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# Catalyzed E/Z isomerization mechanism of stilbene using *para*-benzoquinone as a triplet sensitizer<sup>†</sup>

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Sensitizer molecules affect not only the quantum yield but also the selectivity of photochemical reactions. For an appropriate design of sensitized photochemical processes, we need to elucidate the reaction mechanism in detail. Here we investigated the mechanism of photoisomerization of stilbene via triplet state with *para*-benzoquinone sensitizer using the density functional theory. In general, the isomerization of stilbene via triplet state exhibits (*Z*)-selectivity (*cis*-selectivity); however, *para*-benzoquinone sensitizer changes it to (*E*)-selectivity (*trans*-selectivity). The calculations showed that stilbene and *para*-benzoquinone form stable exciplexes having a preoxetane structure. The E/Z isomerization occurred via this exciplex, in which *para*-benzoquinone acted as a photocatalyst rather than a sensitizer only providing excitation energy. The spin-density distribution of the exciplex differed from the isolated stilbene in the triplet state. Therefore, the stilbene moiety could take (*E*)-conformation in the exciplex. The intermolecular charge-transfer drove the exciplex formation. This specific reaction mechanism was originated from the electron-accepting ability of *para*-benzoquinone in the triplet state.

#### 1 Introduction

Photochemistry directly utilizes the photon energy in a chemical reaction. The photochemical processes commonly involve changes in the electronic state; therefore, photochemical reactions may realize molecular conversions that are difficult in the ground state. However, the quantum yield of photochemical reactions is frequently low because most molecules do not contain an efficient light-harvesting group. Moreover, the reaction yield further diminishes if the process involves a forbidden transition of electronic states such as intersystem crossing between the singlet and triplet states. In order to overcome such difficulty, a photosensitizer is widely used.<sup>1</sup> It is known that the sensitizer affects not only the reaction yield but also the selectivity. Therefore, the optimization of photosensitizer is important for designing photochemical processes.

The photo E/Z isomerization (*trans/cis* isomerization) of olefins is a typical system<sup>2–8</sup> where the reaction proceeds via the triplet excited state. Many studies have examined the reaction mechanisms and the effect of photosensitizers.<sup>7,8</sup> In particular, Hammond and coworkers studied the [Z]/[E] ratio of the prod-

uct for the photoisomerization of stilbene using various sensitizer molecules.<sup>2</sup> They revealed the general reaction mechanisms by applying the kinetic model and assuming the Dexter mechanism to explain the observed Z/E selectivity.<sup>9</sup> Based on these works, we can control the Z/E selectivity of the photoisomerization of stilbene by adjusting the triplet energy of the sensitizer. In short, we need high triplet energy to decrease the [Z]/[E] ratio because to excite (Z)-stilbene (cis-stilbene) requires higher energy than (E)-stilbene (trans-stilbene). However, some exceptions exist. For example, some sensitizers yield specifically low [Z]/[E] ratio even though their triplet energies are low. Particularly, Hammond and coworkers reported that using para-benzoquinone (PBQ) as the sensitizer yields an unexpectedly low [Z]/[E] ratio in the photoisomerization of stilbene in comparison with other sensitizers that have the similar excitation energy to PBQ.<sup>2</sup> That means a specific Z to E conversion pathway may exist despite the required higher energy for (Z)-stilbene to excite than for (E)-stilbene. However, such a reaction pathway cannot be found by the reaction kinetics, and the mechanism remains unclear.

Aside from the common photochemical isomerization, the reaction via cation radical exhibits one-way isomerization of (*Z*)stilbene to (*E*)-stilbene.<sup>10</sup> In the cation radical reaction, stilbene is photochemically oxidized to yield the cation radical using electron-accepting sensitizers such as 9,10-dicianoanthoracene (DCA).<sup>11</sup> Using polar solvent and adding salt improve the conversion efficiency.<sup>10</sup> Duroquinone sensitizer in the micellar environment also exhibits a similar isomerization reaction of stilbene.<sup>12</sup>

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Those studies implied that the shape of potential energy surface in the cation radical state differs from that in the triplet state. <sup>10,13</sup> The formation of ion pairs affects the detail of the reaction kinetics and spectroscopic behaviors; <sup>14,15</sup> however, the effect of the ion pair on the [Z]/[E] ratio in the steady-state has not been considered as important. Particularly, it is not common to use unsubstituted PBQ as a photoredox catalyst of olefin; therefore, previous studies did not consider specific intermolecular interaction or charge transfer between PBQ and stilbene.

In the excited state, an olefin and carboxyl group may form an adduct as a side product or an intermediate. Paternò-Büchi reaction, [2+2] photocycloaddition of a carbonyl and an alkene, is a well-known one.<sup>16</sup> To the best of our knowledge, a stable product has not been known for Paternò-Büchi reaction with unsubstituted PBQ and stilbene;<sup>16–21</sup> however, there is a possibility to form an intermediate exciplex of PBQ and stilbene.<sup>22-26</sup> Additionally, the experimental study showed that the [Z]/[E] ratio in the steady-state depended on the concentration of PBQ sensitizer, although such concentration dependence was not found in the reaction which proceeds in the Dexter mechanism.<sup>2</sup> Those findings suggest that a specific intermolecular interaction plays an essential role in the isomerization of stilbene with PBQ sensitizer.<sup>27</sup> However, a reaction pathway that involves ion pair or exciplex intermediate<sup>14,15,27</sup> is unknown and has not been investigated. To establish such reaction pathway and mechanism will provide new insight into the sensitized photoisomerization reactions, organic photocatalytic reactions, and the chemistry in triplet states.<sup>28</sup>

In this paper, we examined the possible reaction pathways for the photoisomerization of stilbene sensitized by PBQ using quantum chemical methods and provided the reason why PBQ sensitizer specifically yields excess (*E*)-stilbene. We considered the reaction pathways in the lowest triplet and cation doublet states and the possibility of forming an adduct of stilbene and PBQ in the triplet state as an exciplex. We propose the catalyzed mechanism in which a triplet sensitizer adds to an unsaturated bond of an olefin as proposed by Turro.<sup>22</sup> The electronic structure of PBQ plays an essential role in the specific selectivity of photoreaction.

# 2 Methodology

#### 2.1 Models and reaction schemes for sensitized photoisomerization of stilbene

In general, the sensitized photoisomerization reaction proceeds in the Dexter energy-transfer mechanism.<sup>9</sup> We illustrate the energetics of the Dexter mechanism in **Figure 1**. In the Dexter mechanism the excited sensitizer in the singlet state first converts to triplet states via an intersystem crossing. Thus, an efficient intersystem crossing is desired on a suitable sensitizer. Heteroatoms play an essential role in leading the intersystem crossing efficiently. Then, the excitation energy transfer occurs to generate triplet stilbene, and the sensitizer goes to the ground state. The equilibrium geometry in the lowest triplet ( $T_1$ ) state significantly differs from that on the singlet ground ( $S_0$ ) state. Thus, we need to consider the overlap of the electronic wavefunction and the overlap of the vibrational wavefunction to discuss the rate of the energy-transfer reaction.<sup>29,30</sup> After the energy transfer, the isomerization occurs on the potential energy surface of the  $T_1$  state. Finally, the excited stilbene is quenched to yield the ground-state product.



Fig. 1 The Dexter energy transfer mechanism of triplet sensitized (denoted by sen) isomerization of stilbene.

The E/Z selectivity of the isomerization reaction depends on the triplet excitation energy of the sensitizer ( $\Delta E$  (sen)). Throughout the study, we will discuss the selectivity by the ratio of concentration, [Z]/[E], in the photo-stationary state: the ratio observed after photoirradiation in enough long time. The correlation between  $\Delta E$  (sen) and the [Z]/[E] ratio is shown in **Figure 2**, based on the experimental observations.<sup>2</sup> By assuming the Dexter mechanism, we may categorize the sensitizers into three groups by their triplet excitation energies and [Z]/[E] ratio as follows: Group 1: For  $\Delta E$  (sen) > 60 kcal mol<sup>-1</sup>, the [Z]/[E] ratio is almost constant,  $[Z]/[E] \simeq 1.5$ .

Group 2: For  $\Delta E(\text{sen}) < 60 \text{ kcal mol}^{-1}$ , the [Z]/[E] ratio approximately increases with decreasing  $\Delta E(\text{sen})$ , although there are several exceptions. Sensitizers in this group exhibit (*Z*)-selectivity of [Z]/[E] > 1.5.

Group 3: Using some sensitizers (e.g. PBQ, eosin, and 9,10dibromoanthracene), we obtain the reaction product of [Z]/[E]< 1.0. Namely, (*E*)-selectivity is observed with these sensitizers.

The behavior of sensitizers in groups 1 and 2 may be understood in terms of classical reaction dynamics by using a simple two-state model for the energy transfer, which is illustrated in **Figure 3**. We considered two states: excited sensitizer (sen\*) with ground-state stilbene and ground-state sensitizer with excited stilbene (stilbene\*). Their potential energy curve were approximated by identical parabolas. The horizontal axis denotes the reaction coordinate of energy transfer. Because group 1 sensitizer has enough high energy, the system smoothly moves from the initial state (broken-line curve) to the final state (solid-line curve) without a significant barrier. For group 2 sensitizer, the intersection of potential energy curves results in an energy barrier denoted as  $\Delta G^{act}$ . The barrier height can be written as

$$\Delta G^{\rm act} = \frac{\left(\lambda + \Delta G^0\right)^2}{4\lambda} \tag{1}$$

where  $\Delta G^0$  and  $\lambda$  denote the reaction energy and reorganization

energy, respectively. We expect the barrier for (*Z*)-stilbene to be higher than (*E*)-stilbene due to the larger reaction and reorganization energies. The quantum mechanical model can describe the behavior of group 1 or group 2 sensitizers also to predict the transition rates in terms of the Golden rule.<sup>29,30</sup>



Fig. 2 The [Z]/[E] ratio (extrapolated values at infinite dilution) of stilbene at photo-stationary states with respect to the triplet excitation energies of various triplet sensitizers. The figure was created based on the data in Ref.<sup>2</sup>.



Fig. 3 The energy diagram for the excitation energy transfer between sensitizer (sen) and stilbene.

For group 1, the [Z]/[E] ratio is ruled by the quenching process of the T<sub>1</sub> state toward (*E*)- or (*Z*)-conformations branching from the T<sub>1</sub> equilibrium geometry. The branching ratio is an intrinsic property of stilbene molecule; therefore, the [Z]/[E] ratio is almost constant. For group 2, the [Z]/[E] ratio is determined by the rate of the energy transfer that depends on  $\Delta E$  (sen). With using a group 3 sensitizer, the reaction probably proceeds in another mechanism. According to its triplet energy, PBQ molecule belongs to group 2; however, it yields unexpected (*E*)-excess product, [Z]/[E] = 0.71 at the extrapolation to the infinite dilution of PBQ. The photoisomerization to yield (*E*)-excess products is a very limited case, although the (*E*)-isomer is thermally more stable than the (*Z*)-isomer. The reaction sensitized with PBQ undoubtedly proceeds in a pathway other than the Dexter mechanism. Thus, we aimed to find the isomerization mechanism by considering the potential energy surface using quantum chemical computations.

#### 2.2 Computational details

To obtain the potential energy surfaces relevant to the isomerization reaction, we performed the geometry optimization for PBQ, (E) and (Z)-stilbene, and their complexes (exciplexes) in the  $S_0$ and the T1 states. Additionally, we calculated the cation doublet state of stilbene and anion doublet state of PBQ. We used the B3LYP functional  $^{31-33}$  and 6-311+G(d,p) basis sets.  $^{34,35}$  The electronic structure of PBQ in the lowest triplet state of PBQ is somewhat complicated due to the near degeneracy of  $n\pi^*$  and  $\pi\pi^*$  states. We have confirmed that the unrestricted (U) B3LYP works well for this system in the previous study.<sup>36</sup> The expectation values of  $S^2$  in the triplet states were 2.025 <  $\langle S^2 \rangle$  < 2.053 before the annihilation of the first spin contamination and were  $\langle S^2 \rangle = 2.000$  after the annihilation. The atomic charges were evaluated by the natural bond orbital (NBO) analysis.<sup>37</sup> The molecular geometry optimizations and vibrational frequency calculations were performed for isolated systems. The solvent effect (benzene) was considered for the total energy at the singlepoint calculation level with the polarizable continuum model.<sup>38</sup> We used the Gaussian 16 program<sup>39</sup> for the computations.

We also performed geometry optimization for some potential energy crossing points for elucidating the deactivation process  $(T_1 \rightarrow S_0)$  of the exciplexes. In these calculations, we optimized the molecular coordinates, **R**, to minimize the squared energy difference between the ground and excited states,

$$[\Delta E(\mathbf{R})]^2 = [E_1(\mathbf{R}) - E_0(\mathbf{R})]^2$$
(2)

using its gradient with L-BFGS algorithm 40,41

$$\frac{\partial (\Delta E)^2}{\partial \mathbf{R}} = 2(E_1 - E_0) \left( \frac{\partial E_1}{\partial \mathbf{R}} - \frac{\partial E_0}{\partial \mathbf{R}} \right)$$
(3)

Here,  $E_1$  and  $E_0$  are the  $T_1$  and  $S_0$  energies, respectively. We developed the program for optimizing the crossing points using the energy gradient calculated by the Gaussian 16 program. The geometry obtained by this procedure is not the minimum energy crossing point (MECP)<sup>42</sup> but one of the energy crossing points close to the initial geometry. We tried to search the several crossing points near the equilibrium geometry of the exciplexes and adopted the lowest energy one. In other words, the presented energy value toward the crossing point means an upper bound; the existence of lower-energy crossing points never affects our conclusions.

## 3 Results and Discussion

#### 3.1 Overall energetics and optimized geometries

The overall energy diagrams for the reaction,

(*E*)-stilbene + PBQ  $\rightleftharpoons$  (*Z*)-stilbene + PBQ,

are summarized in Figure 4 and Figure 5. The relative energies include the zero-point energy and solvation energy corrections.

We set the energy of (*E*)-stilbene plus PBQ in the S<sub>0</sub> state to zero and considered the relative stability of (*E*)- and (*Z*)-stilbene, *E/Z* isomerization in the S<sub>0</sub>, T<sub>1</sub>, and cation states. Furthermore, we investigated the complex formation of stilbene and PBQ and their 1,4-radical exciplex (**XP**). Additionally, we examined the oxetane (**OX**) formation via [2+2] cycloaddition reaction known as the Paternò-Büchi reaction. The absolute energy values of all the considered systems are given in **Table S1** of the Supporting Information.

We summarized selected structural parameters (bond lengths and dihedral angles) of relevant reactants, intermediates, and products in **Table S2** of the Supporting Information. In the S<sub>0</sub> state, PBQ takes D<sub>2h</sub> point group symmetry, and the structure varies to C<sub>2v</sub> in the T<sub>1</sub> state, having inequivalent C=O bonds. (*E*)-stilbene has C<sub>2h</sub> point group symmetry; (*Z*)-stilbene and the twisted conformation, (*tw*)- stilbene, belong to C<sub>2</sub> point group. We found the bond-length alternation around the central CC bond of stilbene between the S<sub>0</sub> and T<sub>1</sub> states. The three-dimensional structures are given in **Figure S2**.

#### 3.2 Isomerization of stilbene in the lowest triplet state

In the ground state ( $S_0$ ), (*E*)-stilbene exhibited lower energy than (*Z*)-stilbene by 5.1 kcal mol<sup>-1</sup> in benzene (4.8 kcal mol<sup>-1</sup> in *vacuo*). The calculated energy difference agreed with the experimental value<sup>43</sup> (4.59 kcal mol<sup>-1</sup> in *vacuo*). The relevant energies are shown in **Figure 4**. The highest-energy structure along the central CC bond (C1C2 bond in **Figure S1**) torsion was calculated at 33.4 kcal mol<sup>-1</sup> above the (*E*)-conformer. However, this structure did not have any imaginary frequency; therefore, this is not the transition state (TS). We need to consider non-dynamical electron correlation properly for evaluating the accurate TS. We did not try to find the TS furthermore because we did not aim to find the reaction pathway in the ground state.<sup>44</sup>

The most stable structure in the  $T_1$  state was the twisted (*tw*) form existing at 43.5 kcal mol<sup>-1</sup> above the (E)-conformer in the ground state. This calculated energy was a little lower than the experimental estiamation<sup>45</sup> of 46.5 kcal mol<sup>-1</sup>. The T<sub>1</sub> state did not have the minimal structure that corresponds to the (Z)conformer. Therefore, the exited (Z)-stilbene is directly relaxed toward the (tw)-form. The 0-0 transition of (Z)-stilbene is represented by the transition from (Z)-conformer ( $S_0$ ) to (tw)-form (T<sub>1</sub>). The calculated 0-0 transition energy was 38.4 kcal mol<sup>-1</sup>. We also calculated the T<sub>1</sub> energy by fixing the torsion angle to that in the (Z)-conformer of the  $S_0$  state and relaxing other parameters. The energy of this structure was 10.4 kcal mol<sup>-1</sup> higher than the lowest structure (twisted) of the  $T_1$  state. The torsion of the central CC bond involves significant relaxation energy. The previous studies guessed the existence of the local minimum structure that corresponds to the (*E*)-conformer in the  $T_1$  state.<sup>2,43,45</sup> The (E)-conformer in the  $T_1$  state had one imaginary frequency mode (18.2i cm<sup>-1</sup>) by the present computational method. Consequently, the (E)-conformer was calculated to be a TS between (Z)- and (tw)-forms with very flat upward-convex. The calculated 0-0 transition energy of (*E*)-stilbene was 46.2 kcal mol<sup>-1</sup>.

The calculated 0-0 transition energy of PBQ was 44.0 kcal mol<sup>-1</sup>

in the  $T_1$  state. This finding seems significantly lower than the experimental values<sup>46,47</sup> of 52.5 to 53.4 kcal mol<sup>-1</sup>. Because of the quasi-degeneracy of several low-lying states, a quantitative agreement is still challenging by the DFT calculations for this state. In the Dexter mechanism, the excitation energy transfer from triplet PBQ generates triplet stilbene.

The rate of the excitation energy transfer can be represented by the electronic coupling, overlap of the vibrational wavefunctions, reorganization energies, and the free energy change of the energy transfer reaction using the Golden rule and Born-Oppenheimer approximation.<sup>29</sup> Orlandi et al. calculated the rate constant for the triplet energy transfer between a sensitizer and (E)/(Z)stilbene with respect to the free-energy change.<sup>30</sup> They reported that the rate constant decreases with decreasing the excess energy of sensitizer that corresponds to the free-energy change in the total system. For (E)-stilbene, the rate constant decreases when the excess energy lowers than 2 kcal mol<sup>-1</sup>, while for (Z)-stilbene, the rate constant decreases when excess energy lowers than 10 kcal mol<sup>-1</sup>. This difference between (*E*)- and (*Z*)-stilbene mainly arises from the reorganization energy via the CC bond torsion. The model by Orlandi et al. successfully described the [Z]/[E]ratio of isomerization reaction for many sensitizers.

#### 3.3 Isomerization of stilbene in the cation state

In the cation state, the E/Z isomerization becomes easier because of the decrease in the  $\pi$ -bonding character. In the cation state, we could not find the TS along the CC bond torsion. The highest energy structure along the bond torsion was found at 22.7 kcal mol<sup>-1</sup> above (*E*)-conformer and 15.1 kcal mol<sup>-1</sup> above (*Z*)conformer. The height of the potential surface decreased by more than 10 kcal mol<sup>-1</sup> in comparison with the  $S_0$  state. Additionally, the energy difference between (E)- and (Z)-conformer was 7.6 kcal mol<sup>-1</sup>; the (Z)-conformer becomes unstable in comparison with the S<sub>0</sub> state probably because of the Coulomb repulsion between the positive charge distributed in two phenyl groups. Due to the Coulomb repulsion, the dihedral angle around the central CC bond became large in comparison with the neutral (Z)-conformer. The shape of the obtained potential energy surface is favorable for the one-way isomerization from (Z) to (E)stilbene. 10,13

We need to discuss the ionization process and required energy to ionize stilbene by a photochemical process in solution, although the PBQ molecule is not a strong photooxidant. The calculated ionization potential (0-0 transition) of (*E*)-stilbene was 167.6 kcal mol<sup>-1</sup> *in vacuo* (146.8 kcal mol<sup>-1</sup> in benzene), and the calculation slightly underestimated the experimental value<sup>48</sup> of 176.6 kcal mol<sup>-1</sup> (*in vacuo*). The electron affinity (0-0 transition value) of PBQ was calculated to be 51.2 kcal mol<sup>-1</sup> *in vacuo* (77.5 kcal mol<sup>-1</sup> in benzene) with overestimating the experimental value<sup>49,50</sup> about 10 kcal mol<sup>-1</sup>. The electron transfer energy for PBQ and stilbene may be approximated as

$$E_{\rm ET} \approx I_{\rm D} - E_{\rm A} - V_{\rm Coulomb} \tag{4}$$

where  $I_D$  and  $E_A$  denote the ionization potential of the donor (stilbene) and electron affinity of the acceptor (PBQ), respectively.



Fig. 4 Reaction energy diagram for the E/Z isomerization pathways of stilbene in the S<sub>0</sub>, T<sub>1</sub>, and cation state with PBQ sensitizer. The reaction along the CC bond torsion is shown. The relative energies of oxetane products via photocycloaddition are also shown.

The third term represents the Coulomb interaction energy that may be estimated by the point charge interaction with distance R as

$$V_{\text{Coulomb}} = \frac{1}{4\pi\varepsilon_0\varepsilon_r} \frac{e^2}{R}$$
(5)

where  $\varepsilon_0$  and  $\varepsilon_r$  denote the permittivity of vacuum and the dielectric constant of solvent medium. As a solvated ion pair, we considered that one benzene molecule exists between PBQ and stilbene. Based on the electron-density distribution, we calculated the molar volume of PBQ anion, (*E*)- and (*Z*)-stilbene cations, and benzene as 68.4, 173.6, 162.4, and 70.9 cm<sup>3</sup> mol<sup>-1</sup>. Assuming that all molecules are spherical, their approximated radii were 3.0, 4.1, 4.0, and 3.0 Å. Thus, the distance of point charges may be estimated as 13.1 Å. Using  $\varepsilon_r = 2.2706$  for benzene, we finally evaluated the Coulomb interaction energy as 11.2 kcal mol<sup>-1</sup>.

The relative energies of PBQ(-1)–stilbene(+1) solvated pair were consequently evaluated, as shown in **Figure 4**. These values (e.g. 57.8 kcal mol<sup>-1</sup> for PBQ(-1)–(*E*)-stilbene(+1)) would be, however, lower limits because of the overestimation of the electron affinity of PBQ. It is possible to generate the electron transfer states by the visible light energy; however, the necessary energy was significantly higher than the triplet excitation energy. Thus, the isomerization pathway involving photoionization is less important than the triplet one for using PBQ sensitizer, although highly polar environment may promote the photoionization mechanism. In addition, the isomerization reaction with eosin sensitizer would proceed in this cation mechanism. Eosin is known as a photoredox catalyst, and therefore it may exhibit the one-way isomerization.<sup>28</sup>

#### 3.4 Isomerization of stilbene via triplet exciplex with PBQ

We found that stable encounter complexes were formed with triplet PBQ and ground state stilbene, and the encounter complexes were easily converted to exciplexes by forming a C-O bond. In the encounter complexes, the distance was 2.4–2.5 Å between the oxygen of PBQ and carbon in the central CC bond of stilbene. The energy diagram relevant to the exciplex is shown in Figure 5. The gross charge on the stilbene moiety was +0.49 e for (E)-conformer (+0.48 e for (Z)-conformer) in the complex, and therefore, the charge-transfer stabilizes the encounter complex. The stabilization energy was 8.1 kcal mol<sup>-1</sup> for (*E*)-conformer (7.3 kcal mol<sup>-1</sup> for (Z)-conformer). The encounter complex was converted to the exciplex (E-XP or Z-XP), passing the transition state (TS1 or TS2) with a low energy barrier by forming the C-O bond. The exciplex formation was exothermic; the E-XP and Z-XP had lower energies than the encounter complexes by 9.0 and 12.7 kcal mol<sup>-1</sup>, respectively.

The torsion around the central CC bond of the stilbene moiety becomes much easier in the exciplex because the carbon bonding with the oxygen of PBQ takes sp<sup>3</sup> electronic structure. The **Z**-**XP** will be transformed into a twisted form (*tw*-**XP**) by passing through the **TS3** (the barrier is 3.1 kcal mol<sup>-1</sup>). Alternatively, it will be the *E*-**XP** by passing through the **TS5** that is located in the opposite torsional direction (the barrier is 2.5 kcal mol<sup>-1</sup>). The potential energy surfaces between the *E*-**XP** and *tw*-**XP** were almost flat. They had almost the same energy, and the height of **TS4** between them was only 1.8 kcal mol<sup>-1</sup>. By elongating the O-C distance between PBQ and stilbene up to 1.7 Å, the *E*-**XP** and *tw*-**XP** were converted to the same structure.

The exciplexes were unstable in the  $S_0$  state and dissociating to PBQ and stilbene. The intersystem crossing preferentially occurs around the crossing point between the  $S_0$  and  $T_1$ . We obtained



Fig. 5 Reaction energy diagram for the E/Z isomerization pathways of stilbene with PBQ sensitizer via the exciplex formation. The excitation of PBQ to the T<sub>1</sub> state yields the encounter complex. After passing through the TS1 (or TS2), *E*-exciplex: *E*-XP (or *Z*-exciplex: *Z*-XP) is generated. The isomerization proceeds via the triplet exciplex.

crossing points of **CP1** and **CP2** around the geometry of *E*-**XP** and *Z*-**XP**, respectively. During the geometry optimization of **CP1** and **CP2**, we did not consider the solvent effect and zero-point energy, although these corrections depend on the electronic states. Therefore, the  $S_0$  and  $T_1$  energies at the **CP1** and **CP2** structures are not identical. Here, we used the  $S_0$  energy for discussion. The **CP1** was found 12.1 kcal mol<sup>-1</sup> above the *E*-**XP**, and the **CP2** was 14.3 kcal mol<sup>-1</sup> higher than the *Z*-**XP**. The energy difference was 2.2 kcal mol<sup>-1</sup> between *E*-**XP** and *Z*-**XP**. In the exciplex state, the (*E*)-conformer is more stable than the (*Z*)-conformer; therefore, (*E*)- or (*Z*)-stilbene forms triplet exciplex and relaxes to the *E*-**XP** structure. Finally, the *E*-**XP** is quenched to yield PBQ and (*E*)-stilbene in the  $S_0$  state. As a result, the one-way isomerization from (*Z*)- to (*E*)-stilbene is achieved using the triplet state of PBO.

A well-known photochemical reaction of olefin and carbonyl compounds is the Paternò-Büchi reaction: [2+2] photocycloaddition reaction. We found that the products of the Paternò-Büchi reaction, oxetane species, were significantly unstable compared to the exciplexes having a preoxetane structure. The triplet oxetane products (*E*-OX and *Z*-OX) had about 70 kcal mol<sup>-1</sup> higher energy than the ground state reactant, PBQ + stilbene (Figure 4). Therefore, we do not need to consider the photocycloaddition reaction.

#### 3.5 Electronic structures

The spin density distributions can explain the stable conformation of stilbene in the  $T_1$  state. The twisted form is the most stable structure for stilbene in the  $T_1$  state, while the *E*-XP becomes a low-energy structure for the PBQ-stilbene exciplex. The spin density distributions are shown in **Figure 6**. For stilbene in the twisted form, the spin density was distributed in two HC–Ph groups. Those two maximum distributions took a perpendicular direction due to reducing the overlap of unpaired electrons.<sup>51,52</sup> The overlap of unpaired electrons destabilizes the system owing to the Pauli repulsion originated in the exclusion principle. Therefore, stilbene in the  $T_1$  state favors a twisted structure. In the PBQ-stilbene exciplex, on the other hand, the spin density was delocalized in one HC–Ph group and PBQ moiety. Thus, the overlap of unpaired electrons hardly depends on the conformation of the stilbene moiety.

The charge-transfer drives the C-O bond formation in the PBQstilbene exciplex. In a simplified orbital picture, the *n*- and  $\pi^*$ orbitals correspond to the SOMO (singly-occupied molecular orbital) of PBQ in the T<sub>1</sub> state. The valence  $\pi$  electron of stilbene moves to the SOMO *n*-orbital of PBQ to form the C-O bond. Consequently, unpaired electrons remain in the  $\pi$ -orbital of stilbene and  $\pi^*$ -orbital of PBQ, resulting in the  $\pi\pi^*$  charge-transfer type T<sub>1</sub> state. This charge-transfer already occurs partly in the encounter complexes. For the oxetane, *E*-OX, the spin density is distributed in PBQ moiety showing the  $n\pi^*$ -like character.

Since the presented reaction mechanism involves intersystem crossing, spin-orbit coupling (SOC) would be significant. Thus, we estimated the SOC between the  $S_0$  and  $T_1$  states by the TDB3LYP/6-311G(d,p) method and Casida's wavefunction ansatz



**Fig. 6** Spin density distributions in the  $T_1$  state of (a) (*tw*)-stilbene, (b) *E*-XP, (c) encounter complex, and (d) *E*-OX with the isosurface value is 0.008. The blue and yellow regions represent positive and negative values, respectively.

using the PySOC program code.<sup>53</sup> The SOC values for important systems are shown in **Table 1**. The SOCs for PBQ in the S<sub>0</sub> and T<sub>1</sub> equilibrium geometry were 64 and 49 cm<sup>-1</sup>, respectively. Strong SOC arises from the  $n\pi^*$  transition. The SOCs for stilbene and exciplexes are 4 cm<sup>-1</sup> or lower. They have a  $\pi\pi^*$  character, and therefore, SOC becomes weak. Sensitization by the triplet PBQ is effective, and the quenching to S<sub>0</sub> stilbene is expected to be slow.

Table 1 Spin-orbit coupling (SOC) between  ${\rm S_0}$  and  ${\rm T_1}$  states calculated with TDB3LYP.

System	SOC / cm <sup>-1</sup>
PBQ (S <sub>0</sub> geometry)	64
PBQ ( $T_1$ geometry)	49
( <i>E</i> )-Stilbene ( $T_1$ geometry)	0
( <i>tw</i> )-Stilbene ( $\tilde{T}_1$ geometry)	2
(Z)-Stilbene ( $T_1$ geometry)	1
<i>E</i> - <b>XP</b> (T <sub>1</sub> geometry)	4
<i>tw</i> - <b>XP</b> ( $T_1$ geometry)	3
<b>Z-XP</b> ( $T_1$ geometry)	2
<b>CP1</b> (T <sub>1</sub> geometry)	4
<b>CP2</b> ( $T_1$ geometry)	4

#### 3.6 Comparison with diacetyl sensitizer

We investigated the exciplex formation of stilbene with 2,3butanedione (diacetyl, diac) since it helps to understand the exciplex formation that the comparison of PBQ with a similar sensitizer molecule having carbonyl groups. The experimental study showed that the diac sensitizer belongs to group 2 with  $[Z]/[E] \simeq 6.5$ , indicating the Dexter mechanism. The energy diagram for (*E*)-stilbene and diac was shown in **Figure 7** with comparing to the energetics of PBQ.

The exciplex formation of stilbene and diac was not so favorable energetically than that of PBQ; therefore, the exciplex formation will not occur for diac, and the Dexter energy-transfer will be the dominant process. The calculated 0-0 transition energy of diac was 47.0 kcal mol-1 in benzene solution between the  $S_{\rm 0}$  and  $T_{\rm 1}$  states. The transition energy was close to that of PBQ. In contrast to PBQ, diac did not form a stable encounter complex with stilbene in the T<sub>1</sub> state. The calculated stabilization energy was 0.6 kcal mol<sup>-1</sup> by forming the encounter complex, which exhibited only 0.03 e charge transfer by the natural population analysis. The complex of diac yielded the triplet exciplex, which was similar to that of PBQ, after passing the transition state of 7.3 kcal mol<sup>-1</sup> barrier height. The product exciplex had 2.1 kcal mol<sup>-1</sup> lower energy than the reactant; the reaction energy of the exciplex formation was significantly smaller than that of PBQ (17.1 kcal mol<sup>-1</sup>). Additionally, we found that the oxetane structure had about 40 kcal mol<sup>-1</sup> higher energy than the reactant. These findings indicate that the Dexter energy transfer occurs preferentially than the exciplex formation upon using diac as the sensitizer.

Both the exciplexes with PBQ and diac have a similar electronic structure. The sensitizer moieties accepted negative charge about -0.36 e, and the spin density was delocalized in the phenyl and the sensitizer moieties. The C-O bond lengths between sensitizer and stilbene are 1.466 and 1.465 Å for PBO and diac, respectively. Briefly, the intermolecular bond forms with accepting electron by the sensitizer. Thus, the stability of exciplex relates to the electron affinity of sensitizers in the triplet state. The electron affinity in the triplet state can be estimated easily by the computations. The calculated 0-0 energy differences between the triplet and anion radical were -95.2 and -70.3 kcal mol-1 for PBQ and diac, respectively, in vacuo. The negative sign means that anion radical is more stable than the triplet. Thus, the high electron acceptability of PBO is the electronic origin to stabilize the triplet exciplex. This feature also affects the stability of the encounter complexes and their charge-transfer character.

## 4 Conclusions

Based on the quantum chemical calculations, we concluded that the PBQ molecule acts as a sensitizer and a catalyst in the photoisomerization reaction of stilbene by forming a stable exciplex as an intermediate. We found that stilbene and PBQ form a stable complex stabilized by the charge-transfer. This encounter complex was converted to the exciplex by forming a C-O bond. The exciplex formation was energetically more favorable than the Dexter energy transfer. The conformation of the exciplex was flexible, and therefore it was converted to the stable (*E*)conformation. The exciplex was quenched to the S<sub>0</sub> state to yield (*E*)-stilbene after passing this crossing point between the T<sub>1</sub> and S<sub>0</sub> states. Although the present study considered only the low-



Fig. 7 The reaction profiles for the stilbene exciplex formation process with diacetyl (upper green line) and with PBQ (lower blue line). The sensitizer plus (E)-stilbene was set to the reference of energy.

est triplet state within the complicated photochemical reaction, the exciplex mechanism is consistent with the observed Z/E selectivity and whose dependence on the concentration of PBQ. Experimental detection of the exciplex intermediate is necessary to confirm the proposed mechanism.

The exciplex formation is derived by the oxidative addition of triplet sensitizer to stilbene; therefore, the sensitizers having high electron acceptability in the triplet state favor to form exciplex. The high electron acceptability is the characteristic of benzoquinone, and therefore, it works as a photocatalyst. The organic photocatalyst is receiving increasing attention. In the photocatalytic reaction mechanism, the existence of intermediate exciplexes is not well considered because the exciplex formation does not affect the outcome. The present result is an example of that exciplex formation affects the selectivity of photochemical reactions. This study shows the necessity to consider exciplex intermediates in the mechanistic study of photocatalytic reactions.

# Conflicts of interest

There are no conflicts to declare.

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# References

- J. Zhao, W. Wu, J. Sun and S. Guo, Triplet photosensitizers: from molecular design to applications, *Chem. Soc. Rev.*, 2013, 42, 5323–5351.
- 2 G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, Mechanisms of photochemical reactions in solution. XXII. Photochemical cis-trans isomerization, *J. Am. Chem. Soc.*, 1964, **86**, 3197–3217.
- 3 W. G. Herkstroeter and G. S. Hammond, Mechanisms of photochemical reactions in solution. XXXIX. Study of energy transfer by kinetic spectrophotometry, *J. Am. Chem. Soc.*, 1966, **88**, 4769–4777.
- 4 T. Arai and K. Tokumaru, Photochemical one-way adiabatic isomerization of aromatic olefins, *Chem. Rev.*, 1993, **93**, 23– 39.
- 5 Y.-P. Zhao, L.-Y. Yang and R. S. H. Liu, Designing systems for one-way trans to cis photoisomerization for solar reactions, *Green Chem.*, 2009, **11**, 837–842.
- 6 J. B. Metternich and R. Gilmour, A Bio-Inspired, Catalytic  $E \rightarrow Z$  Isomerization of Activated Olefins, *J. Am. Chem. Soc.*, 2015, **137**, 11254–11257.
- 7 J. B. Metternich, D. G. Artiukhin, M. C. Holland, M. von Bremen-Kühne, J. Neugebauer and R. Gilmour, Photocatalytic E → Z Isomerization of Polarized Alkenes Inspired by the Visual Cycle: Mechanistic Dichotomy and Origin of Selectivity, J. Org. Chem., 2017, 82, 9955–9977.
- 8 W. Cai, H. Fan, D. Ding, Y. Zhang and W. Wang, Synthesis of Z-alkenes via visible light promoted photocatalytic  $E \rightarrow Z$  isomerization under metal-free conditions, *Chem. Commun.*, 2017, **53**, 12918–12921.
- 9 D. L. Dexter, A theory of sensitized luminescence in solids, *J. Chem. Phys.*, 1953, **21**, 836–850.
- 10 F. D. Lewis, J. R. Petisce, J. D. Oxman and M. J. Nepras, One-Way Photoisomerization of cis-Stilbene via a Cation Radical Chain Mechanism, J. Am. Chem. Soc., 1985, 107, 203–207.
- 11 L. T. Spada and C. S. Foote, Electron-transfer photooxidation. 3. Detection of radical-ion intermediates in the cyanoaromatic-sensitized photooxidation of trans- and cisstilbene, J. Am. Chem. Soc., 1980, **102**, 391–393.
- 12 Y. Tanimoto, M. Takayama, S. Shima and M. Itoh, Laser Photolysis Study on the Duroquinone-photosensitized Isomerization of Stilbenes in Micellar Solution, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3641–3642.
- 13 Y. Kuriyama, T. Arai, H. Sakuragi and K. Tokumaru, Direct observation of cis-to-trans conversion of olefin radical cations. Electron transfer-induced isomerization of stilbene derivatives, *Chem. Phys. Lett.*, 1990, **173**, 253–256.
- 14 H. D. Roth and M. L. M. Schilling, Nuclear spin polarization effects in radical ion pair reactions. Recombination in the singlet and triplet state, J. Am. Chem. Soc., 1980, 102, 4303– 4310.
- 15 M. Goez and G. Eckert, Olefin Isomerization via Radical-Ion Pairs in Triplet States Studied by Chemically Induced Dynamic

Nuclear Polarization (CIDNP), Helv. Chim. Acta, 2006, 89, 2183–2199.

- M. Fréneau and N. Hoffmann, The Paternò-Büchi reaction
  Mechanisms and application to organic synthesis, J. Photochem. Photobiolog. C Photochem. Rev., 2017, 33, 83–108.
- 17 K. Kokubo, T. Masaki and T. Oshima, Steric Effects in Photoinduced Electron Transfer Reaction of Halogenated 1,4-Benzoquinones with Donor Olefins, *Org. Lett.*, 2000, 2, 1979– 1981.
- 18 J. A. Barltrop and B. Hesp, Organic photochemistry. Part V. The illumination of some quinones in the presence of conjugated dienes and other olefinic systems, *J. Chem. Soc. C*, 1967, 1625–1635.
- 19 D. Bryce-Smith, A. Gilbert and M. G. Johnson, Liquid-phase photolysis. Part X. Formation of spiro-oxetans by photoaddition of olefins to p-benzoquinone, *J. Chem. Soc. C*, 1967, 383– 389.
- 20 E. Bosch, S. M. Hubig and J. K. Kochi, Paterno-Büchi Coupling of (Diaryl)acetylenes and Quinone via Photoinduced Electron Transfer, J. Am. Chem. Soc., 1998, 120, 386–395.
- 21 M. Christl, M. Braun and O. Deeg, Photochemical reactions of tetrachloro-1,4-benzoquinone (chloranil) with tricyclo[4.1.0.02,7]heptane (Moore's hydrocarbon) and bicyclo[4.1.0]hept-2-ene (2-norcarene), *Org. Biomol. Chem.*, 2013, **11**, 2811–2817.
- N. J. Turro, Mechanisms of Sensitized Photochemical cistrans-iso, erization in solution, *Photochem. Photobiol.*, 1969, 9, 555–563.
- 23 R. M. Wilson and A. K. Musser, Photocyclizations involving quinone-olefin charge-transfer exciplexes, J. Am. Chem. Soc., 1980, 102, 1720–1722.
- 24 K. A. Schnapp, R. M. Wilson, D. M. Ho, R. A. Caldwell and D. Creed, Benzoquinone-olefin exciplexes: the observation and chemistry of the p-benzoquinone-tetraphenylallene exciplex, *J. Am. Chem. Soc.*, 1990, **112**, 3700–3702.
- 25 D. Sun, S. M. Hubig and J. K. Kochi, Oxetanes from [2+2] Cycloaddition of Stilbenes to Quinone via Photoinduced Electron Transfer, *J. Org. Chem.*, 1999, **64**, 2250–2258.
- 26 H. Yamamoto, K. Ohkubo, S. Akimoto, S. Fukuzumi and A. Tsuda, Control of reaction pathways in the photochemical reaction of a quinone with tetramethylethylene by metal binding, *Org. Biomol. Chem.*, 2014, **12**, 7004–7017.
- 27 S. M. Hubig, D. Sun and J. K. Kochi, Photodynamics of the Paterno–Büchi cycloaddition of stilbene to quinone. Unusual modulation of electron-transfer kinetics by solvent and added salt, *J. Chem. Soc., Perkin Trans.* 2, 1999, 781–788.
- 28 N. A. Romero and D. A. Nicewicz, Organic Photoredox Catalysis, Chem. Rev., 2016, 116, 10075–10166.
- 29 J. Ulstrup and J. Jortner, The effect of intramolecular quantum modes on free energy relationships for electron transfer reactions, *J. Chem. Phys.*, 1975, **63**, 4358–4368.
- 30 G. Orlandi, S. Monti, F. Barigelletti and V. Balzani, Triplet energy transfer to cis and trans stilbene. A quantum mechanical approach, *Chem. Phys.*, 1980, **52**, 313–319.
- 31 A. D. Becke, Density-functional exchange-energy approxima-

tion with correct asymptotic behavior, *Phys. Rev. A*, 1988, **38**, 3098–3100.

- 32 C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, 1988, **37**, 785–789.
- 33 A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys., 1993, 98, 5648–5652.
- 34 A. D. McLean and G. S. Chandler, Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11–18, J. Chem. Phys., 1980, 72, 5639–5648.
- 35 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, Selfconsistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys.*, 1980, 72, 650–654.
- 36 K. Nakatani, H. Sato and R. Fukuda, Pseudo-Jahn-Teller effect on the lowest triplet state of para-benzoquinone involving inequivalent carbonyl bonds, *Chem. Phys. Lett.*, 2020, 741, 137072.
- 37 A. E. Reed, R. B. Weinstock and F. Weinhold, Natural population analysis, J. Chem. Phys., 1985, 83, 735–746.
- 38 E. Cancès, B. Mennucci and J. Tomasi, A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics, J. Chem. Phys., 1997, 107, 3032–3041.
- 39 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian16 Revision C.01, 2016, Gaussian Inc. Wallingford CT.
- 40 J. Nocedal, Updating Quasi-Newton Matrices with Limited Storage, *Math. Comput.*, 1980, **35**, 773–782.
- 41 D. C. Liu and J. Nocedal, On the limited memory BFGS

method for large scale optimization, *Math. Program. B*, 1989, **45**, 503–528.

- 42 M. J. Bearpark, M. A. Robb and H. Bernhard Schlegel, A direct method for the location of the lowest energy point on a potential surface crossing, *Chem. Phys. Lett.*, 1994, **223**, 269– 274.
- 43 J. Saltiel, S. Ganapathy and C. Werking, The  $\Delta$ H for thermal trans/cis-stilbene isomerization: do S<sub>0</sub> and T<sub>1</sub> potential energy curves cross?, *J. Phys. Chem.*, 1987, **91**, 2755–2758.
- 44 L.-Y. Yang, M. Harigai, Y. Imamoto, M. Kataoka, T.-I. Ho, E. Andrioukhina, O. Federova, S. Shevyakov and R. S. H. Liu, Stilbene analogs in Hula-twist photoisomerization, *Photochem. Photobiol. Sci.*, 2006, **5**, 874–882.
- 45 T. Ni, R. A. Caldwell and L. A. Melton, The relaxed and spectroscopic energies of olefin triplets, *J. Am. Chem. Soc.*, 1989, 111, 457–464.
- 46 H. P. Trommsdorff, Electronic States and Spectra of p-Benzoquinone, J. Chem. Phys., 1972, 56, 5358–5372.
- 47 N. Ohta, I. Yamazaki, M. Sanekata, I. Suzuka and O. Sekiguchi, Rotational effects on singlet-triplet interaction of p-benzoquinone vapor, *J. Phys. Chem.*, 1993, **97**, 7857–7862.
- 48 C. Dietl, E. Papastathopoulos, P. Niklaus, R. Improta, F. Santoro and G. Gerber, Femtosecond photoelectron spectroscopy of trans-stilbene above the reaction barrier, *Chem. Phys.*, 2005, **310**, 201–211.
- 49 P. B. Comita and J. I. Brauman, Photodissociation spectroscopy of the negative ion dimer of toluquinone, *J. Am. Chem. Soc.*, 1987, **109**, 7591–7597.
- 50 J. Schiedt and R. Weinkauf, Resonant photodetachment via shape and Feshbach resonances: p-benzoquinone anions as a model system, *J. Chem. Phys.*, 1999, **110**, 304–314.
- 51 N. C. Baird and R. M. West, Quantum organic photochemistry. I. Intramolecular potential energy surfaces for the lowest  ${}^{3}\pi\pi^{*}$  state of polyenes, *J. Am. Chem. Soc.*, 1971, **93**, 4427–4432.
- 52 K. Fukui and K. Tanaka, A Theoretical Study on Biradicals. I. Theoretical Characteristics of Biradicals, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1391–1398.
- 53 X. Gao, S. Bai, D. Fazzi, T. Niehaus, M. Barbatti and W. Thiel, Evaluation of Spin-Orbit Couplings with Linear-Response Time-Dependent Density Functional Methods, *J. Chem. The*ory and Comput., 2017, 13, 515–524.