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Benzophenone Sensitized Photoisomerization of 1,2-Bispyrazinylethylene

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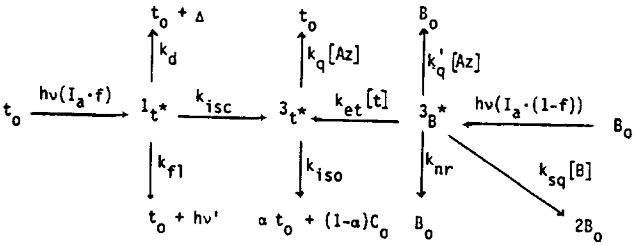
We have proposed a triplet mechanism for direct *trans*→*cis* photoisomerization of 1,2-bispyrazinylethylene(BPyE) on the basis of benzophenone sensitization and azulene quenching studies.[1] Benzophenone sensitizer, however, showed an anomalous concentration effect on the photoisomerization quantum yields[1b] which could not be clearly explained at that time. We now propose a plausible mechanism to explain this anomaly.

A simple analysis of the data[1b] shows a decrease of benzophenone sensitized *trans*→*cis* photoisomerization quantum yields as the concentration of benzophenone increases indicating that not all the benzophenone triplets generate the olefin triplets. The simplest mechanism which will account for this observation is shown in Scheme 1.



Scheme 1. Mechanism of the *trans*→*cis* photoisomerization of *trans*-1,2-bispyrazinylethylene.

When the steady-state approximation is applied on the benzophenone sensitized *trans*→*cis* photoisomerization,

$$\Phi^{obs}_{t\to c}=f(1-\alpha)\Phi_{isc}+(1-f)(1-\alpha)\frac{k_{et}[t]}{k_{nr}+k_{et}[t]+k_{sq}[B]} \qquad (1)$$

and when azulene is added as a triplet quencher, the following Stern-Volmer relationship can be derived,

$$\Phi^{o}_{t\to c}/\Phi_{t\to c}=\frac{(1+k_q[Az]/k_{iso})\left(f\Phi_{isc}+\frac{(1-f)k_{et}[t]}{k_{nr}+k_{et}[t]+k_{sq}[B]}\right)}{\left(f\Phi_{isc}+\frac{(1-f)k_{et}[t]}{k_{nr}+k_{et}[t]+k_{sq}[B]+k'_q[Az]}\right)} \qquad (2)$$

where, $f=E_t[t]$ which is the fraction of photons absorbed by *trans*-BPyE at 366 nm, $(1-\alpha)$ is the fraction of decay from $^3t^*$

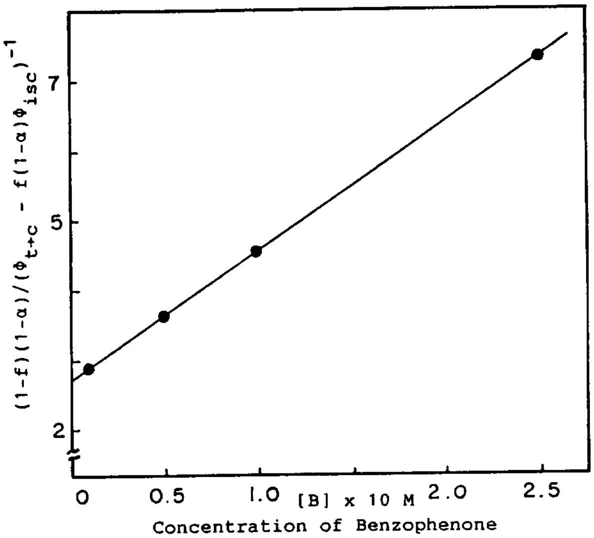


Figure 1. Benzophenone effect on the *trans* → *cis* photoisomerization of BPyE, where the concentration of *trans*–BPyE is 2.5 × 10^{-3} M.

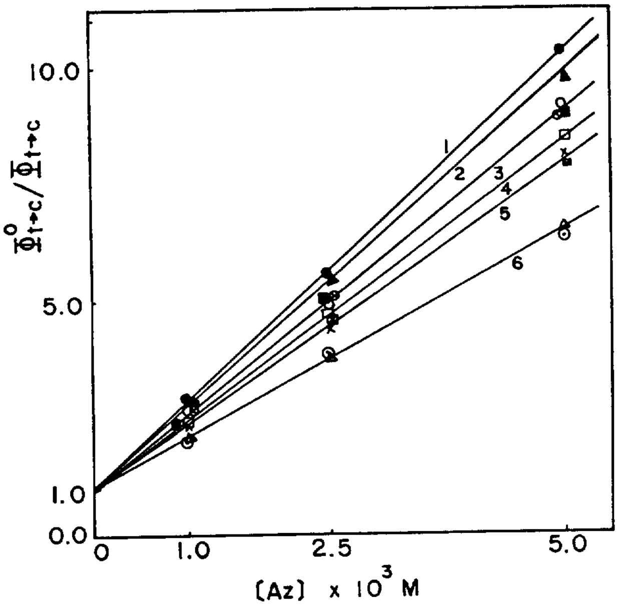


Figure 2. Stern–Volmer plots for direct and sensitized *trans*→ *cis* photoisomerization of BPyE: line 1, in benzene at 366 nm ([*B*] is 2.0 × 10^{-2} M (●)); line 2, in benzene at 366 nm ([*B*] is 1.0 × 10^{-2} M (▲)); line 3, in benzene at 366 nm ([*B*] is zero (■) or 1.0 × 10^{-3} M (○)) and at 435.8 nm ([*B*] is zero (⊗)); line 4, in acetonitrile–water (v/v, 7:3) at 366 nm ([*B*] is 5.0 × 10^{-2} M (□)); line 5, in benzene–dichloromethane (v/v, 1:1) at 366 nm ([*B*] is zero (x)) and at 435.8 nm ([*B*] is zero or 1.2 × 10^{-2} M (⊠)); line 6, in acetonitrile–water (v/v, 7:3) at 366 nm ([*B*] is zero (△) or 1.0 × 10^{-3} M (⊙)), where [*B*] is the concentration of benzophenone.

to c_0 which was found to be 0.43,[1b] [*t*] and [*B*] are the concentration of trans–BPyE and benzophenone, respectively, k_{nr} and k_{sq} are the rate constants of nonradiative decay and self-quenching of benzophenone triplets in benzene which were reported to be $k_{nr} = 1.14 \times 10^4 \sim 1.0 \times 10^5$ sec^{-1} and $k_{sq} = 1.6 \times 10^5$ $\text{M}^{-1}\text{sec}^{-1}$ by Schuster *et al.*[2a] and $k_{nr} = 2.0 \times 10^4 \sim 5.0 \times 10^5$ sec^{-1} and $k_{sq} = 4.4 \times 10^5$ $\text{M}^{-1}\text{sec}^{-1}$ by Singer *et al.*,[2b] respectively, k_{et} is the rate constant of energy transfer from benzophenone triplets to *trans*–BPyE, k_q and k_q' are the quenching rate constants of *trans*–BPyE and benzophenone triplets by azulene, respectively, $1/k_{iso}$ (τ_T) is the lifetime of *trans*–BPyE triplets, Φ_{isc} is the intersystem crossing quantum yield of *trans*–BPyE, and $\Phi^{o}_{t\to c}$ is the *trans* → *cis* photoisomerization quantum yield of *trans*–BPyE in the absence of azulene.

We can derive the following equation (3) from the equation (1).

$$\frac{(1-f)(1-\alpha)}{\Phi^{obs}_{t\to c}-f(1-\alpha)\Phi_{isc}}=1+\frac{k_{nr}}{k_{et}[t]}+\frac{k_{sq}}{k_{et}[t]}[B] \qquad (3)$$

A plot of $(1-f)(1-\alpha)(\Phi^{obs}_{t\text{-}c}-f(1-\alpha)\Phi_{isc})^{-1}$ *vs.* [*B*] gives a good linear relationship as shown in Figure 1, showing the intercept of 2.73 and the slope of 18.4$\text{M}^{-1}\text{sec}^{-1}$, respectively, where the concentration of *trans*–BPyE is 2.5 × 10^{-3}M. The rate constant of the energy transfer from benzophenone triplets to *trans*–BPyE (k_{et}) must be in the range of 3.5 ~ 9.6 × 10^6 $\text{M}^{-1}\text{sec}^{-1}$ and k_{nr} is in the range of 1.5 ~ 4.1 × 10^4 sec^{-1}, respectively if we assume the k_{sq} value to fall in the range of 1.6 ~ 4.4 × 10^5 $\text{M}^{-1}\text{sec}^{-1}$. Rate constant of the energy transfer for other related olefins, however, is ~ 5 × 10^9 $\text{M}^{-1}\text{sec}^{-1}$.

From the results of equation (3) and on the assumption that k_q and k_q' are the same as the diffusion controlled rate constant, we can modify the equation (2) into the equation (4).

$$\Phi^{o}_{t\to c}/\Phi_{t\to c}=$$

$$(1+k_q[Az]/k_{iso})\left(1+\frac{(1-f)k_{et}[t]}{f\Phi_{isc}(k_{nr}+k_{et}[t]+k_{sq}[B])}\right) \qquad (4)$$

The value of second term in equation (4) increases as [*B*] increases because of the increase of (1–*f*) value. The bigger Stern–Volmer constants, therefore, were obtained as [*B*] increases as shown in Figure 2.

These phenomena can be observed when benzophenone triplets are quenched through self-quenching and triplet–triplet annihilations (TTA) of benzophenone or when the triplets of *trans*–BPyE are quenched by benzophenone. Since the triplets of *trans*–BPyE are not quenched by benzophenone when biacetyl is used as a photosensitizer at 435.8 nm, the process may be considered to be negligible. TTA mechanism seems not acceptible either since TTA occurs at high light intensities when long triplet lifetimes are involved. Since the lifetime of benzophenone triplets decreases as [*B*] is increased, any involvement of TTA will diminish. Wolf *et al.*[2b] also reported that *P*–type delayed fluorescence in benzophenone is negligible at concentrations <0.05 M in benzene.

The low energy transfer rate constant of benzophenone triplets to *trans*–BPyE may be explained by proposing the formation of an AD* complex or exciplex[3] where benzophenone triplet is the donor (D) and the ground state *trans*–BPyE is the acceptor (A) and the rate constant for energy transfer as:[3c]

$$k^{obs}_{et}=k_{diff}k_{et}/(k_{et}+k_{-diff}) \qquad (5)$$

The observed energy transfer rate constant (k_{et}^{obs}) depends on the diffusion rate constant (k_{diff}) for diffusion of D* and A and the energy transfer during the lifetime of the exciplex or complex. If we assume the rate of dissociation of the exciplex or complex to be very fast relative to energy transfer ($k_{-diff} \gg k_{et}$)[4] as in the case of triplet-triplet energy transfer of valerophenone to 2,5-dimethyl-2,4-hexadiene,[5] the observed rate constant is a composite of the equilibrium constant (k_{diff}/k_{-diff}) for exciplex or complex formation and the rate constant for energy transfer. In this case, the observed energy transfer rate constant is much smaller than the diffusion controlled rate constant. It indicates that the self-quenching of the benzophenone triplets must compete with energy transfer to *trans*-BPyE and the photoisomerization quantum yields decrease as the concentration of benzophenone, [*B*], increases.

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Rhodium-Olefin Interaction: Double Bond Migration of *cis*-But-2-en-1,4-diol with Rhodium(I) Complexes

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The difference in affinities of rhodium(I) and iridium(I) toward a certain ligand is prominent, *e.g.*, reactions of $IrA(CO)(PPh_3)_2$ (A = monodentate anionic ligand such as halogens and ClO_4) with H_2 give stable $Ir(H)_2A(CO)(PPh_3)_2$ which are quantitatively isolated at room temperature[1] while $Rh(H)_2A(CO)(PPh_3)_2$ has never been isolated from the reactions of $RhA(CO)(PPh_3)_2$ and H_2. The M-P bond in $IrCl(PPh_3)_3$ is stronger than that in $RhCl(PPh_3)_3$: the latter is very effective catalyst for various organic reactions due to the significant dissociation of PPh_3 from rhodium in solution to provide a vacant site around rhodium for organic substrates[2] while the former is hardly employed as a catalyst mainly because the dissociation of PPh_3 from iridium is negligible.

It has been known that $Ir(ClO_4)(CO)(PPh_3)_2$ attacks both hydroxyl groups of *cis*-$HOCH_2CH = CHCH_2OH$ (**1**) to give *trans*-$CH_3CH = CHCHO$ but leaves the olefinic group intact.[3] The rhodium analogue $Rh(ClO_4)(CO)(PPh_3)_2$ (**2**), however, behaves quite differently in the reaction with **1**, which is described in this report along with related experimental results.

Rhodium-olefinic group interaction is apparent in the reactions of **2** and $[Rh(CO)(PPh_3)_3]ClO_4$ (**3**) with **1** but no evidence for interaction between rhodium (in **2** and **3**) and the hydroxyl groups of **1** has been observed (see below). 2-Hydroxytetrahydrofuran (**4**) is catalytically produced in the reactions of **1** with **2** or **3** (Table 1). Proton NMR spectral changes during the reactions clearly showed that a saturated aldehyde, presumably 4-hydroxybutanal (**5**), is produced and disappeared when a mixture of CD_3COCD_3 and $CDCl_3$ is used as a solvent (see Experimental and Table 1). No other products such as but-2-enal (which is produced in the reaction of the iridium complex $Ir(ClO_4)(CO)(PPh_3)_2$ with **1**[3]) has been found. Accordingly, the production of **4** seems to occur through the formation of **5** (equation 1). Formation of **5** is also strongly supported by the fact that complex **2** and **3** are very effective catalysts for the double bond migration of allylic alcohols to produce the corresponding saturated aldehydes[4] and the double bond migration product **5** would readily

Table 1. Catalytic Production of 2-Hydroxytetrahydrofuran (**4**) in the Reactions of *cis*-But-2-en-1,4-diol (**1**) (2.0 mmole) with $Rh(ClO_4)(CO)(PPh_3)_2$ (**2**) (0.1 mmole) and $[Rh(CO)(PPh_3)_3]ClO_4$ (**3**) (0.1 mmole) at 45 °C under Nitrogen

Catalyst	Solvent	Time, (hr)	Yield (%)
2	$CDCl_3$(0.5 m*l*)	32	100
3	$CDCl_3$(0.5 m*l*)	24	100
2	$CDCl_3$(0.4 m*l*) + CD_3OD(0.1 m*l*)	5	100
3	$CDCl_3$(0.4 m*l*) + CD_3OD(0.1 m*l*)	3	100
2	$CDCl_3$(0.4 m*l*) + CD_3COCD_3(0.1 m*l*)	15	100
3	$CDCl_3$(0.4 m*l*) + CD_3COCD_3(0.1 m*l*)	10	100