

## TRIPLET LIFETIME OF DICHLOROBENZENES IN THE VAPOUR PHASE STUDIED BY TIME-RESOLVED AND STATIONARY OBSERVATIONS OF PHOTOSENSITIZED PHOSPHORESCENCE

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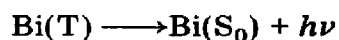
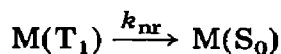
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### Summary

Time-resolved and stationary observations of biacetyl phosphorescence sensitized by dichlorobenzene vapour have led to the determination of the rate constant  $k_{nr}$  for non-radiative decay and the rate constant  $k_{ET}$  for energy transfer to biacetyl from the lowest triplet states of dichlorobenzenes in the vapour phase. The values of  $k_{nr}$  for *p*-dichlorobenzene, *m*-dichlorobenzene and *o*-dichlorobenzene are  $1.4 \times 10^5 \text{ s}^{-1}$ ,  $1.1 \times 10^5 \text{ s}^{-1}$  and  $1.5 \times 10^5 \text{ s}^{-1}$  respectively. The values of  $k_{ET}$  obtained are  $3.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and  $7.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  respectively for *p*-dichlorobenzene, *m*-dichlorobenzene and *o*-dichlorobenzene. The values of  $k_{nr}$  and  $k_{ET}$  for dichlorobenzenes are similar to those for chlorotoluenes and they are rather insensitive to the introduction of the second chlorine atom substituent but are slightly dependent upon its position.

### 1. Introduction

In ref. 1 we demonstrated the close agreement between time-resolved and stationary measurements of the phosphorescence of biacetyl photosensitized by thermalized triplet chlorotoluene molecules and we reviewed references for the photosensitized phosphorescence of biacetyl. A kinetic model assumed for the phosphorescence of biacetyl (Bi) sensitized by thermalized triplet chlorotoluene (M(T<sub>1</sub>)) is represented by



in which the rates for the phosphorescence decay and the self-quenching of thermalized triplet chlorotoluene are negligible compared with the rate  $k_{nr}$  of the non-radiative decay to the ground state or compared with the rate  $k_{ET}[\text{Bi}]$  of the energy transfer to biacetyl [1]. Time-resolved measurements of the rise time of the sensitized biacetyl phosphorescence give the summation  $k_{nr} + k_{ET}[\text{Bi}]$  of the unimolecular and bimolecular decay rates. Stationary observation of the intensity of biacetyl phosphorescence at various biacetyl pressures leads to the ratio  $k_{nr}/k_{ET}$  of the rate constants. Thus by combining the two methods we can evaluate the rate constants  $k_{nr}$  and  $k_{ET}$ . Of course, time-resolved measurements at various biacetyl pressures independently lead to values of  $k_{nr}$  and  $k_{ET}$ . So values for  $k_{nr}$  and  $k_{ET}$  obtained in this way can be compared with those obtained by the stationary method. The very good agreement between the results from the two methods for triplet *p*-chlorotoluene molecules [1] implies that the combination method may be used for other triplet molecules. In this paper we have applied such a treatment to investigate the lowest triplet state of dichlorobenzene molecules.

It was expected that the second chlorine atom substituent in dichlorobenzene would enhance non-radiative transitions. Measurements of the fluorescence quantum yields (about  $10^{-2}$ ) and lifetimes (about 1 ns) of the excited singlet states of dichlorobenzenes, however, indicate that the increase in the number of chlorine atoms does not greatly enhance non-radiative transitions in excited molecules, but the fluorescence quantum yield and lifetime of the excited singlet state are influenced by the position of the second chlorine atom substituent, an effect attributed to molecular symmetry [2]. Rather slow non-radiative transitions and rather fast radiative transitions in *p*-disubstituted benzenes are generally observed relative to those for *m*- or *o*-disubstituted benzenes [3].

The predominant decay process of excited singlet dichlorobenzene molecules seems to be intersystem crossing to triplet levels through the spin-orbit interaction induced by the chlorine substituent. The triplet dichlorobenzene molecules thus formed give rise to the dissociation of the C—Cl bond and relaxation to stable triplet levels and/or the ground electronic state. The photodecomposition quantum yields of the C—Cl bond were estimated to be 0.9 for *p*- and *o*-dichlorobenzene and 0.8 for *m*-dichlorobenzene on irradiation at 253.7 nm [4, 5]. The pressure sensitivity of the photodecomposition quantum yield of *p*-dichlorobenzene is different from that of the other isomers. Collision-induced photodecomposition is observed in the vibrationally excited triplet levels [4].

In the light of these results, we have investigated the photosensitized phosphorescence of biacetyl to clarify our understanding of the formation of triplet dichlorobenzene molecules. The quantum yield of phosphorescence from triplet dichlorobenzene vapour must be very low. It will be shown later that the phosphorescence of biacetyl is sensitized by triplet dichlorobenzene molecules in the vapour phase formed through intersystem crossing from the first excited singlet state.

## 2. Experimental details

The apparatus used in these experiments has been described in detail previously [1] and therefore only a brief description is given here.

The time-resolved photosensitized phosphorescence of biacetyl was observed by exciting a sample mixture (biacetyl, dichlorobenzene vapour and ethane) at 266 nm using the fourth harmonic of a mode-locked Nd-YAG laser output. The sensitized luminescence was detected by a combination of a monochromator and a photomultiplier. The luminescence was observed at  $514 \pm 2$  nm. The photomultiplier output signal was amplified by a preamplifier and then fed to a fast oscilloscope. The signals displayed on the oscilloscope were digitized and analysed by a combination of a video camera and a microcomputer in order to improve the signal-to-noise ratio. The weak signals were usually accumulated and averaged for 40 laser shots.

Stationary intensity measurements of the photosensitized phosphorescence of biacetyl were carried out with the excitation produced by monochromatic light (half-band width, 0.2 nm) from a xenon lamp. Biacetyl vapour of pressure 0.06 - 0.85 Torr was homogeneously mixed with the vapour of the sensitizers *p*-, *m*- or *o*-dichlorobenzene. The vapour pressure of the sensitizer was kept approximately constant at a value of 1 Torr. As a collision partner, ethane was added to the mixture at a pressure of 30 - 760 Torr. The sample mixture was stirred for about 1 h by a glass circulator. The photosensitized phosphorescence of biacetyl was observed by employing a combination of cut-off filters which transmit light of wavelength longer than 490 nm and a photomultiplier operating in d.c. mode. In the case of the 253.7 nm irradiation a monochromator was placed between the reaction cell and the photomultiplier.

Dichlorobenzenes (ortho and meta isomers, Tokyo Kasei) were purified by repeated vacuum distillation. The para isomer (Tokyo Kasei) was purified by repeated recrystallization from methanol solution. Ethane (stated purity, 99.9%) was available commercially from Takachiho and was used without further purification. Biacetyl was obtained from Tokyo Kasei and distilled under vacuum, the middle fraction being retained and stored in the dark.

## 3. Results

### 3.1. Mechanism of photosensitized phosphorescence

Optically excited singlet dichlorobenzene molecules ( $B(S_1)$ ) mostly undergo intersystem crossing to triplet levels with an energy above the C-Cl bond dissociation energy (about 97 kcal mol<sup>-1</sup> [6]). Thus, non-relaxed triplet molecules of dichlorobenzene ( $B(T^*)$ ) initially formed by intersystem crossing can decompose to chlorophenyl radicals and chlorine atoms simultaneously with unimolecular and/or bimolecular relaxation. Unimolecular relaxation involves intramolecular redistribution of electronic and vibrational energy. After some relaxation, the molecules which have energies beyond the

threshold of the C—Cl bond dissociation can still undergo the C—Cl bond dissociation. The molecules that have escaped decomposition are eventually deactivated to lower stable triplet or ground singlet levels by molecular collisions with the third body (X) [7].

The rates of decay of triplet chlorotoluene molecules by phosphorescence and self-quenching were shown to be negligible compared with the rate due to energy transfer to biacetyl or to unimolecular non-radiative processes to the ground state [1, 8]. This seems to be true also for triplet dichlorobenzenes. Thermalized triplet dichlorobenzene molecules ( $B(T_1)$ ) formed with a quantum yield  $\Phi_T$  transfer their excitation energy to biacetyl or relax to the ground state. Thus biacetyl molecules accept the excitation energy from triplet dichlorobenzene molecules and eventually emit phosphorescence with a quantum yield  $\Phi_{bp}$ . Accordingly, the simplified kinetic model for the sensitized phosphorescence of biacetyl by triplet dichlorobenzene can be represented by



on omitting the mechanism of formation of the initial triplet dichlorobenzene ( $B(T^*)$ ).

### 3.2. Time-resolved sensitized phosphorescence of biacetyl

Typical initial rises of the phosphorescence of biacetyl sensitized by *p*-, *m*- and *o*-dichlorobenzene are shown in Figs. 1(a), 1(b) and 1(c) respectively. The observed time profile of the sensitized phosphorescence intensity of biacetyl at  $514 \pm 2$  nm reaches its maximum within a few microseconds. The rise time of the biacetyl phosphorescence varies with the pressure of biacetyl but is insensitive to the change in the pressures of ethane and dichlorobenzene. The decay rate of sensitized phosphorescence is very slow compared with its rise time and has a constant value of 1.8 ms independent of the pressure of biacetyl, dichlorobenzene or ethane. This value is identical with the value reported in ref. 9.

The time profiles shown in Figs. 1(a), 1(b) and 1(c) are simulated using a lifetime of 1.8 ms for the biacetyl phosphorescence to estimate the decay rates of triplet dichlorobenzene molecules. The decay for the triplet dichlorobenzene concentration [ $B(T_1)$ ] is assumed to be single exponential. In Figs. 1(a), 1(b) and 1(c), the simulated curves are shown by broken lines. The decay rates obtained for triplet dichlorobenzenes, which can be

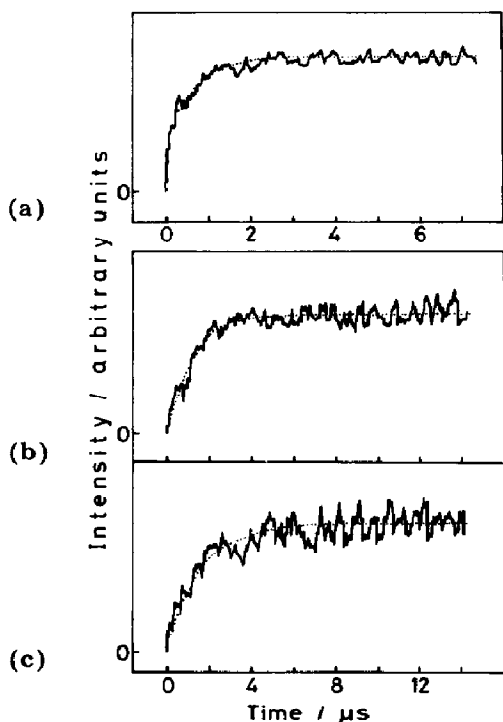


Fig. 1. Time-profile of photosensitized phosphorescence of biacetyl at  $514 \pm 2$  nm by dichlorobenzenes. The decay rate of phosphorescence is 1.8 ms, which is identical with the value reported in ref. 9. (a), (b) and (c) show initial rises of the sensitized biacetyl phosphorescence observed with the 266 nm laser pulse irradiation: (a) *p*-dichlorobenzene (0.5 Torr) + biacetyl (0.68 Torr) + ethane (765 Torr); (b) *m*-dichlorobenzene (0.78 Torr) + biacetyl (0.62 Torr) + ethane (942 Torr); (c) *o*-dichlorobenzene (0.65 Torr) + biacetyl (1.12 Torr) + ethane (935 Torr). Data were accumulated for 50 laser shots in the case of (a) and (b) and 40 laser shots in the case of (c). The broken lines show the curves simulated assuming a single exponential function of the triplet dichlorobenzene concentration.

expressed as  $k_{nr} + k_{ET}[\text{Bi}]$  according to the mechanism discussed above, are listed in Table 1.

### 3.3. Sensitized biacetyl phosphorescence studied by stationary observation

The results for the photosensitized phosphorescence of the dichlorobenzene–biacetyl system in the presence of ethane are shown in Fig. 2. The phosphorescence intensity of biacetyl sensitized by *p*-dichlorobenzene excited at its 0–0 transition at 279.6 nm increases with the pressure of biacetyl. The phosphorescence intensity at a low pressure of ethane is much weaker than that for a high pressure of ethane. This can be interpreted as being the result of the collisional deactivation of vibrationally hot triplet molecules of dichlorobenzene with ethane (reaction (2)). The intensity  $I_p$  of the sensitized phosphorescence of biacetyl can be expressed by the equation

$$I_p = \frac{\Phi_T \Phi_{bp} k_{ET} [\text{Bi}]}{k_{ET} [\text{Bi}] + k_{nr}} \quad (\text{I})$$

TABLE 1

Summary of values of  $k_{\text{ET}}[\text{Bi}] + k_{\text{nr}}$ ,  $k_{\text{nr}}/k_{\text{ET}}$ ,  $k_{\text{ET}}$  and  $k_{\text{nr}}$  for *p*-dichlorobenzene, *m*-dichlorobenzene and *o*-dichlorobenzene

Molecule	$k_{\text{ET}}[\text{Bi}] + k_{\text{nr}}^{\text{a}}$ ( $\times 10^6 \text{ s}^{-1}$ )	$k_{\text{nr}}/k_{\text{ET}}^{\text{b}}$ ( $\times 10^{-6} \text{ M}$ )	$k_{\text{ET}}$ ( $\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ )	$k_{\text{nr}}$ ( $\times 10^5 \text{ s}^{-1}$ )
<i>p</i> -Dichlorobenzene	1.3	4.4	3.2	1.4
<i>m</i> -Dichlorobenzene	0.81	5.4	2.1	1.1
<i>o</i> -Dichlorobenzene	0.61	20	0.76	1.5

<sup>a</sup>Derived from time-resolved measurements (Fig. 1).

<sup>b</sup>Derived from stationary measurements (Fig. 2).

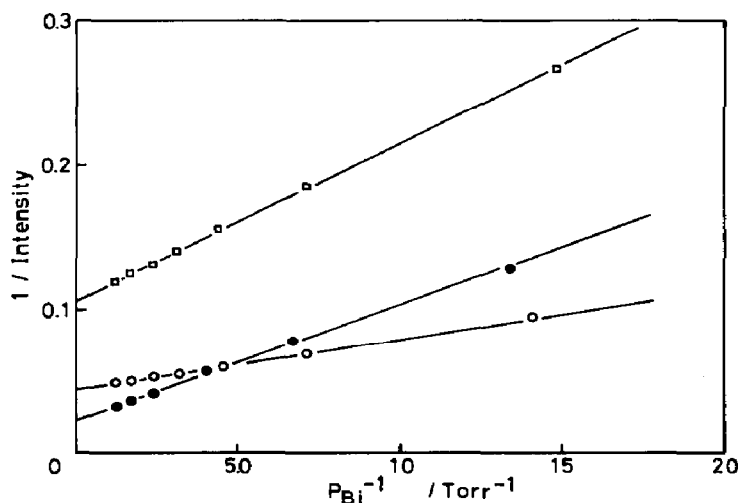


Fig. 2. Sensitized biacetyl phosphorescence intensity vs. pressure of biacetyl under stationary conditions. The inverse of the sensitized phosphorescence intensity is plotted against the inverse of the biacetyl pressure. The experimental conditions are as follows:  $\circ$ , *p*-dichlorobenzene (0.68 Torr) + ethane (590 Torr) excited at 279.6 nm;  $\square$ , *m*-dichlorobenzene (0.92 Torr) + ethane (370 Torr) excited at 276.3 nm;  $\bullet$ , *o*-dichlorobenzene (0.54 Torr) excited at 275.9 nm. The pressure of biacetyl was varied from 0.07 to 0.8 Torr.

derived from the above reaction mechanism assuming stationary conditions and unit efficiency for the system used to detect the sensitized phosphorescence. Thus the inverse of the phosphorescence intensity is expressed by

$$\frac{1}{I_p} = \frac{1 + k_{\text{nr}}/k_{\text{ET}}[\text{Bi}]}{\Phi_T \Phi_{\text{bp}}} \quad (\text{II})$$

Plots of the inverse of the phosphorescence intensity at a fixed pressure of ethane against the inverse of the biacetyl pressure are shown in Fig. 2. The plots can be fitted well to straight lines. The intercepts and the slopes of these straight lines give the ratio of  $k_{\text{nr}}$  to  $k_{\text{ET}}$  (see Table 1). The values of  $k_{\text{nr}}/k_{\text{ET}}$  for dichlorobenzenes are independent of the pressure of ethane from 50 to 760 Torr and also of the pressure of dichlorobenzenes up to 2.0 Torr.

The  $k_{nr}/k_{ET}$  are also insensitive to the excitation wavelength from 280 to 254 nm.

Values of  $k_{nr}$  and  $k_{ET}$  for *p*-, *o*- and *m*-dichlorobenzene were determined from the values of  $k_{nr}/k_{ET}$  by utilizing the values  $k_{nr} + k_{ET}[\text{Bi}]$  deduced from the phosphorescence intensity rise curves in Fig. 1. The values calculated are listed in Table 1.

#### 4. Discussion on $k_{ET}$ and $k_{nr}$

The lack of pressure or excitation energy effects on the values of  $k_{nr}/k_{ET}$  indicates that the sensitizer of the biacetyl phosphorescence must be vibrationally thermalized. Thus the dominant energy donor of the triplet excitation energy to biacetyl is the vibrationally thermalized dichlorobenzene and it should have a unique value of the energy transfer rate constant. The non-thermalized triplet molecule cannot live long enough to transfer its energy to biacetyl, owing to the fast intersystem crossing and/or decomposition. These facts were also deduced for the chlorotoluene-biacetyl system [1].

It may be thought that the values of  $k_{nr}/k_{ET}$  in Table 1 suggest rather large differences between the values of  $k_{nr}$  for the three isomers of dichlorobenzene. The time-resolved observation of sensitized phosphorescence, however, has revealed that  $k_{nr}$  is rather insensitive to the molecular structure while  $k_{ET}$  is sensitive to it. This seems to be reasonable since the energy transfer of triplet energy occurs by electron exchange between the energy donor and acceptor molecules.

The values of  $k_{ET}$  for *p*- and *m*-dichlorobenzenes are very similar and are close to those for toluene and xylenes [10]. This probably indicates that the energy transfer from triplet *m*- or *p*-dichlorobenzene to triplet biacetyl takes place via a mechanism very similar to that from triplet toluene or xylenes to triplet biacetyl. The chlorine atom substituent, therefore, has no marked effect on the mechanism of energy transfer of triplet excitation energy from *m*- or *p*-dichlorobenzenes to biacetyl.

However, *o*-dichlorobenzene has the smallest value among the three isomers of dichlorobenzene: approximately a quarter of the rate constants for the other dichlorobenzenes. For the energy transfer from *m*- or *p*-dichlorobenzene to biacetyl the chlorine atom does not strongly affect the relative orientation and separation between donor and acceptor molecules. In the case of *o*-dichlorobenzene, however, the effects of ortho substitution may prevent the donor and acceptor molecules from being suitably oriented and separated for energy transfer to take place. This ortho-substitution effect was also observed in the energy transfer from triplet *o*-chlorotoluene to biacetyl. The value of  $k_{ET}$  for *o*-chlorotoluene is much smaller than the  $k_{ET}$  for *m*- or *p*-chlorotoluene [1]. Similar trends may be observed for *o*-xylene. The value of  $k_{ET}$  for *o*-xylene is somewhat smaller than the values for *m*- or *p*-xylene [10].

The lifetimes of the lowest triplet state ( $T_1$ ) of dichlorobenzenes are shorter than those for xylenes by more than two orders of magnitude [10]. These short lifetimes for triplet dichlorobenzene isomers are thought to be solely due to the effects of the chlorine atom substituent (spin-orbit interaction). The second chlorine substituent does not markedly affect the lifetimes of chloro-substituted benzene derivatives since triplet chlorotoluene isomers have lifetimes very similar to those of dichlorobenzenes.  $T_1$  for *p*-dichlorobenzene is situated at about 82 kcal mol<sup>-1</sup> above the ground state [11] and the bond dissociation energy of C—Cl is estimated to be 97 kcal mol<sup>-1</sup> [6]. Accordingly, the stabilized  $T_1$  molecules mostly decay through intersystem crossing to the ground state and the dissociation of  $T_1$  molecules seems to be unimportant.

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