Deactivation Mechanism of Triplet Exciplexes between Benzophenone and Sensitized-Triplet Naphthalene Derivatives

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The decay process of the triplet exciplexes formed between triplet naphthalene derivatives and benzophenone was found to be promoted by their charge transfer character since the rate constant of the nonradiative deactivation process increased with decreasing of the oxidation potentials of naphthalene derivatives.

Triplet energy transfer is one of fundamental processes in photochemistry and photobiochemistry, and has been studied extensively in rigid and fluid media spectroscopically and kinetically.[1] Triplet sensitization techniques have been applied to production of the triplet states without direct photoexcitation. However, the deactivation process of triplet-sensitized molecules has been ignored until our reports on triplet naphthylammonium ions, naphthol derivatives and methoxynaphthalenes sensitized by triplet benzophenone ($^3BP^*$).[2-14] For the case of naphthol, hydrogen-atom transfer from triplet naphthol to the sensitizer of benzophenone (BP) has been shown in wet acetonitrile (ACN) both with and without protons,[4,6] while electron transfer from triplet methoxynaphthalene to BP has been found only in the presence of protons.[3,7] These reactions have been interpreted to proceed via triplet exciplexes between triplet naphthol (or methoxynaphthalene) and BP.[7] It has been shown that these triplet exciplexes have loose sandwich-like structures[8] with weak charge-transfer character.[4-13] The thermochemical parameters for the formation of these triplet exciplexes have been obtained.[10] However, the formation and the decay mechanism for triplet exciplexes of other naphthalene derivatives (ND) which have no possibility for hydrogen atom transfer nor electron transfer have not been revealed yet. In the present report, by using 1-cyanonaphthalene (1CNNp), 1-bromonaphthalene (1BrNp), 1- and 2-chloronaphthalenes (1ClNp and 2ClNp), naphthalene (Np), 1- and 2-methoxynaphthalenes (1MeONp and 2MeONp), the mechanism of the deactivation process of their triplet exciplexes with BP was investigated by means of nanosecond laser photolysis techniques in ACN at 295 K.

Figure 1 shows plots of the first-order decay rate (k_{obsd}) of triplet Np ($^3Np^*$) monitored at 413 nm sensitized by $^3BP^*$ observed after 355-nm laser pulsing from a Nd^{3+}:YAG laser in the BP-Np (2.0 x 10^{-3} mol dm^{-3}) system in ACN as a function of concentration of BP ([BP]). The value of k_{obsd} increases nonlinearly with an increase of [BP]. This leveling-off is evidence for formation of the triplet exciplex ($^3(Np\cdots BP)^*$) between $^3Np^*$ and BP expressed by the following equilibrium.[4-7,9-13]

$$^3Np^* + BP \rightleftarrows {}^3(Np\cdots BP)^* \qquad (1)$$

With the use of the rate constants (k_0[15] and k_{ex}) of the decay processes expressed by Eqs. 2 and 3 for $^3Np^*$ and $^3(Np\cdots BP)^*$, respectively, and the equilibrium constant, K (= $[^3(Np\cdots BP)^*][^3Np^*]^{-1}[BP]^{-1}$), k_{obsd} can be formulated by Eq. 4.[4-7,9-13]

$$^3Np^* \rightarrow Np \qquad (2)$$

$$^3(Np\cdots BP)^* \rightarrow Np + BP \qquad (3)$$

$$k_{obsd} = (k_0 + k_{ex}K[BP])(1 + K[BP])^{-1} \qquad (4)$$

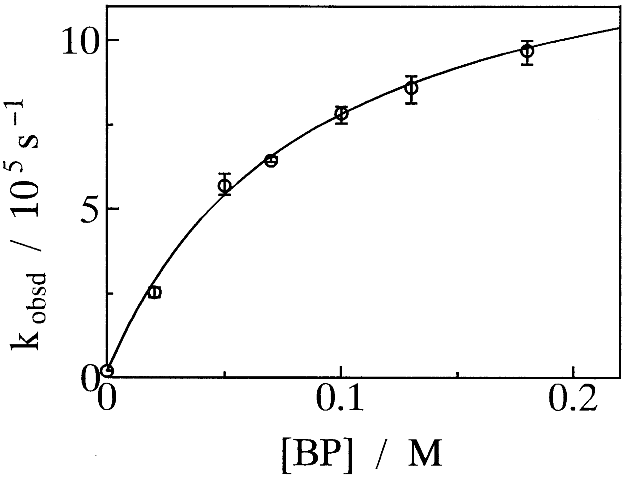

Figure 1. Plots of the decay rate (k_{obsd}) monitored at 413 nm obtained by 355-nm laser photolysis in the BP-Np system in ACN at 295 K. The solid curve was calculated according to Eq. 4. See text for details.

By best-fitting Eq. 4 to the values of k_{obsd} obtained experimentally, the values of k_{ex} and K were determined to be 1.4 x 10^6 s^{-1} and 11.8 dm^3 mol^{-1}, respectively, for the BP-Np system in ACN at 295 K. For other systems, the same procedures for k_{ex} and K were applied on the condition, [ND] = 2.0 x 10^{-3} mol dm^{-3}. The data obtained are listed in Table 1. The values of K are in the same order of magnitude as that in the case for hydrogen atom transfer (~10 dm^3 mol^{-1}).[6] On the other hand, the k_{ex} values are smaller by one order of magnitude than that of naphthol (ca. 1 x 10^7 s^{-1}).[4,6] In our previous reports, the triplet exciplexes have

Table 1. The oxidation potentials of ND and kinetic parameters for the BP-ND system in ACN

ND	E_{ox} [a] / V	k_0 [b] / 10^4 s^{-1}	K [b,c] / dm^3 mol^{-1}	k_{ex} [b,c] / 10^6 s^{-1}
1CNNp	2.17	1.0	6.5	0.67
2ClNp	1.97	1.1	3.4	1.1
1BrNp	1.74	1.3	12.7	1.8
1ClNp	1.71	1.0	9.1	1.7
Np	1.62	2.0	11.8	1.4
2MeONp	1.52	0.9	2.2	1.6
1MeONp	1.38	2.4	7.1	2.2
DMNA[d]	0.75[e]	3.0[e]	10[e]	2.5[e]
DENA[f]	0.75[e]	7.5[e]	9[e]	3.4[e]

[a] vs. SCE in ACN. Data from "Handbook of photochemistry, 2nd Ed., revised and expanded" ed by S.L. Murov, I. Carmichael and G.L. Hug, Marcel Dekker, New York (1993). [b] Errors ± 5%. [c] See text for determinastion. [d] N,N-Dimethyl-1-naphthylamine. [e] Data from Refs. 12 and 13. [f] N,N-Diethyl-1-naphthylamine.

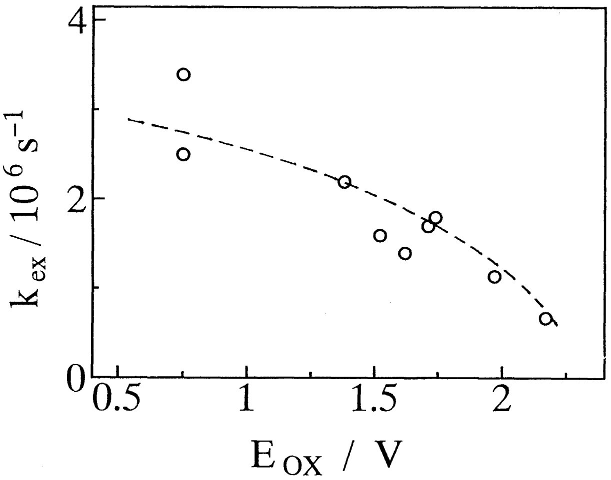

Figure 2. Plots of the decay rate constant (k_{ex}) of $^3(Np\cdots BP)^*$ as a function of the oxidation potential (E_{ox}) of ND.

been considered to have weak charge-transfer character.[4-13] In order to elucidate charge-transfer character of the triplet exciplexes employed in the present study, plots of the obtained k_{ex} are given as a function of the oxidation potential (E_{ox}) of ND in Figure 2. With a decrease of the value of E_{ox}, the k_{ex} value increases up to ca. 3 x 10^6 s^{-1}. The stabilization energy (E_{CT}) of the complex due to the charge-transfer interaction would be proportional to the difference between the redox potentials of the related molecules.

$$E_{CT} \propto E_{ox} - E_{red} \qquad (5)$$

where E_{red} represents the reduction potential of BP. It was impossible to formulate k_{ex} with E_{ox} though the behavior of k_{ex} vs. E_{ox} is similar to that of the Rehm-Weller plots for electron transfer.[16] On the other hand, considering the change in spin-multiplicity, the decay process of the triplet exciplex is intersystem crossing. Lim et al. reported that intersystem crossing in charge transfer complexes was efficient.[17] Therefore, the behavior of k_{ex} against E_{ox} in Figure 2 demonstrates that the deactivation process of the triplet exciplex is correlated with charge transfer interaction. We can conclude that the mechanism of the deactivation of the triplet exciplex between BP and ND is intersystem crossing originated from weak charge transfer character in the triplet exciplexes.

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