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Rate Constant of Bimolecular Triplet Energy Transfer from Chrysene in the Higher Triplet Excited States

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The rate constant of the bimolecular triplet energy transfer from chrysene in the second higher triplet excited state (T_2) to triplet quenchers (Q) such as biphenyl, naphthalene, and carbon tetrachloride was determined based on the lifetime of chrysene(T_2) (45 ± 7 ps) measured directly with ns−ps two-color two-laser flash photolysis method. The rate constant was found to be larger than the diffusion-controlled rate constant in the solvents. The occurrence of the fast bimolecular triplet energy transfer is considered clear evidence of the Ware theoretical model on the energy transfer quenching of the excited species with short lifetimes by the quencher.

Introduction

Triplet−triplet (T−T) energy transfer in fluid solution is very important and has been intensively studied.[1−3] The exchange (collisional) mechanism has been successfully applied to bimolecular energy transfer quenching of excited molecules (M*) in the lowest triplet state (T_1) by the quenchers (Q) having the lower energy (E_{T1}) than those of M*(T_1).[1] Usually, the maximum rate constant for the bimolecular energy transfer with large exothermic free energy change is equal to the diffusion-controlled limit (k_{diff}) in the solvent.[1] However, it has been found that the rate constant of triplet energy transfer (k_{TET}) is not always a linear function of the viscosity of the solvent. In the case of quenching of the valerophenone in the T_1 state by 2,5-dimethyl-2,4-hexadiene, the experimentally estimated k_{TET} value was smaller than the k_{diff} value.[4] A similar phenomenon was also found in the triplet energy transfer from chlorophyll to β-carotene.[5] In these cases, the transfer of the triplet excitation energy is not efficient and the encounter complex separates before energy transfer. On the other hand, very fast bimolecular energy transfer competing with vibrational relaxation process was observed for the quenching of benzophenone in the T_1 state by 1,3-pentadiene or 1-methylnaphthalene, which were used as the solvent.[6] Therefore, the actual processes for a very short period are still unclear. Especially, in the limit of energy transfer from short-lived excited state to highly concentrated quencher, the quenching process is quite complex and the simple diffusional kinetics cannot be applied.

Ware et al.[7] proposed the theoretical model on the quenching processes of M* with a short lifetime by Q (eq 1). According to this model, the bimolecular energy transfer rate constant (k_{ET})-is expressed by lifetime-independent and -dependent terms as in eqs 2 and 3,

$$M^* + Q \xrightarrow{k_{ET}} M + Q^* \tag{1}$$

$$k_{ET} = k_{diff} + k_{diff}\sigma'/(\pi D\tau)^{0.5}, \tag{2}$$

$$k_{diff} = 4\pi N\sigma' D, \tag{3}$$

where σ' is the collisional distance between two molecules, D is the sum of the diffusion coefficients for M* and Q, τ is the lifetime of the excited species, and N is the Avogadro number. Using the theoretical model, the larger k_{ET} value than k_{diff} can be explained without assumption of the complex formation between M and Q. The lifetime-dependent term contributes considerably on the k_{ET} value during the quenching of M* with a short τ, typically $\tau < 100$ ps. Therefore, when the energy transfer proceeds from M* with a short τ, such as the higher singlet and triplet excited (S_n and T_n, respectively) states, the lifetime-dependent quenching process must be considered. The experimental evidence of the Ware theoretical model was obtained only for the quenching of S_1 from the steady-state fluorescence quenching,[7] but not for the S_n or T_n states with short τ. Since the T_1 state has a longer τ than the S_1 state,[2,8] excitation of the T_1 state can be easily performed to give the T_n state. Also, energy-transfer quenching from the T_n state to Q can proceed effectively compared with that from the S_n state. Because no emission from the T_n state is usually observed but absorption of the T_1 state is often observed, transient absorption measurement can be applied to estimate the k_{ET} value of short-lived species.

Recently, several aromatic hydrocarbons such as naphthalene, dibenz[*a*,*h*]anthracene, and chrysene in the T_n states have been studied with ns−ns two-color two-laser flash photolysis in our laboratory.[9,10] Fast triplet energy transfer from the T_n states to Q, whose E_{T1} is lower than E_{Tn} and higher than E_{T1} of such aromatic hydrocarbons, was observed. No complex was formed between the aromatic hydrocarbons in the T_1 state and Qs. Based

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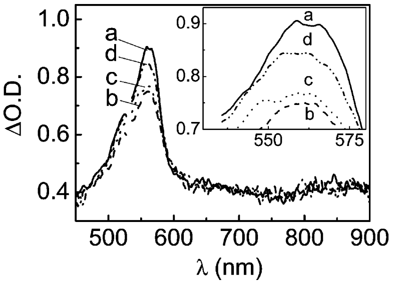


Figure 1. Transient absorption spectra observed at 20 ps before (solid line, a) and 40 ps (dashed line, b), 60 ps (dotted line, c), and 85 ps (two dots and dashed line, d) after a 532-nm and 30-ps laser flash during the two-color two-laser flash photolysis of chrysene (1.0×10^{-3} M) in Ar-saturated cyclohexane at room temperature using the pump-probe system. The delay time of the second 532-nm and 30-ps laser after the first 355-nm and 5-ns laser was 100 ns. The inset shows the amplification of the bleaching and recovery at the peak region of the spectra.

on the accurate τ value of the aromatic hydrocarbons in the T_n states, the rate constant of the bimolecular energy transfer can be determined. Herein, we report determination of the rate constant for the triplet energy transfer from chrysene in the second triplet excited state (chrysene(T_2)) to Q based on the τ value of chrysene(T_2) measured directly using ns−ps two-color two-laser flash photolysis method.

Experimental Section

Materials. Chrysene was purchased from Aldrich Chem. Co. (purity > 98%) and used without further purification. Naphthalene and biphenyl were purchased from Nacalai Tesque Inc. and were recrystallized twice from ethanol before use. Carbon tetrachloride (CCl_4), methylene dichloride (CH_2Cl_2), and 1,2-dichloroethane (DCE) were purchased from Wako Chem. Co. Cyclohexane was purchased from Nacalai Tesque Inc. All liquid compounds were spectral grade. Sample solutions were freshly prepared and deoxygenated by bubbling with argon (Ar) gas before irradiation. A 1 × 0.5 × 2 cm rectangular Suprasil flow cell was used to make sure that each laser shot was irradiated on the fresh sample. All experiments were carried out at room temperature.

Two-color Two-laser Flash Photolysis. The first laser flash at 355 nm was obtained from a ns Nd:YAG laser (Continuum, Surelite II-10; 5-ns fwhm, 10 Hz). The second laser flash at 532 nm was obtained from a ps Nd:YAG laser (Continuum, RGA69−10; 30-ps fwhm, 10 Hz) seeded by a ps diode laser (1064 nm, 5-ps, 100 MHz, Time-bandwidth, GE−100). Two laser flashes were synchronized by a pulse generator with a delay time of 10 ns to 10 ms and overlapped through the sample. Transient absorption spectra in the picosecond region were measured by the pump and probe method. The probe pulse generated by focusing the fundamental light of the ps Nd:YAG laser on a D_2O:H_2O cell was detected with an MOS linear image sensor (Hamamatsu Photonics, M2493−40) equipped with a polychromator (Hamamatsu Photonics, C5094) after passing through the sample. The total system was controlled with a personal computer via GP−IB interface.

Results and Discussion

Direct Measurement of Lifetime of Chrysene(T_2). When chrysene (1.0×10^{-3} M) was irradiated at 355 nm using a ns Nd:YAG laser in Ar-saturated cyclohexane, a transient absorption spectrum of chrysene in the lowest triplet excited state (chrysene(T_1)) with a peak around 570 nm (extinction coefficient, $\epsilon_{570} = 29800$ M^{-1} cm^{-1}) was observed (Figure 1a).[11,12] The quantum yield (Φ_T) of intersystem crossing (ISC) from chrysene(S_1) to chrysene(T_1) is 0.85 and the τ value of chrysene(T_1) is longer than 3.4 μs (eq 4).[8,12] Because chrysene(T_1) has an absorption at 532 nm, chrysene(T_1) is selectively excited to chrysene in the higher triplet excited state (chrysene(T_n)) with the second 532-nm ps laser irradiation to the sample at 100 ns after the first 355-nm ns laser irradiation. Bleaching of the transient absorption of chrysene(T_1) was observed within a 532-nm laser flash duration; then, the transient absorption was completely recovered in the 100−200 ps time range as shown in Figures 1 and 2, which was not observed during the ns−ns two-color two-laser flash photolysis.[10] This result indicates that chrysene(T_1) is excited to chrysene (T_n) (bleaching of the chrysene(T_1)) during the irradiation of the second 532-nm ps laser, then chrysene(T_n) decays through the internal conversion (IC) to regenerate chrysene(T_1) (recovery of the chrysene(T_1)) (eq 5).

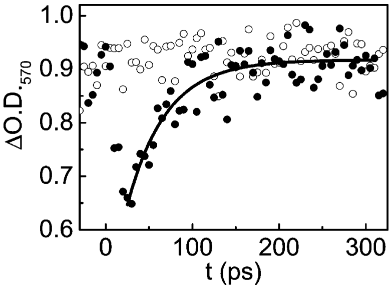


Figure 2. Time profiles of the transient absorption at 570 nm, assigned to chrysene(T_1), during irradiation of one laser (open circles) and two lasers (closed circles). The delay time of the second 532-nm and 30-ps laser after the first 355-nm and 5-ns laser was 100 ns. The solid line is the fit with the single-exponential function.

$$\text{chrysene}(S_0) \xrightarrow{h\nu_{355}} \text{chrysene}(S_1) \xrightarrow{\text{ISC}} \text{chrysene}(T_1) \qquad (4)$$

$$\text{chrysene}(T_1) \xrightarrow{h\nu_{532}} \text{chrysene}(T_n) \xrightarrow{\text{IC}} \text{chrysene}(T_1) \qquad (5)$$

Since the chrysene(T_1) was recovered completely, no reaction (such as ionization) was involved in the decay process of chrysene(T_n). The recovery was fitted well with the single-exponential function. The τ value of chrysene(T_n) was found to be 45 ± 7 ps, which is similar to the previously reported value estimated from eqs 2 and 3 based on the quenching experiments using the ns−ns two-color two-laser flash photolysis method.[9,10] Since a similar τ value of chrysene(T_n) was obtained in acetonitrile, the solvent effect can be negligible.

Since neither unimolecular reaction nor emission was detected, the IC from chrysene(T_n) to chrysene(T_1) is considered to be the main decay pathway. Therefore, the rate constant of the IC (k_{IC}) is defined as a reciprocal of the τ value. The k_{IC} value depends on the energy gap between two states (ΔE) as shown in eq 6,[1]

$$\tau^{-1} = k_{IC} \approx 10^{13} \exp(-\alpha\Delta E), \qquad (6)$$

where α (eV^{-1}) is a constant value, usually smaller than 5 eV^{-1} for rigid aromatic hydrocarbons.[1,13,14] The value $\alpha = 3.3$ eV^{-1} was calculated from the data of anthracene in the T_2 state, which decays through IC with $\tau = 11$ ps and $\Delta E_{T2-T1} = 1.39$ eV.[13] With $\alpha = 3.3$ eV^{-1} and $\tau = 45 \pm 7$ ps ($k_{IC} = (2.3 \pm 0.3) \times 10^{10}$ s^{-1}), the ΔE value between the T_1 and T_n states (ΔE_{Tn-T1}) of chrysene was calculated to be 1.85 ± 0.05 eV. The ΔE_{T2-T1} value between the T_1 ($E_{T1} = 2.48$ eV) and T_2 ($E_{T2} = 4.23$ eV) states for chrysene is theoretically calculated to be 1.75 eV, while ΔE_{T3-T1} of chrysene is 2.03 eV.[11,12] Therefore, the

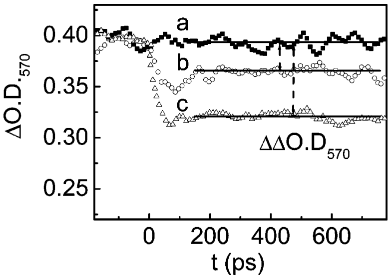


Figure 3. Kinetic traces illustrating the time profiles of $\Delta O.D._{570}$ during 355-nm and 5-ns laser irradiation (a) and during two-color two-laser flash photolysis (the first 355-nm and 5-ns and the second 532-nm and 30-ps lasers) of chrysene (1.0×10^{-3} M) in Ar-saturated cyclohexane at room in the presence of CCl_4 with 0.5 M (b) and 2.0 M (c).

observed IC corresponds to that from chrysene(T_2). Because the energy of the 532-nm photon is 2.33 eV, which is much higher than the ΔE_{T2-T1}, the chrysene(T_n, $n > 2$) states should be initially generated and deactivated through the fast IC to chrysene(T_2) with the longest τ (45 ± 7 ps) among chrysene(T_n) (eq 7),

$$\text{chrysene}(T_n) \xrightarrow{\text{IC}} \text{chrysene}(T_2) \xrightarrow{\text{IC}} \text{chrysene}(T_1) \qquad (7)$$

Triplet Energy Transfer From Chrysene(T_2) to Q. The triplet energy transfer quenching of chrysene(T_2) by Q such as biphenyl, naphthalene, or carbon tetrachloride (CCl_4) has been observed previously.[10] Since E_{T1} of biphenyl or naphthalene is higher than chrysene(T_1) (2.48 eV)[8,12] and lower than chrysene(T_2) (4.23 eV), Q can act as a triplet energy acceptor for chrysene(T_2) with large exothermic energy, but not for chrysene(T_1) (eq 8),

$$\text{chrysene}(T_2) + Q \rightarrow \text{chrysene}(T_1) + Q(T_1) \qquad (8)$$

The ns–ps two-color two-laser flash photolysis experiment in the presence of CCl_4 was also performed as shown in Figure 3.

In the presence of CCl_4, bleaching of the chrysene(T_1) within the second 532-nm laser flash with a duration of 30 ps was observed together with incomplete recovery of the chrysene(T_1) ($\Delta\Delta O.D._{570}$). The $\Delta\Delta O.D._{570}$ increased with the increasing of the concentration of CCl_4 ([CCl_4]). The value of $\Delta\Delta O.D._{570}$ shows that the triplet energy transfer from chrysene(T_2) to CCl_4 and sequential C–Cl bond cleavage (C–Cl bond cleavage energy of CCl_4 is 3.17 eV)[15] occur during the second 532-nm laser irradiation (eq 9).[10,16]

$$\text{chrysene}(T_2) + CCl_4 \rightarrow \text{chrysene}(T_1) + \bullet CCl_3 + Cl^- \qquad (9)$$

Since the triplet energy transfer from chrysene(T_2) to CCl_4 occurs competitively with the IC from chrysene(T_2) to chrysene(T_1), $\Delta\Delta O.D._{570}$ is represented by [CCl_4] as shown in eq 10,[17,18]

$$\Delta\Delta O.D._{570}/\beta = (k_{TET} \times [CCl_4])/(k_{IC} + (k_{TET} \times [CCl_4])), \qquad (10)$$

where β refers to a constant that indicates the ratio of chrysene(T_1) that is excited during the second 532-nm 30-ps laser irradiation. A linear relation was obtained when $|\Delta\Delta O.D._{570}|^{-1}$ was plotted against $[CCl_4]^{-1}$ as expected from eq 10 (Figure 4).

Since $k_{IC} = (2.2 \pm 0.3) \times 10^{10}$ s^{-1} for the IC from chrysene(T_2) to chrysene(T_1), the k_{TET} was calculated to be $(1.2 \pm 0.2) \times 10^{10}$ M^{-1}s^{-1} from the slope and intercept of the line (Figure 4) according to eq 10. The k_{TET} value is larger than k_{diff} (7.4×10^9 M^{-1}s^{-1}, 25 °C) in cyclohexane.[8] Furthermore, $k_{TET} = (2.35 \pm 0.3) \times 10^{10}$, $(2.40 \pm 0.2) \times 10^{10}$, and $(2.60 \pm 0.4) \times 10^{10}$ M^{-1}s^{-1} were calculated for Q = biphenyl, naphthalene, and CCl_4, respectively, in acetonitrile. The k_{TET} values are also larger than k_{diff} (1.9×10^{10} M^{-1}s^{-1}, 25 °C) in acetonitrile.[8] These results show that contributions of the lifetime-dependent term to k_{TET} are 20% and 26% in acetonitrile and cyclohexane, respectively. Such a large contribution of the lifetime-dependent term should be observed for any energy transfer from the excited species with a short τ. This can be easily understood from eq 2. When the τ value is smaller, the contribution of the lifetime-dependent term ($k_{diff}\sigma'/(\pi D\tau)^{0.5}$) to k_{TET} becomes larger.

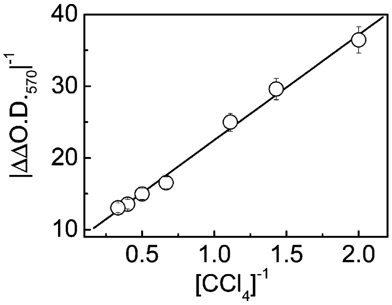
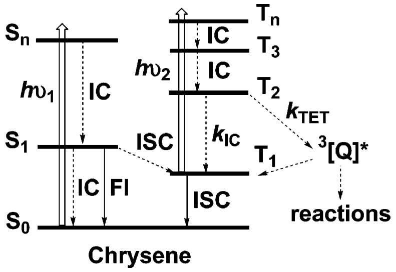


Figure 4. Plots of $|\Delta\Delta O.D._{570}|^{-1}$ vs $[CCl_4]^{-1}$.

SCHEME 1: Schematic Energy Diagram of Chrysene, $h\nu_1$: the First 355-nm Laser, $h\nu_2$: the Second 532-nm Laser, Solid and Dotted Lines Indicate Radiation and Radiationless Processes, Respectively. IC: Internal Conversion; ISC: Intersystem Crossing; Fl: Fluorescence



Formation of a complex between M and Q in the ground state also makes the k_{TET} value larger than k_{diff}.[19–21] This is not the case for the bimolecular triplet energy transfer from chrysene(T_2) to CCl_4, because no complex forms between chrysene(T_1) and CCl_4 (0.5–3.0 M). The transient absorption of chrysene(T_1) was bleached without recovery in the case of CCl_4, while the bleaching and recovery of chrysene(T_1) were observed together with the growth and decay of the transient absorption of biphenyl(T_1) or naphthalene(T_1) during the two-color two-laser flash photolysis.[9,10] No complex formation between chrysene(T_1) and biphenyl or naphthalene was also confirmed. For the recovery of chrysene(T_1), bimolecular collisional quenching of biphenyl(T_1), or naphthalene(T_1) by chrysene(S_0) occurred at k_{diff} to give chrysene(T_1) and biphenyl(S_0) or naphthalene(S_0).

Consequently, the energy-level diagram involving chrysene(T_1) and chrysene(T_n) is summarized in Scheme 1.

Chrysene in the ground state (chrysene(S_0)) is excited by the first 355-nm laser irradiation to give chrysene in the singlet excited state (chrysene(S_1)), from which ISC occurs to give chrysene(T_1). Chrysene(T_1) is excited to chrysene(T_n) during the second 532-nm laser irradiation, from which fast IC occurs to give chrysene(T_2) with the τ value of 45 ± 7 ps. Neither bimolecular energy transfer directly from chrysene(T_n) to Q nor inverse intersystem crossing from chrysene(T_n) to chrysene(S_n) was observed, indicating that very fast IC occurs from chrysene(T_n) to chrysene(T_2) from which bimolecular triplet energy transfer to Q and IC to give chrysene(T_1) occurs competitively.

Triplet Energy Transfer Rate from Chrysene(T_2) to Q Faster Than Diffusion-controlled Rate. The maximum value of k_{TET} is k_{diff} according to the classical triplet energy transfer theory. Therefore, the bimolecular energy transfer processes become possible only when the τ values of T_2 are longer than 53 and 135 ps ($1/k_{diff}$) in the presence of 1 M of Q in acetonitrile and cyclohexane, respectively. However, bimolecular energy transfer processes were clearly observed in the presence of 0.05 M of Q during the quenching of chrysene(T_2) with the τ value of 45 ± 7 ps.

It has been observed that the rate constant for the singlet energy transfer is larger than k_{diff}, since singlet energy transfer from $^1M^*$ to Q proceeds via dipole−dipole interaction, even at distances longer than 10 Å.[1,22] On the other hand, the exchange mechanism operates in the T−T energy transfer,[1] where $^3M^*$ and Q must collide each other. From the measured k_{TET} values and eqs 2 and 3, the σ' values were calculated to be 3.8 and 3.7 Å in cyclohexane and acetonitrile, respectively. This indicates that the collision between chrysene(T_2) and Q occurs in the triplet energy transfer quenching of chrysene(T_2) by Q with the exchange mechanism. The k_{TET} value larger than k_{diff} can be attributed to the short τ value of chrysene(T_2) in the lifetime-dependent term of eq 2. The present result clearly demonstrates that the Ware theoretical model is suitable not only for the singlet energy transfer from the S_1 state, but also for the triplet energy transfer from the T_n states, having short τ values, to Q.

Conclusions

We have first succeeded in measuring directly the τ value of chrysene(T_2) (45 ± 7 ps) with the ns−ps two-color two-laser flash photolysis method, and determined the k_{TET} values of the triplet energy transfer from chrysene(T_2) to Q, $(1.2 \pm 0.2) \times 10^{10}$ $M^{-1}s^{-1}$ in cyclohexane (Q = CCl_4), $(2.35 \pm 0.3) \times 10^{10}$ in acetonitrile (Q = biphenyl), $(2.40 \pm 0.2) \times 10^{10}$ in acetonitrile (Q = naphthalene), and $(2.60 \pm 0.4) \times 10^{10}$ $M^{-1}s^{-1}$ in acetonitrile (Q = CCl_4), which are larger than k_{diff}. It is demonstrated that the Ware theoretical model is suitable not only for the singlet energy transfer but also for the triplet energy transfer. Consequently, the lifetime-dependent quenching processes must be considered during bimolecular energy transfer processes from short-lived species such as the T_n states. We would like to emphasize that the present ns−ps two-color two-laser flash photolysis method can be applied to study bimolecular energy transfer processes between short-lived species and Q.

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