# TRIPLET ← SINGLET AND SINGLET → SINGLET RADIATIONLESS TRANSITIONS OF SOME CARCINOGENIC COMPOUNDS

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## Summary

From the measurements of the lifetimes of some carcinogenic compounds as a function of temperature, singlet → singlet and triplet ← singlet radiationless transition rate parameters have been determined and are discussed. It was found that the temperature-independent part of the decay time equation could be the result of intersystem crossing or internal conversion for monomers and excimers, depending on the system used. The temperature-dependent part, however, was found to be due to internal conversion of the form $S_m \rightarrow S_n$ ($m = 2$, $n = 1$ or $m = 1$, $n = 0$) or to be of negligible value.

## 1. Introduction

There are two main radiationless processes through which a molecule can be internally quenched:

(1) intersystem crossing from the first electronic excited singlet state $S_1$ to any of the triplet states $T_n$ where $n \geqslant 1$;

(2) internal conversion between any two states of the same multiplicity.

One of the most powerful techniques used for determining internal quenching processes and in differentiating experimentally between processes (1) and (2) is the measurement of fluorescence lifetimes as a function of the absolute temperature. According to the kinetic theory of reactions, the molecular lifetime $\tau$ can be written as

$$1/\tau = K_F + K_I \tag{1}$$

where $K_F$ and $K_I$ are the fluorescence and internal quenching rate parameters respectively. $K_I$ can be written [1] as

$$K_I = K_I^0 + K_I' \exp\left(-W_I/kT\right) \qquad (2)$$

where $K_I^0$ is independent of the absolute temperature $T$, and the temperature-dependent component of $K_I$ has a frequency factor $K_I'$ and an activation energy $W_I$; $k$ is the Boltzmann constant.

Previous assignment by various researchers of the temperature-dependent and temperature-independent components of $K_I$ to the two processes (1) and (2) has been confusing. For example, process (1) has been assigned to the temperature-dependent component of $K_I$ for benzene and its derivatives while process (1) was assigned for higher condensed aromatic hydrocarbons such as naphthalene [2]. Similarly, for anthracene derivatives [3] process (1) was assigned to the temperature-dependent component of $K_I$. Furthermore, Birks and King [4, 5] assigned both the temperature-dependent components of $K_{IM}$ and $K_{ID}$ (where M stands for monomer and D for excimer components) to intersystem crossing (or process (1)) when they measured the lifetime of 1,6-dimethyl naphthalene as a function of temperature. From these measurements they obtained the following values for $K_{IM}^0, K_{ID}^0, K_{IM}'$ and $K_{ID}'$ respectively: $11.6 \times 10^6$, $5.1 \times 10^6$, $2.7 \times 10^8$ and $6 \times 10^9$. In spite of the large values of the frequency factors $K_{IM}'$ and $K_{ID}'$, process (1) was assigned to the temperature-dependent component of eqn. (2). They based their conclusion on the results obtained by Medinger and Wilkinson [6] who indicated that at room temperature the quenching process of aromatic hydrocarbons is solely due to intersystem crossing from $S_1$ to $T_1$ and that the internal conversion from $S_1$ to $S_0$ is negligible. However, studies of the influence of environment on the radiative and radiationless transition rates of pyrene excimers in solution and in crystalline forms by Birks *et al.* [7] have led them to conclude that the temperature-independent radiationless parameter $K_{ID}^0$ is due to process (1) while the temperature-dependent part $K_{ID}' \exp(-W_{ID}/kT)$ is due to process (2) in the case of liquid pyrene. For pyrene crystal, they determined the temperature-dependent component $K_{ID}' \exp(-W_{ID}/kT)$ to be entirely due to intersystem crossing.

During the work for this article, we investigated processes (1) and (2) for five compounds. These compounds were studied because they have been proven to cause cancer [8] and, since some of them are emitted into the air from car exhausts and factory chimneys, they are dangerous environmental pollutants. This investigation represents part of our research in a broader program to study the spectroscopic properties of carcinogenic compounds.

## 2. Experimental

A pulsed nanosecond fluorimeter system that uses the matching signals technique was used for the measurement of lifetimes. This system is discussed in detail in ref. 9 and the reader is referred to it. In addition, in order

to raise the temperature of the sample above room temperature, the quartz sample cell was placed inside a copper–brass jacket. A mixture of 50% water and 50% ethylene glycol was circulated through this jacket, using a Haak Model FT-67145 closed liquid circulator and heater. To lower the temperature of the sample, a slightly modified Air Product model AC-1-110 heat exchange nitrogen cooler was used. For oxygen removal, an ultrahigh purity grade of dry argon was continuously bubbled inside the sample before and during the lifetime measurements. The monomer and excimer bands of each compound studied were separated using appropriate filters from Corning and Ditric Optics, Inc. The temperatures of the samples were measured with a copper–constantan thermocouple and a Fluke Instruments model 8120 A digital multimeter. To ensure a true reading of the temperature, the thermocouple junction was dipped inside the sample.

The compounds used in this work were of the highest purity available commercially (99.9%+) and were used without further purification. Special precautions were taken in the handling of the carcinogenic compounds. These precautions included the building of special hoods for the entire set-up, as well as other measures.

## 3. Results

The emission spectra of 3,4,9,10-dibenzopyrene–toluene, 20-methyl cholanthrene–benzene and 2- and 1-aminoanthracene–alcohol solutions have been investigated by Lopez [10]. He has studied the spectroscopic properties of these compounds as a function of concentration and temperature and has carefully determined the monomeric (M) and excimer (D) bands of each compound. Based on his data, we investigated both monomer and excimer lifetimes of the specified compounds as a function of temperature. We used solvents of low viscosities so that Stern–Volmer [11] kinetics could be applied to the behaviour of each solution studied. Equations (1) and (2) were used for analyzing the data obtained. It has been established [5, 12] that the radiative fluorescence rate parameter can be written as

$$K_F = n^2 K_F^0,$$

where $n$ is the solvent refractive index and $K_F^0$ is the value of $K_F$ when $n = 1$. $K_F^0$ is thus independent of the temperature and of the solvent. Since $n$ is a slowly varying function of temperature, for all practical purposes and within the limits of experimental error, we can consider $K_F$ to be constant [13] and eqn. (1) becomes

$$1/\tau_{M(D)} = K_{FM(D)} + K_{IM(D)}^0 + K'_{IM(D)}\exp(-W_{IM(D)}/kT) \tag{3}$$

The experimental values of the different rate parameters of eqn. (3) are obtained from Figs. (1) - (4) and are presented in Table 1. For all compounds studied, the agreement between the theoretical and experimental values of eqn. (3) was extremely good as is clear from the figures. The
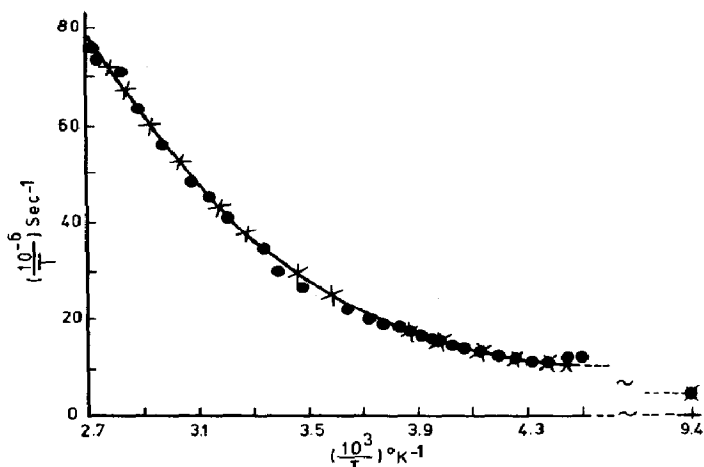
Fig. 1. Variation of the monomer lifetime $\tau$ of 0.01 g $l^{-1}$ of 3,4,9,10-dibenzopyrene in toluene at an absolute temperature $T$: ●, experimental; ×–×–×–, theoretical.
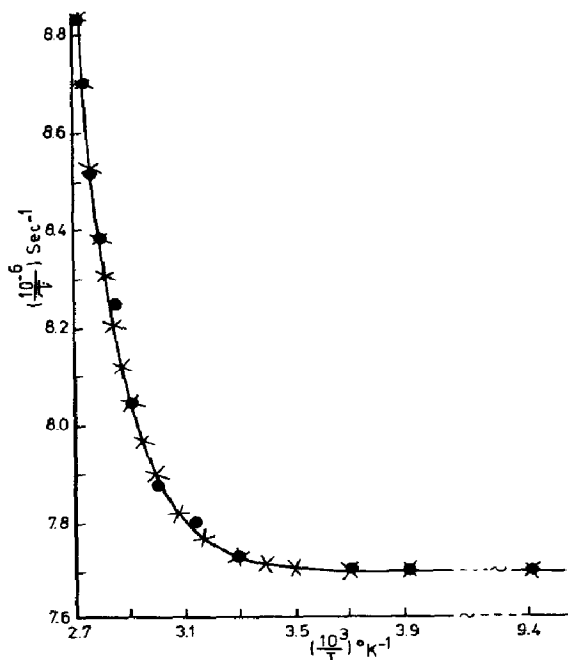


Fig. 2. Variation of the excimer lifetime $\tau$ of 1.0 g $l^{-1}$ of 3,4,9,10-dibenzopyrene in toluene at an absolute temperature $T$: ●, experimental; ×–×–×–, theoretical.

separation of the temperature-independent term in eqn. (3) into $K_{FM(D)}$ and $K^0_{IM(D)}$ requires the measurement of the absolute quantum efficiency of each compound studied. This has been postponed for the time being to await the completion of the single-photon counting and time-resolved pulse nanosecond fluorimeter system which is now under construction in our laboratory. However, a rough comparison of the emission spectra of the
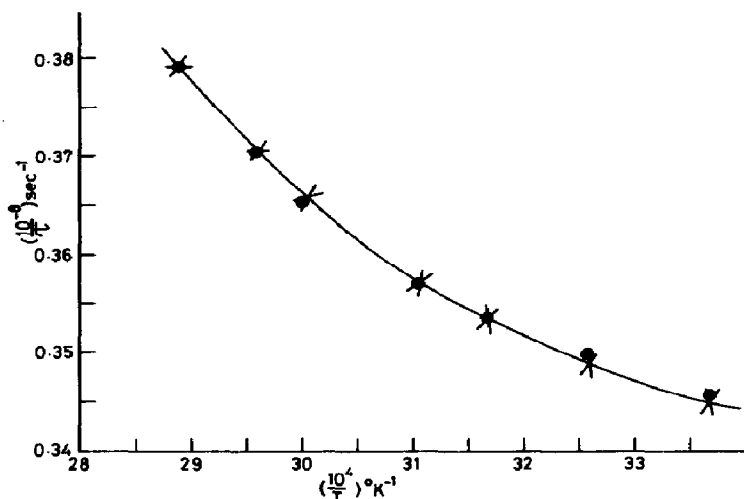
Fig. 3. Variation of the excimer lifetime $\tau$ of 2.0 g $l^{-1}$ of 2-aminoanthracene in alcohol at an absolute temperature $T$: ●, experimental; ×-×-×-, theoretical.
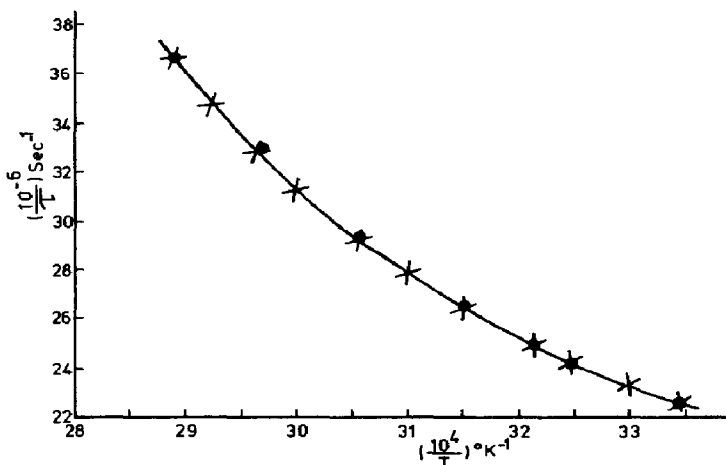


Fig. 4. Variation of the excimer lifetime $\tau$ of 20 g $l^{-1}$ of 20-methyl cholanthrene in benzene at an absolute temperature $T$: ●, experimental; ×-×-×-, theoretical.

compounds we studied with that of pyrene under the same experimental conditions indicates that the quantum efficiencies of our compounds are less than that of pyrene. Since the quantum efficiency of pyrene at room temperature is about 0.65 for the monomer and 0.68 for the excimer [14], the values of $K_{IM}^0$ were roughly estimated to be $10^6$ - $10^7$ $s^{-1}$ for the monomer and excimer of 3,4,9,10-dibenzopyrene and for the excimers of 20-methyl cholanthrene and 2-aminoanthracene. These values are small enough to be due to internal conversion but could also be due to inter-system crossing. This is in agreement with recent data of Birks et al. [7] and Cundall and Pereira [15].

TABLE 1

Values of different rate constants and activation energies of some carcinogenic compounds

| Compound | Component | $K_F + K_I^0$ $(\times 10^7\,s^{-1})$ | $K_I'$ $(\times 10^{11}\,s^{-1})$ | $W_I$ (eV) |
|---|---|---|---|---|
| 3,4,9,10-Dibenzopyrene–toluene | M | 0.77 | 2.69 | 0.54 |
| | D | 0.40 | 0.04 | 0.13 |
| 20-Methyl cholanthrene–benzene | M | 3.79 | — | — |
| | D | 1.8 | 1.26 | 0.26 |
| 2-Aminoanthracene–alcohol | M | 2.91 | — | — |
| | D | 0.34 | 0.46 | 0.27 |
| 1-Aminoanthracene–alcohol | M | 5.62 | — | — |
| | D | 6.67 | — | — |

For 20-methyl cholanthrene, we obtained a constant value of 26.5 ns for the monomer decay time throughout the range of temperatures used. This means that the temperature-dependent part of eqn. (3) is either zero or of negligible value compared with the temperature-independent part. The same behavior was observed in the cases of the excimer or 1-aminoanthracene and the monomers of 1- and 2-aminoanthracene. In all these cases values of $K_{IM(D)}^0$ are about $10^8$ - $10^9$ $s^{-1}$. These values are large enough not to be assigned to spin-forbidden transitions such as intersystem crossing. However, they could be assigned to internal conversion processes. Since they are of almost the same order of magnitude as the values of $K_{FM(D)}$, the assignments of $S_1 \rightarrow S_0$ and $D_1 \rightarrow D_0$ radiationless transitions for the $K_{IM(D)}^0$ values are perhaps correct in these cases. Although the radiative processes $S_1 \rightarrow S_0 + h\nu_M$ and $D_1 \rightarrow D_0 + h\nu_D$ compete efficiently with the corresponding nonradiative processes, it has been shown that the latter processes exist [16].

The temperature-dependent parts of eqn. (3) are perhaps worth analyzing individually for each compound since we cannot draw a general conclusion regarding all of them as in the case of $K_{IM(D)}^0$. For 3,4,9,10-dibenzopyrene, $K_{IM}' = 2.69 \times 10^{13}$ $s^{-1}$ is too large to be due to a spin-forbidden transition. Therefore, it must be due to internal conversion. However, owing to its large value, a very fast radiationless process is indicated. This process is much faster than the normal radiation fluorescence process for such a compound. As a result, assignment of the temperature-dependent part of eqn. (3) as due to the $S_1 \rightarrow S_0$ radiationless transition is incorrect in this case but it could be due to the $S_1 \rightarrow S_2$ radiationless process as follows: $S_1$ can be thought of as emitting and simultaneously thermally populating $S_2$. Although the decay of $S_1$ would not in general be exponential, under suitable conditions it might be, as in our case. This is not surprising, since thermally populated second excited electronic singlet states have been observed by several scientists[†] in systems similar to that studied

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[†] A strong emission from the second electronic excited singlet state of this compound,

here. As mentioned before, many authors [21 - 24] have suggested that the $S_1 \nrightarrow S_0$ radiationless transition probability is extremely small or even zero compared with the radiative probability between the same two levels. Forster and Dadley [16], however, disagreed with these authors' conclusion and showed that the $S_1 \nrightarrow S_0$ radiationless transition is possible. Nevertheless, in the present work, the second excited singlet state $S_2$ of 3,4,9,10-dibenzo-pyrene might be thermally populated and decayed to $S_1$ and/or $S_0$ via partially radiative and partially non-radiative processes.

$K'_{1D}$ for this compound was found to be $4 \times 10^9$ s$^{-1}$, which indicates a radiationless transition of the form $D_1 \rightarrow D_0$. Although this transition competes efficiently with the $D_n \rightarrow D_1$ ($n > 1$) radiationless transitions, it does not mean that the $D_n \rightarrow D_1$ radiationless transition probability is zero for all systems. If $D_n$ states are associated, the previous process can take place. For example, $K'_{1D}$ for 20-methyl cholanthrene is equal to $1.26 \times 10^{11}$ s$^{-1}$. This value is again relatively large and the temperature-dependent component of eqn. (3) could not be due to a $D_1 \rightarrow D_0$ radiationless transition. The proper assignment for it is the $D_2 \rightarrow D_1$ radiationless transition; $D_1$ in this case is emitting and thermally populating $D_2$. This was also found to be the case for 2-aminoanthracene excimer, where $K'_{1D} \exp(-W_{1D}/kT)$ could only be assigned to the $D_2 \rightarrow D_1$ radiationless transition.

## Acknowledgment

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at the concentration of 0.01 g l$^{-1}$, has been observed by Abu-Zeid *et al.* [17]. This emission was much enhanced and became almost of the same intensity as that due to $S_1 \rightarrow S_0$ emission when the sample was excited by a powerful (100 kW) main pulsed $N_2$ laser line ($\lambda$ = 3371 Å). For emission from second electronic excited singlet states of (a) pyrene and 3,4-benzopyrene (in the vapor phase), see ref. 18; (b) azulene, see ref. 19; (c) 1,2-benzanthracene and 3,4-benzopyrene solutions, see ref. 20.

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