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Journal of Photochemistry and Photobiology A: Chemistry 139 (2001) 37–43

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Catalysis of a photochemical quantum chain process Optimal conditions for catalyzed quantum chain *cis–trans* photoisomerizations of a styrylpyrene

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Received 30 October 2000; accepted 22 November 2000

Abstract

In an experimental study of catalyzed photosensitized *cis–trans* isomerization of 1-(3,5-di-tertbutylstyryl)pyrene, three different catalysts, anthracene, 9-methylanthracene and 9,10-di-chloroanthracene were used. The most efficient catalytic process was observed when anthracene was used as the catalyst. The quantum yield was 11.5 times higher than that of the uncatalyst isomerization. The use of different catalyst shows that the quantum yield for the photoisomerization strongly depends on properties of the added catalyst. The most important properties of the catalyst seem to be proper triplet energy and long triplet lifetime.

The limits for the catalysis of *cis–trans* isomerization chain process was also investigated by model calculation. From this calculation it is concluded that a high quantum yield is not equivalent with efficient catalysis. The most efficient catalysis is reached when the triplet state energy of the catalyst is around 1.5 kcal/mol above the triplet energy of the *E*-isomer. For this optimum of the catalytic effect, quantum yield in the absence of the catalyst is close to unity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: *cis–trans* isomerization; *E*-isomer; Anthracene; Photoisomerization; Triplet state energy

1. Introduction

The photochemical *cis–trans* isomerization of olefins is one of the simplest, but also one of the most interesting and studied photoreactions. This reaction can occur in the singlet as well as the triplet state[1] (see, e.g. [1,15,16]) by a diabatic or an adiabatic process. In a diabatic process, the reaction starts on the excited state surface and is completed on the ground state energy surface. The decay from the excited state to the ground state usually occurs when the isomerization is halfway with a 90° twist around the C=C double bond. In an adiabatic process the product is formed in an excited state. It is the shape of the excited state potential energy surface that determines the reaction path.

The first adiabatic triplet state *cis–trans* photoisomerization was reported in the beginning of the 1980s by Tokumaru and co-workers [2]. They termed this reaction as "one-way photoisomerization". Shortly thereafter, Sandros and Becker [3] reported an adiabatic singlet state photoisomerizations. In most cases, the absorption of one photon is needed to isomerize one double bond. Our interest in *cis–trans* photoisomerization started when we found that multiple intramolecular isomerizations could occur in large macrocycles via an initial absorption of only one photon [4]. This eventually led us to examine linear molecules with several conjugated double bonds. We have reported both intramolecular multiple photoisomerization as well as intermolecular quantum chain reactions [5,17–21]. The probability for multiple photoisomerization is higher in the triplet state than in the singlet state due to the longer lifetime of the triplet state. However, one case of a twofold isomerization in the singlet state has been reported [5].

In system that follows an adiabatic mechanism, the isomerization usually occurs by an intermolecular quantum chain process. This system can show a quantum yield that exceeds unity since the initial excitation energy is used several times [1,15,16].[2] In a quantum chain process the excitation energy of, i.e. a triplet state excited *trans*-isomer, $^3trans^*$, is transferred to a ground state *cis*-isomer producing a $^3cis^*$ which isomerizes into a new $^3trans^*$. Such quantum chain process will show high efficiency provided that the lifetime of the excited product ($^3trans^*$) is sufficiently long

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[1] For general overviews of *cis–trans* isomerization of olefins.

[2] See Footnote 1.

PII: S1010-6030(00)00419-6

for energy transfer to occur. If the excited state lifetime of ^{3}*trans** is short, the addition of a second compound with similar triplet energy as ^{3}*trans** but with a longer triplet lifetime could function as a catalyst and increase the length of the quantum chain process. We have shown that it is possible to catalyze an adiabatic *cis–trans* isomerization by adding such a catalyst [6,7]. We have also found that the efficiency of the quantum chain process depends strongly on the properties of the catalyst.

In this paper, we report a study of the optimal conditions for catalyzed quantum chain *cis–trans* photoisomerizations. Complementary experiments to the earlier study as well as calculations based on a theoretical reaction model have been carried out.

In the experimental part of the investigation we have studied the effect of the triplet energy and triplet lifetime of the catalyst on the catalytic efficiency by using different catalysts. The photoisomerization of 1-(3,5-di- tertbutylstyryl)pyrene (SP) was chosen and camphorquinone (CQ) was used as the triplet sensitizer (Fig. 1). The concentration of the catalyst was varied while the concentration of substrate (SP) and the triplet sensitizer (CQ) was held constant. We have used anthracene and some anthracene derivatives as catalysts since their photophysical and photochemical properties are well known. The triplet lifetime of the catalyst and the substrate were varied by changing the oxygen concentration in the solution, and consequently the oxygen quenching rate.

2. Experimental

2.1. Materials

1-(3,5-di-tertbutylstyryl)pyrene (SP) [8] was synthesized by a Wittig reaction from (3,5-di-tertbutylbenzyl)triphenylphosphonium bromide and 1-pyrencarboxaldehyde. A standard procedure for the Wittig reaction, and the purification of the product mixture and separation of the isomers by HPLC, was used [9]. The purity obtained was >99.5% and the total yield of the different isomers were 90%.

2.2. Isomerizations

The solutions of SP were irradiated in an optical bench arrangement from applied photophysics, using a 150 W xenon arc lamp and a monochromator adjusted to 480 nm. The isomerization was followed by analytical HPLC (spherisorb CN 5 μ, with hexane as eluent). The photon fluxes were determined by ferrioxalate actinometry. The reduction of the oxygen concentration in the sample of *cis*-SP/CQ/catalyst in toluene was accomplished either by nitrogen flushing or degassing by five freeze-pump-thaw cycles.

2.3. Laser flash photolysis

Excitation of CQ by using a tripled Nd:YAG laser pumped dye laser (coumarine 480, ~7 ns FWHM) [10] made it possible to determine the triplet lifetime of SP and the catalysts, as well as the diffusion constant of the system SP/CQ/catalyst. The triplet lifetimes are corrected for triplet–triplet annihilation by extrapolating to zero intensity.

3. Theoretical modeling of catalysis of a quantum chain process

3.1. Reaction model

The photoisomerization was assumed to proceed by a quantum chain process and to follow an adiabatic triplet sensitized *cis–trans* isomerization pathway, described by the following reactions.

Excitation:

$$\mathrm{Sens} \rightarrow {}^1\mathrm{Sens}^* \quad I,\ \text{excitation rate} \tag{1}$$

$$^1\mathrm{Sens}^* \rightarrow {}^3\mathrm{Sens}^* \quad \Phi\mathrm{isc} \tag{2}$$

Energy transfer:

$$^3\mathrm{Sens}^* + Z \rightarrow \mathrm{Sens} + {}^3Z^* \quad Ix_Z \tag{3}$$

$$^3\mathrm{Sens}^* + E \rightarrow \mathrm{Sens} + {}^3E^* \quad Ix_E \tag{4}$$

$$^3E^* + Z \rightarrow E + {}^3Z^* \quad k_{\mathrm{et}EZ} \tag{5}$$

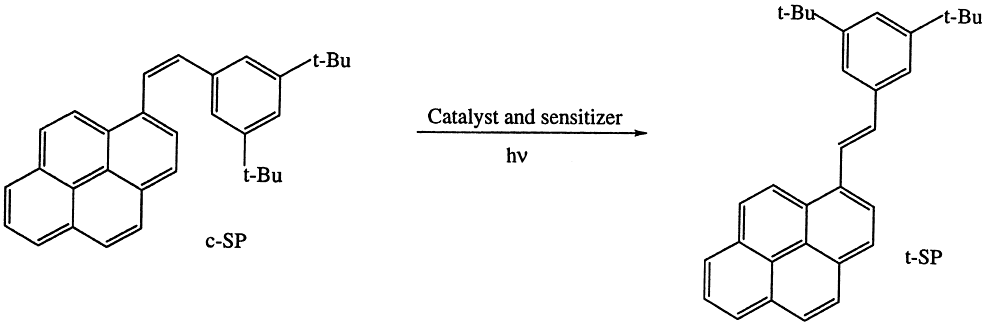

Fig. 1. *cis–trans* isomerization in the presence of a catalyst, anthracene, 9-methylanthracene or 9,10-di-chloroanthracene and CQ as the sensitizer.

Isomerization:

$$^3Z^* \rightarrow {}^3\mathrm{p}^* \rightarrow {}^3E^* \tag{6}$$

$$^3E^* \rightleftarrows {}^3\mathrm{p}^* \quad K \tag{7}$$

Unimolecular decay:

$$^3E^* \rightarrow E \quad k_E \tag{8}$$

$$^3\mathrm{p}^* \rightarrow \alpha Z + (1-\alpha)E \quad k_\mathrm{p} \tag{9}$$

To derive at Eq. (14), valid for the catalyzed triplet-sensitized *cis–trans* isomerization, energy transfer to and from the catalyst as well as the decay of the triplet state of the catalyst have to be considered.

Energy transfer with catalyst:

$$^3\mathrm{Sens}^* + \mathrm{Cat} \rightarrow \mathrm{Sens} + {}^3\mathrm{Cat}^* \quad Ix_\mathrm{Cat} \tag{10}$$

$$^3E^* + \mathrm{Cat} \rightarrow E + {}^3\mathrm{Cat}^* \quad k_{\mathrm{et}E\mathrm{Cat}}, k_{\mathrm{etCat}E} \tag{11}$$

$$^3\mathrm{Cat}^* + Z \rightarrow \mathrm{Cat} + {}^3Z^* \quad k_{\mathrm{etCat}Z} \tag{12}$$

Unimolecular decay with catalyst:

$$^3\mathrm{Cat}^* \rightarrow \mathrm{Cat} \quad k_\mathrm{Cat} \tag{13}$$

In an earlier paper [6] the theoretical treatment of such catalytic processes has been discussed and the following equation is proposed to describe the catalysis of the isomerization:

$$\frac{\partial[E]}{I\partial t} = \frac{\begin{array}{l}(1-\alpha) + k_{\mathrm{et}EZ}[Z]/Kk_\mathrm{p} + k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}]/Kk_\mathrm{p} - (k_{\mathrm{etCat}E}(x_\mathrm{Cat} + k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}]/Kk_\mathrm{p})[E])/\\ \quad (k_\mathrm{Cat}(1-x_\mathrm{Cat}) + k_{\mathrm{etCat}E}[E] + k_{\mathrm{etCat}Z}[Z]))\end{array}}{1 + k_\mathrm{Cat}(x_\mathrm{Cat} + k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}]/Kk_\mathrm{p})/(k_\mathrm{Cat}(1-x_\mathrm{Cat}) + k_{\mathrm{etCat}E}[E] + k_{\mathrm{etCat}Z}[Z])} - x_E \tag{14}$$

In earlier papers we have investigated three other catalytic systems [6,7]. The agreement between the experimental results and calculations using Eq. (14) has been good. For the catalytic system of *cis*-SP/CQ/catalyst only the linear part of Eq. (14) is considered because the isomerization was run to low conversion only. Thus, Eq. (14) can be simplified assuming $[E] = 0$, to Eq. (15). This simplification has been used in the evaluation of two of the earlier catalytic systems [7].

$$\frac{\partial[E]}{I\partial t} = \frac{(1-\alpha) + k_{\mathrm{et}EZ}[Z]/Kk_\mathrm{p} + k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}]/Kk_\mathrm{p}}{1 + k_\mathrm{Cat}(x_\mathrm{Cat} + k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}]/Kk_\mathrm{p})/(k_\mathrm{Cat}(1-x_\mathrm{Cat}) + k_{\mathrm{etCat}Z}[Z])} \tag{15}$$

The rate constants of the energy transfer, $k_{\mathrm{et}EZ}$, $\mathrm{k}_{\mathrm{et}E\mathrm{Cat}}$ and $k_{\mathrm{etCat}Z}$ in Eq. (15) can be calculated using the Sandros [11] equation (Eq. (16)) if the diffusion constant (k_diff) and the differences between the triplet energies of the energy donor and acceptor (ΔE_T) are known:

$$k = \frac{k_\mathrm{diff}}{1 + \exp(-\Delta E_\mathrm{T}/RT)} \tag{16}$$

4. Results and discussion

4.1. The effect of the triplet energy of the catalyst

The isomerization of *cis*-SP (0.2 mM) to *trans*-SP was studied using three different catalysts (0–20 mM), CQ (50.0 mM) as triplet sensitizer, and with toluene as solvent. The oxygen concentration flushing was minimized by flushing the solution with nitrogen. Anthracene, 9-methylanthracene and 9,10-di-chloroanthracene were selected as catalysts, which have the triplet energies 42.5, 41.4 and 40.7 kcal/mol, respectively [12]. The triplet energy levels are 43.0 kcal/mol for *cis*-SP and 40.8 kcal/mol for *trans*-SP [8]. The diffusion constant was determined by laser flash photolysis to $6.9 \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. The triplet lifetimes of *trans*-SP (Kk_p) and the catalyst (k_Cat) were also measured by laser flash photolysis. The triplet lifetimes of the catalysts were corrected for self-quenching. The k_Cat was substituted for $k_\mathrm{Cat} + k_\mathrm{sqCat}[\mathrm{Cat}]$. No photodegradation of the catalysts was observed. When the concentration of the catalyst is varied, the quantum yield for the isomerization shows a maximum at a certain concentration of the catalyst. At much higher concentrations of the catalyst the quantum chain process is terminated by self-quenching of the catalysts triplets (Fig. 2).

The efficiency of the quantum chain process is strongly dependent on the triplet energy of the catalyst. The efficiency decreases with decreasing triplet energy of the catalyst. The efficiency is about 11.5 times and 2.5 times higher with anthracene and 9-methylanthracene, respectively, than that of the uncatalyst isomerization. Almost no catalytic effect was observed for 9,10-dichloroanthracene.

4.2. The effect of oxygen quenching

Different methods of oxygen removal were tested, in order to see how the effective triplet lifetime of the catalyst and the substance influences the catalytic efficiency. In this study the most efficient catalytic system from the earlier experiments above was chosen, i.e., anthracene 15 mM. At first oxygen was removed from the sample simply by flushing with nitrogen. The catalytic efficiency was about 11.5 times the efficiency of the uncatalyzed reaction. Then, for comparison, the sample was degassed by five freeze-pump-thaw

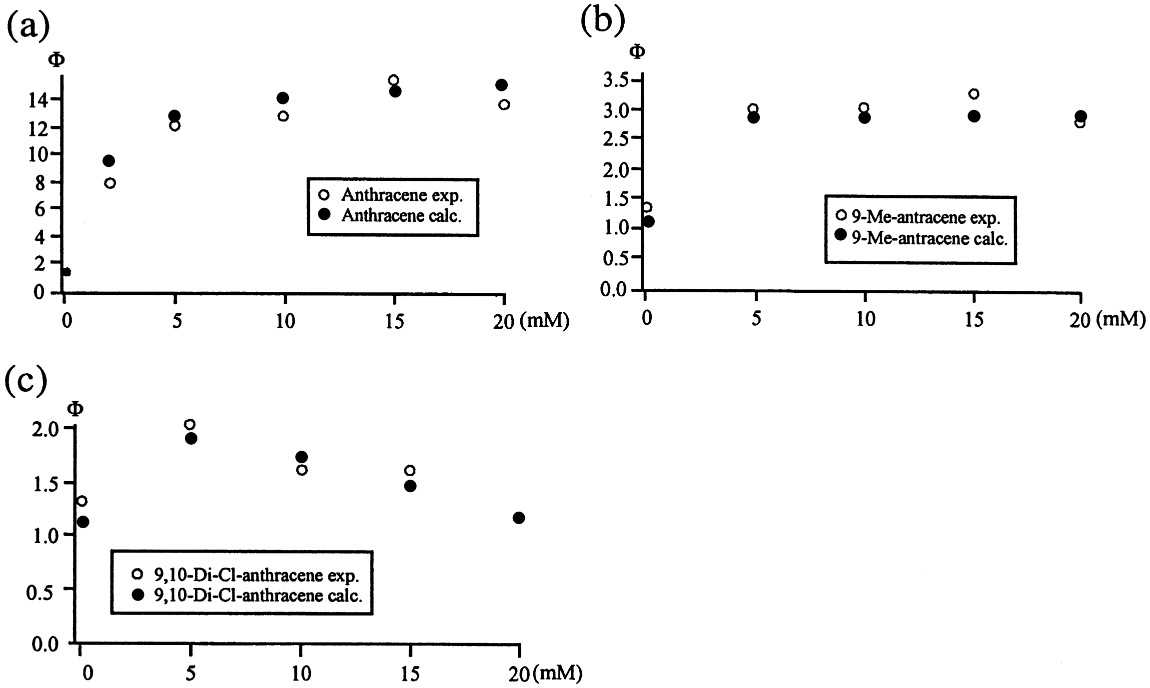

Fig. 2. Experimentally obtained and calculated quantum yields for the isomerization of *cis*-SP as a function of the concentration of the catalysts: (a) anthracene, (b) 9-methylanthracene, (c) 9,10-di-chloroanthracene. The concentration of *cis*-SP was 0.2 mM at I_t.

cycles to lower the oxygen concentration in the solutions more efficiency. The quantum yield was then increased to 30 and the catalytic efficiency was 23 times the efficiency of the uncatalyzed reaction.

5. Model calculations

The theoretical modeling of the catalysis of the quantum chain process was done by calculations using Eq. (15) as described above. The equation has six independent variables, which all can be varied. Two of these are the energy differences between the triplet states of the *Z*- and *E*-isomers ($\Delta E\,^3Z^*–^3E^*$) and between the triplet states of the *E*-isomers and catalyst ($\Delta E\,^3Z^*–^3\mathrm{Cat}^*$). Another two are the concentrations of the *Z*-isomer and the catalyst and the last two are the lifetimes of the *E*-isomer and the catalyst. This study focuses on the catalytic optimum and how to maximize the quantum yield. The experimentally studied system was used as a starting point to find whether or not the catalytic process has a maximum value.

The variables were given realistic values based on the previous experimental results. It is not realistic to use very high concentrations of the catalyst and the substrate since the quantum chain process will then be terminated by self-quenching of the triplets. Such self-quenching is not included in the model. Calculations assuming very long triplet lifetimes of the catalyst and reactants are not realistic since oxygen quenching will always occur even in carefully degassed solutions.

Furthermore, the triplet energy difference $\Delta E\,^3\mathrm{Z}^*–^3E^*$ was assumed to be at almost 5 kcal/mol, which is a large value for aromatic compounds with extended π-systems likely to undergo *Z*/*E*-photoisomerizations.

Our basic idea is that for most *Z*/*E* photoisomerizations, which can undergo quantum chain processes, i.e., are adiabatic, it is possible to catalyze the photoisomerization by adding a compound with a proper triplet energy and long triplet lifetime. If the triplet lifetime of the *E*-isomer of the substrate is very long and if the triplet energy difference between *Z*-and *E*-isomers is zero there is no point in adding an extra compound. However, in most cases the triplet lifetime of the *E*-isomer is short and there is a small but significant difference between the triplet energies of the *Z*-and *E*-isomers. In Fig. 3, we show some results of our model calculations.

The values of the variables which depend on the catalyst that lead to a maximum of the quantum yield are shown in the diagram. The choice of the concentrations and the lifetimes are based on our experimental system SP/CQ/anthracene. The maximum of the quantum yield and the catalytic efficiency is plotted as a function of the triplet energy difference between the *cis*- and *trans*-isomers (20 mM, triplet lifetime 20 μs) and a catalyst (15 mM, triplet lifetime 500 μs). The quantum yield decreases but the catalytic efficiency increases with increasing energy difference. A large value of the quantum yield does not have to be the same as an efficient catalytic process. A typical triplet energy difference between the *E*- and the *Z*-isomers of a substrate, which can isomerize adiabatically, is 1–3 kcal/mol

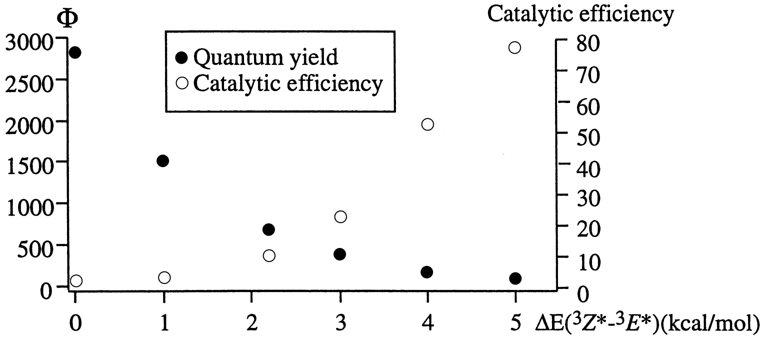

Fig. 3. Calculated quantum yield and catalytic efficiency for the *cis–trans* isomerization as functions of the triplet energy different between the *cis*- and *trans*- isomers. The calculations were preformed on a *cis*-isomer concentration of 20 mM and a triplet liftime of $\tau = 21\,\mu$s and a catalyst concentration of 15 mM and a lifetime of $\tau_{\mathrm{Cat}} = 500\,\mu$s.

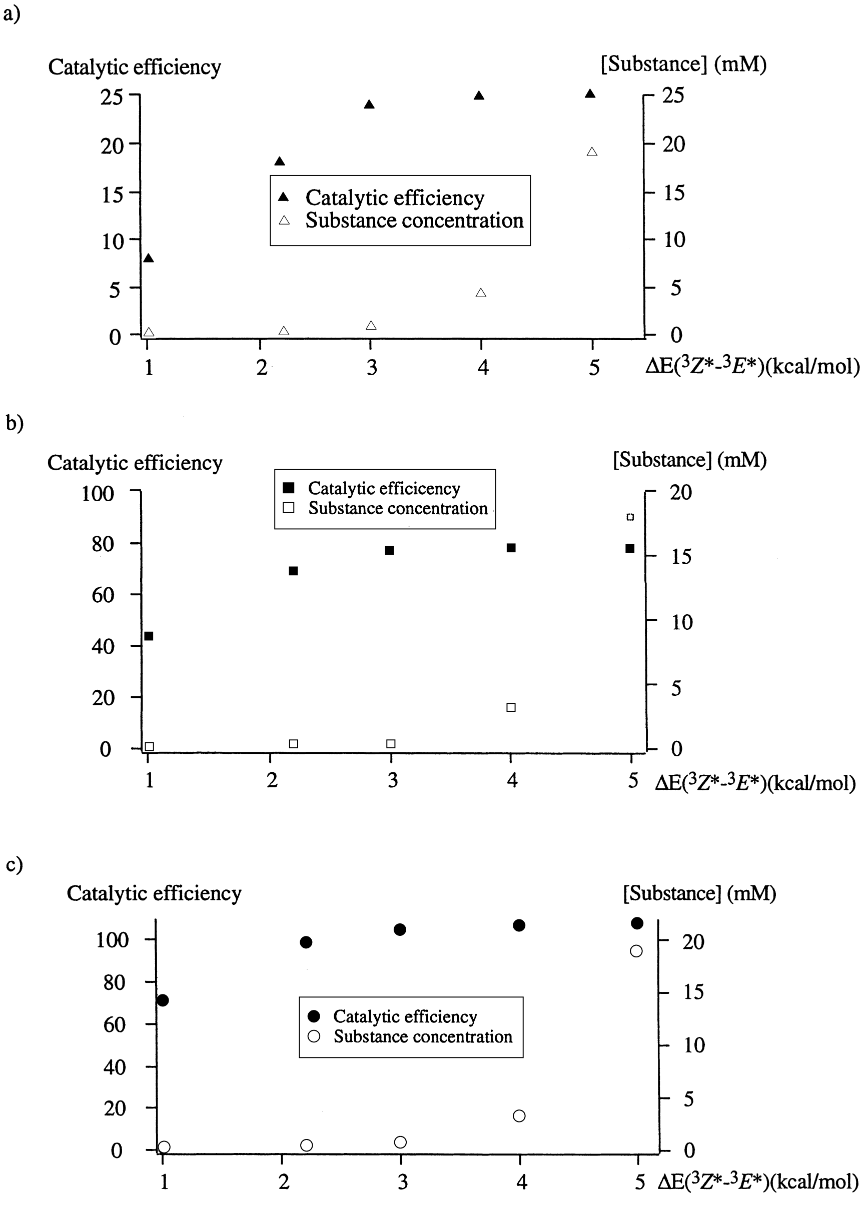

Fig. 4. Calculated values of catalytic efficiency and the substance concentration as functions of the triplet energy different between the *cis*- and *trans*-isomer. The catalytic efficiency is strongly dependent of the triplet lifetime of the catalyst. In the diagrams the triplet lifetimes are the following: (a) 50 μs; (b) 500 μs; (c) 1 ms.

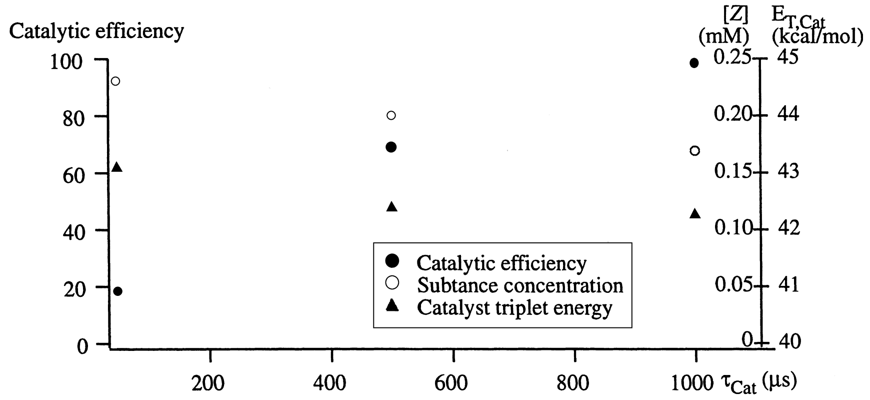

Fig. 5. Calculation of the optimum catalytic efficiency is showing a strong effect of the triplet lifetime of the catalyst. In the diagram the optimum catalytic efficiency, the concentration and the catalyst triplet energy are shown as functions of the triplet lifetime of the catalyst. The calculations were preformed on the substance SP ($\Delta E\,^3Z^*–^3E^* = 40.8–43.0$ kcal/mol, $\tau_{SP} = 21\,\mu s$) and a catalyst concentration of 15 mM.

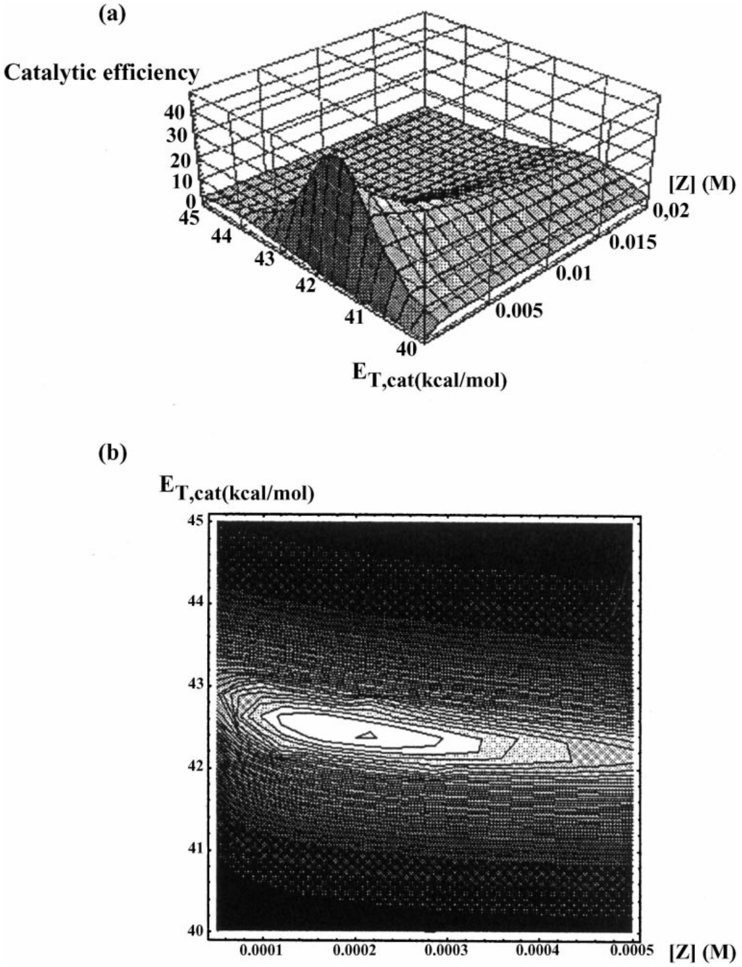

Fig. 6. An optimum of the catalytic efficiency exsists for the catalytic process. This is clearly seen in the three dimension plot (a) and a contour plot (b). In this plot the catalytic efficiency is shown as a function of the concentration of the *cis*-isomer and the triplet energy of the catalyst. The calculation was performed on the substance SP ($\Delta E\,^3Z^*–^3E^* = 40.87–43.0$ kcal/mol, $\tau_{SP} = 21\,\mu s$) and a catalyst concentration of 15 mM and $\tau_{Cat} = 500$ s.

[13]. In this energy interval the catalytic effect is limited to a 5–25 fold increase in quantum yield for the chain process compared to the uncatalyzed reaction. However, by variation of all of the variables the catalytic efficiency can be improved. The influence of the substrate concentration and triplet energy difference on the catalytic efficiency is shown in Fig. 4 for three different triplet lifetimes of the catalyst.

The efficiency at the optimum value increases with increasing triplet lifetime as expected. It is possible to achieve high catalytic efficiency at low substrate concentrations and relatively small energy differences between the triplets of the *cis*- and *trans*-isomers. At the optimum point for the catalytic effect the quantum yield for the uncatalyzed isomerization is close to unity. Thus, it is not necessary to have a high quantum yield for the uncatalyzed process. An added catalyst that increases the quantum yield above one acts as a triplet reservoir.

In our search for optimum conditions for the catalytic process we have also included the relative energy of the triplet state of the catalyst. Fig. 5 shows some results.

The optimum catalytic efficiency is calculated as a function of triplet energy and lifetime of the catalyst (15 mM) and the concentration of the substrate. The optimum efficiency is not very sensitive to either the substrate concentration or the energy of the catalyst triplet state. The last observation requires some comments. Originally, we had the idea that the triplet energy of the catalyst should be in between the triplet energies of the *Z*- and *E*-isomers. Calculations have shown this to be only partially correct. The optimum triplet state energy of the catalyst is around 1.5 kcal/mol above the triplet energy of the *E*-isomer. This optimum energy of the catalyst decreases slightly with increasing triplet lifetime of the catalyst.

The catalytic efficiency for the catalysis as a function of substrate concentration and triplet energy of the catalyst is shown in Fig. 6. Clearly, there is a maximum with a catalytic efficiency of 69 for the case where the triplet energy of the catalyst is ca. 42.4 kcal/mol and the substrate concentration is 0.2 mM.

Are these conditions and the catalytic efficiency realistic? As already mentioned we have been able to achieve very similar results experimentally with our model system. It should be possible to reach the catalytic effect shown in Fig. 6 with proper equipment to decrease the oxygen concentration in the solution and thus lowering the oxygen quenching rate.

6. Concluding remarks

We have found four examples of triplet-sensitized photocatalytic processes. We have also investigated the scope and limitations of this catalytic process by the calculations based on a tentative mechanism. Further search for new and simpler systems will continue. As an example, we are looking for efficient systems where the catalyst and the sensitizer are the same. All the studied systems follow a quantum chain process where energy transfers between the molecules involved occur by fast collisions. An alternative mechanism for catalyzed photoisomerizations is also possible. Energy transfer and isomerization could occur within an excited molecular complex between the catalyst and the substrate. Such system has been reported by Whitten et al. [14,22]. Further work on the catalysis of photoisomerization will clarify the different possibilities with respect to the various mechanistic schemes and whether or not catalytic photoisomerization do occur in nature. Catalyzed quantum chain processes are certainly very effective ways of initiating biological processes by light and constitute very sensitive photoprocesses.

Acknowledgements

Financial support from the Swedish Research Council for Engineering Sciences (TFR), and the Swedish Natural Science Research Council (NFR) is gratefully acknowledged.

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