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Catalysis of triplet state *cis–trans* isomerizations making a quantum chain process more efficient

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Abstract

Photocatalysis of *cis–trans* isomerizations is treated in this paper. Two systems, 8-(3,5-di*tert*-butylstyryl)fluoranthene/camphorquinone/acridine and 1,6-bisstyryl-1,3,5-cycloheptatriene/C60 were studied. In the first system Z-8-(3,5-di*tert*-butylstyryl)fluoranthene is photoisomerized with acridine as the catalyst and camphorquinone as triplet sensitizer, and in the second *Z,E*-1,6-bisstyryl-1,3,5-cycloheptatriene is isomerized with C60 as both catalyst and triplet sensitizer. The quantum efficiencies were found to increase 5.5 times in the first case and to be doubled in the second. The effect of concentration of both the catalyst and the reactant were investigated. The results are explained as an increased efficiency of a quantum chain process, and a theoretical model is used to evaluate the results.

Keywords: Cis–trans isomerization; Photocatalysis; Quantum chain reaction

1. Introduction

Multiple photoisomerizations, where a single photon isomerizes several double bonds, have been a topic of our research group for about a decade now. We have shown that multiple isomerizations can occur within a molecule or intermolecularly in several molecules [1–11]. An adiabatic photo reaction mechanism favours multiple isomerizations and the product is formed in the excited state. This is important both for the intermolecular and the intramolecular type. Multiple isomerizations can occur in the singlet excited state but are more common for triplet state reactions. In the intermolecular type of isomerization the reaction has always been a triplet state reaction. This paper is focused on such quantum chain reactions. In particular, we have recently shown that it is possible to catalyze triplet state *cis–trans* isomerizations, by a new type of catalysis [12]. The catalyst acts as a chain carrying species within a quantum chain process, making this process more efficient. The excited state of the reactant, the product and the catalyst are all involved. A large number of papers on *cis–trans* isomerizations proceeding by a quantum chain process are found in the literature. The group headed by Professor K. Tokumaru has done a particularly great deal of work in this area [13]. It is the efficiency of this type of quantum chain isomerization which can be further increased by the addition of a substance, a catalyst, with the right properties [12].

A study of two systems is presented in this paper. One system is the photoisomerization of *Z*-8-(3,5-di*tert*-butylstyryl)fluoranthene (*c*-SF) to the *trans* configuration (*t*-SF) with camphorquinone (CQ) as the triplet sensitizer and acridine (Acr) as the catalyst and the other is the photoisomerization of a *Z,E*-1,6-bisstyryl-1,3,5-cycloheptatriene (*c*-BSCH) to the *E,E*-configuration (*t*-BSCH) with C60 as both the sensitizer and the catalyst (Figs. 1 and 2).

2. Experimental

8-(3,5-di*tert*-butylstyryl)fluoranthenes (SF) were prepared in five steps.

2.1. *Methylfluoranthene-8-carboxylate*

A mixture of methylcoumalate (10.2 g, 66.2 mmol) and acenaphthylene (3.02 g, 19.9 mmol) in dry DMF (60 ml) was refluxed for 9 h in a nitrogen atmosphere under vigorous stirring. The solution was poured into water and extracted with chloroform. The crude product was purified using flash chromatography on silica gel with methylene chloride as the eluent to give yellow crystals (82%) [14].

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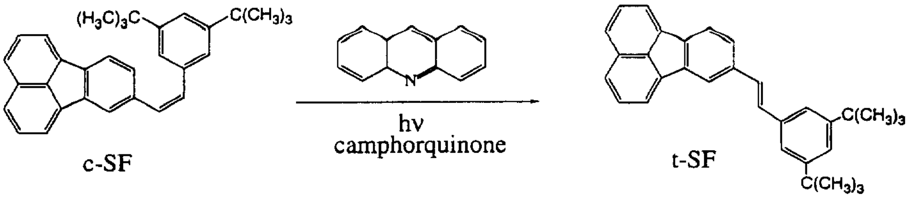

Fig. 1. *Cis–trans* isomerization in the presence of acridine as catalyst and camphorquinone as sensitizer.

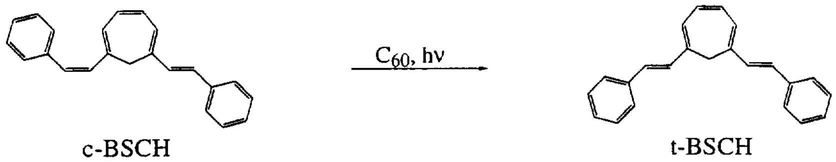

Fig. 2. *Cis–trans* isomerization in the presence of C60 as catalyst as well as sensitizer.

2.2. 8-(hydroxymethyl)fluoranthene

Lithium aluminium hydride (0.60 g) was added to a dried round-bottomed flask containing methyl flouranthene-8-carboxylate (4.23 g, 16.3 mmol) and dry diethyl ether (100 ml). The mixture was refluxed in a nitrogen atmosphere under vigorous stirring. After 2 h, when the reduction was complete, ethyl acetate (0.75 ml) and 5% aqueous sodium hydroxide (50 ml) were added successively to the ice-cooled reaction mixture under vigorous stirring. The ether layer was separated and the solvent removed. The residue was stirred with 10% aqueous sodium hydroxide (50 ml) for 1 h. The solution was then extracted three times with methylene chloride, and the methylene chloride phase was washed with water, 6 M HCl, and water again. Evaporation of the solvent yielded red crystals (60%) [15].

2.3. 8-(bromomethyl)fluoranthene

8-(bromomethyl)fluoranthene was prepared from phosphoroustribromide (1.16 g, 4.3 mmol) and 8-(hydroxymethyl)fluoranthene (2.25 g, 9.7 mmol) according to Ref. [15]. The crude product was purified using flash chromatography (silica gel) with methylene chloride as the eluent. Evaporation of the solvent yielded yellow crystals (1.13 g, 40%).

2.4. (8-fluoranthenemethyl)triphenylphosphoniumbromide

8-(bromomethyl)fluoranthene (0.55 g, 1.9 mmol) was mixed with triphenylphosphine (0.54 g, 2.05 mmol) in xylene (50 ml). The mixture was refluxed for 2 h and then cooled for one more hour. The reaction mixture was poured into a Büchner funnel and the yellow crystals obtained (60%) were washed with ice-cooled ether.

2.5. 8-(3,5-ditert-butylstyryl)fluoranthene (SF)

8-(3,5-di*tert*-butylstyryl)fluoranthenes were prepared with a Wittig reaction between (8-fluoranthenylmethyl)-triphenylphosphoniumbromide (0.16 g, 1.1 mmol) and (3,5-di*tert*-butyl)benzaldehyde (0.25 g, 1.1 mmol) in dry DMF (50 ml). Lithium ethoxide in ethanol was used as the base. Purification using column chromatography (silica gel) with methylene chloride as the eluent yielded a mixture of *c*-SF and *t*-SF (82%). The isomers were separated using preparative HPLC, using hexane as the eluent and a medium-polar column packed with Spherisorb S10 CN. The isomeric purities thus obtained were >99.9%.

2.6. 1,6-bisstyryl-1,3,5-cycloheptatriene (BSCH)

1,6-bisstyryl-1,3,5-cycloheptatrienes were synthesized using a twofold Wittig reaction from benzyltriphenylphosphonium chloride and 1,6-cycloheptatrienedicarbaldehyde [10].

2.7. Isomerization measurements

Irradiations were performed in an optical bench arrangement from Applied Photophysics, using a 150 W Xenon arc lamp and a monochromator. The isomerizations were followed by analytical HPLC, using hexane as the eluent and a medium-polar column, Sperisorb CN 5μ. Quantum yields were determined using ferrioxalate actinometry. Samples of *c*-SF/CQ/Acr in toluene were degassed with four freeze–pump–thaw cycles and irradiated at 480 nm. Samples of *c*-BSCH/C60 in toluene were freed from oxygen by nitrogen flushing and irradiated at 509 nm.

3. Results and discussion

3.1. Isomerization efficiency with varying catalyst concentration

3.1.1. 8-(3,5-ditert-butylstyryl)fluoranthene (SF)

The isomerization of *c*-SF (2.0 mM) to *t*-SF was studied using CQ (50.0 mM) as triplet sensitizer and Acr (0–30.0 mM) as catalyst with toluene as the solvent. The efficiency

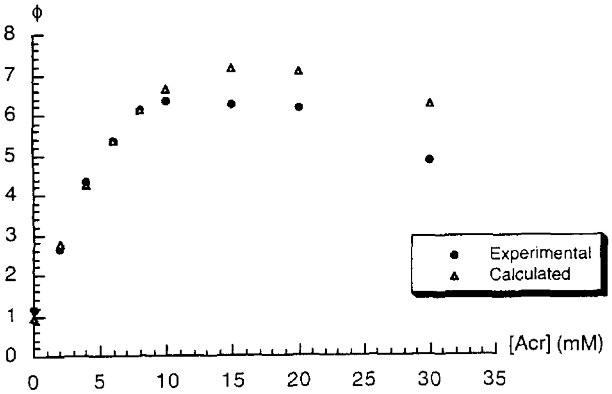

Fig. 3. Experimentally obtained quantum yields for the isomerization of *c*-SF plotted against the concentration of acridine and the quantum yields calculated according to the theory of quantum chain processes. The concentration of *c*-SF at It = 0 is 2.0 mM.

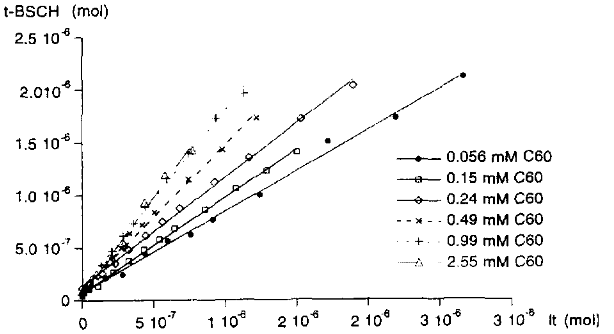

Fig. 4. The amount of *t*-BSCH (mol) obtained at isomerization plotted against the total number of absorbed photons (mol) for various concentrations of C60. The concentration of *c*-BSCH at It = 0 is 5.0 mM.

of the isomerization of *c*-SF shows a maximum at a certain concentration of Acr (Fig. 3).

Below, it is shown that this is the initial effect of a more efficient quantum chain process, but that it is later destroyed owing to self-quenching of Acr triplets. The efficiency of the *c*-SF to *t*-SF isomerization is increased by about 5.5 times at the most.

3.1.2. 1,6-bisstyryl-1,3,5-cycloheptatriene (BSCH)

The isomerization of *c*-BSCH (5.0 mM) to *t*-BSCH was studied using C60 as both triplet sensitizer and catalyst (0.05–2.5 mM), with toluene as the solvent. The efficiency of the isomerization of *c*-BSCH is increased with increasing C60-concentration, reaching a maximum with about doubled isomerization efficiency (Figs. 4 and 5).

This can be explained in a similar way as above. We have previously investigated this system without using a catalyst, and shown that it is mainly an adiabatic triplet state reaction [10].

3.2. Isomerization efficiency with varying reactant concentration

3.2.1. 8-(3,5-ditert-butylstyryl)fluoranthene (SF)

The isomerization of *c*-SF (2.0–12.0 mM) to *t*-SF is studied using camphorquinone (50.0 mM) as triplet sensitizer and acridine (8.0 mM) as catalyst with toluene as the solvent. The efficiency of the isomerization of *c*-SF increases with increasing *c*-SF concentration (Fig. 6).

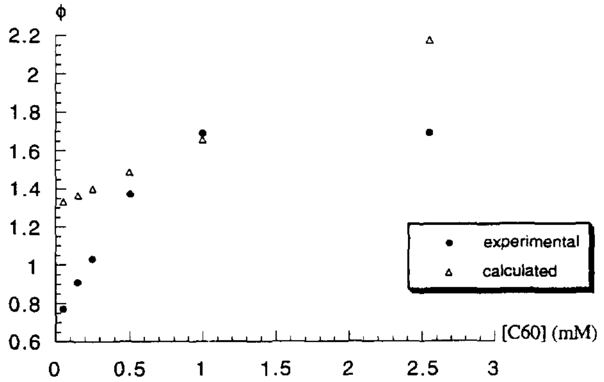

Fig. 5. Experimentally obtained quantum yields for the isomerization of *c*-BSCH plotted against the concentration of C60 and the quantum yields calculated according to the theory of quantum chain processes. The concentration of *c*-BSCH at It = 0 is 5.0 mM.

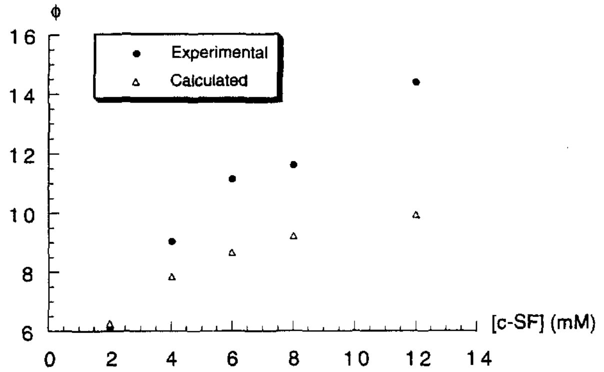

Fig. 6. Experimentally obtained quantum yields at various concentrations of *c*-SF, and quantum yields calculated according to quantum chain processes. The concentration of acridine is 8 mM.

The increase in quantum yield is due to the fact that the quantum chain process is more efficient at higher concentrations of *c*-SF. A similar system without using a catalyst has been studied by Tokumaru and co-workers [16]. They investigated the mechanism for triplet state isomerization of a *c*-SF without *tert*-butyl groups. The concentration effect on the quantum yield in that case was 0.34 mM^{-1}, that is an increase of 0.34 per mM.

3.2.2. 1,6-bisstyryl-1,3,5-cycloheptatriene (BSCH)

The isomerization of *c*-BSCH (0.2–2.3 mM) to *t*-BSCH is studied using C60 as both triplet sensitizer and catalyst (1.0 mM) with toluene as the solvent. The efficiency of the isomerization of *c*-BSCH is increased with increasing *c*-BSCH concentration. This can be explained in a similar way as above.

3.3. Laser flash photolysis

3.3.1. 8-(3,5-ditert-butylstyryl)fluoranthene (SF)

The laser flash photolysis studies were focused on the *c*-SF/CQ/Acr system. The acridine triplet lifetime was deter-

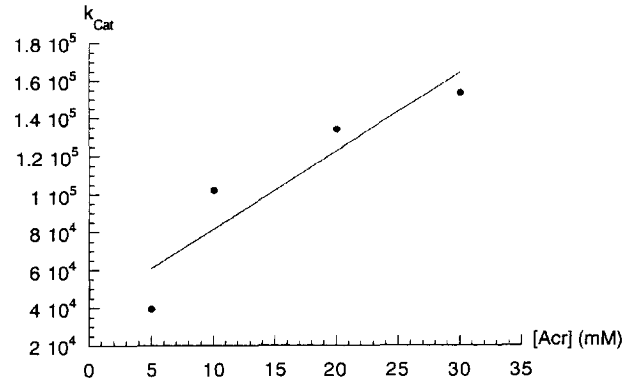

Fig. 7. The rate constant for the decay of triplet state of acridine at various concentration of acridine.

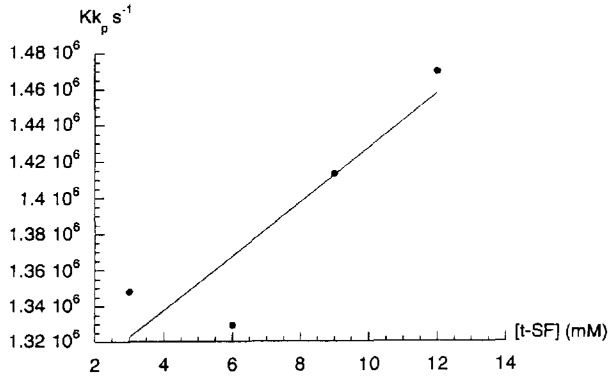

Fig. 8. The rate constant for the decay of triplet state of *t*-SF at various concentrations of *t*-SF.

mined at different concentrations of Acr (5.0–30.0 mM) using CQ (20.0 mM) as triplet sensitizer (Fig. 7).

The CQ is excited at 480 nm using a tripled Nd:YAG laser pumped dye laser (coumarine 480, ≈7 ns FWHM). The lifetimes are corrected for triplet–triplet annihilation by extrapolating to zero laser dose. The lifetime decreases with increasing Acr concentration owing to self-quenching of the Acr triplets by ground state Acr. The experimental rate constant for self-quenching is calculated to 4.15×10^6 M^{-1} s^{-1}, although the error is probably large. The effect of the concentration of *t*-SF on the *t*-SF triplet state lifetime has also been investigated using similar conditions as above (*t*-SF 3.0–12.0 mM and CQ 15.0 mM). In this case no triplet–triplet annihilation could be observed but self-quenching of *t*-SF triplets by ground state *t*-SF was observed (Fig. 8). The experimental rate constant for self-quenching is calculated to 1.50×10^7 M^{-1} s^{-1}, but similar as above the error is probably large.

3.3.2. *1,6-bisstyryl-1,3,5-cycloheptatriene (BSCH)*

Self-quenching of C60 triplets has been studied by Fraelich and Weisman [17].

3.4. *Reaction model*

In a previous paper [12], the catalysis of the triplet state isomerization of a *Z,E*-styrylstilbene to the *E,E*-isomer with anthracene as the catalyst was presented as well as a theoretical treatment of the processes included. The efficiency of the isomerization was increased as much as 50 times. The equation describing the catalysis of the isomerizations is as follows:

$$\begin{aligned} \mathrm{d}[E]/I\,\mathrm{d}t= & \\ & \{(1-\alpha)+k_{\mathrm{etEZ}}[Z]/Kk_{\mathrm{p}}+k_{\mathrm{etECat}}[\mathrm{Cat}]/Kk_{\mathrm{p}} \\ & -k_{\mathrm{etCatE}}(x_{\mathrm{Cat}}+k_{\mathrm{etECat}}[\mathrm{Cat}]/Kk_{\mathrm{p}})[E]/ \\ & (k_{\mathrm{Cat}}(1-x_{\mathrm{Cat}})+k_{\mathrm{etCatE}}[E]+k_{\mathrm{etCatZ}}[Z])\}/ \\ & \{1+k_{\mathrm{Cat}}(x_{\mathrm{Cat}}+k_{\mathrm{etECat}}[\mathrm{Cat}]/Kk_{\mathrm{p}})/(k_{\mathrm{Cat}}(1-x_{\mathrm{Cat}}) \\ & +k_{\mathrm{etCatE}}[E]+k_{\mathrm{etCatZ}}[Z])\}-x_E \end{aligned} \quad (1)$$

The isomerizations were only carried out to low conversions, hence only the linear part of Eq. (1) was considered. With $[E]=0$ Eq. (1) reduces Eq. (2).

$$\begin{aligned} \mathrm{d}[E]/I\,\mathrm{d}t= & \\ & \{(1-\alpha)+k_{\mathrm{etEZ}}[Z]/Kk_{\mathrm{p}}+k_{\mathrm{etECat}}[\mathrm{Cat}]/Kk_{\mathrm{p}}\}/ \\ & \{1+k_{\mathrm{Cat}}(x_{\mathrm{Cat}}+k_{\mathrm{etECat}}[\mathrm{Cat}]/Kk_{\mathrm{p}})/ \\ & (k_{\mathrm{Cat}}(1-x_{\mathrm{Cat}})+k_{\mathrm{etCatZ}}[Z])\} \end{aligned} \quad (2)$$

Some of the rate constants are measured and others are calculated using the Sandros Eq. (6) [18]. The rate constants k_{etEZ}, k_{etECat} and k_{etCatZ} can be described by the following reactions:

$$^3E^*+Z \rightarrow E+{}^3Z^* \qquad k_{\mathrm{etEZ}} \qquad (3)$$

$$^3E^*+\mathrm{Cat} \rightarrow E+{}^3\mathrm{Cat}^* \qquad k_{\mathrm{etECat}} \qquad (4)$$

$$^3\mathrm{Cat}^*+Z \rightarrow \mathrm{Cat}+{}^3Z^* \qquad k_{\mathrm{etCatZ}} \qquad (5)$$

Using the Sandros equation, these rate constants can be calculated if the diffusion constants (k_{diff}) and the differences between the triplet energies (ΔE_{T}) are known. For *c*-SF/CQ/Acr k_{diff} has been determined experimentally (4.81×10^9 M^{-1} s^{-1}) and the triplet energy levels used in this case were 44.5 kcal/mol for *t*-SF, 46.1 kcal/mol for *c*-SF and 45.0 kcal/mol for Acr [16,19]. For *c*-BSCH/C60 a value of 1.1×10^{10} M^{-1} s^{-1} has been used for k_{diff} [19] and the triplet energy levels used for this system were 34.0 kcal/mol for *t*-BSCH, 37.0 kcal/mol for *c*-BSCH and 36.0 kcal/mol for C60 [610,19].

$$k=k_{\mathrm{diff}}/\{1+\exp(-\Delta E_{\mathrm{T}}/RT)\} \qquad (6)$$

Lifetime measurements of the compounds and the catalysts give values of the rate constants k_{Cat} and Kk_{p}. These rate constants are described by the reactions below:

$$^3\mathrm{Cat}^* \rightarrow \mathrm{Cat} \qquad k_{\mathrm{Cat}} \qquad (7)$$

Table 1
Rate constants and α for *c*-SF and *c*-BSCH

	c-SF	*c*-BSCH
k_{etEZ} (M^{-1} s^{-1})	2.89×10^{8}	1.48×10^{8}
k_{etECat} (M^{-1} s^{-1})	1.43×10^{9}	3.43×10^{8}
k_{etCatZ} (M^{-1} s^{-1})	6.32×10^{8}	3.27×10^{9}
Kk_p (s^{-1})	738×10^{-9}	1.0×10^{-6}
α	0.5	0

$$^3Z^* \rightarrow {}^3p^* \rightarrow {}^3E^* \qquad (8)$$

$$^3E^* \leftrightarrows {}^3p^* \qquad K \qquad (9)$$

$$^3p^* \rightarrow \alpha E + (1-\alpha)E \qquad k_p \qquad (10)$$

What was not considered in the previous paper [12] was the self-quenching of triplets. This can be done by substituting k_{Cat} for $k_{Cat} + k_{sqCat}[Cat]$ and Kk_p for $Kk_p + k_{sqZ}[Z]$. Doing this and using Eq. (2) gives the curves fitted in Figs. 3 and 6. The following constants were used:

The rate constants in Table 1 may contain errors mainly due to the uncertainty in the triplet energies. This uncertainty may also explain the discrepancy in Fig. 6. A small change in triplet energies will affect the quantum yield substantially. Furthermore, the rate constant for self-quenching of *t*-SF triplets seems rather high. In Fig. 5 the calculated quantum yields are higher than those obtained experimentally. This might be due to *c*-BSCH not being a Franck–Condon triplet. Another reason might be aggregation of C60 at higher concentrations. Then there will always be effects that cannot be included in a model.

A rather complex catalytic reaction has been treated and there are still some effects which are not considered, such as the effect of possible triplet exciplexes and reactions within such exciplexes. Such a possibility might further increase the catalytic effect, giving even more efficient catalysis. Another effect which might destroy the catalysis is if the catalyst is not a 'Franck–Condon triplet', that is, if there is not as much energy available for sensitization using the catalyst as is required to excite the catalyst.

4. Concluding remarks

Three examples of this new photocatalytic process have been found to date. We will continue to study new systems, hoping to find a more efficient and simple system. It is our goal to find a more efficient system where the catalyst and the sensitizer are the same. Another goal is to design efficient systems where the reaction occurs in an excited state complex. There are examples of such systems in the literature, where a complex is needed to explain the results. Further work along this line might give very efficient systems. Finally it is a challenging thought whether there are examples of this catalytic process in nature.

Acknowledgements

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