Decay of Naphthalene Phosphorescence in the Presence of Some Chlorinated Compounds. An External Heavy Atom Effect

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The decay of the phosphorescence of naphthalene in the mixed solutions of methylcyclohexane and several chlorinated compounds has been analyzed. In many cases the decay was almost exponential and the decay constant was a function of the concentration of chlorinated compounds. In the case of carbon tetrachloride, the decay was distinctly non-exponential. The decay was analyzed by a Laplace transformation method. In this case a complex was formed, in equilibrium with the free naphthalene molecule, and the decay constant of the former increased when the concentration of CCl_4 increased. The external heavy atom effect takes place in two ways: one by complex formation with the molecule containing heavy atoms and another by a long range interaction through a statistical distribution of the latter molecules around the phosphorescing molecule.

The interaction of a molecule with molecules containing heavy atoms may frequently result in an apparent decrease in the triplet lifetime of the former. This external heavy atom effect has been the subject of a number of experimental and theoretical investigations. Quantitative treatment of the effect has led to an elucidation of the mechanism in terms of enhanced spin-orbit interaction through formation of CT complexes in which emitting triplet species may be either a locally excited state of one of the component molecules[1-9)] or a CT state.[10-13)] Previous investigators have laid stress on a particular route of enhancement, for example,

a) mixing of the triplet state with the locally excited singlet state,[1-3)]

or

b) mixing of the triplet state with the CT singlet state.[4,5,13)]

The heavy atom effect on the phosphorescence of stable CT complexes has been investigated.[7-12)] It has been shown that the rate constants of both $S_1 \rightsquigarrow T_1$ and $T_1 \rightarrow S_0$ transitions are increased. Furthermore, it has also been demonstrated that the $T_1 \rightsquigarrow S_0$ radiationless transition is not much enhanced and the observed reduction in the triplet lifetimes is mainly due to a change in the radiative lifetime.[7)]

The decay of benzene phosphoresence in rare gas hosts has been reported.[14-20)] It has been found that heavy atoms such as Kr or Xe have a drastic effect on the decay rate. Moreover, the geometrical arrangement of the heavy atoms around the molecule has been found to affect its lifetime. The mechanism has been elucidated by K. C. Lin and S. H. Lin[3)] in terms of enhanced spin-orbit coupling in the benzene ring in the presence of a heavy atom perturber. Najbar[17-20)] has discussed their experimental results in terms of a mean lifetime averaged over different sites, each occupied by a benzene molecule and a variable number of heavy atoms.

The dependence of the heavy atom effect on the distance between the emitting molecule and the heavy atom has also been investigated. Kavarnos *et al.*[21)] have synthesized several bromine-substituted naphthonorbornanes and have measured their radiative as well as non-radiative lifetimes. Giaccino and Kearns[22)] have doped naphthalene molecules into crystals of various halogen-containing molecules and have measured the phosphorescence lifetimes. None of them, however, could find any distinct relationship between the lifetime and the halogen–naphthalene distance.

Eisenthal[8)] has found that in the presence of tetrachloro- or tetrabromophthalic anhydride or in the presence of propyl iodide the phosphorescence of 2-chloronaphthalene becomes very similar to that of naphthalene. He claimed that the CT singlet state playes an important role in the donor phosphorescence. Similar observations were also reported by other authors.[23)]

It has been shown that the lifetime is dependent on the concentration of concomitant heavy atom compounds. If the heavy atom effect manifests itself through formation of a CT complex, the decay of phosphorescence would consist of two exponential components, one for the complex and another for naphthalene itself, and the ratio of their coefficients would be a function of the concentration. In a separate experiment on the phosphorescence of haloalkylnaphthalenes, we have found some evidence for a non-complexed external heavy atom effect. If such is the case, the concentration dependence is a function of the distribution of heavy atom molecules around the phosphorescing molecule.

In the following, we have employed chlorinated compounds because they seemed least liable to form complexes with naphthalene. The decay curve of naphthalene molecule in the presence of chlorinated moleculas was analyzed as a function of the concentration of the latter.

Experimental

Naphthalene-d_0 and naphthalene-d_8 were zone-refined several times. Methylcyclohexane (MCH) and the following liquid samples were purified by column chromatogram or distilled: carbon tetrachloride, dichloromethane, propyl chloride, butyl chloride, cyclohexyl chloride, benzyl chloride, chlorobenzene, *o*-dichlorobenzene, and *m*-dichlorobenzene. Naphthalene was dissolved in a chlorinated compound–MCH mixture in various mole fractions from 0 : 1 to 1 : 0. The concentration of naphthalene molecule was kept at 5×10^{-3} mol dm^{-3} in every case. Samples were excited at 315 nm at 77 K and the decay of phosphorescence was displayed on a recorder. In the photoselection experiment, the exciting light was passed through a Gran-Thomson prism and the emission was observed through a plastic polarizer.

Results and Discussion

The decay of naphthalene phosphorescence in the presence of the above chlorinated compounds was almost exponential, except for the case of carbon tetrachloride (Figs. 1—3). The decay constants were sometimes very sensitive to the presence of chlorinated molecules and sometimes quite insensitive. There seemed no distinct relation to the extent of CT interaction. Generally, compounds with one chlorine atom were insensitive and compounds with more than one chlorine atom were sensitive. In the latter case, the concentration dependence was remarkable, although the exponential behavior seemed to appear quite clearly. There were two characteristic observations to be noted.

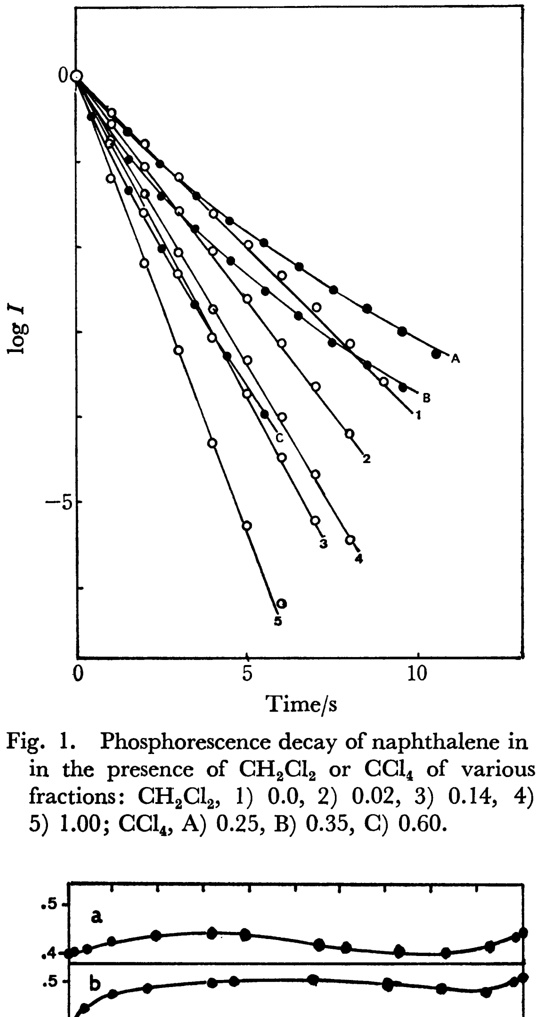

Fig. 1. Phosphorescence decay of naphthalene in MCH in the presence of CH_2Cl_2 or CCl_4 of various mole fractions: CH_2Cl_2, 1) 0.0, 2) 0.02, 3) 0.14, 4) 0.87, 5) 1.00; CCl_4, A) 0.25, B) 0.35, C) 0.60.

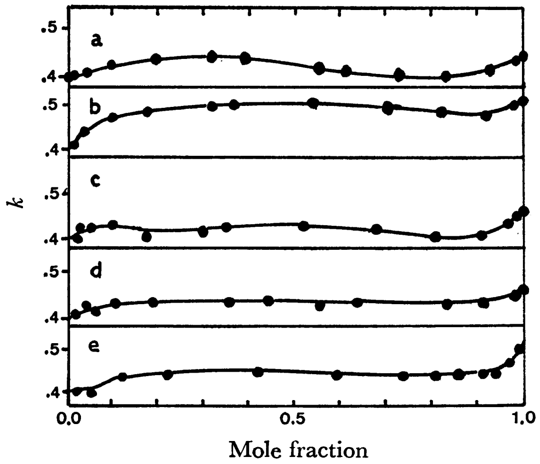

Fig. 2. Phosphorescence decay constant of naphthalene in the mixed solution of MCH and monochloro compounds: a) C_6H_5Cl, b) $C_6H_5CH_2Cl$, c) $C_6H_{11}Cl$, d) C_4H_9Cl, e) C_3H_7Cl.

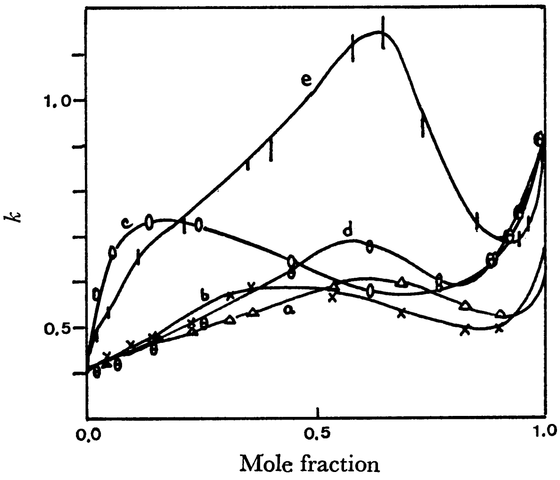

Fig. 3. Phosphorescence decay constant of naphthalene in the mixed solution of MCH and di- or tetrachloro compounds: a) o-$C_6H_4Cl_2$, b) m-$C_6H_4Cl_2$, c) CH_2Cl_2, d) CH_2Cl_2 in EtOH, e) CCl_4.

(1) The decay constant increased when the mole fraction of chlorinated compound increased, until it reached a maximum. After this concentration, the solid solution lost its transparency, indicating that two solid phases separated out.

(2) The decay constant increased again when the mole fraction of chlorinated compound approached 1.0. However, the rate constant in this region was less than the maximal value. As this region was very near to the pure phase of chlorinated compound, it may be reasonable to assume that the sample was again single phase.

Hence, the regions of monotonic increase (from the mole fraction of 0.0 to the maximum of k and from the minimum of k to mole fraction 1.0) seem to be important.

If the concentration dependence is the result of complex formation, the decay should be non-exponential. One may well think that the experimental accuracy had failed to detect its bicomponent character, but then the observed large change in the rate constant should be within this inaccuracy, which is unrealistic. Moreover, the molecule employed seemed quite unsusceptible to complex formation. It can be shown by a model calculation that a decay of a statistical body, of which the distribution of the decay constant has a fairly sharp peak, seems like a true exponential decay. Hence, it may be concluded that the decay is not bicomponent, but is multicomponent and that the decay component distribution has a sharp peak around a point which moves toward larger values with increasing concentration of the chlorinated compound.

We assume that the distribution of chlorinated compound around naphthalene molecules is random but statistically uniform, and that the decay constant of each naphthalene molecule is determined by its environment. As the heavy atom effect is short-range, the decay constant of each naphthalene molecule is mainly determined by the distance to its nearest chlorinanated molecule. The distribution of the nearest distance is expressed[24] by

$$\rho \mathrm{d}r = 4\pi r^2 C \exp(-4\pi r^3 C/3)\mathrm{d}r$$

with a peak at

$$r_{\max} = (2\pi C)^{-1/3}$$

where C is the concentration of the chlorinated molecule in Å^{-3} and r in Å (Fig. 4). The distribution of k itself can not be estimated, but it is a sharp function of r and would have a sharp peak at the respective value of $k(r_{\max})$, which would shift monotonically toward larger values according to the concentration.

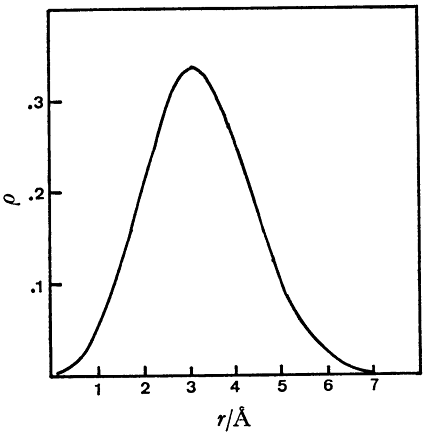

Fig. 4. Distribution of nearest distance $\rho(r)$ at C=5.3 × 10^{-3} Å^{-3}.

It may be asked that the observed effect may be ascribed to a medium-range CT interaction, rather than a heavy atom effect. It can be discarded because the observed effect seemed irrelevant to the extent of the donor character of the chlorinated compounds. It is often suggested that the overlap integrals between orbitals of the heavy atom and those of atoms participating in the triplet state serve as a measure of the heavy atom effect. In our experiment, however, they are somewhat smaller to account for the observed concentration dependence of the heavy atom effect. We assume that the effect is mainly carried by the framework of the surrounding solvent molecules, as can be shown by a CNDO calculation. In addition, the heavy molecule would exert an out-of-plane interaction. In this respect, we have carried out a photoselection measurement of the phosphorescence of naphthalene in the mixture solution of CCl_4 and EPA (Fig. 5). The phosphorescence tended to depolarize when CCl_4 was added, indicating that the phosphorescence has some in-plane character. It follows that the triplet state mixed with π-π* singlet states by the presence of a perturber. If the interaction of the perturber destroys the planar symmetry of the molecule, one center spin-orbit integral on the heavy atom suffices to effectively mix the π-π* triplet state with the π-π* singlet states, thereby remarkably decreasing the radiative lifetime.

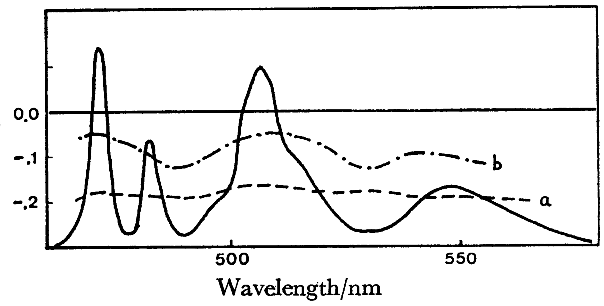

Fig. 5. Polarization of the phosphorescence of naphthalene in a) EPA and b) CH_2Cl_2–EPA (mole fraction 0.23).

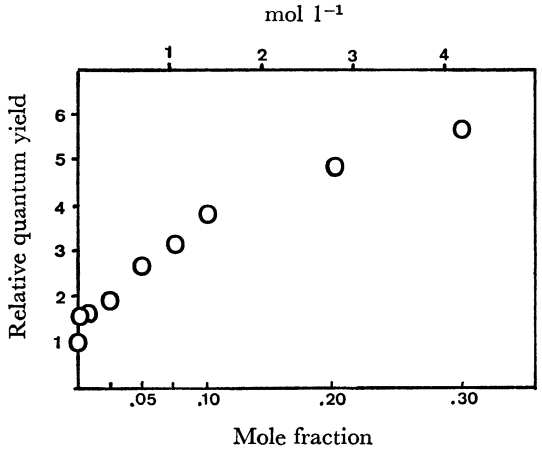

Fig. 6. Apparent quantum yield of $C_{10}D_8$ in EPA in the presence of CCl_4.

We have measured a relative quantum yield of the phosphorescence as a function of the concentration of CCl_4 in the EPA–CCl_4 mixture solution (Fig. 6). If we assume that the radiationless lifetime is not affected and that the lifetime of $C_{10}D_8$ (22 s) is equal to the radiative lifetime of $C_{10}H_8$, then a six time increase of the radiative decay constant leads to a mean total decay constant of 0.59—0.64 s^{-1} at 0.3 mole fraction, according to the extent to which the fluorescence (q=0.18) is quenched by an enhanced intersystem crossing. This value of the decay constant can be compared with the observed mean value of 0.78 s^{-1}. Thus the experiment of Eisenthal, in which the phosphorescence spectrum of chloronaphthalene becomes very similar to that of naphthalene in the presence of alkyl bromide or iodide, may also be interpreted by assuming that the totally-symmetric bands acquire large oscillator strengths from π-π* singlet states.

If the solvent molecules participate in the heavy atom effect, the latter may be sensitive to the kind of solvent. In Fig. 3 the same chlorinated compound CH_2Cl_2 was examined with two different solvents, methylcyclohexane and ethanol. They had quite different profiles, although the decay constant of naphthalene was the same in either solvent when the perturber was absent.

In the case of monochloro compounds (Fig. 2), the heavy atom effect manifested itself only slightly. The decay constant in the presence of the perturber is always very near to that in the absence of the perturber. In contrast, the change was remarkable in the case of dichloro compounds (Fig. 3). There seemed to be no parallelism between the heavy atom effect and the ability of forming a CT complex. Only a tentative explanation can be given at present. The contraction of MCH when chilled from room temperature to 77 K was measured to be 75%, so that the mean distance between two solvent molecules is 5.4 Å, which we assume to be the same as the mean distance between a naphthalene molecule and a nearest solvent molecule. In a solution of 0.6 mole fraction of chlorobenzene the mean distance from a naphthalene molecule to the nearest chlorobenzene molecule is 6.4 Å, and the mean distance from a naphthalene molecule to the nearest chlorine atom is also 6.4 Å, assuming a free rotation for the chlorobenzene molecule. But in the case of *p*-dichlorobenzene, the mean distance to the nearest chlorine atom is reduced by 1.6 Å, a half of the center-of-molecule chlorine distance. The difference may give rise to a drastic change, as the distance dependence of the heavy atom effect is large.

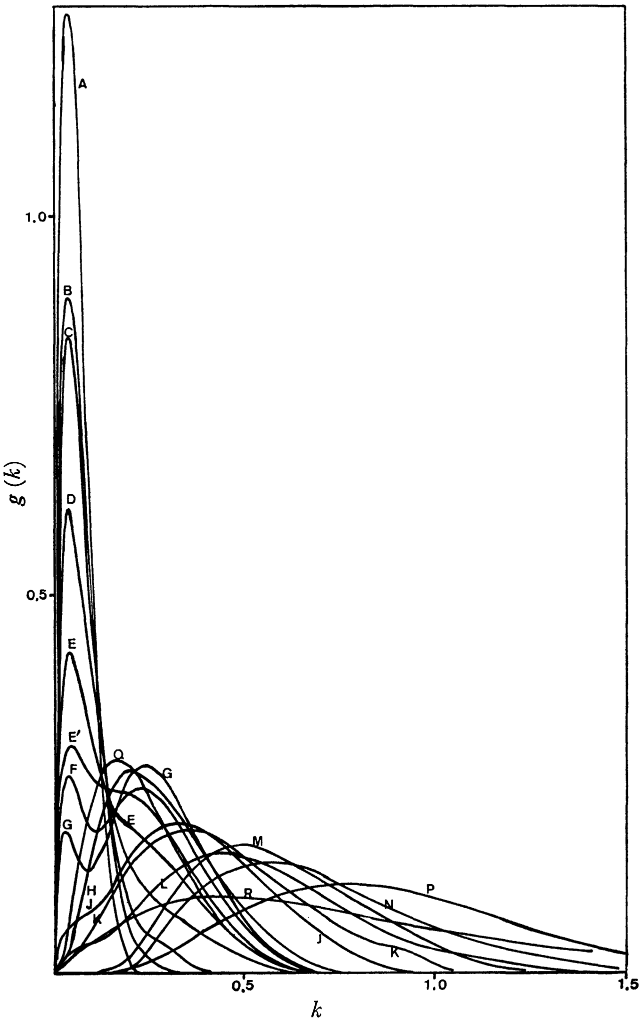

Fig. 7. Distribution function of the decay constant of $C_{10}D_8$ in the mixed solution of CCl_4 and MCH in varying mole fraction of CCl_4: A) 0.00, B) 0.005, C) 0.01, D) 0.025, E) 0.05, F) 0.07, G) 0.10, H) 0.15, J) 0.20, K) 0.25, L) 0.30, M) 0.41, N) 0.51, P) 0.60, Q) 0.99, R) 1.00.

The decay of naphthalene in CCl_4 was non-exponential (Fig. 1). As CCl_4 can form a CT complex with naphthalene, we expected that the decay had two components and the peak of the complex would move in accordance with the advent of statistical heavy atom effect. Very rough estimates of the mean rate constants are illustrated in Fig. 3; these show a similar inflecting profile. The decay curves were analyzed by a method of Laplace transformation developed by one of the authors.[25] The decay function can be expressed as

$$f(t) = \int_{s_0}^{\infty} g(s) \exp(-st)\mathrm{d}s$$

where $g(s)$ is a normalized distribution function of the decay constant. $g(s)$ is approximated by a power series with an exponential function which guarantees the convergence:

$$g(s) = \sum_{i}^{N} A_i(s-s_0)^i \exp(-Bs)$$

where A_i's are the coefficients to be determined and N and B are ajustable parameters. A method of least squares was applied for A_i's to obtain the best fit to the observed decay curve. The results are shown in Fig. 7. The peak of the complex is gradually formed at the expense of that of free naphthalene molecule, and the former moves according to the concentration. Thus the external heavy atom effect takes place in two ways: one by forming a CT complex with a molecule containing heavy atoms, and the other by a statistical approach of heavy molecules to the phosphorescing molecule.

When the mole fraction of the halogenated compound was large, the rate constant became small again, contrary to expectation. It might be supposed that in an incommodious crystal lattice of the halogenated compound the naphthalene molecule is deprived of the solvent molecules which bring the heavy atom effect in a favorable position or that the disposition of the naphthalene molecule itself is unfavorable. The singular nature at high concentration limit is open to future investigation.

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