The data in Table IV are in agreement with eq 7, as shown in Figure 2. However, the scatter of the points is appreciable, and, moreover, at greater dilutions fairly large conversions had to be used. The slope to intercept ratio gives a value of about 2.5 for $\gamma'k'_{Ci}/\gamma k_{Ci}$. The value larger than unity suggests that cyclodimerization occurs perhaps only within a restricted range of mutual orientations of the two 2-butene molecules at the time of their encounter.

It should be stressed that although the reaction scheme employed treats formally the effect of dilution as a competitive collisional deactivation, implicit in the treatment is the notion that the diluent decreases the probability of encounters (or perhaps of complex formation as a precursor to cyclodimerization) between a ground state and an electronically excited state of cis-2-butene during the effective lifetime of the latter. This effect could be to some extent likened to a solvent cage effect.

The ratios of the yields of the other butene isomerization products (butene-1 + methylcyclopropane, not shown in Table IV) to the yield of trans-2-butene are not affected by dilution. The effect of dilution on the acyclic C_8 products in Table IV will be discussed in the next section.

Fragmentation Reactions and Cyclodimer Rearrangement. The data in Tables II, III, and IV show that, even in the liquid phase, an appreciable fragmentation (photolysis) of 2-butene takes place and is followed by the usual free radical combination and disproportionation reactions. The extent of photolysis is greater at room temperature than at -78 °C and is much enhanced by a decrease in wavelength to 184.9 nm, at which wavelength relatively little cyclodimerization is observed. These trends are easily understandable in terms of the large amount of energy acquired by the molecule which absorbs a photon (and perhaps enhanced formation of a different electronic state at 184.9 nm[11,12]) and the greater probability of dissipation of energy in liquid phase. In agreement with this, Table III shows very much enhanced photolysis in the gas phase relative to geometric isomerization and very little cyclodimerization even at 213.9 nm. It is not the primary object of the present paper

to discuss in detail the mechanism of photolysis, although, as already stated, most of the reaction paths leading to the products listed in Tables II, III, and IV are obvious (and have been indicated by writing each compound symbolically as a dimer of the two radicals from which it has been formed by combination).

It should be mentioned also that, at higher temperatures and shorter wavelengths, the photolytic reactions may be accompanied to some extent by partial rearrangement of the "hot" cyclodimer to acyclic C_8 products. This may in particular apply to 3,4-dimethyl-2-hexene (indicated in the tables by the symbol V·sB), which is affected by dilution in a manner which parallels more closely the trend shown by the cyclodimers A and B than by trans-2-butene. Support for this view comes also from the fact that some other products which would be expected if free vinylic radical $CH_3\dot{C}=CHCH_3$ were present are not observed. The rearrangement may be visualized as ring opening to form a 1,4-biradical, which then rearranges by a 1,5-H atom shift. 3,4-Dimethyl-1-hexene (M_1·sB) may also be formed to a certain extent by cyclodimer rearrangement, although it must also be formed in this system by radical recombination.

References and Notes

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Kinetic Study of Triplet Excimer Formation in Fluid Solution by Means of Phosphorimetry

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Abstract: The kinetics of the triplet excimer formation has been studied by means of phosphorimetry for naphthalene and 1-chloronaphthalene in isooctane at 293 K. The decay of the monomer phosphorescence and the rise and decay of the excimer phosphorescence following flash excitation were observed. From an analysis of the results obtained, the existence of the triplet excimer was confirmed for both naphthalene and 1-chloronaphthalene. The time behavior of the monomer and excimer phosphorescence is well explained by eq 6 in the text. In isooctane at 293 K the rate constants for the various processes involved were found to be: $k_1 = 0.2 \times 10^3$ s^{-1}, $k_2 = 0.8 \times 10^3$ s^{-1}, $k_d + k_1' = 2.0 \times 10^7$ M^{-1} s^{-1}, and $k_{dis} = 7.0 \times 10^3$ s^{-1} for naphthalene, and $k_1 = 0.6 \times 10^3$ s^{-1}, $k_2 = 0.6 \times 10^3$ s^{-1}, $k_d + k_1' = 6.0 \times 10^7$ M^{-1} s^{-1}, and $k_{dis} = 1.0 \times 10^3$ s^{-1} for 1-chloronaphthalene.

The excimer phosphorescence or the triplet excimer has been studied by several workers for aromatic compounds under various conditions.[1-14] Existence of the triplet excimer is relatively well established for some halobenzenes.[3,4] Langelaar et al.[6] indirectly obtained excimer phosphores-

cence spectra for naphthalene and phenanthrene by subtracting the phosphorescence spectrum at 140 K (just below the melting point of the solvent, 95% ethanol) from the spectrum at higher temperatures, but the emission assigned to the triplet excimer of phenanthrene turned out to origi-
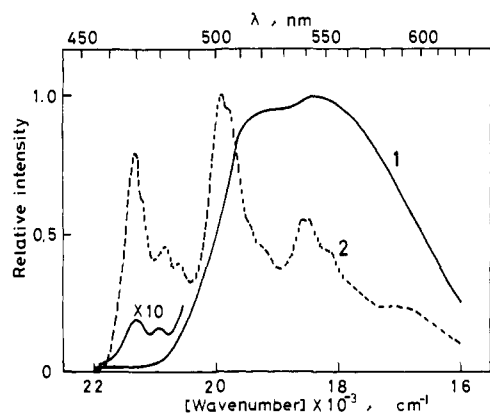
Figure 1. The corrected phosphorescence spectra of naphthalene in isooctane (1.52×10^{-4} M) at 293 K (1) and in EPA at 77 K (2). Relative intensity represents the relative spectral quantum yield per unit wavelength interval.
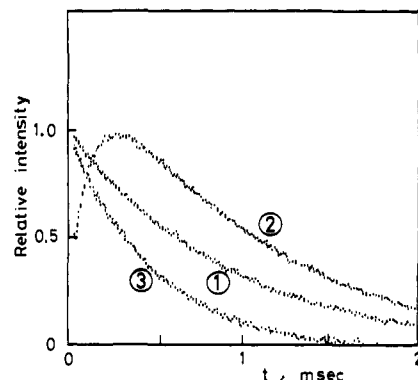

Figure 2. Some representative $I(t)$ curves for naphthalene in isooctane at 293 K. The monitoring wavelengths are (1) 470 nm, (2) 510 nm, and (3) 340 nm.

nate from an impurity.[14] Briegleb et al.[8] also reported excimer phosphorescence for naphthalene and phenanthrene in glassy n-propyl ether solutions at temperatures near 100 K; however, the excimer phosphorescence was observed when the hydrocarbon molecules formed charge-transfer complexes with electron acceptors. Thus, whether or not unsubstituted aromatic hydrocarbons give excimer phosphorescence still remains open to question.

We have recently observed phosphorescence of naphthalene in nonviscous fluid solution with the aid of a sensitive spectrophotometer and found that the phosphorescence spectrum is ascribable mainly to the triplet excimer of naphthalene on the basis of the following experimental results:[1] (1) The phosphorescence spectrum in isooctane solution at temperatures near 300 K is distinctly different from the spectrum in rigid-glass solution; (2) the phosphorescence excitation spectrum is in complete agreement with the absorption spectrum of monomeric naphthalene; (3) the phosphorescence quantum yield and the reciprocal of the phosphorescence lifetime increase with increasing solute concentration; (4) the dependence of the phosphorescence spectrum in glycerol on the solvent viscosity and solute concentration shows that the phosphorescence consists of emissions from both the monomer and the excimer; and (5) the phosphorescence disappears by aeration.

In this study we have kinetically examined the phosphorescence of naphthalene and 1-chloronaphthalene in isooctane under fluid conditions in order to establish the existence of the triplet excimer and to explore the mechanism of triplet excimer formation.

Experimental Section

Naphthalene was carefully purified by vacuum sublimation, zone refining, and chromatography using activated silica gel. 1-Chloronaphthalene was purified by repeated vacuum distillation. Spectrograde isooctane was passed through a silica gel column. Solutions of the sample in isooctane were fully degassed by repeated freeze-thaw cycles (seven or eight times).

Emission spectra were measured with a high-resolution, high-sensitivity emission spectrophotometer which has recently been constructed in our laboratory by means of the photon-counting method, using a Hamamatsu R585 photomultiplier that shows at room temperature a very low dark current corresponding to ~1 count/s.

In the emission spectrophotometer, light from a 150-W xenon arc lamp is dispersed by a Czerny-Turner double monochromator with an f number of 4.5, consisting of a quartz prism and a grating (1200 lines/mm), to give monochromatic excitation beam. The emission obtained at right angles to the excitation beam is dispersed by another Czerny-Turner monochromator with f of 4.5,

which includes a single 1200 lines/mm grating, and the resulting monochromatic emission is detected by an R585 photomultiplier. Both excitation and emission wavelengths are scanned discontinuously with the aid of a pulse motor. Emission with a quantum yield as low as 10^{-7} can be measured with this spectrophotometer, provided that an optimum concentration of sample material can be used. A phosphoroscope is attached to the spectrophotometer.

A specially designed spectrophosphorimeter was used for measuring the intensity of phosphorescence or delayed fluorescence emission as a function of time, in a range of 10^{-5} to 10^2 s, as well as for obtaining their time-resolved spectra.

The spectrophosphorimeter consists of excitation and emission grating monochromators ($f/\sim4$) of a Hitachi MPF-2A fluorescence spectrophotometer and an R585 photomultiplier detector. It is based on the photon-counting method combined with a multichannel digital boxcar technique.[15] Two sorts of light sources were used for excitation: (1) a 150-W xenon arc lamp, the light from which is chopped mechanically by a variable frequency synchronous motor (10-400 rps) to provide light pulses of constant intensity and relatively short duration (down to 50 μs); (2) a xenon flash lamp of 3 μs duration. Also, two sorts of photoelectron-counting systems were employed: (1) a homemade 16-channel counter with the shortest resolvable time of 50 ns; (2) a commercial multichannel pulse-height analyzer (Northern 720 PHA, 1024 channels) with the shortest resolvable time of 10 μs. These light sources and counting systems are appropriately combined according to the purpose of measurement. Thus, for example, the time-resolved phosphorescence spectrum is observed by combining the source (1) and the counting system (1), while the phosphorescence intensity as a function of time is measured by the use of the source (2) and the counting system (2). A phosphoroscope is also attached to this spectrophosphorimeter to obtain an emission spectrum from which the prompt fluorescence is eliminated.

The phosphorescence spectra were corrected for the spectral sensitivity of the monochromator-photomultiplier system, after the method reported in a previous paper[16] using a standard tungsten filament lamp. The phosphorescence quantum yields were determined by comparing the corrected phosphorescence spectra with a corrected fluorescence spectrum of quinine sulfate in 0.5 M sulfuric acid, which has a fluorescence quantum yield of 0.51.

Results

Figure 1 shows the corrected phosphorescence spectrum of naphthalene in isooctane at 293 K. The weak structured phosphorescence band in a wavelength region near 470 nm, which is similar to that observed in EPA at 77 K, is due to the triplet monomer of naphthalene, and the broad emission band with its intensity maximum at about 540 nm is attributed to the triplet excimer according to the assignment given in the previous paper.[1]

The emission intensity as a function of time after flash excitation, monitored at a given wavelength, is denoted by $I(t)$. Figure 2 shows some representative $I(t)$ curves for naphthalene in isooctane at 293 K. The emission detected at 470 nm is presumed to consist predominantly of the mono-
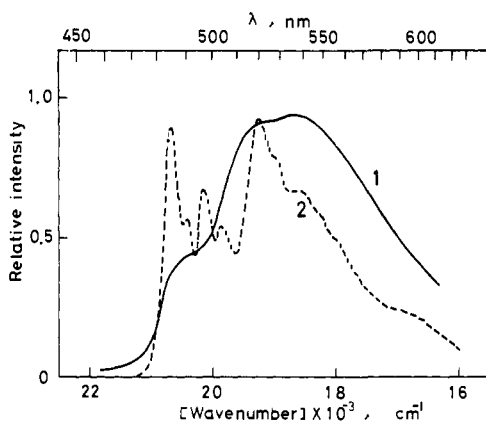
Figure 3. The corrected phosphorescence spectra of 1-chloronaphthalene in isooctane (0.50×10^{-4} M) at 293 K (1) and in EPA at 77 K (2). Relative intensity represents the relative spectral quantum yield per unit wavelength interval.

mer phosphorescence, and that detected at 510 nm is due essentially to the triplet excimer. The figure includes also the $I(t)$ curve for the delayed fluorescence observed at 340 nm.

Each of the $I(t)$ curves obtained by monitoring the emission at 470 and 340 nm represents a first-order decay; the rate constant for the decay is denoted by $\kappa(470)$ or $\kappa(340)$. The $I(t)$ curve monitored at 510 nm shows a rise for small values of t and a decay for large t. The plot of log $I(t)$ vs. t for the decay part of the curve yields a straight line with a slope leading to a first-order decay constant, $\kappa(510)$. It is found that $\kappa(510)$ agrees with $\kappa(470)$ and with one-half the value of $\kappa(340)$. It should be noted that the functions $I(t)$ obtained at various wavelengths longer than 510 nm also have both rise and decay parts, and that the decay constants κ obtained in the same way as before are essentially equal to $\kappa(510)$.

The phosphorescence spectrum of 1-chloronaphthalene in isooctane at 293 K is shown in Figure 3, together with the spectrum in EPA at 77 K. As in the case of naphthalene, the phosphorescence band in a short-wavelength region near 490 nm, appearing as a shoulder, can be assigned mainly to the monomer, and the broad phosphorescence band in the region longer than 510 nm, having its intensity maximum at about 540 nm, may be ascribed to the excimer. The $I(t)$ curves for 1-chloronaphthalene monitored at 490 and 510 nm are shown in Figure 4. They are qualitatively similar to the corresponding curves for naphthalene.

Under the present experimental conditions where the excitation intensity is very low and the solution is of very low viscosity, the kinetic scheme for the deactivation of the triplet state involving excimer formation may be assumed to be as follows:[1,9,14]

$$^3M^* + {}^1M \underset{k_{dis}}{\overset{k_f}{\rightleftharpoons}} {}^3D^* \qquad (1)$$
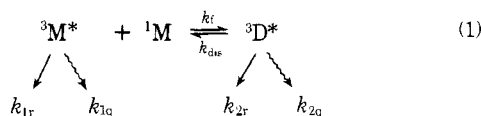
$$k_{1r} \quad k_{1q} \qquad k_{2r} \quad k_{2q}$$

where ^1M, $^3M^*$, and $^3D^*$ stand for the ground singlet monomer, excited triplet monomer, and excited triplet dimer (triplet excimer), respectively; k_{1r}, k_{1q}, k_{2r}, and k_{2q} are the radiative (r) and nonradiative (q) decay constants for the triplet monomer and excimer. k_f and k_{dis} denote the rate constants for formation and dissociation of the triplet excimer. Because of the very low intensity of the exciting light, the T–T annihilation process need not be considered.

Solving the rate equations appropriate to the kinetic scheme 1, with initial conditions $[^3M^*] = [^3M^*]_0$, $[^3D^*] = 0$ at $t = 0$, one obtains the following expressions for the time dependence of the intensities of the monomer (m) and
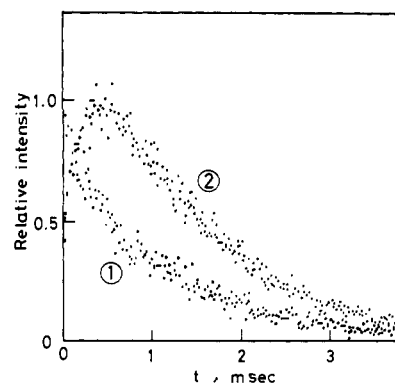

Figure 4. The $I(t)$ curves for 1-chloronaphthalene in isooctane at 293 K. The monitoring wavelengths are (1) 490 nm and (2) 510 nm.

excimer (d) phosphorescence:

$$I_m(t) = \frac{k_{1r}[^3M^*]_0(\theta_2 - X)}{(\theta_2 - \theta_1)}\{e^{-\theta_1 t} + Ae^{-\theta_2 t}\} \qquad (2)$$

$$I_d(t) = \frac{k_{2r}[^3M^*]_0 k_f[^1M]}{(\theta_2 - \theta_1)}\{e^{-\theta_1 t} - e^{-\theta_2 t}\} \qquad (3)$$

where

$$\theta_{1,2} = \frac{1}{2}[X + Y \mp \{(Y - X)^2 + 4k_f k_{dis}[^1M]\}^{1/2}] \qquad (4)$$

and

$$A = (X - \theta_1)/(\theta_2 - X)$$

$$X = k_1 + k_f[^1M] \qquad Y = k_2 + k_{dis} \qquad (5)$$

$$k_1 = k_{1r} + k_{1q} \qquad k_2 = k_{2r} + k_{2q}$$

According to eq 3, the excimer phosphorescence should yield a rise-and-decay curve, which is to be approximated at sufficiently long times by an exponential curve associated with a first-order decay with a rate constant θ_1. In Figures 2 and 4, the $I(t)$ curves monitored at 510 nm for both naphthalene and 1-chloronaphthalene correspond well to $I_d(t)$ given by (3), so that the $\kappa(510)$ values may be assigned to θ_1. The values of θ_2 can be obtained from the difference between the $I(t)$ curve observed and the first-order decay curve extrapolated toward shorter times by the use of θ_1, or from the value of t at which $I(t)$ reaches a maximum.

On the other hand, eq 2 predicts that the monomer phosphorescence should display a curve consisting of two exponential decays. Contrary to this prediction, the $I(t)$ functions obtained by monitoring at 470 and 490 nm, respectively, for naphthalene and 1-chloronaphthalene (Figures 2 and 4) can be described each as a single exponential decay; the values of $\kappa(470)$ and $\kappa(490)$ are in good agreement with the respective $\kappa(510)$ values for the two compounds which have been assigned to θ_1. These results may be understood by assuming that the coefficient A in eq 2 is too small for the decay component with the rate constant θ_2 to be detected. In fact, it will be seen from the data shown later in Table I that the fast decay component, characterized by the rate constant θ_2, is difficult to detect unambiguously under our experimental conditions.

Figures 5 and 6 show plots of θ_1 and θ_2 against the concentrations of naphthalene and 1-chloronaphthalene, respectively. As the concentration of naphthalene increases, θ_1 increases and reaches a constant value in a relatively high concentration region. On the other hand, the value of θ_1 for 1-chloronaphthalene is independent of concentration over a wide range of 10^{-2}–10^{-6} M. The θ_2 values increase with increasing solute concentration for both compounds.

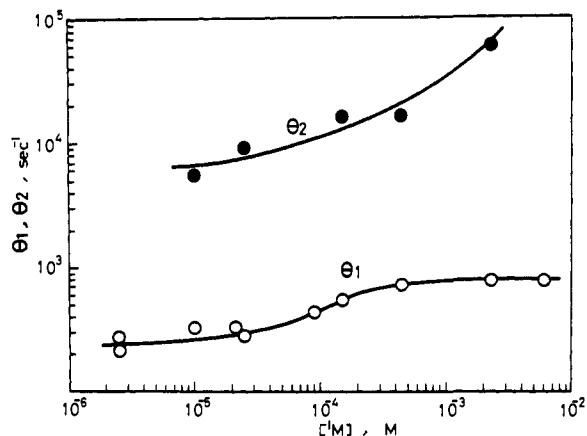The rate constants k_1, k_2, k_f, and k_{dis} in reaction scheme 1 can be evaluated from the data on θ_1 and θ_2 as a function

Figure 5. The plots of θ_1 and θ_2 against the concentration of naphthalene in isooctane at 293 K.

Figure 7. The plots of $\theta_1 + \theta_2$ against the concentration of naphthalene (1) and 1-chloronaphthalene (2) in isooctane at 293 K.

Figure 6. The plots of θ_1 and θ_2 against the concentration of 1-chloronaphthalene in isooctane at 293 K.

Table I. Rate Constants for Naphthalene and 1-Chloronaphthalene in Isooctane at 293 K

	$k_1 \times 10^{-3}$ s^{-1}	$k_2 \times 10^{-3}$ s^{-1}	$k_f \times 10^{-7}$ $M^{-1} s^{-1}$	$k_{dis} \times 10^{-3}$ s^{-1}	$\rho \times 10^3$
Naphtha-lene	0.2	0.8	2.0	7.0	0.9
1-Chloro-naphtha-lene	0.6	0.6	6.0	1.0	2.7

of the concentration, [^{1}M], using eq 4 and 5. The following limiting properties of θ_1 and θ_2 were taken into consideration for the evaluation of the rate constants.[14] (i) As [^{1}M] $\rightarrow$ 0, $\theta_1 \rightarrow k_1$ and $\theta_2 \rightarrow k_2 + k_{dis}$; (ii) as $1/[^1M] \rightarrow 0$, $\theta_1 \rightarrow k_2$; and (iii) at any solute concentration, $d(\theta_1 + \theta_2)/d[^1M] = k_f$. Figure 7 shows plots of $\theta_1 + \theta_2$ against [^{1}M] at 293 K for naphthalene and 1-chloronaphthalene; the plots give good straight lines within our experimental errors. From the slopes of the lines, the values of k_f are immediately found to be 2.0×10^7 and 6.0×10^7 M^{-1} s^{-1} for naphthalene and 1-chloronaphthalene, respectively. The rate constants for naphthalene and 1-chloronaphthalene determined from the experiments under transient conditions are summarized in Table I.

Discussion

There have hitherto been many cases where emission assigned to the triplet excimer of an aromatic hydrocarbon turned out to originate from an impurity. Chandross and Dempster studied the naphthalene dimer phosphorescence in a rigid matrix by means of the sandwich dimer technique,[12] and were led to the conclusion that the excimer phosphorescence of naphthalene would be very difficult to observe.

In a previous paper,[1] we suggested through a phosphorimetric investigation by steady irradiation of naphthalene in fluid solution that the broad emission band with its intensity maximum at about 510 nm (uncorrected for the spectral sensitivity) may be attributed to the naphthalene excimer phosphorescence, and that it cannot be due to any impurity
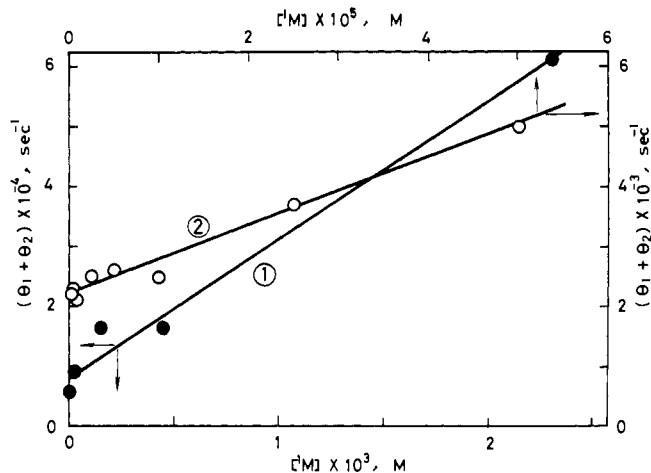
contained originally in the solvent. When a phosphorescent impurity is contained in the solute itself, however, one is not able to decide conclusively on the basis of the spectral data obtained by steady irradiation alone whether the emission is due to the triplet excimer or to the impurity. It should be noted that the broad emission is not due to a photochemical product, because practically no change was produced in the intensity of the broad emission by exposing the sample solution to uv light for a long time.

In order to definitely establish the existence of the triplet excimer in fluid solution, let us examine the possibility that the emission originates from a solute impurity. If the emission assigned to the excimer phosphorescence were to be due to an impurity triplet, ^{3}Q*, resulting from irreversible triplet–triplet energy transfer from naphthalene or 1-chloronaphthalene to the impurity, the mechanism of the occurrence of the broad emission would be represented by a reaction scheme which is similar to the scheme in (1), with ^{1}Q substituted for ^{1}M and ^{3}Q* for ^{3}D*, but is different from (1) because of the irreversibility of energy transfer.

Thus, if $k_2 < k_1 + k_f[^1Q]$, we have

$$I_m(t) = C_1 \exp(-\theta_2 t)$$

$$I_q(t) = C_2\{\exp(-\theta_1 t) - \exp(-\theta_2 t)\}$$

where $\theta_1 = k_2$, $\theta_2 = k_1 + k_f[^1Q]$, and $C_1, C_2 > 0$. In this case, the decay rate constants for the monomer phosphorescence observed at 470 nm (naphthalene) and 490 nm (1-chloronaphthalene) are expected to coincide with the rise rate constants in the early stages of the $I(t)$ curves monitored at 510 nm. The expected results were not obtained in the range of the solute concentration examined for both compounds.

Next, if $k_2 > k_1 + k_f[^1Q]$ for any solute concentrations examined, it follows that

$$I_m(t) = C_1 \exp(-\theta_1 t)$$

$$I_q(t) = C_2\{\exp(-\theta_1 t) - \exp(-\theta_2 t)\}$$

where $\theta_1 = k_1 + k_f[^1Q]$, $\theta_2 = k_2$, C_1, $C_2 > 0$. In this case it is expected that θ_2 is independent of the solute concentration and θ_1 increases linearly with the same concentration, if the impurity is originally contained in the sample. These expectations obviously contradict the present experimental results (see Figures 5 and 6).

In the preceding discussion, we assumed irreversibility of the energy transfer reaction, which seems to be reasonable.[14,17,18] Taking into consideration the reverse energy transfer from the impurity to naphthalene or 1-chloronaphthalene, in addition to the forward transfer, we can show the following relations. When $[^1M] \to 0$, $\theta_1 \to k_1$ and $\theta_2 \to k_2$, and when $1/[^1M] \to 0$, $\theta_1 \to k_2$. The experimental results shown in Figures 5 and 6, therefore, cannot be explained even if we assume the energy-transfer reaction to be reversible.

Thus, the present experiments under transient conditions afford strong evidence that the broad emission band with its intensity maximum at 540 nm should be attributed to the triplet excimer of naphthalene or 1-chloronaphthalene.

Here we might note the discrepancies between the experimental results of Chandross and Dempster[12] and ours. They observed the normal excimer fluorescence from a naphthalene sandwich pair, but no excimer phosphorescence. We carried out the same experiments as they did. The results were identical with theirs in rigid matrix, but when the sample solution became fluid the excimer phosphorescence appeared as well as the excimer fluorescence. This may be explained by assuming that the geometries of singlet and triplet excimers are considerably different.

The rate constant k_f for the formation of triplet excimer in (1) is anomalously small compared with the diffusion-controlled rate constant for singlet excimer formation.[14] This observation is in qualitative agreement with the result of a study by Langelaar et al.[9] In an analysis of the decay rate of delayed fluorescence, they suggested indirect evidence for the excimer formation on the basis of various assumptions. Following Langelaar et al., we write

$$k_f = \rho k_{dif}$$

where k_{dif} is the diffusion-controlled rate constant, and ρ is the efficiency with which an encounter complex forms the triplet excimer. In Table I the ρ values are shown which are determined from k_f and k_{dif}, the latter being obtained by the use of the relation $k_{dif} = 8RT/3000\eta$.[18] The extreme smallness of ρ values means that the triplet excimer formation is unusually inefficient. This in turn indicates that the triplet excimer is formed in very limited steric arrangement of the two molecules of naphthalene or 1-chloronaphthalene.

The energy separation between the 0-0 band of the monomer phosphorescence and the maximum of the excimer phosphorescence is about 3000 cm^{-1} for both naphthalene and 1-chloronaphthalene. The repulsion energy I_G in the ground state at the equilibrium triplet excimer configuration cannot exactly be evaluated, but it is expected to have a similar value to the binding energy of the triplet excimer or $-\Delta H_T$, where ΔH_T represents the enthalpy change accompanying excimer formation in the triplet state. Thus, assuming tentatively that $I_G = -\Delta H_T$, we may evaluate ΔH_T to be about -5 kcal/mol, because the value of $I_G - \Delta H_T$ is about 3000 cm^{-1}. If we further assume that the entropy change for excimer formation $\Delta S_T = -10$ cal mol^{-1} deg^{-1} by reference to the case of singlet excimer for methylnaphthalene,[21] k_f/k_{dis} is estimated to be about 10^2 M^{-1}.
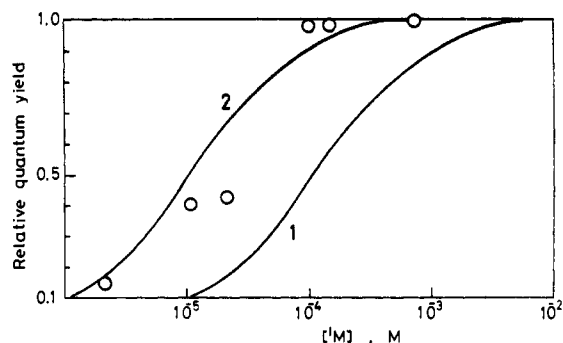

Figure 8. A plot of relative quantum yield of the excimer phosphorescence against the concentration of naphthalene in isooctane at 293 K (O). See the text for curves 1 and 2.

This is probably a maximum value of k_f/k_{dis} in this system, since the absolute values of ΔH_T and ΔS_T described above are estimated as a maximum and a minimum, respectively. On the other hand, from the data given in Table I the values of k_f/k_{dis} were calculated to be 10^3–10^4 M^{-1}. Such a discrepancy between the results of experiments carried out under the photostationary and transient conditions appears to be ascribable to an imperfection of the reaction in eq 1.

For quenching of the pyrimidine triplet state in fluid solution, Fenster and Johns[19] showed that a self-quenching pathway involving encounter of $^3M^*$ with ^1M must be taken into account in addition to the dimer formation. If we consider such a self-quenching pathway, the kinetic scheme 1 should be modified as follows:[20]

$$^3M^* \underset{k_{dis}}{\overset{k_d[^1M]}{\rightleftharpoons}} {^3D^*} \qquad (6)$$

It is easily seen that the rate constants k_1 ($=k_{1r} + k_{1q}$) and k_f defined in (1) correspond, respectively, to $k_1 + k_1'[^1M]$ and k_d in (6). Since k_1 and k_f in (1) were determined by the use of the relations $\theta_1 \to k_1$ as $[^1M] \to 0$ and $d(\theta_1 + \theta_2)/d[^1M] = k_f$, the k_f values given in Table I must be identified with the values of $k_1' + k_d$, that is,

$$k_f = k_1' + k_d \qquad (7)$$

with the other rate constants in (1) (i.e., k_1, k_2, and k_{dis}) being left unchanged. It should be noted here that the validity of the discussion given before with respect to the possibility of impurity emission is not affected by changing the scheme from (1) to (6).

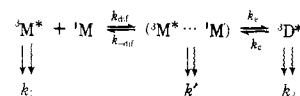According to (6), the quantum yield of excimer phosphorescence, Φ_D, is given by

$$\Phi_D = \frac{\Phi_T k_{2r} K_e[^1M]}{k_1 + (k_1' + k_2 K_e)[^1M]} \qquad (8)$$

where Φ_T is the quantum yield of the formation of the triplet state from the excited singlet, and $K_e = k_d/(k_2 + k_{dis})$. It is expected from eq 8 that Φ_D increases with increasing $[^1M]$ and finally approaches a constant value, which will be denoted by Φ_D^{max}. The quantum yield Φ_D as observed under photostationary conditions was found to meet the above expectation. The relative value of Φ_D observed for naphthalene is plotted against $[^1M]$ in Figure 8; the yield appears to reach Φ_D^{max} at $[^1M]$ of about 10^{-4} M. Curves 1 and 2 given in Figure 8 show relative values of Φ_D calculated from eq 8 as functions of $[^1M]$. In Figure 8, Φ_D^{max} is taken as unity for depicting both observed and calculated results. Curve 1 refers to the case of the scheme in (1), i.e., $k_1' = 0$ and $k_d = k_f$, and curve 2 to the case of $k_1' = k_f -$

k_d and $k_d/k_{dis} = 10^2$ M^{-1}, the latter relation being roughly estimated from the phosphorescence spectral data. Obviously, the experimental results agree, at least qualitatively, with the curve 2 rather than with the curve 1. It is thus concluded that the self-quenching pathway, namely, the quenching by the ground state of the solute molecule is likely to participate in the deactivation of the triplet state.

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(20) Of several detailed mechanisms represented by the general scheme in (6), the following is supposed to be most probable:

$$^1M^* + {}^1M \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} (^3M^* \cdots {}^1M) \underset{k_c}{\overset{k_e}{\rightleftharpoons}} {}^3D^*$$
$$\Big\downarrow k_i \qquad\qquad \Big\downarrow k' \qquad\quad \Big\downarrow k_d$$

where k_{-dif} denotes the diffusion-controlled rate constant for dissociation of the encounter complex, ($^3M^* \cdots {}^1M$). Under the conditions of $k_{-dif} \gg k_e$, k', the rate constants in (6) are expressed as $k_1' = \gamma k'$, $k_d = \gamma k_e$, and $k_{dis} = k_c$, with $\gamma = k_{dif}/k_{-dif}$.
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The Optical Activity of Low-Symmetry Ketones in Absorption and Emission

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Abstract: The optical activity in the n → π* transition of a series of ketones is studied in absorption and emission. For a number of ketones the comparison of the experimental CD and CPL spectra reveals marked differences: both the magnitude of the integrated optical activity and the band shape may be utterly different in absorption and emission. In this paper a relation is laid between these phenomena. The often large discrepancy between the value of the rotational strength in absorption and fluorescence (for some compounds up to sign) points to a large distortion of the ^{1}nπ* state of ketones with respect to their ground state. On the other hand it is shown from general principles that a negative value of the ratio R^{abs}/R^{em} requires a change of sign in either the CD or the CPL curve, i.e., can cause a bisignate Cotton effect. To get a better insight in the observed phenomena, a model is constructed to predict the qualitative band forms of the CD and CPL. Based on the large shift in equilibrium geometry between ground and excited state, the model makes use of an expansion of the electronic rotational strength about those points of normal coordinate space where the Franck–Condon overlap for a particular vibronic transition is peaked. When a linear relationship between the rotational strength and one normal coordinate is assumed, the observed band shapes of CD and CPL of the ketones studied can be successfully explained. In addition to a better understanding of the origins of bisignate Cotton effects, this study leads to the conclusion that the optical activity in the n → π* transition of ketones still can be understood with the relatively simple theory of Moffitt and Moscowitz, provided proper allowance is made for a legitimate role of the excited state.

The optical activity of an electronic transition is governed by its rotational strength,[2] which in turn is defined by the scalar product of the quantum mechanical electric and magnetic dipole transition moments. The molecular wave functions, incorporated in the integrands of the spectral transition moments, depend heavily on the nuclear coordinates and thus a connection between optical activity and molecular geometry is laid—at least in principle, for the actual road leading from experimental circular dichroism (CD) to molecular architecture is sometimes long and slippery owing to the well-known difficulties encountered in finding satisfactory wave functions. It is not surprising therefore that chemists have tried to find other, easier routes and often with considerable success. We refer here to the many well-known sector rules which correlate in an empirical way the contributions to the optical activity of the separate atoms and their relative positions in a molecule. One of the most famous sector rules is the octant rule for chiral ketones,[3] which has proven to be extremely useful, e.g., in the field of conformational analysis.[4] Notwithstanding the generally greater accuracy and applicability of diffraction methods and NMR techniques in the elucidation of molecular structures, it is in particular these sector rules which permit one to consider the study of optical activity as an indispensable tool in structural chemistry, this being more so since it recently turned out to be possible to measure the optical activity of excited species[5] (circular polarization of luminescence, CPL). While circular dichroism provides information on the chirality of the molecule in its ground state, the CPL incorporates the essential features of the structure in the excited state. This information, emitted by the fluorescent or phosphorescent molecule by means of