Short Communication

Self-quenching and dimerization of singlet *trans*-stilbene

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The photodimerization of *trans*-stilbene was first observed by Ciamican and Silber [1] and has subsequently been reinvestigated several times [2]. Unlike the two unimolecular photochemical reactions of the stilbenes (*cis*–*trans* interconversion [3] and *cis*-stilbene–dihydrophenanthrene interconversion [4]) the photodimerization reaction has eluded quantitative study. In the course of our investigations of stilbene photoaddition reactions [5 - 8], kinetic evidence for the involvement of a stilbene excimer at stilbene concentrations above 10^{-2} M was obtained [8]. It thus became necessary to determine the concentration dependence of *trans*-stilbene isomerization and dimerization.

Experimental

 trans-Stilbene (Aldrich) was recrystallized twice from benzene–hexane and twice from absolute ethanol. Spectroquality benzene (Aldrich) was refluxed over two successive portions of phosphorus pentoxide and distilled, the middle 70% being retained. Benzene solutions containing varying stilbene concentrations and two internal standards (hexadecane, 1.5×10^{-3} M, and eicosane, 1.2×10^{-3} M) were degassed and sealed in 15 mm o.d. Pyrex test tubes. The solutions were irradiated on a merry go round apparatus at 25 °C using a 450 W Hanovia lamp with a potassium chromate filter solution to isolate 313 nm light. Irradiated solutions were analyzed by gas chromatography on a 4 in × 1/8 in column containing 5% SF 96 on Chromosorb G calibrated with authentic samples of *cis*-stilbene and stilbene dimers. Conversions of *trans*-stilbene to *cis*-stilbene were less than 10% in all cases. Light intensities were determined using benzophenone–benzhydrol actinometers [9]. Stilbene dimers were stable under the conditions of irradiation and analysis.

Results and discussion

 Quantum yields for stilbene *trans* to *cis* isomerization (Φ_t) and dimerization (Φ_{dim}) are summarized in Table 1. The value of Φ_t is independent of stilbene concentration below 0.1 M, but decreases at higher concentrations. Self-quenching of *trans*-stilbene fluorescence can also be detected at concen-

TABLE 1

Quantum yields for *trans*-stilbene isomerization and dimerization

[*trans*-stilbene] (M)	Φ_t	Φ_{dim}
0.01	0.45 ± 0.02	<0.01
0.05	0.45	0.03 ± 0.01
0.10	0.44	0.08 ± 0.02
0.25	0.38	0.19
0.40	0.31	0.26
0.55	0.27	0.33

trations above 0.1 M. Stilbene dimerization competes efficiently with isomerization at concentrations above 0.1 M. Determination of accurate dimerization quantum yields at lower concentrations would require extrapolation of measured values to zero conversion. The increase in dimerization with increasing stilbene concentration is proportional to the decrease in isomerization and obeys the following empirical formula:

$$\Phi_{dim} = 1.6 \, (\Phi_t^\circ - \Phi_t) \tag{1}$$

The simplest mechanism for stilbene isomerization and dimerization is given by the equations

$$t\text{-S}^* \xrightarrow{k_t} c\text{-S} \tag{2}$$

$$t\text{-S}^* \xrightarrow{k_d} t\text{-S} \tag{3}$$
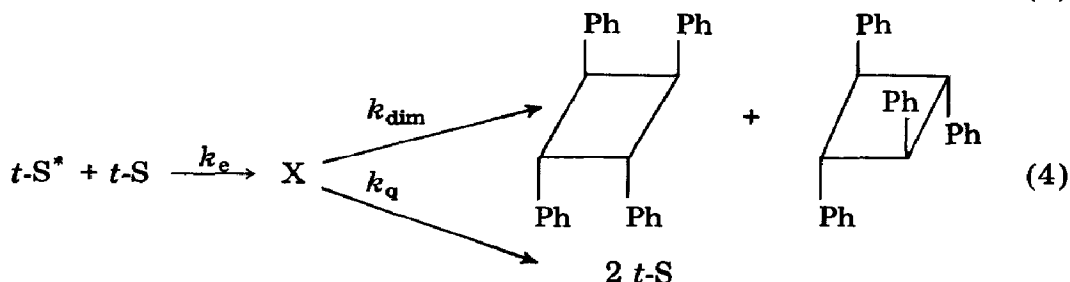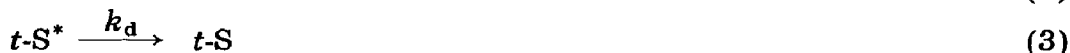
where k_d includes radiative and non-radiative decay and X is an encounter complex or excimer. This mechanism yields the following expressions for stilbene isomerization and dimerization:

$$\Phi_t^{-1} = \frac{k_d + k_t}{k_t} + \frac{k_e \, [t\text{-S}]}{k_t} \tag{5}$$

$$\Phi_{dim}^{-1} = \frac{k_{dim} + k_q}{k_{dim}} \left(1 + \frac{k_d + k_t}{k_e \, [t\text{-S}]}\right) \tag{6}$$

A plot of Φ_t^{-1} *versus* [*t*-S] has an intercept of 2.0 ± 0.1 and a slope of 3.1 ± 0.2, which afford the kinetic relationship $k_t = k_d$ and $k_e = 3.1 \, k_t$.

A plot of $\Phi_{dim}{}^{-1}$ *versus* $[t\text{-S}]^{-1}$ has an intercept of 1.3 ± 0.2 and a limiting slope of 1.0 ± 0.1, which afford the kinetic relationships $k_{dim} = 3.3\,k_q$ and $k_e = 1.3\,(k_t + k_d)$. In the absence of self-quenching, half of the stilbene singlets isomerize. Self-quenching leads to dimerization with a quantum yield of 0.8 ± 0.2, thus accounting for the empirical relationship given in eqn. (1).

The calculation of absolute rate constants is prevented by the occurrence of double exponential fluorescence decay at room temperature [10]. The short lived component (0.07 ns) is presumably due to prompt fluorescence from the planar singlet state and the long lived component (1.5 ns) is due to delayed fluorescence resulting from thermal repopulation of the planar singlet from a twisted singlet. The effective singlet lifetime in singlet quenching experiments is most likely a weighted average of the prompt and delayed lifetimes. The rate constant k_e for self-quenching must fall in the range 10^9 - 2×10^{10} s^{-1}. If stilbene excimer formation is reversible, then this range provides a lower limit for the rate constant for excimer formation. Stilbene excimer has been observed following γ irradiation of a squalene glass at 77 K [11], but is non-fluorescent at room temperature in benzene solution. Rapid dimerization of the stilbene excimer can readily account for the absence of excimer fluorescence [7].

Acknowledgments

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