Isomerization of stilbene photocatalyzed with diphenyldiselenide via a radical mechanism

I.K. Lednev, E.N. Ushakov and M.V. Alfimov

Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka,
Moscow Region 142 432, Russia

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The highly efficient process of cis to trans isomerization of stilbene photocatalyzed with diphenyldiselenide in *n*-hexane solution with quantum yield up to 3500 has been studied. The rate constant of stilbene isomerization catalyzed with PhSe$^\cdot$ radical, the quantum yield of diphenyldiselenide dissociation and the rate constant of PhSe$^\cdot$ radicals recombination have been obtained in the temperature region from 288 to 323 K. Oxygen has been found to inhibit the isomerization at high stilbene concentration.

Keywords: Stilbene; diphenyldiselenide; isomerization; catalysis

1. Introduction

Photosensitized isomerization of arylethylenes and their analogs can have chain [1–4] or catalytic [5–10] character. Such reactions can proceed via at least three different types of mechanism, i.e. via the ion radical one [1,2] or at the expense of energy transfer [3,4] or via the free radical process [5–10].

Iodine-photocatalyzed cis to trans isomerization of stilbenes [5–8,10] and azobenzenes [9] is an example of the reaction of the third type. An earlier suggested [5,6] radical mechanism of the process is described by the following simplified scheme:

$$R_2 \underset{k_1}{\overset{h\nu,\varphi}{\rightleftarrows}} R^\cdot + R^\cdot, \tag{1}$$

$$C + R^\cdot \xrightarrow{k_2} T + R^\cdot, \tag{2}$$

where C and T denote cis and trans isomers, respectively, and R_2 the molecule photogenerating the radical $R^\cdot$ – for example, molecular and atomic iodine, respectively.

The reversible character of the photoinduced atomic iodine interaction with arylethylene molecules allows us to realize the isomerization process with quantum yield $\Phi_{\mathrm{ism}} \gg 1$ [10]. The presented scheme describes well both the kinetics and the concentration dependencies of the isomerization process [5,6,10]. But it does not show the detailed mechanism of the reaction (2) and cannot explain, for instance, the low catalytic activity of iodine in the case of the isomerization of phenanthryl substituted ethylene [8]. The latter has been attributed to the steric effect [8]. When this steric effect acts either on the radical–cis-isomer collisions or during the intramolecular rotation of the adduct is an open question up to now. The investigation of the mechanism of the catalytic isomerization process in iodine–stilbene systems is difficult because of the impossibility to observe the atomic iodine in organic solvent by standard methods such as ESR or absorption spectroscopy. As far as the authors know, the intermediate complex of a cis-isomer molecule and atomic iodine has not been discovered in liquid up to now.

Form the viewpoint of the possibility of detection the photoinduced multiatomic radical with analogous catalytic properties should be more convenient. As an example, the $PhS^{\cdot}$ radical formed after diphenyldisulfide photolysis, which is an effective catalyst of polybutadiene isomerization, can be considered [11]. However, in this case efficient secondary reaction caused by hydrogen atom abstraction takes place. Less reactive analogs of the $PhS^{\cdot}$ radical are compounds with an active center on Se atom. The latter reversibly connects with the double bond of vinyl monomers [12] and catalyzes isomerization of dimethylmaleate [13]. Diphenyldiselenide (DPDS) can serve as a source of Se centered radicals. It has been reliably established by the spin-trap method, that Se–Se bond rupture occurs with forming $PhSe^{\cdot}$ radicals under DPDS photolysis in solution [14]. The radicals have efficient absorbance at 490 nm in an organic solvent [12].

The aim of the present work is to study kinetic and concentration laws of DPDS-photosensitized cis–trans isomerization of stilbene in hexane.

2. Experimental

Cis-stilbene from EGA-Chemie (95%) was used after additional purification [15]. DPDS was purified by recrystallization from methanol. The photosensitized isomerization process was carried out in quartz cells of 1 and 0.2 cm thickness under illumination by high pressure Hg lamp light with $\lambda = 436$ nm. The intensity of light was measured by the thermoelement RTN-2OS. Isomer composition and stilbene concentration were determined from the absorption spectrum of the solution. The quantum yield of DPDS photodissociation in *n*-hexane under irradiation with $\lambda = 436$ nm has been measured by the method of free radical acceptors. Styrene in the presence of air oxygen has been used as an acceptor. The decrease of DPDS concentration has been controlled by optical density of the solution at $\lambda = 401$ nm (the products of the reaction in this region of spectrum do not absorb). The following measured values of the DPDS molar absorption coefficient ϵ (in $\mathrm{mol}^{-1}\ \ell\ \mathrm{cm}^{-1}$) have been used:

T (K)	288	298	310	323
ϵ(401 nm)	287	293	302	310
ϵ(436 nm)	72	76	81	87

The recombination rate constant k_1 of radicals PhSe$^{\cdot}$ in n-hexane has been determined by a sector method [16].

3. Results and discussion

The concentration of DPDS in hexane under irradiation with Hg lamp ($\lambda = 436$ nm) remains constant both in presence and in absence of STB. This evidently signifies that the only reaction of PhSe$^{\cdot}$ radicals decay under these conditions is their bimolecular recombination. Besides that the STB cis to trans isomerization, photosensitized by DPDS, is irreversible. The obtained kinetics of this reaction on steady state irradiation is monoexponential for various concentrations of STB and DPDS in the region 2×10^{-5}–0.65 and 3×10^{-5}–7.5×10^{-4} mol/ℓ, respectively, both for air saturated samples and for degassed ones. Therefore, one can evidently accept the above scheme of eqs. (1), (2) of the isomerization process where R_2 and $R^{\cdot}$ are considered to be DPDS and PhSe$^{\cdot}$ radical, respectively.

According to this scheme the expression for the initial rate of the isomerization in the case of low ($\ll 1$) optical density of the solution at the exciting wavelength can be presented as

$$\left.\frac{\mathrm{d}C}{\mathrm{d}t}\right|_0 = -k_2\sqrt{\varphi/k_1}\sqrt{\frac{\epsilon \times 10^3 \ln 10}{N_\mathrm{A}}}\sqrt{I}\sqrt{[\mathrm{DPDS}]}\,C_0, \tag{3}$$

where I denotes the intensity of the exciting light ($\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$), ϵ the molar absorption coefficient of DPDS at the wavelength of excitation, φ the quantum yield of DPDS photodissociation, t the duration of an illumination, C_0 the initial cis-isomer concentration and N_A Avogadro's number.

Figs. 1 and 2 show the dependence $-\mathrm{d}C/\mathrm{d}t\,|_0$ on C_0, I and [DPDS], obtained at $T = 293$ K. It can be seen that the experimental data satisfy eq. (3) in a wide range of C_0, I and [DPDS] in the case of reaction proceeding in a degassed solution. In the presence of air oxygen the noticeable deviation of experimental data from the theoretical dependence has been found only with STB concentration > 0.1 mol/ℓ (fig. 1). Slowing down of the isomerization

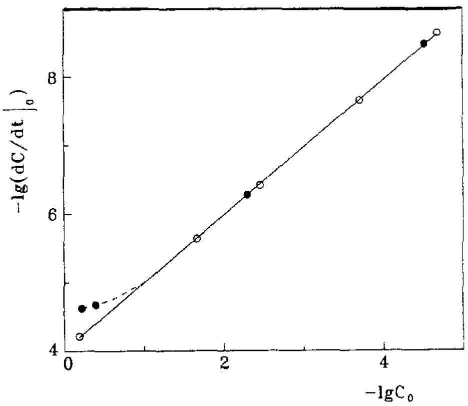

Fig. 1. The initial rate of DPDS-photosensitized cis to trans isomerization of STB as a function of cis-STB concentration in degassed solution (o) and at the air oxygen presence (●). $T = 293$ K, $\lambda_{ex} = 436$ nm, $[\mathrm{DPDS}] = 1.8 \times 10^{-4}$ mol/ℓ, $I = 3.5 \times 10^{14}$ cm^{-2} s^{-1}.

reaction by oxygen at large concentration of STB can evidently be explained by the interaction of oxygen with an adduct of PhSe˙ and STB molecule:

$$\mathrm{PhSe}^{\cdot} + \mathrm{STB} \rightleftarrows (\mathrm{PhSeTB}^{\cdot}) \xrightarrow{O_2} \text{peroxy radical.} \tag{4}$$

In this case, in addition to the quadratic decay of PhSe˙, the first-order reaction of radical disappearance takes place.

For the degassed solution with initial concentration of cis-STB 0.65 mol/ℓ the value of quantum yield $\Phi_{ism} = 3500$ has been obtained at $I = 3.5 \times 10^{14}$ cm^{-2} s^{-1} and $[\mathrm{DPDS}] = 1.8 \times 10^{-4}$ mol/ℓ.

Thus, all data given above confirm the radical catalytic character of the process of cis-STB isomerization photosensitized by DPDS. The kinetic mea-

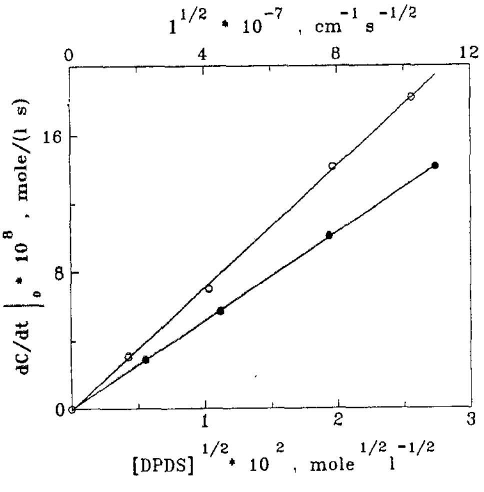

Fig. 2. The initial rate of DPDS-photosensitized cis to trans isomerization of STB as a function of (●) light intensity at $[\mathrm{DPDS}] = 7.5 \times 10^{-4}$ mol/ℓ, and (o) DPDS concentration at $I = 6.2 \times 10^{15}$ cm^{-2} s^{-1}. $T = 293$ K, $\lambda_{ex} = 436$ nm and $C_0 = 1.5 \times 10^{-4}$ mol/ℓ.

surements allow us to determine the value of the combination of constants $k_2\sqrt{\varphi/k_1}$. For a number of temperatures the following values of $k_2\sqrt{\varphi/k_1}$ (in $\ell^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$) were found:

T (K)	288	298	310	232
$k_2\sqrt{\varphi/k_1}$	0.74	0.93	1.13	1.39

where the estimated absolute error is about 10%.

In order to calculate the rate constant k_2 we have measured the quantum yield of DPDS photodissociation φ and PhSe$^\cdot$ radicals recombination rate constant k_1 in n-hexane.

3.1. QUANTUM YIELD OF DPDS PHOTODISSOCIATION

In agreement with Ito's work [12], the process of DPDS photolysis in the presence of styrene and air oxygen can be presented as

$$\mathrm{PhSeSePh} \underset{}{\overset{h\nu}{\rightleftarrows}} 2\mathrm{PhSe}^\cdot, \tag{5}$$

$$\mathrm{PhSe}^\cdot + \mathrm{CH_2{=}CHPh} \rightleftarrows \left(\mathrm{PhSeCH_2\dot{C}HPh}\right) \xrightarrow{\mathrm{O_2}} \mathrm{ROO}^\cdot. \tag{6}$$

Kinetic measurements of DPDS decay have shown that the rate of bimolecular recombination of PhSe$^\cdot$ radicals is negligible relative to the first-order decay of these radicals (eq. (6)) in the presence of air oxygen, in the range of styrene concentration 0.02–0.1 mol/ℓ and at the light absorption rate by the solution of unit volume $G < 2.5 \times 10^{14}$ cm^{-3} s^{-1}, where $G = I[\mathrm{DPDS}]\epsilon \ln 10$ at low optical density of the sample at the wavelength of excitation.

The following values of DPDS photodissociation quantum yield field φ have been obtained at $I = 2.4 \times 10^{15}$ cm^{-2} s^{-1}, styrene concentration 0.1 mol/ℓ and [DPDS] = 4.9×10^{-4} mol/ℓ:

T (K)	288	298	310	323
φ	0.34	0.38	0.42	0.44

The absolute error of measurement of φ, mainly related to the accuracy of measuring I and ϵ, is about 20% and the incidental one is ≈ 5%.

3.2. PhSe$^\cdot$ RECOMBINATION RATE CONSTANT

It has been shown above that the rate of STB cis to trans isomerization photosensitized by DPDS is first-order relative to PhSe$^\cdot$. This fact permits the use of the reaction in a sector method [16] in order to determine the mean lifetime of PhSe$^\cdot$ radicals $\tau = (2k_1R_s)^{-1}$, where R_s is the PhSe$^\cdot$ stationary concentration under constant irradiation of the solution. For each temperature mean value τ at $I = 4.2 \times 10^{15}$ cm^{-2} s^{-1}, $C_0 = 2.2 \times 10^{-5}$ mol/ℓ and [DPDS] =

4.0×10^{-5} mol/ℓ has been measured. The PhSe˙ recombination rate constant has been calculated with the help of above data on φ in accordance with formula [16]: $k_1 = (4\varphi G\tau^2 \times 10^3 N_A^{-1})^{-1}$. The following values of k_1 have been obtained (in $\text{mol}^{-1}\ \ell\ \text{s}^{-1}$):

T (K)	288	298	310	323
$k_1 \times 10^{-9}$	9.1	9.4	9.8	10.2

It should be noted that the absolute error of k_1 measurement is about 40%, and the incidental one is ≈ 15%.

3.3. CATALYTIC ISOMERIZATION RATE CONSTANT k_2

Making use of the measured values of $k_2\sqrt{\varphi/k_1}$, φ and k_1 constants one can easily calculate the value of rate constant k_2 for each temperature used (in $\text{mol}^{-1}\ \ell\ \text{s}^{-1}$):

T (K)	288	298	310	323
$k_2 \times 10^{-5}$	1.21	1.46	1.73	2.12

where the absolute error is about 40% and the incidental one is 10%. The given data in the 288–323 K temperature range satisfy the ordinary Arrhenius equation $k_2 = A \exp(-E/RT)$, where $\lg A = 7.3 \pm 0.5$ and $E = 2.9 \pm 0.6$ kcal/mol.

The comparison of the results presented here with that obtained [5,6] for the molecular iodine–stilbene system shows the higher efficiency of DPDS as a photosensitizer of cis to trans isomerization of STB in n-hexane solution. The value of k_2 in the case of stilbene isomerization photosensitized by iodine at room temperature is $7.2 \times 10^4\ \text{mol}^{-1}\ \ell\ \text{s}^{-1}$ [6].

In addition it should be noted that DPDS can be used as a sensitizer of cis to trans isomerization for a number of other arylethylenes and some stilbazole salts. In contrast to iodine, DPDS has been found to be an effective sensitizer of the isomerization process in various solutions including benzene, alcohols and aqueous micellar solutions. These data are planned to be published in details in near future.

4. Conclusion

The process of cis to trans isomerization of stilbene photosensitized with diphenyldiselenide in n-hexane solution has been studied quantitatively in the temperature region of 288–323 K. The high efficiency of this radical catalytic process permits to obtain the quantum yield up to 3500. An air oxygen has been found to inhibit the isomerization process at high concentration of stilbene.

Diphenyldiselenide as a radical photosensitizer of arylethylenes isomerization has a few advantages relative to the molecular iodine used earlier. PhSe˙ radical has been found to have higher catalytic activity relative to atomic iodine for stilbene isomerization. Diphenyldiselenide exhibits photocatalytic properties in a wide variety of solvents with different polarity. It can be modified chemically for application in organized systems. PhSe˙ radicals are easily registered by absorption spectroscopy which may give an additional possibility to study the process of catalytic isomerization by flash photolysis techniques.

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