (Laser Instruments Ltd.). Stationary irradiations were carried out with a xenon lamp (Osram XBO 450 W) using a 260 nm interference filter No. B 7315002 (Balzer, 260 ± 2 nm) which was protected by a cell (1 cm thickness) containing an aqueous solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (240 g l^{-1}).

Acknowledgments

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