

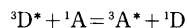
Triplet-Triplet Energy Transfer between Naphthalene and Various Alkyl Phenyl Ketones

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ABSTRACT : The yield of the phosphorescence of alkyl phenyl ketones as functions of naphthalene concentration in triplet-triplet energy transfer was measured in a rigid solution. The volume of the "sphere of action" of quenching for this energy transfer was calculated by F. Perrin's equation. A close correlation was found between the volume of the sphere of action and the branching of alkyl group of alkyl phenyl ketones.

INTRODUCTION

Triplet-triplet energy transfer is a radiationless process, due to interaction between the donor and acceptor molecules during the excitation lifetime of the donor, prior to its emission of a photon. The principle process of triplet-triplet energy transfer from the excited donor molecule in a triplet state ($^3D^*$) to an acceptor molecule in a ground singlet state (1A), raising the latter directly to the triplet state is written as follow



The energy (E_{ex}) of the exciting light and the singlet excitation energies (E_{1D} and E_{1A}) of the donor and acceptor molecules are chosen such that

$$E_{1A} > E_{ex} > E_{1D}$$

and the triplet excitation energies (E_{3D} and E_{3A}) of donor and acceptor are such that

$$E_{3D} - E_{3A} = \Delta E_{3DA} > 0$$

These conditions are required for triplet-triplet

transfer.

Triplet-triplet energy transfer was first clearly demonstrated by Terenin and Ermolaev(1). They have observed the phenomenon of this energy transfer for various combinations of donors and acceptors. They have also studied the "active sphere" of quenching for these combinations, but there was no discussion about the relation between the active sphere of quenching and molecular structure.

In this paper, we intend to report on the effect of the position of the methyl group (CH_3) in alkyl group of alkyl phenyl ketone $[C_6H_5CO(CH_2)_nCH_3-m(CH_3)_m]$ ($n=0, 1; m=0, 1, 2, 3$ and $n=3; m=0$) on triplet-triplet energy transfer from alkyl phenyl ketone molecules to naphthalene molecule.

EXPERIMENTAL

Acetophenone ($n=0, m=0$), propiophenone ($n=0, m=1$ or $n=1, m=0$), butyrophenone ($n=1, m=1$ or $n=2, m=0$), and valerophenone ($n=3,$

m=0) were of Tokyo Kasei's Guaranteed Reagent grade.

Isobutyrophenone ($n=0$, $m=2$), isovalerophenone ($n=1$, $m=2$), and 3, 3-dimethylbutyrophenone ($n=1$, $m=3$) were synthesized by Friedel-Crafts reaction(2), and pivalophenone ($n=0$, $m=3$) was prepared according to the method of Pearson (3). The typical procedures were following:

3, 3-dimethylbutyrophenone. 3, 3-Dimethylbutyric acid (30 ml, 0.235 mol) was added to thionyl chloride (30 ml) with stirring. Soon, an evolution of hydrogen chloride took place. The solution was stirred for 30 min. at room temperature and then heated to complete the reaction for 1 hr under gentle reflux. Excess thionyl chloride was removed by distillation. The residual liquid was distilled through a short Vigreux column to give 3, 3-dimethyl-1-butyryl chloride (20.4g, 64.5%). b. p. : 118.0-121.0, °C.

To an ice-cooled mixture of 20.5g (0.125 mol) of anhydrous aluminium chloride and 120 ml of dry benzene (dried over sodium) was added 20.4g (0.125 mol) of 3, 3-dimethylbutyryl chloride dropwise with stirring over a 1 hr period. After an additional stirring for 3 hr the ice bath was removed, and the mixture was allowed to stir overnight at room temperature. The reaction mixture was heated under reflux for 1 hr, and then allowed to cool to room temperature. The resulting brown solution was poured onto 250 ml of ice-water containing 50ml of concentrated hydrochloric acid, and was extracted with ether. The combined extracts were washed successively with water (50 ml x 2), sodium bicarbonate solution (10%, 50 ml), and finally brine and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure. The remaining pale yellow oil was distilled twice under reduced pressure to give a colorless oil. b. p. : 132.0-132.5 °C (37.0 mmHg), 18.8 g (70.3%)

Isobutyrophenone, 23.0g (72.0%), b. p. : 109.5-111.0 °C (33.0 mmHg), and isovalerophenone, 25.1 g (75.6%), b. p. : 119.0-120.0 °C (27.0 mmHg), were prepared by the similar procedures to 3, 3-dimethylbutyrophenone.

Pivalophenone. An ether solution of phenylmagnesium bromide was prepared in the usual manner starting from 3.79 g (0.156 g-atom) of

magnesium turnings and 24.5 g (0.156 mol) of bromobenzene in 120 ml of dry ether (dried over sodium) under a stream of dry N₂ (dried through CaCl₂). To the stirred phenylmagnesium bromide solution 13.0 g (0.156 mol) of pivalonitrile was added in a dropwise fashion and then the resulting mixture was refluxed with stirring for 2 hr. The mixture was cooled in ice, and 150 ml of cold 20% hydrochloric acid was added dropwise. The mixture was stirred overnight at room temperature to complete hydrolysis. The ether and aqueous layers were separated. The aqueous layer was thoroughly ether extracted and the combined ether extracts were washed with dilute hydrochloric acid, water, sodium bicarbonate solution, and finally brine. After drying on anhydrous magnesium sulfate, removal of the solvent under reduced pressure afforded a pale yellow oil which was distilled under reduced pressure. b. p. : 78.0-80.0 °C (6mmHg). The resulting oil was distilled again. b. p. : 222.0-224.0 °C, a colorless oil, 16.9 g (66.9%)

Alkyl phenyl ketones described above were used as donors, while naphthalene was used as acceptor. Naphthalene was recrystallized from alcohol. (m. p. 80-81 °C).

A Toshiba H 400-p mercury lamp was used as the excitation source. A Shimadzu Bausch & Lomb monochromator was employed to isolate to lines near 3650 or 3340 Å. The samples contained in a quartz tube of diameter 8 mm were held in a transparent quartz dewar containing liquid nitrogen. The luminescence from the samples emitted at right angles to the direction of the exciting light passes through a Hitachi 139 monochromator and was detected by a Hamamatu R-106 photomultiplier. The detected signal was displayed on a Sanei Galvanograph HR-101 recorder.

Measurements were made at liquid nitrogen temperatures (77 °K) and the concentrations used in the analysis of data were corrected for shrinkage of the solution upon freezing (20% by volume).

EPA was used as solvent. EPA is a mixture of ether, isopentane, and ethyl alcohol in the ratio 5:5:2 by volume and forms a clear glass at 77 °K, which showed no emission when

Table I. Alkyl phenyl ketones used as donor in this experiment.

Donor	$C_6H_5CO(CH_2)_nCH_3-m(CH_3)_m$	E_D	
		(\AA)	(cm^{-1})
Valerophenone	($n = 3, m = 0$)	3840	26040
Propiophenone	($n = 0, m = 1$ or $n = 1, m = 0$)	3845	26000
Butyrophenone	($n = 1, m = 1$ or $n = 2, m = 0$)	3850	25970
Acetophenone	($n = 0, m = 0$)	3860	25910
Isobutyrophenone	($n = 0, m = 2$)	3900	25640
Isovalerophenone	($n = 1, m = 2$)	3915	25540
Pivalophenone	($n = 0, m = 3$)	3955	25280
3,3-Dimethylbutyrophenone.	($n = 1, m = 3$)	3990	25060

irradiated with light of the wavelength of 3650 or 3340 \AA .

RESULTS AND DISCUSSION

When studying the phenomenon of triplet-triplet energy transfer, we must, from energy considerations, select the donor and acceptor molecules such that the lowest excited singlet level of the donor is lower than the singlet level of the acceptor and the lowest triplet level of the donor is higher than that of the acceptor.

We selected alkyl phenyl ketones (hereafter, it will be described APK) as donors and naphthalene as acceptor. Table I lists the triplet level of the donors: the height of the triplet level is determined from the position of the short-wavelength band of the phosphorescence spectrum for solution in EPA at 77 $^{\circ}\text{K}$. The compounds in the upper part of the Table I are well excited by the light of the mercury line at 3340 \AA (29940 cm^{-1}) and in the compounds from propiophenone to valerophenone, increasing the linear alkyl group from one to three CH_2 groups (increase in n) does not significantly alter the height of the triplet level. On the other hand, the compounds in the lower part is excited with the light of 3650 \AA (27400 cm^{-1}) and its triplet level decrease with increase of CH_3 -branching in alkyl group (increase in m).

The phosphorescence spectrum of APK used in this experiment has a four main peaks in the 3800-5400 \AA region and show a well defined vibrational pattern that is characteristic

of the $\text{C}=\text{O}$ vibrational stretch in the ground state. The separation of the bands in this emission spectrum is about 1700 cm^{-1} . Such a vibrational pattern suggests that the transition is localized on the $\text{C}=\text{O}$ group in the triplet state. In the case of naphthalene, the lowest excited singlet and triplet levels are at 31700 and 21250 cm^{-1} respectively and its phosphorescence spectrum shows the characteristic $\text{C}=\text{C}$ vibrational pattern of the aromatic ring in the ground state. Thus, when one illuminates a mixed solution of APK and naphthalene with the mercury line at 3340 or 3650 \AA , which is not absorbed or only very poorly absorbed by naphthalene, only APK molecules absorb light and be excited. The fluorescence spectrum of naphthalene does not appear under these condition but the phosphorescence bands of naphthalene appear in the phosphorescence spectrum of APK. This appearance of the naphthalene emission is explained as radiationless triplet-triplet energy transfer from APK in the triplet state to naphthalene in the ground state, raising the latter to the triplet state.

The appearance of the phosphorescence of the acceptor by triplet-triplet energy transfer is accompanied by strong quenching of the phosphorescence of the donor. As an example, the quenching of the phosphorescence yield of valerophenone to various concentration of naphthalene is shown in Fig. 1. Here, the concentration of valerophenone was kept constant.

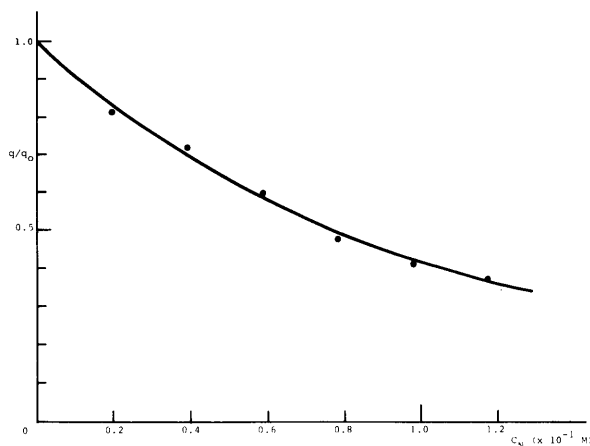


Fig. 1. Quenching of the phosphorescence of valerophenone as a function of the naphthalene concentration

Though the limited solubility of naphthalene in EPA at low temperatures prevents a measurement over a higher range of concentration, it is apparent that the phosphorescence intensities of valerophenone decrease with increase in concentration of naphthalene.

It was shown (4) that the curve for quenching of the phosphorescence of the donor as a function of the acceptor concentration is well described by the formula

$$q/q_0 = e^{-\alpha[C]} \quad (1)$$

where q_0 is the quantum yield of the phosphorescence of the donor in the absence of the acceptor, q is the yield in the presence of the acceptor at a concentration $[C]$, and α is a constant with the dimensions of reciprocal molarity. This exponential concentration dependence of the quenching q/q_0 was first derived theoretically by F. Perrin (5) for the concentration quenching of the fluorescence of dyes. He introduced the conception of the 'active sphere' of quenching, a volume of interaction around a quencher molecule such that a fluorescent molecule excited within this volume is quenched instantaneously, while fluorescent molecules excited outside this volume are unquenched.

The volume of the active sphere of quenching, which serves to determine the value of the constant α , is obtained from the slope of the quenching curves plotted in semilogarithmic

coordinates:

$$V = \frac{\ln(q_0/q)}{N'[C]} \quad (2)$$

where V is the volume of the sphere of quenching in cubic centimeters, $N' = 6.02 \times 10^{20}$ is the number of molecules per millimole and $[C]$ is the acceptor concentration in mole/liter.

Under the assumption that both interacting molecules are spherical in shape, the radius R of the active sphere of quenching can be calculated easily by following equation:

$$R = \left(\frac{3}{4\pi} V \right)^{1/3} \quad (3)$$

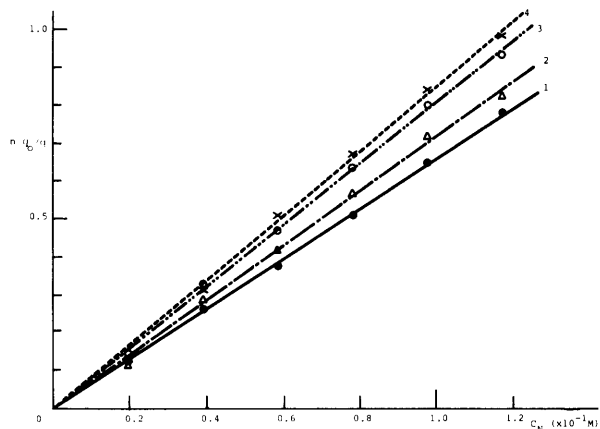


Fig. 2. The natural logarithm of the amount of quenching of the phosphorescence of the donor ($\ln q_0/q$) as a function of the naphthalene concentration (C_N) for various APK-naphthalene combinations.

- 1-Pivalophenone + naphthalene:
 - 2-isobutyrophenone + naphthalene:
 - 3-propiophenone + naphthalene:
 - 4-acetophenone + naphthalene
- in EPA at 77 ° K.

Figure 2 gives the relation of the quenching of the phosphorescence of acetophenone, propiophenone, isobutyrophenone, and pivalophenone to the concentration of naphthalene. The plots are semilogarithmic. Each plot was obtained from the averaged value of several measurements and scattering. The concentration of the donor was held at about 5×10^{-2} mole/liter

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for each donor. As can be seen from Fig. 2, the quenching curve of acetophenone is very similar to that of propiophenone but on going from propiophenone to pivalophenone ($n=0$; increase in m) the slope of the curve decreases with increasing the number of the CH_3 group. A similar tendency is also found in a series of propiophenone, butyrophenone, isovalerophenone, and 3,3-dimethyl butyrophenone ($n=1$; $m=0, 1, 2, 3$) (See Fig. 3).

From the curve of the exponential dependence on the acceptor concentration, the volume and radius of the active sphere of quenching were calculated by using Eq. (2) and (3). This result is summarized in Table II. As we see from Table II, in the molecules with the methylene chain $(\text{CH}_2)_n$ ($n=1-3$) from propiophenone to valerophenone, the value of R are almost the same with that of acetophenone within the experimental error. Thus, it is apparent that an increase in n corresponding to an extend of the methylene chain exerts no significant influence on the energy transfer from the $\text{C}=\text{O}$ group of the donor to the aromatic ring of the acceptor.

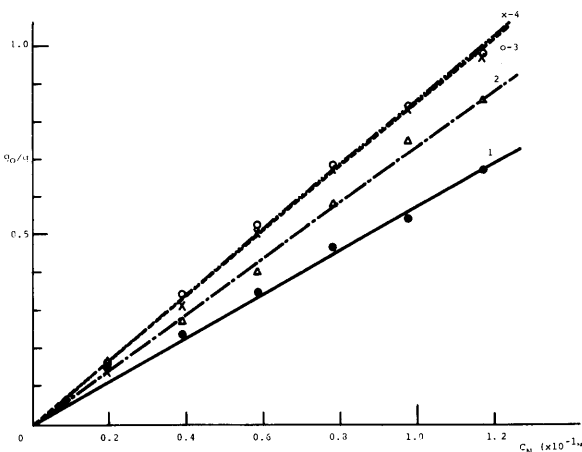


Fig. 3. The natural logarithm of the amount of quenching of the phosphorescence of the donor ($\ln q_0 / q$) as a function of the naphthalene concentration (C_N) for various APK + naphthalene pairs. 1. 3,3-Dimethylbutyrophenone: 2. isovalerophenone: 3. butyrophenone: 4. propiophenone.

Table II. Active sphere and its radius of quenching in triplet-triplet energy transfer.

Donor	Acceptor	$V (10^{-21} \text{cm}^3)$	$R (\text{\AA})$	$\Delta E_{3DA} (\text{cm}^{-1})$
Valerophenone	Naphthalene	14.2	15.0	4790
Propiophenone	"	13.8	14.9	4750
Butyrophenone	"	13.8	14.9	4720
Acetophenone	"	13.6	14.8	4660
Isobutyrophenone	"	11.9	14.2	4390
Isovalerophenone	"	12.5	14.4	4290
Pivalophenone	"	11.1	13.8	4030
3,3-Dimethylbutyrophenone	"	9.8	13.3	3810

Increasing the number of the CH_3 -branch in alkyl group of APK (increase in m) causes to a decrease of the active sphere. In an attempt to obtain information about the geometries, molecular model (Maruzen HGS model) were constructed. The model showed that an increase in m does not substantially alter the distance between the CH_3 group and the $\text{C}=\text{O}$ group but a chance of the approach of the CH_3 group to the $\text{C}=\text{O}$ group increases, and that in $m = 3$, the CH_3 group of

3,3-dimethylbutyrophenone situates closely in the $\text{C}=\text{O}$ group than that of pivalophenone in stable state. Therefore, it can be seen that the CH_3 group situated closely in the $\text{C}=\text{O}$ group prevents an approach of the donor and acceptor molecules, in other words, the bulkiness of the alkyl group situated in the neighborhood of the $\text{C}=\text{O}$ group causes to a decrease of the active sphere.

Table II also gives the value of the energy difference between the triplet levels of the

donors and acceptor. It seems that a decrease in energy difference (ΔE_{3DA}) is closely related to the decrease of the active sphere, but such a correlation was not found in the data of the reference (lb).

The discrepancy of 30% between our data and Ermolaev's data was found in the value of R for acetophenone+naphthalene pair. These difference may be attributed to the difference in estimation of the shrinkage of the solution upon freezing (no statement in the reference (lb)), in solubility of naphthalene (up to 0.5 mole/liter in alcohol-ether mixture in (lb)), in exciting light (in our case, acetophenone does not excite by 3650 Å).

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