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Mechanistic Approach to the Sensitization Process of Aromatic Ketones in the Isomerization between Norbornadiene and Quadricyclane

Tatsuo ARAI,* Takahisa OGUCHI, Toshio WAKABAYASHI, Masahiro TSUCHIYA, Yoshinobu NISHIMURA, Shigero OISHI,†,§ Hirochika SAKURAGI, and Katsumi TOKUMARU*
Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki 305
†Sagami Chemical Research Center, Sagamihara, Kanagawa 229

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The quantum yields for norbornadiene(N) → quadricyclane(Q) and Q → N isomerization were determined in acetonitrile using several substituted benzophenones (BPs) as triplet sensitizers. For the N → Q isomerization, BPs with electron-donating substituents exhibited higher quantum efficiency (0.4—0.6) than BPs with electron-accepting substituents. The quantum yields for Q → N isomerization increased with electron-accepting ability of the substituents on BPs, but were lower than 0.1. The rate constants for quenching of triplet BPs by N and Q were also determined in acetonitrile by means of laser flash photolysis. The rate constants for N were not dependent on the triplet energies (E_T) of BPs but dependent on electronic properties of the substituents on BPs. On the contrary, those for Q increased with decreasing E_T of BPs and with increasing Hammett's σ constants of the substituents of BPs. Based on these observations an addition-elimination process is proposed for the N → Q isomerization, and an electron transfer process for the Q → N isomerization.

Recently much attention has been paid to isomerization of norbornadiene (N) to quadricyclane (Q) under solar light irradiation to accomplish molecular storage of energy.$^{1-3)}$ One of the problems of this system is that N absorbs only light in the UV region. In order to utilize solar irradiation efficiently, two ways of approach have been attempted. The first one using N itself, which is readily supplied as a petrochemical product, employs either sensitizers or reagents capable of forming a complex with N to absorb longer-wavelength light than does N.$^{1-4)}$ The second is to use substituted norbornadienes exhibiting absorption at much longer wavelengths than N.$^{5-7)}$

As for the first approach, benzophenones (BPs) and some other aromatic ketones are known to sensitize N → Q isomerization with light longer than 300 or 350 nm.$^{8)}$ However, there remain some questions regarding the sensitization mechanism. It is still unclear whether the isomerization of N and Q proceeds through energy transfer from sensitizer or not.

Another problem of this system is consumption of the sensitizer ketones during irradiation due to the formation of addition products. It is desirable to find suitable sensitizers which solely bring about the N → Q isomerization but are not seriously consumed by addition to N or Q.

From these viewpoints we have made a mechanistic approach to the sensitizing ability of substituted BPs for N → Q and Q → N photoisomerization.$^{9)}$ In this paper we report effects of structural factors of sensitizer ketones on the isomerization efficiency, and propose an addition-elimination mechanism for the BP sensitized N → Q isomerization and an electron-transfer interaction in the quenching of triplet BPs by Q, on the basis of the quantum yields, of the quenching rate constants measured in laser flash photolysis, and of the time profile of the isomerization and adduct formation.

Experimental

Norbornadiene (N) and quadricyclane (Q) were purchased from Aldrich Chemical Co., and purified by distillation. Solvent acetonitrile was Luminasol from Dojin Chemical Co. 4-Cyanobenzophenone was prepared according to the literature.$^{10)}$ Other substituted benzophenones were purchased from Wako or Nakarai Chemical Co. All the benzophenones were crystallized from methanol, ethanol, hexane, or diethyl ether.

The phosphorescence spectra of some sensitizers were measured on a Hitachi MPF-2A fluorescence spectrophotometer and the triplet energies were determined.

The redox potentials of N, Q, and sensitizers were determined by cyclic voltammetry in acetonitrile with respect to an SCE in the presence of 0.1 mol dm^{-3} tetraethylammonium perchlorate as a supporting electrolyte.

Isomerization quantum yields were determined using potassium tris(oxalato)ferrate(III) actinometry. Benzophenone sensitized N → Q isomerization was carried out in Pyrex tubes with 366 nm light through a UVD-36B glass filter from a 400 W high pressure mercury lamp under nitrogen atmosphere. The conversions were determined by gas chromatography, a Shimadzu GC-4CM PF gas chromatograph equipped with an FID.

Laser flash photolyses were performed as described elsewhere.$^{11)}$ Sample solutions were deaerated by bubbling with nitrogen for 30 min. The first order decay rate constants (k_{obs}) of triplet benzophenones were measured as a function of N or Q concentration by monitoring their T-T absorptions around 530 nm, and the quenching rate constants (k_q^N and k_q^Q) were obtained from linear plots based on the following equation:

$$k_{obs} = \tau_T^{-1} + k_q^S[S], \quad S = N \text{ or } Q.$$

Results

Quantum Yields for N → Q and Q → N Isomerization. The quantum yields for sensitized isomerization of N (0.1 mol dm^{-3}) and Q (0.1 mol dm^{-3}) were determined at low

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[§] Present address: Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

Table 1. Quantum Yields for N→Q Isomerization ($\Phi_{t\to c}$) in Acetonitrile[a)]

Sensitizer	E_T[b)] kcal mol^{-1}	$\Phi_{N\to Q}$	$\Phi_{Q\to N}$	$\Sigma\sigma$[c)]
4,4′-Dimethoxybenzophenone (**1**)	70.3	0.56	0.05	−0.54
4,4′-Dimethylbenzophenone (**2**)	69.3	0.59		−0.34
4-Methylbenzophenone (**3**)	69.2	0.50		−0.17
Benzophenone (**4**)	69.2	0.45	0.06	0
3-Benzoylpyridine (**5**)	69.0	0.36		
4-Methoxybenzophenone (**6**)	69.0	0.53		−0.27
4-Chlorobenzophenone (**7**)	68.8	0.29		0.23
4,4′-Dichlorobenzophenone (**8**)	68.4[d)]	0.29		0.46
4-Hydroxybenzophenone (**9**)	68.3[d)]	0.42		−0.37
2-Benzoylpyridine (**10**)	67.4	0.35		
4-Benzoylpyridine (**11**)	67.2	0.40		
4-Cyanobenzophenone (**12**)	67.0[d)]	0.33	0.10	0.66
Triphenylene (**13**)	66.5	0.02		
Michler's ketone (**14**)	62	0.04		
4-Phenylbenzophenone (**15**)	60.7	0.23		
Benzil (**16**)	54.3	0.009		

a) Concentration of N, 0.1 mol dm^{-3}. b) Triplet excitation energies of sensitizers taken from Ref. 12, unless otherwise indicated. c) Hammett's sigma constants for substituted benzophenones (O. Exner, "Advances in Linear Free Energy Relationships," ed by N. B. Chapman and J. Shorter, Plenum (1972)). d) Estimated from phosphorescence spectra measured in EPA at 77 K.

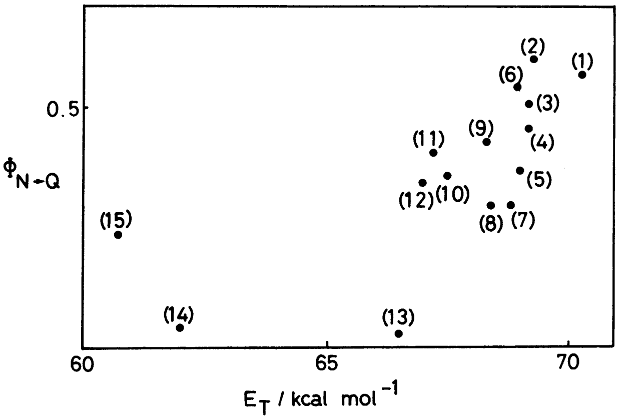


Fig. 1. Plots of isomerization quantum yields ($\Phi_{N\to Q}$) against the triplet energies (E_T) of sensitizers. The numerals refer to the sensitizers in Table 1.

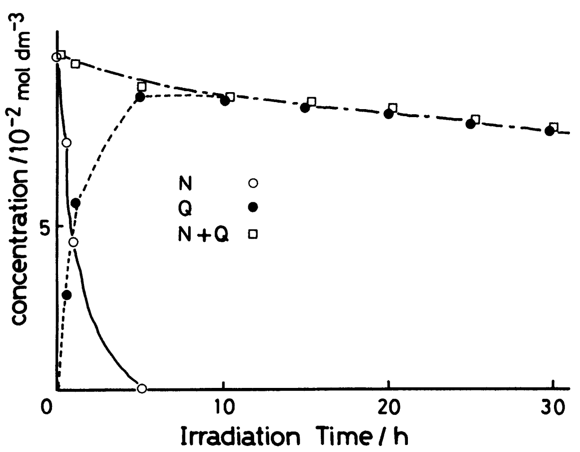


Fig. 3. Irradiation time dependence of concentrations of N, Q, and N+Q in a degassed acetonitrile solution containing 4,4′-dimethoxybenzophenone (0.1 mol dm^{-3}) and N (0.1 mol dm^{-3}).

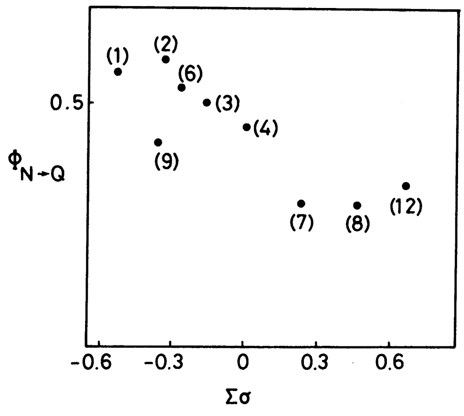


Fig. 2. Plots of isomerization quantum yields ($\Phi_{N\to Q}$) against Hammett's sigma constants. The numerals refer to the sensitizers in Table 1.

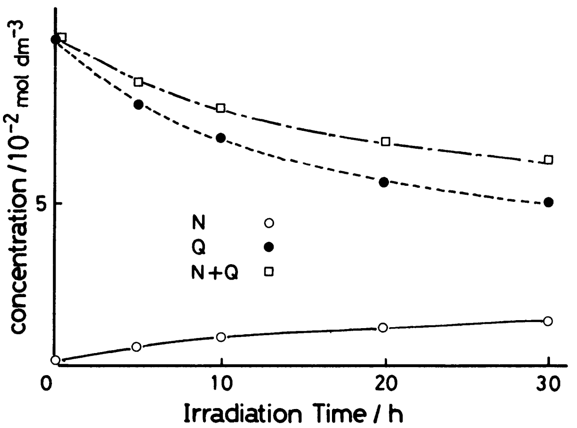


Fig. 4. Irradiation time dependence of concentration of N, Q, and N+Q in a degassed acetonitrile solution containing 4,4′-dichlorobenzophenone (0.1 mol dm^{-3}) and Q (0.1 mol dm^{-3}).

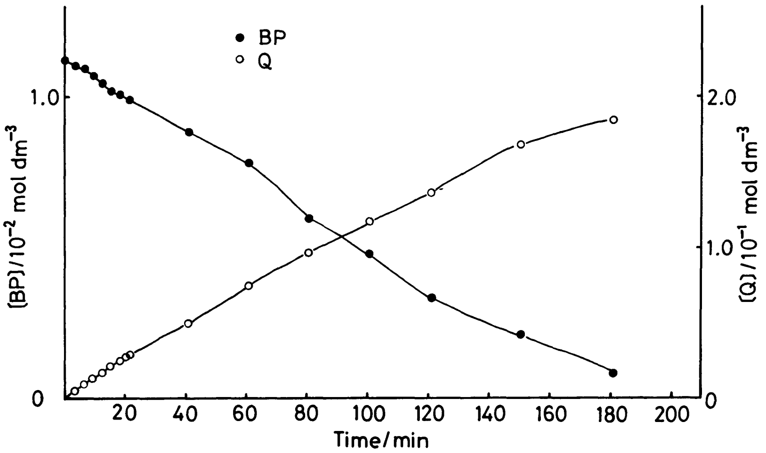


Fig. 5. Time dependence of concentrations of Q and benzophenone in neat N.

Table 2. Quenching Rate Constants of Substituted Benzophenones by Norbornadiene and Quadricyclane

Sensitizer	E_{red}	E_T	$(E_{red}+E_T)$	k_q^N	k_q^Q	ΔG_N° a)	ΔG_Q° b)
	V vs. SCE	eV	eV	mol^{-1}dm^{3}s^{-1}	mol^{-1}dm^{3}s^{-1}	eV	eV
4,4′-Dimethoxybenzophenone (**1**)	−2.01	3.05	1.04	2.02X10^9	2.04X10^8	0.75	0.01
4,4′-Dimethylbenzophenone (**2**)	−1.96	3.01	1.05	1.62X10^9	6.09X10^8	0.74	0
4-Methoxybenzophenone (**6**)	−1.88	2.99	1.11	2.81X10^9	9.50X10^8	0.68	−0.06
Benzophenone (**4**)	−1.82	3.00	1.18	6.44X10^8	8.78X10^8	0.61	−0.13
4-Chlorobenzophenone (**7**)	−1.73	2.98	1.25	2.35X10^9	3.02X10^9	0.54	−0.20
4,4′-Dichlorobenzophenone (**8**)	−1.67	2.97	1.30	2.35X10^9	3.86X10^9	0.49	−0.25
4-Bromobenzophenone (**17**)	−1.65	2.99	1.34	1.84X10^9	3.43X10^9	0.45	−0.29
4-Benzoylpyridine (**11**)	−1.56	2.91	1.35	1.14X10^9	2.37X10^9	0.46	−0.28
4-Cyanobenzophenone (**12**)	−1.48	2.91	1.43	2.46X10^9	6.53X10^9	0.38	−0.36

a) $\Delta G_N^{\circ}=E_{ox}(N)-(E_{red}+E_T)-0.06$. b) $\Delta G_Q^{\circ}=E_{ox}(Q)-(E_{red}+E_T)-0.06$.

conversion using several BPs and other triplet sensitizers (0.1 mol dm^{-3}) in deaerated acetonitrile solutions. The results are summarized in Table 1 together with the triplet excitation energies (E_T) of sensitizers employed and Hammett's σ constants ($\sum\sigma$) of the substituents on BPs. Figure 1 plots the quantum yields against E_T of the sensitizers and Fig. 2 plots the quantum yields against Hammett's σ constants of the substituents on BPs. The quantum yield of N → Q isomerization in neat N was also determined on sensitization with benzophenone (1.12X10^{-2}mol dm^{-3}) to be 0.9.

Reaction of Triplet Benzophenones with N and Q. To see the consumption of N and Q clearly, benzophenone (BP), 4,4′-dimethoxybenzophenone [$(MeO)_2BP$], and 4,4′-dichlorobenzophenone (Cl_2BP) were used in extremely high initial concentrations, the same concentration as N or Q (0.1 mol dm^{-3}). Figures 3 and 4 depict typical results starting from N and Q, respectively. BPs examined induced the N → Q isomerization with a rate decreasing in a sequence of $(MeO)_2BP$, BP, and Cl_2BP, which is in parallel to their sensitized N → Q isomerization quantum yields in the initial stage (Table 1). Starting from both Q and N, the total amount of Q+N decreased most remarkably in the presence of Cl_2BP and to a least extent in the presence of $(MeO)_2BP$. On irradiation of BP (1.12X10^{-2} mol dm^{-3}) in neat N, particular attention was paid to follow the reaction with frequent intervals in the early stage. Figure 5 shows the results.

Table 3. Triplet Energies of Sensitizers (S) and Energies of Intermediates over the Ground States of the Sensitizers and N (or Q)[a)]

Sensitizer	E_T b)	$E(S^{-\cdot}\cdots Q^{+\cdot})$	$E(S^{-\cdot}\cdots N^{+\cdot})$
1	3.05	3.12	3.86(2.86)
2	3.01	3.07	3.81(2.81)
6	2.99	2.99	3.73(2.73)
4	3.00	2.93	3.67(2.67)
7	2.98	2.84	3.58(2.58)
8	2.97	2.78	3.52(2.52)
17	2.99	2.76	3.50(2.50)
11	2.91	2.67	3.41(2.41)
12	2.91	2.59	3.33(2.33)
Chloranil	2.69 c)	1.10	1.84(0.84)

a) In eV. In parentheses are indicated those for $S^{-\cdot}$ and $N^{+\cdot}$ based on the energies of the sensitizers and Q. b) See footnote in Table 1. c) From Ref. 28.

Quenching Rate Constants of Triplet Sensitizers by N and Q. The quenching rate constants of the BPs triplets by N and Q measured in acetonitrile by means of laser flash photolysis are summarized in Table 2. All the benzophenones examined here have nπ^* character in the triplet state.[10b)] This table also lists redox potentials measured in acetonitrile, and the change in the Gibbs function (ΔG°) for electron transfer from N or Q to BPs triplets estimated according to Eq. 1.

$$\Delta G^\circ/\text{eV}=E_{ox}-E_{red}+z_1z_2e^2/\varepsilon r-E_T \qquad (1)$$

The redox potentials E_{ox} and E_{red} refer to E ($N^{+\cdot}/N$) or E ($Q^{+\cdot}/Q$) and E ($BP/BP^{-\cdot}$), respectively, and the term $z_1z_2e^2/\varepsilon r$ represents the Coulombic energy associated with bringing separated radical ions of charges z_1 and z_2 at the encounter

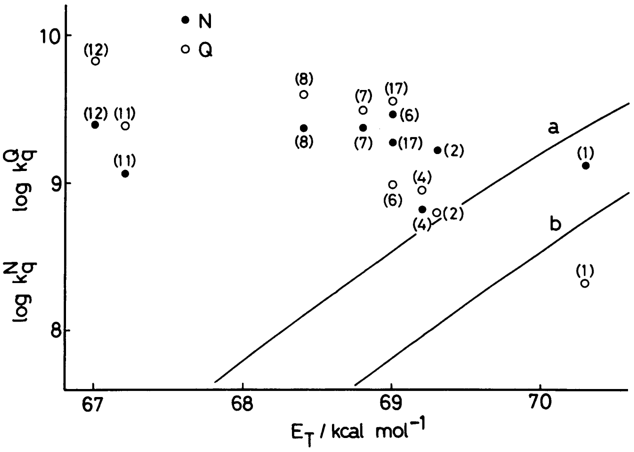


Fig. 6. Plots of quenching rate constants of triplet benzophenones by norbornadiene (k_q^N) and quadricyclane (k_q^Q) vs. triplet energies of benzophenones (E_T). Curves a and b are calculated by Eq. 2 assuming E_T(N)=70 and 72 kcal mol^{-1}, respectively.

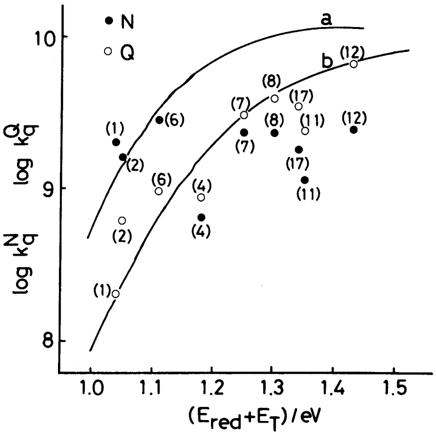


Fig. 8. Plots of quenching rate constants of triplet benzophenones by norbornadiene (k_q^N) and quadricyclane (k_q^Q) vs. E_{red}+E_T of benzophenones. Curves a and b are calculated according to Eq. 3 assuming $\Delta G^{\circ\neq}(0)$=2.4 and 3.5 kcal mol^{-1}, respectively.

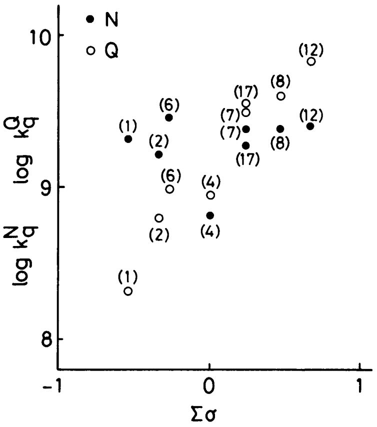
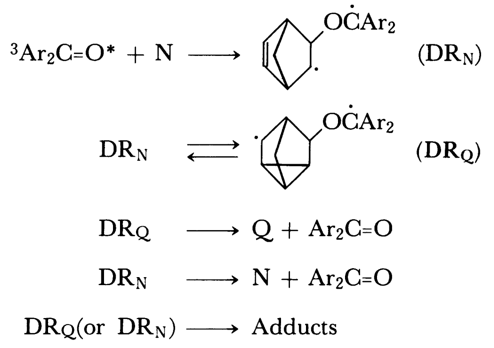


Fig. 7. Plots of quenching rate constants of triplet benzophenones by norbornadiene (k_q^N) and quadricyclane (k_q^Q) vs. Hammett's sigma constants of substituents on benzophenones.



Scheme 1.

distance r in a solvent of dielectric constant ε.[13] The oxidation potentials of Q and N are 1.10 and 1.85 V, respectively, with respect to SCE. The energies of the ion pairs, as calculated as $E_{ox}-E_{red}$ are shown in Table 3. Figures 6 and 7 show logarithmic plots of the quenching rate constants (k_q^N and k_q^Q) against E_T and Hammett's σ constants of BPs, respectively. The plots of log k_q^N and log k_q^Q against the reduction potentials of triplet BPs, as estimated as E_{red}+E_T, are illustrated in Fig. 8.

Discussion

Isomerization of N to Q. Three mechanisms are possible for the sensitization of isomerization of N: 1) Triplet energy transfer, 2) electron transfer, and 3) addition-elimination (Scheme 1). As Fig. 1 shows, the efficiency of the N→Q isomerization is not fully governed by the triplet energies of sensitizers. Thus, triphenylene (E_T: 66.5 kcal mol^{-1}, 1 kcal=4.184 kJ) is far less effective than benzophenone (E_T: 69.2 kcal mol^{-1}) and even than 4-phenylbenzophenone with much lower E_T (E_T: 60.7 kcal mol^{-1}). Figure 2 shows that BPs carrying electron-donating substituents act as more effective sensitizers. Accordingly, it is clear that the efficiency of the sensitizer is not fully controlled by its triplet excitation energy, but among BPs some electronic effects of the substituents play an important role in the sensitization.

It is remarkable and consistent with the above results that k_q^N is independent of E_T of the sensitizers and much lower than diffusion controlled limit (Fig. 6). The lack of correlation between k_q^N and E_T suggests that the quenching of triplet BPs by N does not proceed through a simple energy transfer. The curves in Fig. 6 were calculated assuming that the quenching of triplet BPs by N proceeds through energy transfer and obeys Eq. 2,[14] where k_{dif} is the diffusion controlled rate constant, 10^{10} mol^{-1}dm^{3}s^{-1}, and ΔE is the triplet energy difference between a BP and N.

$$k_q^N = k_{dif}\exp(-\Delta E/RT)/\{1+\exp(-\Delta E/RT)\} \qquad (2)$$

The triplet energy of N was assumed to be 70—72 kcal mol^{-1}.[1,3,15,16] The calculated curves do not fit the plot of the observed rate constants, especially for low energy sensitizers such as 4-cyanobenzophenone, suggesting an important role of quenching processes other than triplet energy transfer.[17]

Electron transfer plays no significant role in the isomerization of N, since the plots of k_q^N against the σ (Fig. 7) and $E_{red}+E_T$ values (Fig. 8) are scattered and seem to have no correlation. From the calculated ΔG° values in Table 2, the electron transfer from N to triplet BPs is estimated to be more than 0.38 eV endothermic, being in accordance with no correlation in Fig. 6. The rate constant associated with an electron-transfer process usually obeys the Rehm-Weller equation (Eq. 3), where $\Delta G^{\circ\neq}(0)$ is the change in the Gibbs function of activation at $\Delta G^\circ=0$ kcal mol^{-1}; $\Delta G^{\circ\neq}(0)$ is related to the change in nuclear positions occurring prior to electron transfer, and is 2.4 kcal mol^{-1} for usual electron transfer.[13]

$$k_q = \frac{2\times10^{10}\ \mathrm{mol^{-1}dm^3s^{-1}}}{1+0.25\{\exp(\Delta G^{\circ\neq}/RT)+\exp(\Delta G^\circ/RT)\}} \tag{3}$$

$$\Delta G^{\circ\neq} = \Delta G^\circ/2 + \{(\Delta G^\circ/2)^2 + [\Delta G^{\circ\neq}(0)]^2\}^{1/2} \tag{4}$$

Because of the large endothermicity (0.38 eV) the rate constant of electron transfer from N to triplet BPs is as low as 2×10^4 mol^{-1}dm^{3}s^{-1} according to Eqs. 3 and 4, suggesting less importance of this process.

The addition-elimination mechanism explains reasonably the observed dependence of sensitizing ability of N→Q isomerization on the substituents of BPs[9] and the formation of addition products.[18,19] Comparison of the plot of log k_q^N against E_T with the calculated curve in Fig. 6 suggests that the quenching might proceed mainly through the addition-elimination process for lower energy sensitizers like 4-cyanobenzophenone, while the energy transfer might play a more important role for sensitizers with higher triplet energy like 4,4′-dimethoxybenzophenone.

Shima reported that triplet BP adds to N to give oxetane products.[18] However, later Gorman reported that the formation of the oxetane products is not due to the addition of triplet BP to N but due to the addition to Q resulting from N isomerization.[19] In order to reveal whether the consumption of BP during the irradiation of N is due to its addition to N or to the resulting Q, we carefully reinvestigated irradiation of BP (1.12×10^{-2} mol dm^{-3}) in neat N. Figure 5 clearly shows that the amount of the resulting Q increased linearly with irradiation time and BP decreased even at the very early stage without any induction period.

The present results are in contrast with Gorman's work. Gorman et al. reported that on irradiation of BP in neat N, Q was produced linearly with irradiation time, while the consumption of BP started after an induction period until Q was accumulated in 1.8×10^{-2} mol dm^{-3}.[19] From these results they concluded that the adducts were formed through addition of triplet BP to Q but not to N.[19]

In this concentration of Q, the molar ratio of N (neat: 9.3 mol dm^{-3}) and Q is ca. 520 : 1, and thus by using 6.4×10^8 and 8.8×10^8 mol^{-1}dm^3 s^{-1} as the rate constants for quenching of BP triplets by N and Q, respectively, the fraction of triplet BP to be quenched by Q is estimated to be only 1/380. Inspection of Gorman's data indicates that the relative rate of the Q formation to that of adduct formation is nearly 6—7. This value gives a quantum yield for the adduct formation as strangely high as 49—57 by using 0.9 as the quantum yield for N→Q isomerization determined in the present investigation. Gorman et al. explained their results shortly that the N→Q isomerization must be very inefficient in neat N because of the self quenching of triplet N.[19] However, it is not the case as shown above. The present results are in keeping with the report by Shima which claimed Gorman's arguments and reconfirmed the addition of BP triplets to N.[20]

When the quenching of triplet BPs by N proceeds solely through the addition-elimination mechanism, the observed quenching rate constant (6.4×10^8 mol^{-1} dm^{3}s^{-1}) could be supposed to be slightly higher than that expected for the addition of $n\pi^*$ triplet to unsaturated bonds. However, from the analysis of the quantum yields for oxetane formation in the stationary irradiation of benzophenone with furan and for isomerization of *cis*- and *trans*-2-butene induced by benzophenone, the rate constants for the quenching of triplet BP by furan and the cis-alkene mostly by addition are estimated as 4.2×10^7 and 7×10^7 mol^{-1}dm^{3}s^{-1}, respectively.[21,22] Also, 4-methoxybenzoyloxyl radical, which has similar electronic configuration to benzophenone triplet carrying an unpaired electron on the oxygen atom, adds to 1,4-cyclohexadiene with a rate constant of ca. 5×10^8 mol^{-1}dm^{3}s^{-1} as determined by laser flash photolysis recently.[23] Furthermore, this radical abstracts a hydrogen atom from cyclohexane with ca. 10^6 mol^{-1}dm^{3}s^{-1}, nearly the same rate constant for the abstraction of hydrogen atom from 2-propanol by triplet benzophenone.[16] Therefore, it is reasonable to propose that triplet BPs add to N with nearly the same rate constant as that for the addition of 4-methoxybenzoyloxyl radical.

Isomerization of Q to N. As shown in Fig. 6, k_q^Q decreases with increasing E_T of sensitizers. The inverse correlation suggests that E_T of Q is much higher than 58 kcal mol^{-1}, a previously reported value,[15,16] and thus the energy transfer quenching is not important. The fact that the rate constants k_q^Q increases with Hammett's σ of the substituents on BPs indicates that the electron transfer plays an important role in the quenching by Q. The curve a in Fig. 8 was calculated from the Rehm-Weller equation (Eq. 3) using $\Delta G^{\circ\neq}(0)=2.4$ kcal mol^{-1} for typical electron transfer.[13] The plot does not fit this curve but fits the curve b calculated by assuming $\Delta G^{\circ\neq}(0)=3.5$ kcal mol^{-1}. This means that the electron transfer between BP triplets and Q needs a higher activation energy and thus larger geometrical changes than the usual electron transfer.[24]

The isomerization of Q to N in acetonitrile was not so efficient as the N → Q isomerization.[8] The quantum yield for Q ($0.1\ \mathrm{mol\,dm^{-3}}$) → N isomerization were 0.05, 0.06, and 0.10 in the presence of $(\mathrm{MeO})_2\mathrm{BP}$, BP, and 4-cyanobenzophenone, respectively (Table 1). On the other hand, Roth reported that chloranil (CA) sensitized the Q → N isomerization with a high quantum yield, 0.64, and pointed out that the quenching of CA triplets by Q resulted in the production of its radical cations having a geometry close to the transition state of $\mathrm{Q^{+\bullet}} \rightarrow \mathrm{N^{+\bullet}}$ isomerization.[25] Furthermore, it has been reported that quadricyclane radical cations $\mathrm{Q^{+\bullet}}$ generated by γ-irradiation or electrochemical oxidation of Q easily convert into norbornadiene-like radical cations $\mathrm{N^{+\bullet}}$ and that the barrier of conversion of $\mathrm{Q^{+\bullet}} \rightarrow \mathrm{N^{+\bullet}}$ is significantly lower than that for Q → N.[26,27] The low quantum yields observed in the present work could be attributed to the production of N triplets from the radical ion pair consisting of $\mathrm{Q^{+\bullet}}$ and $\mathrm{BP^{-\bullet}}$. Thus, the isomerization in a radical pair $(\mathrm{BP^{-\bullet}} \cdots \mathrm{Q^{+\bullet}}) \rightarrow (\mathrm{BP^{-\bullet}} \cdots \mathrm{N^{+\bullet}})$ is exothermic since the ground state of Q is nearly 1 eV higher in energy than that of N.[1] Accordingly, on quenching of triplet BP with Q followed by $\mathrm{Q^{+\bullet}} \rightarrow \mathrm{N^{+\bullet}}$ isomerization in the pair, the resulting triplet radical pair $^3(\mathrm{BP^{-\bullet}} \cdots \mathrm{N^{+\bullet}})$ has a higher energy than triplet N (E_T=3.1 eV)[1,3,15,16] as indicated in Table 3, and thus can produce the N triplet effectively. The N triplets deactivate to the ground state to give mainly the starting material Q, therefore leading to low quantum yields of the Q → N isomerization. After the quenching of triplet BP by Q, the resulting radical ion pairs will undergo sequential reactions very quickly since $\mathrm{BP^{-\bullet}}$ was not observed after 30 ns of a laser pulse in the nanosecond spectroscopy.

In the case of CA sensitization, however, even if the radical pair $^3(\mathrm{CA^{-\bullet}} \cdots \mathrm{N^{+\bullet}})$ [triplet energy: 1.84 eV, $E(\mathrm{CA/CA^{-\bullet}})$= +0.01 V (SCE)][28] is effectively produced in the quenching of triplet CA by Q, it has a lower energy than has an N triplet (Table 2) and deactivates only to CA+N in the ground state resulting in the higher quantum yield of N.

$$
\begin{aligned}
&{}^3\mathrm{BP}^* + \mathrm{Q} \rightarrow {}^3(\mathrm{BP^{-\bullet}} \cdots \mathrm{Q^{+\bullet}}) \rightarrow {}^3(\mathrm{BP^{-\bullet}} \cdots \mathrm{N^{+\bullet}}) \\
&{}^3(\mathrm{BP^{-\bullet}} \cdots \mathrm{N^{+\bullet}}) \rightarrow {}^1(\mathrm{BP^{-\bullet}} \cdots \mathrm{N^{+\bullet}}) \\
&{}^3(\mathrm{BP^{-\bullet}} \cdots \mathrm{N^{+\bullet}}) \rightarrow \mathrm{BP} + {}^3\mathrm{N}^* \\
&{}^1(\mathrm{BP^{-\bullet}} \cdots \mathrm{N^{+\bullet}}) \rightarrow \mathrm{BP} + \mathrm{N} \\
&{}^3\mathrm{N}^* \rightarrow \mathrm{Q} + \mathrm{N}
\end{aligned}
$$

Scheme 2.

In summary, the quenching of triplet BPs by Q proceeds through electron transfer to give norbornadiene-like radical cations, which subsequently recombine with a partner $\mathrm{BP^{-\bullet}}$ to generate triplet N reverting to Q finally (Scheme 2). On the other hand, the quenching of triplet BPs by N is proposed to proceed mainly in the addition-elimination fashion which leads finally to effective isomerization to Q (Scheme 1).

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