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Important Role of Fluorescence Reabsorption Mechanism in Sensitized Reaction of Unsaturated Lactones. Evidence against "the Orbital Symmetry Correlations in Sensitization"

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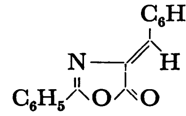
Evidence are presented against Ullman's "the orbital symmetry correlations" between excited aromatic hydrocarbon sensitizers and 4-benzylidene-2-phenyl-5-oxazolone. It is now shown that the oxazolone efficiently quenches the triplet sensitizers regardless of Ullman's classification, and the fluorescence emitted from the sensitizers is reabsorbed by the oxazolone and its wavelength seems to govern the reported reaction course.

Previously Ullman and Baumann reported that under irradiation unsaturated lactones, 4-benzylidene-2-phenyl-5-oxazolone (I) and 2-benzylidene-4-phenyl-3-buten-4-olide (II), depending upon the wavelength of light irradiated or the sensitizers employed, either "selectively" undergo only geometrical isomerization or "unselectively" undergo hydrogen atom abstraction from solvent together with the isomerization.[2] Thus, on direct irradiation of the lactones, 313 nm light caused both reactions, whereas 366 nm light caused only the isomerization. In sensitized reactions, sensitization with biphenyl, fluorene, and naphthalene led to both reactions, whereas sensitization with phenanthrene, triphenylene, and chrysene resulted in only the isomerization. In order to explain the relation between the selectivity of the reaction course and the structure of the sensitizers, they proposed the "orbital symmetry correlations between the excited sensitizers and the lactones" which implied that the close matching of the orbital symmetry between the lowest unfilled molecular orbital of the lactone and a certain part of the highest occupied orbital of the sensitizer led only to the "selective reaction," the isomerization. They stated that matching of the orbital symmetry between the sensitizer and the lactone molecules would lead to effective excitation of the lactone to its $T_1(\pi,\pi^*)$ state to cause the "selective reaction," whereas no matching of the symmetry would lead to inefficient unselective energy transfer to cause the "unselective reactions."[2]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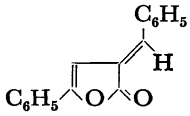
II

In a previous communication[3] we presented an aspect against Ullman's postulate by showing that not the triplet but the singlet excited aromatic hydrocarbons played an important role in the sensitized reaction of the lactone II; fluorescence emitted from the hydrocarbon sensitizers was reabsorbed by the lactone and the fluorescence wavelength seemed to govern the course of the reaction.

In this paper we report firm evidence against Ullman and Baumann's postulate on "the orbital symmetry correlations between the excited sensitizer and the substrate." Contrary to their previous proposition, the oxazolone I is now shown to effectively quench the triplet states of the hydrocarbon sensitizers irrespective of "selective" or "unselective" sensitizers on the ground of direct determination of rate constants for the quenching of the triplet hydrocarbons by the oxazolone. Therefore the reported dependence of the reaction course on sensitizers employed does not result from the difference between the sensitizers in rate constants for the quenching of their triplet states by the oxazolone but is shown to be mostly governed by wavelengths of fluorescence emitted from the singlet excited sensitizers which is reabsorbed by the oxazolone.

Results and Discussion

Absorption and Emission Spectra. Figure 1 shows the absorption spectra of the oxazolone in EPA at 77 K and at ambient temperature together with its emission spectrum in EPA at 77 K. The emission was observed only at 77 K and it is attributable to fluorescence, since the emission starts from the end of absorption and shows mirror image relationship with the absorption. Lack of phosphorescence might be due to rapid radiationless deactivation of the triplet state probably resulting in the facile isomerization of the benzylidene group. The singlet excitation energy of the oxazolone is estimated to be 72 kcal/mol from the above result and its triplet excitation energy was reported to be 43 kcal/mol from its singlet-triplet absorption.[2]

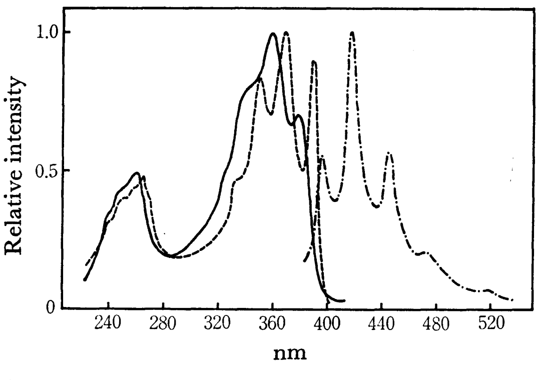

Fig. 1. Absorption and emission spectra of 4-benzylidene-2-phenyl-5-oxazolone in EPA. Absorption at ambient temperature: —, at 77 K: ---, emission at 77 K: -·-·-.

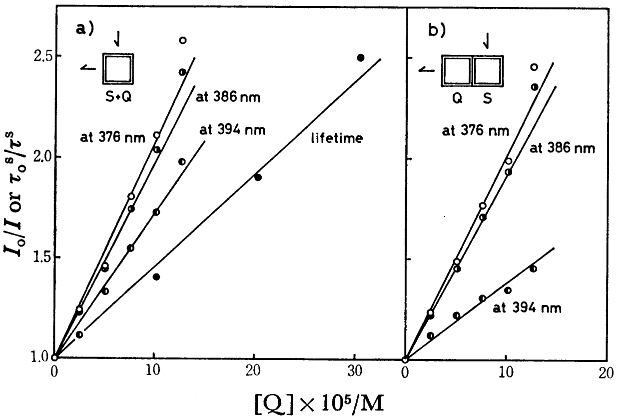

Fig. 2. Stern-Volmer plots. a) Quenching of fluorescence of pyrene (S) by 4-benzylidene-2-phenyl-5-oxazolone (Q) in benzene, b) reabsorption of fluorescence of pyrene (S) by the oxazolone (Q) in benzene.

TABLE 1. QUENCHING OF HYDROCARBON FLUORESCENCE BY 4-BENZYLIDENE-2-PHENYL-5-OXAZOLONE IN BENZENE$^{a)}$

Hydrocarbon	fl$^{b)}$	k_q^{app} $^{c)}$ $\times 10^{-12}$	k_q^S $^{c)}$ $\times 10^{-11}$	$I_0/I^{d)}$	$(I_0/I)_{reabs}$ $^{d)}$	τ_0^S/τ^S $^{d)}$
Biphenyl	316	2.4	0.87	1.45	1.26	1.02
Fluorene	318	3.5	1.5	1.48	1.30	1.02
Naphthalene	336	2.8	4.9	1.98	1.63	1.17
p-Terphenyl	343	55	—	2.31	2.12	—
Triphenylene	364	8.3	1.1	3.27	2.10	1.03
Phenanthrene	366	9.4	4.2	2.95	2.51	1.06
Pyrene	376	7.4	27	3.64	3.34	1.95
Chrysene	383	6.5	3.9	2.72	1.97	1.11

a) Conducted under the aerated condition; the concentration of the hydrocarbon: 10^{-5}—10^{-2} M, the concentration of the oxazolone: 0—5×10^{-5} M for the intensity measurement and 0—10^{-4} M for the lifetime measurement. b) Maximum wavelength of fluorescence in nm. c) In M^{-1} s^{-1}. d) Values at the oxazolone concentration of 2×10^{-5} M.

Quenching of Hydrocarbon Fluorescence by the Oxazolone. Fluorescence of the aromatic hydrocarbons (10^{-5}—10^{-2} mol/l) such as biphenyl, fluorene, naphthalene, triphenylene, chrysene, *p*-terphenyl, phenanthrene, and pyrene was quenched for the intensity and the lifetime by the added oxazolone in benzene solution. Plots of the fluorescence intensity ratio, I_0/I, against the concentration of the oxazolone, [Q], (0—2×10^{-5} mol/l) were, for the most cases, linear only in the lower concentration range of the oxazolone and curved upwards in the higher concentration range as indicated in Fig. 2, where I_0 and I denote the fluorescence intensity of the hydrocarbon in the absence of the oxazolone and that in the presence of the oxazolone in concentration of [Q], respectively. If, in the lower concentration range of the oxazolone, the plots are assumed to obey the Stern-Volmer relationship

$$I_0/I = 1 + k_q^{app}\tau_0^S[Q] \qquad (1)$$

(Eq. 1), the apparent quenching rate constants, k_q^{app}, can be obtained from their slopes divided by the lifetimes of the singlet states of the hydrocarbons in the absence of the oxazolone, τ_0^S. The shapes of fluorescence spectra of some hydrocarbons were varied with increase in the concentration of the oxazolone and the fluorescence intensity ratio, I_0/I, was also varied with wavelength at which the emission is observed. These results suggest, as will be discussed later, that the quenching of hydrocarbon fluorescence is mostly due to the reabsorption of fluorescence by the quencher. In Table 1 are listed the apparent quenching rate constants, k_q^{app}, measured at the emission maximum of each hydrocarbon.

For the quenching of the singlet lifetimes of the aromatic hydrocarbons by the oxazolone, plots of τ_0^S/τ^S against the concentration of the oxazolone fitted the

$$\tau_0^S/\tau^S = 1 + k_q^S\tau_0^S[Q] \qquad (2)$$

Stern-Volmer relationship (Eq. 2) over the concentration range of the oxazolone employed (0—5×10^{-4} mol/l) (Fig. 2), where τ^S denotes the lifetime of a singlet hydrocarbon in the presence of the oxazolone in concentration [Q]. The bimolecular rate constants, k_q^S, for the quenching process of the excited singlet hydrocarbons by the oxazolone are summarized in Table 1, which shows that k_q^{app} values are several to eighty times larger than k_q^S values. Table 1 also contains I_0/I and τ_0^S/τ^S values obtained at $[Q]=2.0\times10^{-5}$ mol/l, showing that I_0/I values are significantly higher than the corresponding τ_0^S/τ^S values.

The above difference between I_0/I and τ_0^S/τ^S values at the same concentration of the oxazolone is reasonably attributable to reabsorption of the fluorescence from the excited singlet hydrocarbons by the oxazolone by the following reasons. If the added oxazolone acts only to quench the excited singlet hydrocarbon with a rate constant of k_q^S, the fluorescence intensity of the hydrocarbon would be decreased to the same extent as the singlet lifetime, so I_0/I would be equal to τ_0^S/τ^S, but it is not the case. When the fluorescence from the hydrocarbon is reabsorbed by the oxazolone in the surrounding medium, the actually observed fluorescence is to be further reduced in intensity, so, as was actually observed, I_0/I value is to be higher than τ_0^S/τ^S value by an extent corresponding to the reabsorption. A possibility that apparent reduction of the sensitizer fluorescence by the oxazolone would be due to formation of complex between ground states of the sensitizer and the oxazolone is excluded since no new absorption appeared on the mixing of the both compounds in solution.

A fact that the absorption spectrum of the oxazolone effectively overlaps with the emission spectra of the hydrocarbon sensitizers suggests that the singlet hydrocarbons could undergo efficient radiative transfer to the oxazolone, which could cause distortion of the shape of the emission spectra. Actually, as mentioned previously, the emission spectra of some hydrocarbons were changed in the shape with the increase in the concentration of the oxazolone, and slopes of Stern-Volmer plots of I_0/I gave higher values in the region of 340—390 nm where the oxazolone shows higher molecular extinction coefficient. Thus, triphenylene, phenanthrene, and pyrene, which have emission maxima in the region of 360—380 nm, gave higher apparent quenching rate constants $k_q^{app}\tau_0^S$ than biphenyl and fluorene which have emission maxima near 320 nm.

Reabsorption of the fluorescence emitted from the hydrocarbons by the oxazolone was further confirmed

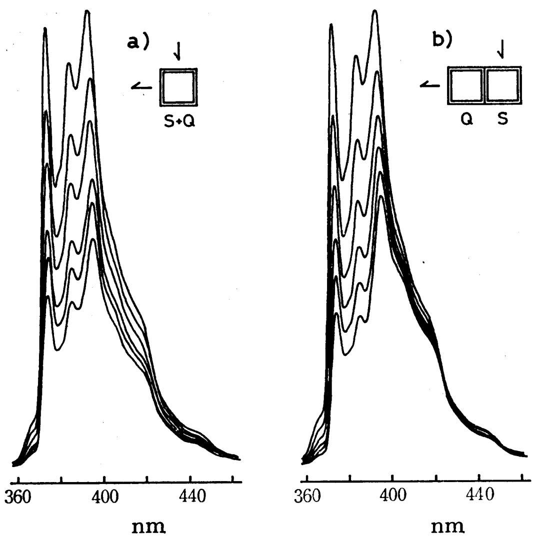

Fig. 3. Changes of fluorescence spectra with the concenration of 4-benzylidene-2-phenyl-5-oxazolone (Q). a) Quenching of fluorescence of pyrene (S) by the oxazolone in benzene, b) reabsorption of fluorescence of pyrene (S) by the oxazolone in benzene.

by the following experiment. A cell containing benzene solution of an emissive hydrocarbon without the oxazolone was placed adjacently to a cell containing benzene solution of the oxazolone in various concentrations, and the fluorescence emitted from the former solution was observed after passing the latter solution. A typical example is shown in Figs. 2 and 3 for pyrene, which has the highest k_q^S value among the sensitizers employed, showing that the spectral change of the fluorescence of the hydrocarbon with added oxazolone in the solution closely resembles that of the fluorescence of the hydrocarbon solution without the oxazolone observed through its reabsorption by the oxazolone solution.

These facts undoubtedly indicate that the fluorescence emitted from the hydrocarbons is effectively reabsorbed by the oxazolone in the surrounding medium, and the reported "selectivity" of the sensitized reaction course seems to depend on the fluorescence wavelength of the sensitizers. In Table 1 are listed $(I_0/I)_{\rm reabs}$ values at $[Q]=2\times10^{-5}$ mol/l which denote estimated values for I_0/I when the decrease of the fluorescence intensity with the oxazolone is assumed to be due only to its reabsorption by the oxazolone, and these values are evaluated from $k_q^{\rm app}$, k_q^S, and τ_0^S, according to Eq. 3.

$$(I_0/I)_{\rm reabs} = 1 + (k_q^{\rm app} - k_q^S)\tau_0^S[Q] \qquad (3)$$

Quenching of Hydrocarbon Triplet by the Oxazolone. Since the triplet energies of the aromatic hydrocarbons employed are in the range between 56.6 kcal/mol for chrysene and 68.0 kcal/mol for fluorene in a nonpolar solvent,[4] and the first excited triplet energy of the oxazolone has been estimated to be 43.0 kcal/mol[2] in chloroform, triplet energy transfer from the hydrocarbons to the oxazolone is expected to be sufficiently exothermic and to proceed with nearly diffusion-controlled rate constants.

In order to examine whether the quenching of the triplet states of the hydrocarbons by the oxazolone would proceed in different manner between "selective" and "unselective" hydrocarbon sensitizers as was proposed by Ullman, rate constants for the quenching of the triplet hydrocarbons by the oxazolone were measured by flash spectrophotometry. The oxazolone did not show any detectable transient absorption in the region of 380—600 nm on flash excitation. So, the decay of the triplet-triplet absorption of the hydrocarbon was followed in the absence and in the presence of various concentrations of the oxazolone in cyclohexane solution at room temperature.

Figures 4 and 5 show typical oscilloscopic traces of triplet-triplet absorption of naphthalene and triphenylene in the absence (a) and in the presence (b) of the oxazolone obtained by monitoring the absorption at 420 and 430 nm, respectively, and Figs. 6 and 7 contain

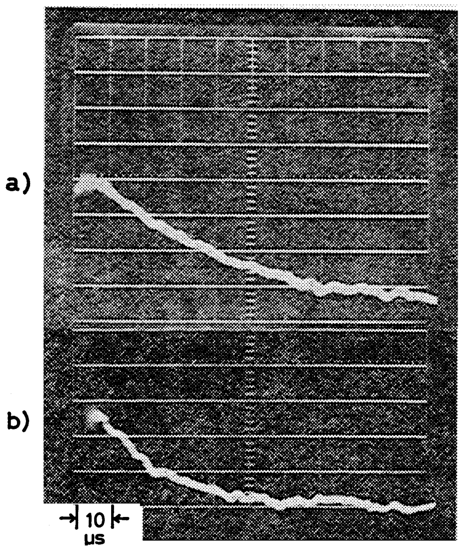

Fig. 4. Oscilloscopic traces of triplet-triplet absorption of naphthalene (7.5×10^{-5} M) in cyclohexane in the absence of 4-benzylidene-2-phenyl-5-oxazolone (a) and in the presence of the oxazolone in 5.5×10^{-6} M (b).

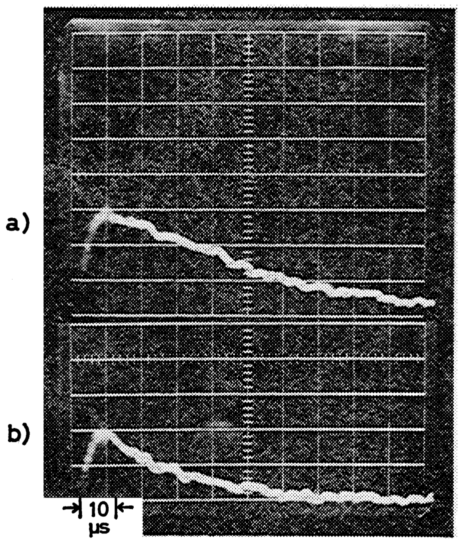

Fig. 5. Oscilloscopic traces of triplet-triplet absorption of triphenylene (3.5×10^{-5} M) in cyclohexane in the absence of 4-benzylidene-2-phenyl-5-oxazolone (a) and in the presence of the oxazolone in 5.5×10^{-6} M (b).

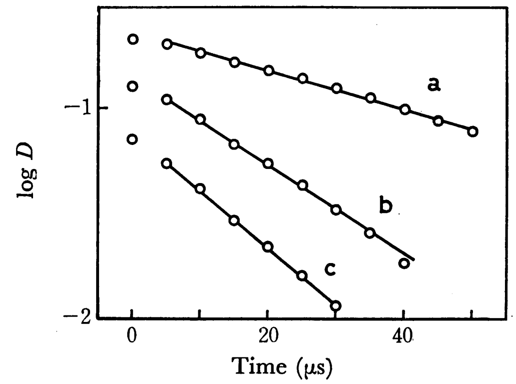

Fig. 6. First-order rate plots for the decay of triplet-triplet absorption (intensity: D) of naphthalene in cyclohexane in the absence of 4-benzylidene-2-phenyl-5-oxazolone (a), in the presence of the oxazolone in 5.5×10^{-6} M (b), and in 1.1×10^{-5} M (c).

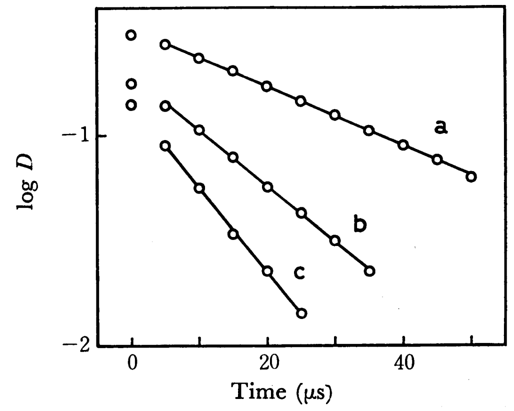

Fig. 7. First-order rate plots for the decay of triplet-triplet absorption (intensity: D) of triphenylene in cyclohexane in the absence of 4-benzylidene-2-phenyl-5-oxazolone (a), in the presence of the oxazolone in 5.5×10^{-6} M (b), and in 1.1×10^{-5} M (c).

first-order plots for the decays of the transients in the presence of different concentrations of the oxazolone. These figures indicate that intensities of triplet-triplet absorptions of the hydrocarbons were reduced and their decay rates were accelerated by the added oxazolone. The slope of the above plots yields the pseudo first-order overall decay coefficient, k', for a particular concentration of the added oxazolone. The coefficient, k', is expressed in the following form:

$$k' = k_d^T + k_q^T[Q] \tag{4}$$

where k_q^T is the second-order rate constant for the triplet quenching and k_d^T represents the first-order coefficient for the unimolecular decay. The observed k' values actually obeyed Eq. 4 to give k_q^T values. The obtained values for k_q^T are summarized in Table 2, together with k_q^{app}, k_q^S, singlet lifetimes, τ_0^S, quantum yields for fluorescence and intersystem crossing, Φ_f and Φ_{IS}, respectively.

Table 2 shows that the triplet states of all sensitizers employed are quenched by the oxazolone with rate constants close to the diffusion-controlled limit regardless of "selective" or "unselective" sensitizers, or of the triplet excitation energy and the structure of the sensitizer. The k_q^T values of fluorene, phenanthrene, and chrysene are larger than those of naphthalene and triphenylene. This result is in contrast with the previous postulate[2] that fluorene and naphthalene classified as "unselective" sensitizers would be more facilely quenched by the oxazolone than the other sensitizers classified as "selective" ones.

New Account for the Effect of the Sensitizers on the Reaction Course. The simplest mechanistic scheme to account for the sensitized reaction is shown in Eqs. 5—15, where S denotes the hydrocarbon sensitizer and Q denotes the oxazolone.

$$\begin{array}{lll}
 & \text{rate constant} & \\
S \xrightarrow{h\nu} {}^1S^* & & (5) \\
{}^1S^* \longrightarrow S_0 + h\nu_f & k_f & (6) \\
{}^1S^* \longrightarrow S_0 & k_d^S & (7) \\
{}^1S^* \longrightarrow {}^3S^* & k_{IS} & (8) \\
{}^1S^* + Q \longrightarrow S_0 + {}^1Q^* & k_q^S & (9) \\
Q \xrightarrow{h\nu_f} {}^1Q^* & k_{reabs} & (10) \\
{}^3S^* \longrightarrow S_0 & k_d^T & (11) \\
{}^3S^* + Q \longrightarrow S_0 + {}^3Q^*(\pi,\pi) & k_q^T & (12) \\
{}^3Q^*(\pi,\pi) \longrightarrow \text{isomerization} & & (13) \\
{}^1Q^* \longrightarrow {}^3Q^*(n,\pi) & & (14) \\
{}^3Q^*(n,\pi) \longrightarrow \text{H-abstraction} & & (15)
\end{array}$$

Thus, a sensitizer molecule, on absorption of photon, is excited to its singlet state (Eq. 5). The singlet state either undergoes fluorescence emission (Eq. 6), radiationless deactivation to the ground state (Eq. 7), intersystem crossing to the triplet state (Eq. 8), or is quenched by the oxazolone (Eq. 9). The emitted fluorescence

TABLE 2. QUENCHING RATE CONSTANTS AND SPECTRAL CHARACTERISTICS OF AROMATIC HYDROCARBONS

Hydrocarbon	τ_0^S a) ns	k_q^{app} b) $\times10^{-12}$	k_q^S b) $\times10^{-12}$	τ_0^T c) μs	k_q^T c,d) $\times10^{-9}$	Φ_f e)	Φ_{IS} e)
Fluorene	10	3.5	0.15	10.4	14.8	0.68	0.31
Naphthalene	96	2.8	0.49	32.7	5.4	0.23	0.40
Triphenylene	37.4	8.3	0.11	39.5	4.1	0.10	0.90
Phenanthrene	57.5	9.4	0.42	15.3	13.0	0.13	0.82
Chrysene	43.7	6.5	0.39	19.5	10.0	0.14	0.69

a) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd Ed., Academic Press, New York, N. Y. (1971). b) In $M^{-1}\,s^{-1}$, in benzene. c) Conducted under nitrogen in cyclohexane; the concentration of the hydrocarbon: $(4—8)\times10^{-5}$ M, the concentration of the oxazolone: $0—1\times10^{-5}$ M. d) In $M^{-1}\,s^{-1}$. e) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," John Wiley and Sons, New York, N. Y. (1969) p. 118.

TABLE 3. ESTIMATED QUANTUM YIELDS FOR SENSITIZED REACTIONS OF THE OXAZOLONE IN 2×10^{-5} M THROUGH APPARENT FLUORESCENCE (Φ_f^{app}), INTERSYSTEM CROSSING (Φ_{IS}), QUENCHING OF THE SINGLET SENSITIZERS (Φ_q^S), REABSORPTION OF THE FLUORESCENCE FROM THE SINGLET SENSITIZERS (Φ_{reabs}), AND QUENCHING OF THE TRIPLET SENSITIZERS (Φ_q^T)

	Φ_f^{app}	Φ_{IS}	Φ_q^S	Φ_{reabs}	Φ_q^T
Fluorene	0.46	0.30	0.02	0.21	0.23
Naphthalene	0.19	0.33	0.18	0.05	0.26
Triphenylene	0.05	0.89	0.01	0.05	0.68
Phenanthrene	0.05	0.77	0.06	0.07	0.62
Chrysene	0.07	0.66	0.05	0.06	0.52

can be reabsorbed by the oxazolone and the latter is excited to its singlet state (Eq. 10). The triplet state of the sensitizer either undergoes radiationless deactivation (Eq. 11) or is quenched by the oxazolone to give the lowest triplet state of the latter (Eq. 12). The quantum yields for the singlet quenching (Φ_q^S), for the reabsorption of fluorescence (Φ_{reabs}), for the apparent fluorescence (Φ_f^{app}), and for the triplet quenching (Φ_q^T) by the oxazolone are estimated in the presence of 2×10^{-5} mol/l of the oxazolone according to the following equations 16—20 and summarized in Table 3.

$$\Phi_f^{app} = \frac{k_f\tau_0^S}{1+k_q^{app}\tau_0^S[Q]} \tag{16}$$

$$\Phi_{IS} = \frac{k_{IS}\tau_0^S}{1+k_q^S\tau_0^S[Q]} \tag{17}$$

$$\Phi_q^S = \frac{k_q^S\tau_0^S[Q]}{1+k_q^S\tau_0^S[Q]} \tag{18}$$

$$\begin{aligned}\Phi_{reabs} &= \frac{k_f\tau_0^S}{1+k_q^S\tau_0^S[Q]} - \frac{k_f\tau_0^S}{1+k_q^{app}\tau_0^S[Q]} \\ &= \Phi_f - \Phi_f^{app}\end{aligned} \tag{19}$$

$$\Phi_q^T = \Phi_{IS}\frac{k_q^T\tau_0^T[Q]}{1+k_q^T\tau_0^T[Q]} \tag{20}$$

Table 3 shows that fluorene and naphthalene, which fluoresce at shorter wavelengths, transfer singlet energy to the oxazolone more efficiently by both bimolecular interaction and reabsorption mechanism, but transfer triplet energy less efficiently than triphenylene, phenanthrene, and chrysene, which fluoresce at longer wavelengths; that is, the "unselective" sensitizers interact with the oxazolone in the singlet state as well as in the triplet state, while the "selective" sensitizers interact more effectively in the triplet state than in the singlet state. These results clearly account for Ullman's observation concerning the dependence of the sensitized reaction course on the structure of the sensitizers employed.

Thus, on taking account of an assumption by Ullman and Baumann that the lowest triplet state of the oxazolone undergoes isomerization and the higher triplet state abstracts hydrogen atom from a solvent, the oxazolone can be easily excited to its $T_1(\pi,\pi^*)$ state by all the sensitizers employed resulting in the isomerization (Eq. 13), but to its higher excited state, for example, T_2 (n, π^*) state, it would be efficiently excited through its singlet state only by sensitization with fluorene and naphthalene (Eqs. 10 and 14) resulting in hydrogen abstraction (Eq. 15).

Finally it should be stressed that reabsorption mechanism can play an important role in some photochemical systems.[5]

Experimental

Materials. 4-Benzylidene-2-phenyl-5-oxazolone was prepared by treating benzaldehyde with *N*-benzoylglycine and recrystallized from benzene.[6] Most sensitizers were purified by column chromatography and recrystallization, and their purities were checked by absorption and fluorescence spectra, and fluorescence lifetimes. Anthracene was prepared by reduction of anthraquinone and recrystallized.[7] Benzene (Wako special grade) was distilled over calcium hydride before use. Cyclohexane (Dotite Spectrosol) was used as received.

Spectra. Absorption spectra were measured with a Hitachi EPS-3 Recording Spectrophotometer. Emission spectra and fluorescence intensities were determined with a Hitachi MPF-2A Fluorescence Spectrophotometer. Reabsorbed emission spectra were measured by observing the emission from hydrocarbon solution in benzene placed in a quartz cell (1 cm in length and 1 cm in width) after passing through an adjacent quartz cell (1 cm in length and 1 cm in width) containing benzene solution of the varying concentration of the oxazolone.

Fluorescence lifetime was measured with a JASCO FL-10 Phase Fluorimeter.

Flash Spectrophotometry. A sample solution contained in a quartz cell (8 cm in length and 2 cm in diameter) was deaerated by bubbling nitrogen. A quartz flash photolysis lamp (10 cm in length and 2 cm in diameter) filled with xenon was operated at 11 kV and 2 μF, dissipating an energy of 120 J; the duration of the flash was 10 μs. The decays of triplet-triplet absorption of hydrocarbons were determined with a xenon lamp (Toshiba 500 W), a plane grating spectrograph (Shimadzu GE-100), a photomultiplier tube (RCA 1P28), and a synchroscope (Toshiba 3054).

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