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Decay Mechanism of the Aromatic Hydrocarbon Biradical, 1,1′-Biacenaphthene-2,2′-diyl. Effects of Solvent and Heavy-atom Perturbation

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Effects of solvents and heavy-atom (H–A) containing compounds on the lifetime of the title biradical (**1**) have been examined to elucidate the decay mechanism of **1** in fluid solutions by means of nanosecond laser spectroscopy. **1** was quenched effectively by H–A compounds such as diethylmercury and iodoethane. The decay rates of **1** showed no explicit correlation with solvent polarities, while a linear correlation was found between the decay rate and the sum of squares of the spin-orbit (S–O) coupling factors of heavy atoms involved in the solvents; chlorobezene, 1,2-dichloroethane, dichloromethane, bromobenzene, and dibromomethane. It has been shown that (i) the biradical lifetime is determined by intersystem crossing (ISC) from the triplet to singlet spin state prior to chemical reactions, (ii) ISC is enhanced by H–A perturbation through the S–O interaction, and (iii) the reactivity of the singlet biradical (^{1}**1**) but not the triplet one (^{3}**1**) sways the product distribution in the triplet-sensitized photodimerization of acenaphthylene.

Since a direct detection of Norrish type II biradicals in fluid solution,[1] dynamic properties of these biradicals have been studied considerably.[2] However, our knowledges about dynamic behavior of aromatic hydrocarbon biradicals have been still scarce in comparison with those for type II biradicals.[3]

Previously we reported an observation of aromatic hydrocarbon biradical **1** as an intermediate in the triplet-sensitized photocycloreversion of trans-dimer (t-D) of acenaphthylene.[4] The biradical **1** is also supposed as an intermediate for the triplet-sensitized photodimerization of acenaphthylene (A).[5,6] This reaction is known to be a typical example of a photochemical H–A effect[7] and to undergo a significant effect of solvent polarity.[6] Therefore, examinations of solvent and H–A effects on the biradical lifetime may be favorable for elucidating the decay behavior of **1** in relation to the dimerization reaction.

This paper deals with a nanosecond laser photolysis study of the biradical **1** under the influence of H–A compounds and solvents with various polarities, in order to clarify the decay mechanism of **1** having a characteristic structure different from the type II biradicals. It was of interest whether the decay rate of a triplet biradical would be determined by a chemical reaction or by ISC prior to chemical reactions. We here make it clear that the decay of **1** proceeds *via* the latter mechanism. We also intend to relate quantitatively the decay rates of **1** to the S–O interaction factors, because the already-known results of H–A effects on biradicals are only qualitative.[1a,3a] The present results show an explicit correlation between them, indicating that the decay rate is enhanced by H–A compounds through the S–O interaction. At the same time, a complex formation between **1** and EtI is proposed and a role of the biradical in the dimerization reaction is also discussed.

Experimental

Materials. The trans-dimer of acenaphthylene (t-D) and benzophenone (BP) were the same as those reported previously.[4] Benzene, toluene, 1,4-dioxane, and acetone were all spectrograde reagents (Dotite). Dibromomethane (Wako, GR grade) was used without further purification. Dichloromethane, 1,2-dichloroethane, chlorobenzene, bromobenzene, pyridine, and acetonitrile were purified by the usual methods. Iodoethane (Wako, GR grade), diethylmercury (Wako, CP grade), and diethyl sulfide (Wako, EP grade) were distilled under vacuum just before use.

Nanosecond Laser Photolysis. The 1,1′-biacenaphthene-2,2′-diyl (**1**) was observed by a nanosecond laser photolysis method at 347 nm.[4] The solutions used contained both t-D ($\geq 2\times10^{-3}$ mol dm^{-3}) and BP ($\approx 4\times10^{-3}$ mol dm^{-3}) as a triplet sensitizer. The lifetime of **1** was measured by monitoring the time-dependent intensity of its characteristic absorption band at 380 nm. When the absorption band of **1** was overlapped by a long-lived absorption of byproduct, *e.g.*, benzophenone ketyl radical, the interference absorption at 380 nm was subtracted from the observed absorption to obtain a true decay time of **1**. The quenching experiments of **1** by Et_2Hg, EtI, and Et_2S were performed in benzene solutions. All solutions were degassed by the usual freeze-pump-thaw method. The lifetime measurements were performed at 20±1 °C.

Results and Discussion

Transient Absorption Spectra. Before examination of the external solvent effects, transient absorption spectra of **1** were observed in each solvent at room temperature. The typical spectra are illustrated in Fig. 1. Figure 1a is the previously observed spectra in benzene given for comparison.[4] Figure 1b shows time-resolved absorption spectra observed in dichloromethane. The spectral profiles resemble well those given in Fig. 1a. Namely, in the early stage of time after excitation, absorption bands due to ^{3}BP and ^{3}t-D are observed around 530 and 450 nm respectively. Both bands decay rapidly and a strong absorption band grows around 380 nm. This is the characteristic absorption band of **1** (Fig. 1b-2). This band decays with the first-order kinetics. Figure 1c pictures the transient spectra in 1,4-dioxane. The absorption of **1** is observed also around 380 nm. In this case, a distinct absorption band with maximum at 545 nm still remains after disappearance of **1**. The absorption band monitored at 545 nm

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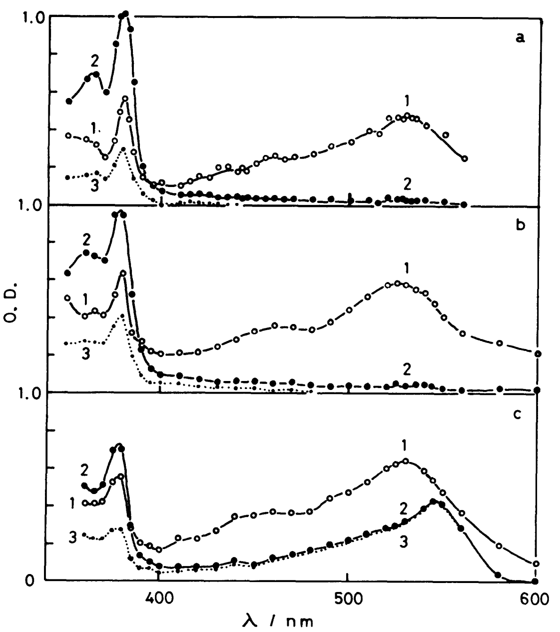

Fig. 1. Transient absorption spectra observed in the BP–t-D system. Solvent and delay time after the beginning of laser oscillation:
a) Benzene; (1) 40 ns, (2) 230 ns, (3) 730 ns, b) dichloromethane; (1) 40 ns, (2) 260 ns, (3) 660 ns, c) 1,4-dioxane; (1) 60 ns, (2) 280 ns, (3) 660 ns.

decayed slowly with the second-order kinetics. This long-lived transient can be identified to benzophenone ketyl radical (BPH·) from comparing the spectrum and decay kinetics with those of BPH· in the literatures.[8] The BPH· observed here is not a transient produced by a reaction between **1** and BP, because the absorbance of BPH· around 545 nm does not increase as the absorbance of **1** at 380 nm decreases during the time interval 280—660 ns (Fig. 1c). Furthermore, if BP in the ground state caused H-atom abstraction from ^{3}t-D, the abstraction reaction should occur in benzene or in dichloromethane as well. But no BPH· absorption is observed in these solvents (Figs. 1a and b). The BPH·, therefore, is not also a transient originated from the reaction between ^{3}t-D and BP. It is considered that BPH· forms through H-abstraction reaction by ^{3}BP from the solvent 1,4-dioxane which is a fairly good H-donor.[9] Because BPH· disappears much slower than **1**, the decay of BPH· is negligible in the time range required to analyze the biradical lifetime (τ_B). Then, the value of τ_B in 1,4-dioxane can be estimated by a simple procedure in which the absorbance of BPH· ($D_{BPH\cdot}$) is subtracted from the observed absorbance (D_{obsd}) using the following equation:

$$D_{obsd} - D_{BPH} = (D^0_{obsd} - D_{BPH\cdot})\exp(-t/\tau_B),$$

where D^0_{obsd} is the observed absorbance at the time origin arbitrarily taken in the time domain where the decay curve is exponential.

Quenching of 1 by H–A Containing Compounds. Figures 2a, 2b, and 2c present the Stern-Volmer plots of lifetimes against concentrations of the quenchers Et_2Hg, EtI, and Et_2S, respectively, in benzene. The quenching by Et_2Hg shows a good linear relation

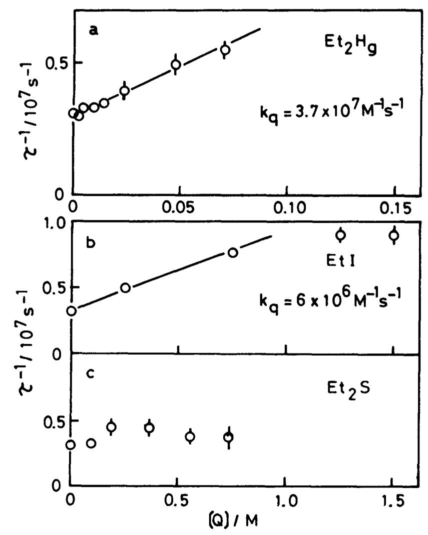

Fig. 2. Stern-Volmer plots of the inverse lifetime τ^{-1} *vs.* quencher concentration [Q]. The quencher Q: a) Et_2Hg, b) EtI, c) Et_2S. (1 M = 1 mol dm^{-3})

with the rate constant k_q: 3.7×10^7 dm^3 mol^{-1} s^{-1} (Fig. 2a). The quenching curve by EtI approaches gradually the maximum value near *ca.* 1×10^7 s^{-1} with increasing [EtI]. In the range of [EtI]<1 mol dm^{-3} the curve can be approximated by a straight line corresponding to k_q: *ca.* 6×10^6 dm^3 mol^{-1} s^{-1}. This line is added into Fig. 2b. Figure 2c indicates that Et_2S is not an effective quencher for **1**. Thus, the quenching efficiencies correspond to the order of magnitude of the atomic number of heavy atoms (Hg, I, and S) in the quenchers, suggesting that the quenching events are caused by external H–A effect.

The nonlinearity of the Stern-Volmer plots, as shown in Fig. 2b, has been frequently observed in the high concentration region of quenchers (>1 mol dm^{-3}). As for the quenching mechanism there are some interpretations in terms of the decrease of the activity coefficients of quenchers,[10] the change of radiationless transition induced by change of solvent composition,[11] and the formation of ground- or excited-state complex.[12,13] In recent studies the exciplex mechanism appears to be an appropriate one to the H–A effect of EtI on the quenching of both excited singlet and triplet states of aromatic hydrocarbons.[14,15] Since **1** is composed of aromatic hydrocarbon moieties similar to chromophores in the exciplex forming systems noted above, a weak complex formation may be expected between **1** and EtI. We attempted to analyze the quenching curve for EtI from a view point of the complex formation, although no explicitly spectral evidence indicating the complex formation was observed up to the heighest concentration (2.5 mol dm^{-3}) of EtI so far as we examined.[16] The quenching curve bending downward suggests the existence of the so-called dynamic equilibrium[17] represented as follows:

$$\begin{tikzcd} \mathbf{1} + \mathrm{EtI} \arrow[r, shift left, "k_a"] \arrow[dl, "\tau_B^{-1}"] & \mathbf{1} \cdots \mathrm{EtI}, \arrow[l, shift left, "k_b"] \arrow[dr, "\tau_C^{-1}"] & {} \\ {} & {} & {} \end{tikzcd} \qquad (1)$$

where τ_B and τ_C are the lifetimes of **1** in the absence of EtI and the complex **1**···EtI respectively, k_a and k_b are the rate constants of association and dissociation processes respectively, and the equilibrium constant K is defined by k_a/k_b. When the dynamic equilibrium condition,

$$k_a[\mathrm{EtI}],\ k_b \gg \tau_B^{-1},\ \tau_C^{-1}, \qquad (2)$$

holds completely, the apparent lifetime (τ) of **1** in the presence of EtI should satisfy the following two relations expressed by Ware *et al.*[18] and Rayner and Wyatt[19] respectively:

$$(\tau^{-1}-\tau_B^{-1})^{-1} = (\tau_C^{-1}-\tau_B^{-1})^{-1}(1+K^{-1}[\mathrm{EtI}]^{-1}), \qquad (3)$$

and

$$[\mathrm{EtI}]^{-1}(\tau^{-1}-\tau_B^{-1}) = K(\tau_C^{-1}-\tau^{-1}). \qquad (4)$$

Although both equations are derived from the same kinetic assumption (Eq. 2), Eq. 3 is sensitive to τ values in the relatively low concentration region of the quencher and Eq. 4 reflects rather well the variation in τ in the relatively high concentration region. Figures 3a and 3b show the relations corresponding to Eqs. 3 and 4 respectively for the lifetimes (τ) measured at 8 different concentrations of EtI in the range of 0.25—2.5 mol dm^{-3}. Both equations fit well the experimental results. The values of K 0.64±0.06 dm^3 mol^{-1} and τ_C 65± 5 ns are obtained from Fig. 3a and K 0.72±0.09 dm^3 mol^{-1} and τ_C 69±13 ns are obtained from Fig. 3b. A good agreement in each K and τ_C values estimated from the two different kinetic expressions suggests strongly the existence of **1**···EtI in the equilibrium as indicated in Eq. 1. The complex formation contributes to enhancement of the biradical decay through the S-O interaction as is indicated later.

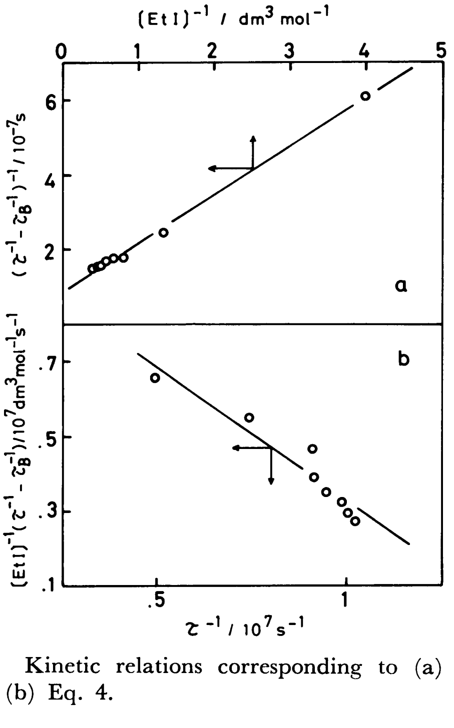

Fig. 3. Kinetic relations corresponding to (a) Eq. 3 and (b) Eq. 4.

Table 1. Decay times of **1** in various solvents at 20 °C

Solvent	ε	$\Sigma\zeta^2/10^6\ \mathrm{cm}^{-2}$	τ_B/ns
1,4-Dioxane	2.21		270
Benzene	2.28		300
Toluene	2.38		290
Bromobenzene	5.39	6.05	152
Chlorobenzene	5.71	0.34	289
Dibromomethane	7.04	12.1	84
Dichloromethane	8.93	0.69	295
1,2-Dichloroethane	10.66	0.69	350
Pyridine	13.23		290
Acetone+1,2-Dichloroethane (1 : 1 in volume)	15.7[a]		380
Acetonitrile+Benzene (1 : 1 in volume)	24.6[a]		310

a) The values of mixed solvents are obtained by assuming additivity: $\varepsilon_{\mathrm{mix}}=\Sigma\chi_i\varepsilon_i$, where χ_i is the molar fraction and ε_i corresponds to ε of i-th component solvent.

Effects of H-A Solvents and Solvent Polarities. Table 1 lists the values of biradical lifetimes (τ_B) measured in several solvents together with those of dielectric constant (ε) of the solvents. The errors in τ_B values are *ca.* 10%. The mixed solvents were employed as highly polar solvents because of low solubility of t-D in neat acetone or acetonitrile. For H-A solvents of bromobenzene, chlorobenzene, dibromomethane, dichloromethane, and 1,2-dichloroethane the sum of squares of S-O interaction factors (ζ) of halogen atoms involved in the solvents are additionally given in Tabel 1.[20] The $\Sigma\zeta^2$ values are a measure of the magnitude of transition probability induced by S-O interaction; $k_{\mathrm{ISC}}\propto\langle{}^1\phi|H_{\mathrm{SO}}|{}^3\phi\rangle^2\propto\Sigma\zeta^2$, where k_{ISC} is the probability of ISC induced by heavy atoms and $\langle{}^1\phi|H_{\mathrm{SO}}|{}^3\phi\rangle$ is the S-O coupling matrix element between singlet and triplet states.

The τ_B values in the H-A solvents decrease with the order of 1,2-dichloroethane, dichloromethane, chlorobenzene, bromobenzene, and dibromomethane. This tendency is parallel to that for the quenching rate constants in the addition effect of H-A compounds. To show this effect quantitatively, Fig. 4 illustrates a relation between τ_B^{-1} and $\Sigma\zeta^2$. There exists a linear relation. Therefore, it is evident that the S-O interaction is the origin of the H-A solvent effect enhancing the decay rate of **1**. Although the compounds involving Cl- or S-atom show no recognizable H-A effect, this seems due to much smaller S-O interaction factors of these atoms than those of Br- and I-atoms.

Next we notice the effect of solvent polarity on the lifetime. The τ_B values in Table 1 do not show any appreciable correlation with solvent polarities and are close to one another except for the lifetimes in bromobenzene and dibromomethane (H-A solvents). Accordingly, the biradical lifetimes can be regarded to be almost independent on solvent polarity. In contrast, it is known that a lifetime of the Norrish type II biradical **2** derived from 4-methyl-1-phenyl-1-pentanone depends strongly on the polarity and hydrogen-bonding strength of solvents.[1a,2a] Such influence of H-bonding ability is not found for the case of **1**. These different

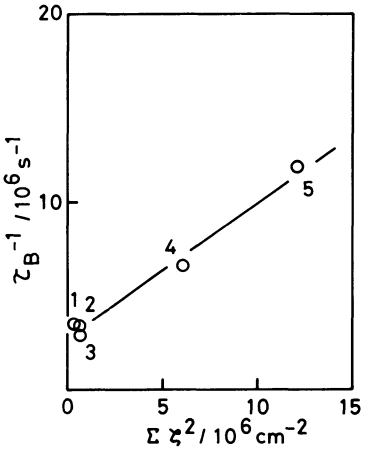

Fig. 4. The relation between the inverse lifetime of **1** (τ_B^{-1}) and the S–O interaction parameter ($\sum\zeta^2$); 1) chlorobenzene, 2) dichloromethane 3) 1,2-dichloroethane, 4) bromobenzene, and 5) dibromomethane.

features between **1** and **2** as to the solvent effects seem to arise from difference in their molecular structures. That is, **1** has a structure composed of two identical aromatic π-radical sites with no or weak H-bonding property but **2** consists of two different radical sites one of which has a hydroxyl group to cause readily H-bonding with basic solvents. Besides **1** would have a smaller dipole moment than **2**. Therefore, it is understood that **1** is less sensitive to the solvent polarity as well as H-bonding ability.

Decay Mechanism of 1 and Photodimerization of Acenaphthylene. A previous report[4)] demonstrated that (i) **1** is a triplet-derived biradical with a fairly long life, (ii) its decay rate is approximately temperature-independent, (iii) the frequency factor of an Arrhenius plot for the decay rate constant is so small ($1.9\times10^6\,s^{-1}$ in benzene) as to suggest a spin-forbidden nature of the decay process, and (iv) **1** is quenched by oxygen, a paramagnetic molecule, with a nearly diffusion-controlled rate constant $0.9\times10^{10}\,dm^3\,mol^{-1}\,s^{-1}$ in benzene at 20 °C. These properties of **1** resemble quite well those of familier triplet state type II biradicals. From these knowledges, **1** has been ascribed to be a biradical in the triplet spin state (^{3}**1**). We here discuss the decay mechanism of ^{3}**1** relating the mechanism of photodimerization of A on the basis of the previously-mentioned results together with already-known results of the photodimerization reaction.

In an examination of solvent effect on the triplet-sensitized dimerization of A, it has been reported that the logarithm of the ratio between the yields of the products t-D and c-D, log[t-D]/[c-D], correlates linearly with the Kirkwood-Onsager parameter $(\rho/M)(\varepsilon-1)/(2\varepsilon+1)$ where ρ is the solvent density and M is the molecular weight of solvent.[6,21)] Nevertheless, as seen from Table 1, the decay rate of ^{3}**1** is not governed by the above relation and other solvent polarity parameters. It turns out, therefore, that ^{3}**1** does not concern directly the reaction steps determining the product distribution of c- and t-D. Since the τ_B values are approximately unaltered in the several kinds of light-atom solvents, it is supposed that ^{3}**1** does not react directly with the solvents. The validity of this supposition may be justified by the fact that the material balance of the dimerization reaction is approximately 100% in several solvents; cyclohexane, benzene, and methanol.[5)] Because byproduct formation is negligible even in the H-A solvent, 1-bromopropane,[5,22)] it may be also plausible that the biradical quenching by the H-A perturbers is not due to chemical reactions between ^{3}**1** and the perturbers. The spin-allowed dissociation of $^3\mathbf{1}\rightarrow{}^3A^*+A$ is thermally forbidden, so that this process is difficult to take place. ^{3}**1** is considered to exist in the potential minimum, *i.e.*, the relaxed state, since its lifetime was observably long. Then, a fairly high activation energy (at least, a few kcal mol^{-1}) would be required for the biradical decay if ^{3}**1** caused spin inversion concomitantly with bond beaking (*i.e.*, $^3\mathbf{1}\rightarrow 2A$) in which ^{3}**1** must be activated thermally in the triplet state potential surface to take a conformation favorable for the dissociation yielding 2A. However, no activation energy was observed for the decay rate of ^{3}**1** in benzene.[4)] Therefore, the spin-forbidden process of $^3\mathbf{1}\rightarrow 2A$ does not seem to participate in the radiationless decay of ^{3}**1**. Hence, the lifetime of ^{3}**1** must be determined by the rate of ISC as a physical process from the triplet to the singlet spin state (^{1}**1**) both in the presence and absence of the perturbers (X). The most reasonable decay routes of ^{3}**1** can be represented as follows:

$$ {}^3\mathbf{1} \xrightarrow[(+X)]{\text{ISC}} {}^1\mathbf{1} \begin{array}{l} \nearrow \text{c-D} \\ \rightarrow \text{t-D}, \\ \searrow 2A \end{array} \qquad (5) $$

where ^{1}**1** decays so rapid as unable to be observed by the nanosecond laser photolysis. Since ^{3}**1** involves no decay process other than ISC, the increase in the rate of ISC induced by the H-A compounds does not lead to increase in the total yield of the dimers in the triplet-sensitized dimerization reaction. This suggestion is consistent with the previous results that a kinetic analysis for the yield of the dimers can be treated without regard to the enhancement of biradical spin relaxation and hence H-A solvents may act only as solvents with certain polarities on the product distribution.[22,23)]

It is known that the quantum yields for directly excited photodissociation of c- and t-D, which are assumed to dissociate via respective biradical states in the singlet multiplicity,[24,25)] are different from each other.[25–27)] These results imply that the reactivity of ^{1}**1** depends strongly on its conformation immediately after generation. Such importance of biradical conformation in determining product distribution has been proposed for type II biradicals.[2b,28)] On the other hand, the present result regarding effect of solvent polarity suggests that the conformations of ^{3}**1** in various solvents are not so much different from one another as to vary the ISC rate depending on difference of solvent polarities, since the rate of ISC is determined normally by the magnitude of S–O interaction matrix element which is sensitive to conformation of a biradical. Such circumstance would be the case for ^{3}**1** at the moment when ISC occurs. If the conformation does not change during ISC, the conformations of ^{1}**1** immediately after generation would be nearly identical to one another in different solvents as the case for ^{3}**1** is so. Therefore, it may be thought that the product distribution of c- and t-D is swayed by the solvent-dependent rate constants of ^{1}**1** producing c- and t-D but not by difference in the conformations of ^{1}**1** immediately after generation.[29] However, further study about dynamic nature of the short-lived singlet biradical ^{1}**1** will be needed to elucidate a detailed mechanism of the solvent effect on the product distribution.

It has been pointed out that two types of spin inversion concerning the mechanism of ISC in a triplet biradical are assumed: One is a spin inversion leading to singlet biradical prior to chemical reactions (Mechanism I) and the other is a spin inversion occuring concurrently with reactions to yield some products of the singlet state (Mechanism II).[30] In the present case, it is clear that ISC corresponds to Mechanism I, since no direct chemical reaction occurs in the triplet biradical while the singlet biradical may be an actual intermediate which plays an essential role in determining the product distribution.

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