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Catalysis of a photochemical reaction; a *cis–trans* isomerization proceeding by a quantum chain process

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Abstract

The quantum efficiency for the biacetyl-sensitized isomerization of (*Z,E*)-3,3″,5,5″-tetra(*tert*-butyl)-4′-styrylstilbene to (*E,E*)-3,3″,5,5″-tetra(*tert*-butyl)-4′-styrylstilbene can be increased by more than fifty times by the addition of anthracene to the reaction mixture. The results are explained as being due to a more efficient energy transfer within a quantum chain process. The chain length of the process increases with increasing concentration of anthracene.

Keywords: Triplet state; *cis–trans* photoisomerization; Quantum chain process; Photocatalysis; Energy transfer; Adiabatic photoreaction

1. Introduction

Catalysis in photochemical reactions does not usually involve the excited state of the pure catalyst but is often a case of ground-state complexation prior to the excitation, e.g. Lewis acid catalysis of photochemical reactions [1]. There is also a possibility that an intermediate reactive towards a catalyst is formed, as is the case in the deconjugation of cyclohexenones [2]. In our study, the excited triplet states of the reactant, the product and the catalyst are all involved in the reaction. To our knowledge this is a new type of catalysis. A prerequisite for such a catalytic process is the presence of an adiabatic photoreaction, in which the product is formed in its excited state. In a previous paper it was shown that a similar type of catalysis could occur in stilbene photoisomerization, although this required the formation of an excited state complex in terms of either an encounter complex or a triplet exciplex [3]. This complex has to be sufficiently long lived for the isomerization and energy transfer processes to proceed before the complex is dissociated.

In a series of papers by us and others, an adiabatic mechanism has been shown to be important for certain *cis–trans* photoisomerizations [4]. The adiabatic mechanism has been shown to be valid not only for triplet-state [4b–d,g–h] but also for singlet-state [4a,e,f–h] isomerizations. In triplet-state reactions the excited product may have rather a long lifetime, and this may lead to energy transfer from the excited product to a ground-state reactant, initiating a new isomerization process, provided that the triplet energy of the reactant is not much higher than that of the product. The reactions can then proceed by quantum chain processes with quantum yields exceeding unity [5]. In this paper, we present an example of how the quantum efficiency of such a process can be further increased, i.e. how such a reaction can be catalysed.

2. Experimental details

Solutions of (*Z,E*)-3,3″,5,5″-tetra(*tert*-butyl)-4′-styrylstilbene (*Z*), anthracene and biacetyl were irradiated at 436 nm. An optical bench with a 150 W xenon arc lamp and a monochromator was used. Samples without anthracene were irradiated to permit the light flux to be determined. The styrylstilbene was prepared as previously described [4a]; anthracene (test substance for elemental analysis, Merck) and biacetyl (Aldrich, greater than 99% (gas chromatography)) were used as received. All measurements were performed in nitrogen-flushed solutions with spectroscopic-grade methylene chloride as solvent. The compositions of the irradiated solutions were determined by analytical high-performance

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liquid chromatography using hexane as eluent and a medium polar column; Spherisorb S5 CN. The detection method was UV absorption (313 nm).

3. Theory

The following reactions are of importance in a triplet-sensitized *cis–trans* isomerization proceeding by a quantum chain process: excitation (x denotes the molar fraction of the respective compounds):

$$\mathrm{Sens} \longrightarrow {}^1\mathrm{Sens}^* \qquad I,\ \text{excitation rate} \tag{1}$$

$$ {}^1\mathrm{Sens}^* \longrightarrow {}^3\mathrm{Sens}^* \qquad \phi_{\mathrm{isc}} \approx 1\ \text{(for biacetyl)} \tag{2}$$

energy transfer:

$$ {}^3\mathrm{Sens}^* + Z \longrightarrow \mathrm{Sens} + {}^3Z^* \qquad Ix_Z \tag{3}$$

$$ {}^3\mathrm{Sens}^* + E \longrightarrow \mathrm{Sens} + {}^3E^* \qquad Ix_E \tag{4}$$

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

isomerizations:

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

$$ {}^3E^* \rightleftharpoons {}^3\mathrm{p}^* \qquad K \tag{7}$$

unimolecular decay:

$$ {}^3E^* \longrightarrow E \qquad k_E \tag{8}$$

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

In a photoreaction proceeding by a quantum chain process, energy is transferred from the product-excited state to a ground-state reactant (Eq. (5)). This energy transfer is usually an endothermic reaction and the rate of the reaction is thus lower than that of a diffusion-controlled reaction [6]. The length of the chain in the chain process depends of course on the efficiency of this energy transfer step, which also depends on the lifetime of the excited product. Knowing the relative energy of the species, the rate constant of this energy transfer reaction can be calculated from the Sandros [6] equation

$$k_{\mathrm{et}} = \frac{k_{\mathrm{diff}}}{1+\exp(-\Delta E/RT)} \tag{10}$$

By the addition of a substance Cat, with a triplet energy intermediate between those of the reactant and the product, the reaction can, provided that the triplet lifetime of this substance is longer than that of the product, be catalysed. The additional reactions which then need to be considered are

$$ {}^3\mathrm{Sens}^* + \mathrm{Cat} \longrightarrow \mathrm{Sens} + {}^3\mathrm{Cat}^* \qquad Ix_{\mathrm{cat}} \tag{11}$$

$$ {}^3E^* + \mathrm{Cat} \rightleftharpoons E + {}^3\mathrm{Cat}^* \qquad k_{\mathrm{et}E\mathrm{cat}},\ k_{\mathrm{etCat}E} \tag{12}$$

$$ {}^3\mathrm{Cat}^* + Z \longrightarrow \mathrm{Cat} + {}^3Z^* \qquad k_{\mathrm{etCat}Z} \tag{13}$$

$$ {}^3\mathrm{Cat}^* \longrightarrow \mathrm{Cat} \qquad k_{\mathrm{cat}} \tag{14}$$

Some assumptions are made, namely that equilibration between the different triplets is much faster than decay of triplets, that ${}^3Z^*$ has an infinitesimal lifetime and that ${}^3E^*$ is much more populated than ${}^3\mathrm{p}^*$, that the dominating reactions of the sensitizer triplet is energy transfer to the reactant, to the catalyst and to the product and, furthermore, that the unimolecular decay from ${}^3EE^*$ to the ground state is too slow to be of importance ($k_{\mathrm{p}}K \gg k_E$). These assumptions have been shown to be valid for the biacetyl-sensitized isomerization of (Z,E)-3,3″,5,5″-tetra(*tert*-butyl)-4′-styrylstilbene (Z) to (E,E)-3,3″,5,5″-tetra(*tert*-butyl)-4′-styrylstilbene (E) [4b]. The experimental work presented in this paper demonstrates the catalysis of this isomerization by anthracene.

Steady-state treatments of the total triplet and of the Cat triplet give

$$\frac{\mathrm{d}[{}^3\mathrm{total}^*]}{\mathrm{d}t} = I - k_{\mathrm{p}}[{}^3\mathrm{p}^*] - k_{\mathrm{Cat}}[{}^3\mathrm{Cat}^*] = 0 \tag{15}$$

$$\begin{aligned}\frac{\mathrm{d}[{}^3\mathrm{Cat}^*]}{\mathrm{d}t} = {} & Ix_{\mathrm{Cat}} + k_{\mathrm{et}E\mathrm{Cat}}[{}^3E^*][\mathrm{Cat}] \\ & - k_{\mathrm{etCat}E}[{}^3\mathrm{Cat}^*][E] - k_{\mathrm{etCat}Z}[{}^3\mathrm{Cat}^{*2}][Z] \\ & - k_{\mathrm{Cat}}[{}^3\mathrm{Cat}^*] = 0\end{aligned} \tag{16}$$

Equations (15) and (16) give

$$[{}^3\mathrm{Cat}^*] = \frac{(x_{\mathrm{Cat}}Kk_{\mathrm{p}} + k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}])[{}^3E^*]}{k_{\mathrm{Cat}}(1-x_{\mathrm{Cat}}) + k_{\mathrm{etCat}E}[E] + k_{\mathrm{etCat}Z}[Z]} \tag{17}$$

The rate of isomerization to E is

$$\begin{aligned}\frac{\mathrm{d}[E]}{\mathrm{d}t} = {} & (1-\alpha)k_{\mathrm{p}}[{}^3\mathrm{p}^*] + k_{\mathrm{et}EZ}[{}^3E^*][Z] \\ & + k_{\mathrm{et}E\mathrm{Cat}}[{}^3E^*][\mathrm{Cat}] - k_{\mathrm{etCat}E}[{}^3\mathrm{Cat}^*][E] - Ix_E\end{aligned} \tag{18}$$

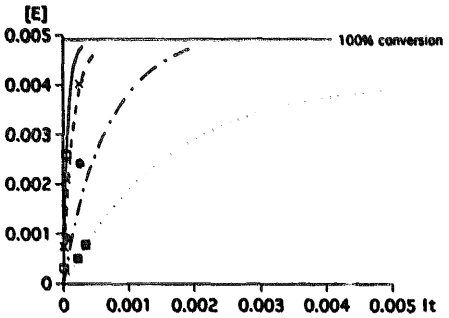

Fig. 1. The concentration of E plotted against the total number of absorbed photons per litre in Einsteins per litre. The concentration of Z at $It = 0$ was 4.91 mmol l^{-1}. The curves are theoretically calculated for the various anthracene concentrations used: □, 15 mmol l^{-1}; ×, 6.31 mmol l^{-1}; ●, 4.1 mmol l^{-1}; ■, 0 mmol l^{-1}.

Equations (17) and (18) give

$$\frac{\mathrm{d}[E]}{\mathrm{d}t}=(1-\alpha)Kk_{\mathrm{p}}[{}^3E^*]+k_{\mathrm{et}EZ}[{}^3E^*][Z]+\mathrm{k}_{\mathrm{et}E\mathrm{Cat}}[{}^3E^*][\mathrm{Cat}]-\frac{k_{\mathrm{etCat}E}(x_{\mathrm{Cat}}Kk_{\mathrm{p}}+k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}])[E][{}^3E^*]}{k_{\mathrm{Cat}}(1-x_{\mathrm{Cat}})k_{\mathrm{etCat}E}[E]+k_{\mathrm{etCat}Z}[Z])}-Ix_E \tag{19}$$

Equations (15), (17) and (19) give

$$\frac{\mathrm{d}[E]}{I\,\mathrm{d}t}=\frac{(1-\alpha)+k_{\mathrm{et}EZ}[Z]/Kk_{\mathrm{p}}+k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}]/Kk_{\mathrm{p}}-k_{\mathrm{etCat}E}(x_{\mathrm{Cat}}+k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}]/Kk_{\mathrm{p}})[E]/[k_{\mathrm{Cat}}(1-x_{\mathrm{Cat}})+k_{\mathrm{etCat}E}[E]+k_{\mathrm{etCat}Z}[Z]]}{1+k_{\mathrm{Cat}}(x_{\mathrm{Cat}}+k_{\mathrm{et}E\mathrm{Cat}}[\mathrm{Cat}]/Kk_{\mathrm{p}})/[k_{\mathrm{Cat}}(1-x_{\mathrm{Cat}})+k_{\mathrm{etCat}E}[E]+k_{\mathrm{etCat}Z}[Z]]}-x_E \tag{20}$$

4. Results

Samples of Z and biacetyl in methylene chloride containing anthracene in various concentrations were irradiated at 436 nm. The quantum efficiency for the formation of E was clearly dependent on the anthracene concentration (Fig. 1). Numerical integration of Eq. (20) with different values of the rate constants was carried out. The photon flux was determined in the absence of anthracene (Fig. 1) using the rate constant for energy transfer from ${}^3E^*$ to Z which had previously been found to be 1.2×10^8 M^{-1} s^{-1} [4b].[1] One set of parameters which gives a fairly good fit to the experimental data from irradiations of samples in the presence of anthracene is (Fig. 1) $\alpha=0.5$, $k_{\mathrm{et}E\mathrm{Cat}}=1.7\times10^9$ M^{-1} s^{-1}, $k_{\mathrm{Cat}}=1\times10^4$ s^{-1}, $1/Kk_{\mathrm{p}}=3.5\times10^{-6}$ s, $k_{\mathrm{etCat}E}=3.0\times10^9$ M^{-1} s^{-1} and $k_{\mathrm{etCat}Z}=2.1\times10^9$ M^{-1} s^{-1}.[2]

5. Discussion

In Fig. 2, a simple description of the catalytical process is attempted. For simplicity, the ^{3}p* state is ignored here since it in principle does not affect this discussion. Two important features of the catalyst are a long triplet lifetime and a triplet energy intermediate between those of the reactant and the product. Anthracene has a long triplet lifetime (about 100 μs) and its triplet energy (42.5 kcal mol^{-1}) is intermediate between those of Z and E, which are 43 kcal mol^{-1} and 41 kcal mol^{-1} respectively. Furthermore, the catalyst should have a Franck–Condon triplet, i.e. there should be as much energy available for sensitization as is required for excitation. Another important feature is photostability. The triplet state of anthracene is photostable in this system (no degradation could be detected under the conditions used).

The presence of a triplet exciplex or a long-lived encounter complex combined with "non-vertical" energy transfer might also further enhance the efficiency of the catalytical process. In our case a long-lived excited-state complex is not needed to explain the catalysis although it might contribute to a minor extent. In the photocatalytic stilbene isomerization, sensitized by metalloporphyrins, a complex long-lived enough for the isomerization and energy transfer processes to occur has to be present [3].

We intend to design other systems to study this type of catalysis. One objective is to find a catalyst which can also conveniently be used as a sensitizer.

6. Conclusion

We have found a new and simple way to catalyse adiabatic *cis–trans* photoisomerizations. It is to early to say whether this mechanism is of any importance in biological systems, such as in the chemistry oı vision at very low light fluxes.

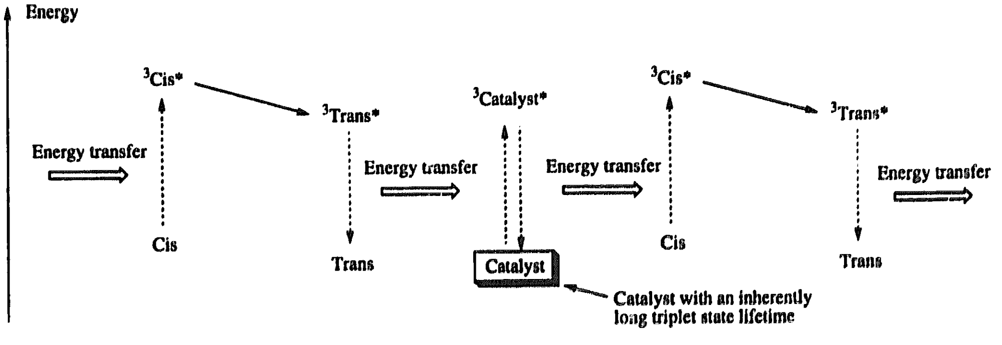

Fig. 2. Illustration of the effect of a catalyst on a quantum chain process.

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[1] This value is for a methylcyclohexane solution, although the experiments reported in this paper have been done in methylene chloride to allow for higher anthracene concentrations. No correction has been made for this solvent change. Thus there may be some minor numerical deviations, but this should have no effect on the principle.

[2] Obviously, several other combinations of rate constants might also give good fits to the experimental values, so that the values of these rate constants should not be taken too literally.

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