

PHOTOLYSIS OF *r*-1,*c*-2,*t*-3,*t*-4-TETRAPHENYLCYCLOBUTANE: QUANTUM YIELD DETERMINATIONS VIA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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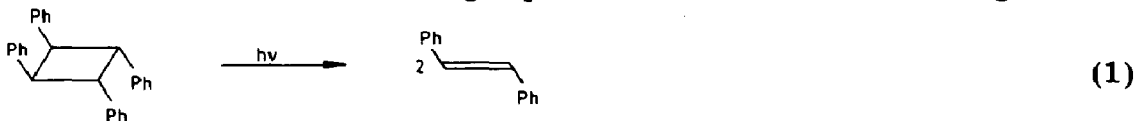
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Summary

r-1,*c*-2,*t*-3,*t*-4-tetraphenylcyclobutane (TPCB) was irradiated in *n*-butyl chloride solution using 15 ns flashes of 265 nm light. Significant amounts of *cis*-stilbene were produced during the flash via isomerization of *trans*-stilbene which is formed with a rate constant $k_1 > 5 \times 10^8 \text{ s}^{-1}$ according to the reaction $\text{TPCB} + h\nu \rightarrow 2 \text{ trans-stilbene}$. The quantum yield for the cycloreversion of TPCB is $\phi(-\text{TPCB}) \approx 1.0$. The same result was obtained for continuous irradiation using light from a xenon lamp ($\lambda = 240 - 280 \text{ nm}$).

1. Introduction

It has been pointed out previously by Kaupp and Stark [1] that *r*-1,*c*-2,*t*-3,*t*-4-tetraphenylcyclobutane (TPCB) and similar compounds undergo a selective $2\sigma \rightarrow 2\pi$ bond cleavage upon direct excitation with UV light:



This reaction attracted our attention some years ago [2] because it appeared to be appropriate for the actinometry of light of wavelengths between 240 and 270 nm where TPCB possesses absorption bands. In contrast, the product of reaction (1), *trans*-stilbene, absorbs strongly near 300 nm where TPCB is almost transparent. Uncertainty has recently arisen regarding the quantum yield of reaction (1). Values of $\phi(-\text{TPCB})$ ranging from 0.13 [2] (solvent, *n*-butyl chloride) to 0.42 [3] (solvent, cyclohexane) have been reported. Reasons for these discrepancies were sought in terms of the simultaneous formation of *cis*- and *trans*-stilbene and subsequent *trans* \rightarrow *cis* isomerization during the irradiation. *Cis*-stilbene ($\epsilon = 5.5 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ [4]) absorbs significantly less light at 300 nm than is absorbed by *trans*-stilbene ($\epsilon = 2.9 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ [4]), which may lead to misinterpretations of the results of optical density measurements if the conversion of *trans*-stilbene is neglected.

To clarify the situation, we have performed product analyses using high performance liquid chromatography (HPLC) following irradiation of dilute

solutions of TPCB in *n*-butyl chloride. The irradiations were performed either continuously using UV light (240 - 280 nm), selected from the emission spectrum of a xenon lamp by means of a filter combination, or using 15 ns single flashes (wavelength, 265 nm) produced by a neodymium-doped yttrium aluminium garnet (Nd-YAG) laser system operated in conjunction with two frequency doublers.

2. Results

2.1. Flash photolysis experiments

Figure 1 shows the formation of *cis*- and *trans*-stilbene in solutions of TPCB in *n*-butyl chloride at concentrations of 1.4×10^{-4} and 0.8×10^{-4} mol l⁻¹ as a function of the absorbed dose per flash. The upward curvature observed for *cis*-stilbene and the corresponding downward curvature observed for the formation of *trans*-stilbene indicate that *cis*-stilbene is not formed via bond scission in TPCB but via *trans* → *cis* isomerization during the 15 ns flash, *i.e.* subsequent to reaction (1) *trans* → *cis* isomerization occurs following the absorption of another photon:



This conclusion is supported by the observation that the *cis*-to-*trans* ratio $r(c/tr)$ increases with increasing dose as shown in the inset in Fig. 1. A constant *cis*-to-*trans* ratio would be observed if *cis*- and *trans*-stilbene were formed simultaneously from the decomposition of TPCB. This behaviour becomes feasible if the lifetime of the excited TPCB molecules is markedly shorter than the duration of the flash. In fact a rather short fluorescence lifetime of TPCB in cyclohexane solution ($\tau_{F1} \approx 1.8$ ns) was determined in this work on excitation at $\lambda = 254$ nm. According to Shizuka *et al.* [3] τ_{F1} is 0.8 ns. Therefore, a rate constant k_1 for reaction (1) of at least 5×10^8 s⁻¹ must be assumed.

The initial slope of the curve representing the total formation of stilbene gives a value of 2 for the quantum yield $\phi(\text{stilbene})$ which corresponds to $\phi(-\text{TPCB}) = 1$. This result disagrees with the conclusion of Shizuka *et al.* [3], which was reached on the basis of fluorescence measurements only, that about half the excited TPCB molecules deactivate to the ground state by bond cleavage and the other half deactivate by internal conversion. It should be noted that, with respect to the quantum yield balance, fluorescence does not play a role since its contribution to the total deactivation is almost negligible ($\phi_{F1} \approx 5 \times 10^{-3}$ [3]).

2.2. Continuous irradiation

The results are similar to those obtained by flash photolysis. The quantum yield for total stilbene formation when TPCB was irradiated in *n*-butyl chloride ($[\text{TPCB}] = 1.4 \times 10^{-4}$ mol l⁻¹) was also found to be 2.

3. Experimental details

An Nd-YAG laser system operated in conjunction with a neodymium glass amplifier (J. K. Lasers Ltd.) was used for the flash photolysis experiments (flash duration, 15 ns; $\lambda = 265$ nm). The actinometry was performed using an argon-saturated aqueous solution of $K_4Fe(CN)_6$ at a concentration of 1.4×10^{-5} mol l^{-1} . The concentration of hydrated electrons was measured at the end of the flash at 600 nm ($\epsilon = 1.32 \times 10^4$ l mol $^{-1}$ cm $^{-1}$ [5]; $\phi(e_{aq}^-) = 0.51$ at $\lambda = 265$ nm [6]).

A xenon lamp was used for the continuous irradiation. Light of wavelength 240 - 280 nm was selected by means of a filter combination (2 mm Schott UG5 and 1 cm of an aqueous solution of 2,7-dimethyl-3,6-diazacyclohepta-2,6-diene perchlorate at a concentration of 0.2 g l^{-1} [7]). In this case the ferrioxalate actinometer was used.

All irradiations were performed in deaerated *n*-butyl chloride solutions. The solvent, which was obtained from E. Merck, was washed with concen-

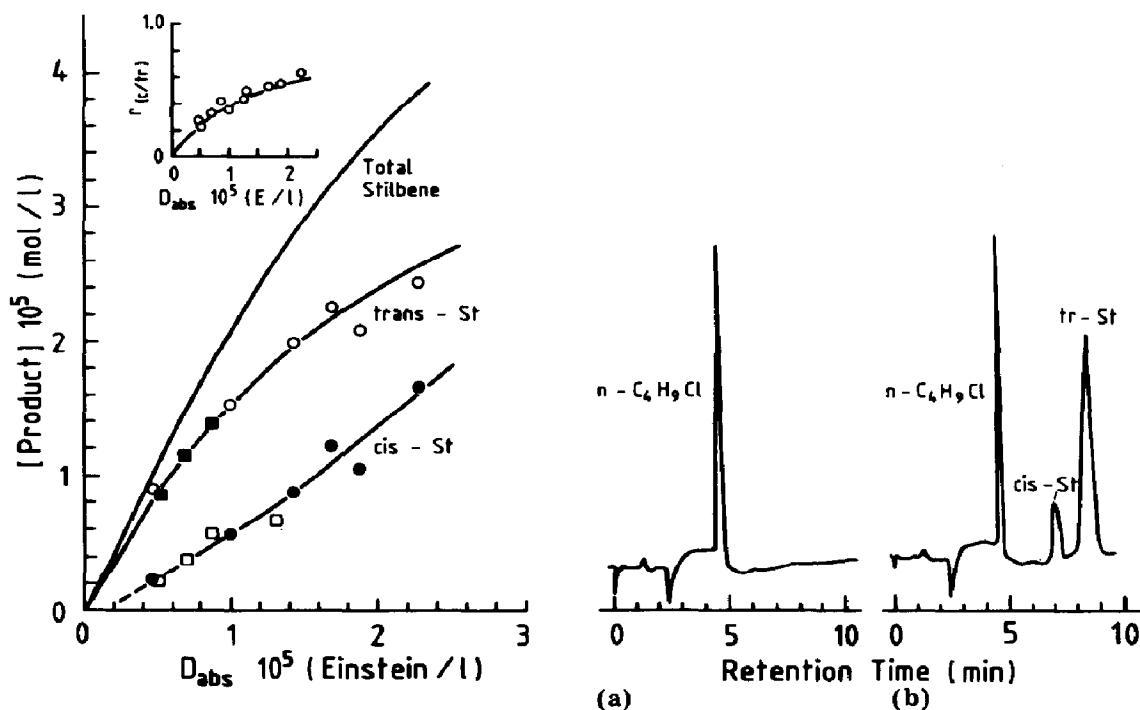


Fig. 1. Product formation during the flash photolysis of TPCB in deaerated *n*-butyl chloride at concentrations of 1.4×10^{-4} mol l^{-1} (\circ , \bullet) and 0.8×10^{-4} mol l^{-1} (\square , \blacksquare). The product concentration is plotted against the dose absorbed per flash by TPCB. The inset shows the change in the *cis*-to-*trans* ratio $r(c/tr)$ as a function of the absorbed dose.

Fig. 2. Typical chromatograms obtained with (a) non-irradiated and (b) irradiated solutions of TPCB in *n*-butyl chloride at a concentration of 1.4×10^{-4} mol l^{-1} . In case (b) the solution was irradiated using a single flash of 265 nm light (absorbed dose, 1.9×10^{-5} einstein l^{-1}).

trated H₂SO₄ and water, dried over CaCl₂, passed through an Al₂O₃ (neutral) column and distilled via a 1 m splitting tube column (Fischer, Bonn). The boiling point was 77 - 78 °C.

Quantitative HPLC analyses based on calibrations using the two stilbene isomers were performed using a Varian model 5000 instrument in conjunction with an integrator (Varian CDS 111) and a UV detector (Knauer) set at $\lambda = 280$ nm. A 30 cm Micropack reversed phase column (MCH 10) of internal diameter 0.4 cm was used. The eluent was a mixture of 70 vol.% methanol and 30 vol.% water. Figure 2 shows typical chromatograms.

4. Conclusions

The photolysis of TPCB in dilute solution results in the formation of *trans*-stilbene with a quantum yield of 2. The cyclobutane ring is split with a rate constant of at least 5×10^8 s⁻¹. In a simultaneous process *trans*-stilbene undergoes isomerization on absorption of light. Therefore, the final product of the photolysis of TPCB consists of both *trans*- and *cis*-stilbene. It appears that the photocleavage of TPCB can be used for actinometric purposes only after careful calibration.

Acknowledgments

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