

Short Communication

Low temperature fluorescence lifetime of aromatic solutes in 3-methylpentane: investigation using Čerenkov radiation

J. MAYER, M. SZADKOWSKA-NICZE and J. KROH

The Institute of Applied Radiation Chemistry, Technical University, 93-590 Łódź, Wróblewskiego 15 (Poland)

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The fluorescence lifetime-temperature dependences for naphthalene and pyrene in 3-methylpentane were investigated in the temperature range 92 - 298 K using Čerenkov light as the source of photochemical excitation. The results are explained in terms of temperature-dependent intersystem crossing from S_1 to the adjacent triplet levels.

1. Introduction

Čerenkov radiation can be considered to be an electromagnetic shock wave generated when a charged particle traverses a transparent medium with a velocity exceeding the speed of light. Since Čerenkov radiation has a continuous spectrum from the IR to the UV, most molecules can be excited optically on its absorption [1, 2].

In this communication we report the results of a study of the fluorescence lifetime temperature dependence for naphthalene (Nph) and pyrene (Py) in 3-methylpentane (3MP) between 295 and 90 K. The excited singlet states of the aromatic compound were produced by absorption of the Čerenkov radiation accompanying electron pulses delivered from a linear accelerator.

By using a concentration of 10^{-5} mol dm⁻³ of the guest compound the ion recombination mechanism of excited state formation during the duration of the electron pulse as well as excimer production may be neglected.

Lifetime studies can provide information on the local structure of the solution as well as on the radiationless transitions in the guest molecule.

2. Experimental details

Nph (POCh, Poland, analytical grade) was purified by vacuum sublimation, and Py (UEB, Belgium, analytical grade) was recrystallized twice from ethanol. 3MP (Fluka pure grade) was chromatographed through a freshly activated silica-gel column and kept under argon. All solutions were deoxygenated in a Spectrosil A sample cell by prolonged bubbling with argon or

helium. The sample cell was kept in a home-made styrofoam-copper cryostat through which cold nitrogen was passed, and this enabled experiments to be carried out at temperatures down to 90 K. The error in the temperature determination is estimated as ± 1 K. 3MP solutions form transparent glasses when in the frozen state.

A linear accelerator (ELU-6, made in the U.S.S.R.) delivering 17 ns electron pulses was used for the irradiation.

A Hamamatsu R-928 photomultiplier (input resistance, 50Ω) in conjunction with a Tektronix 7834 storage-type oscilloscope was used as the detection system. More details concerning the accelerator and the detection equipment can be found elsewhere [3].

3. Results and discussion

The decay curves for the Nph and Py fluorescence in the 3MP system at 298 K and 90 K are shown as insets to Fig. 1 and Fig. 2. All the observed decay curves can be approximated by a single exponential function over at least four half-lives (Fig. 1).

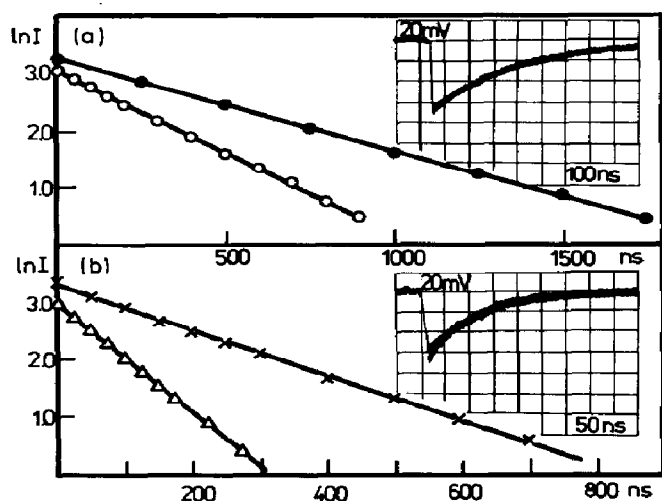


Fig. 1. Semilogarithmic (natural) plots of the fluorescence decay with least mean-squares fit giving the decay rate constant. (a) Py at 400 nm: \circ , 298 K; \bullet , 92 K. (b) Nph at 325 nm: \triangle , 298 K; \times , 92 K. The insets show oscilloscope traces of the fluorescence decay at 298 K: (a) Py, 100 ns per division; (b) Nph, 50 ns per division.

The resulting rate constants of singlet excited state deactivation for Nph and Py are plotted against temperature in Fig. 2. The fluorescence decay rates for both guest molecules can be represented by

$$k = k_0 + a \exp\left(-\frac{\Delta E}{kt}\right) \quad (1)$$

The parameters k_0 , a and ΔE are listed in Table 1, together with the available literature data.

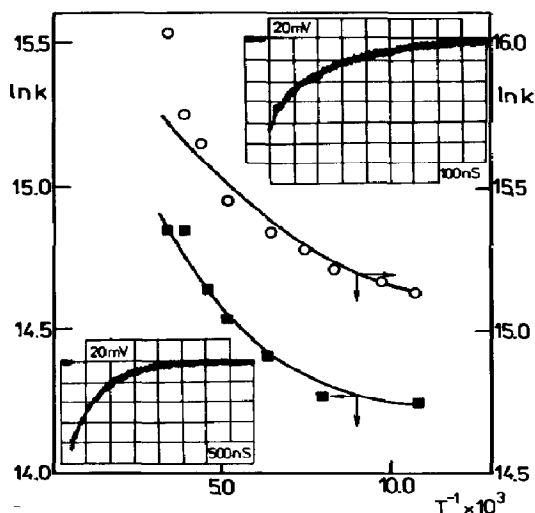


Fig. 2. Natural logarithm of the fluorescence decay rate constants *vs.* the reciprocal of the temperature: ○, Nph fluorescence monitored at 325 nm; ■, Py fluorescence monitored at 400 nm. The insets show oscilloscope traces of the fluorescence decay at 92 K: upper, Nph, 100 ns per division; lower, Py, 500 ns per division.

TABLE 1

Temperature-dependent intersystem crossing from S_1 (a , frequency factor; ΔE , activation energy; k_0 , temperature-independent parameter)

<i>Solvent</i>	$10^{-6}k_0$ (s^{-1})	$10^{-8}a$ (s^{-1})	ΔE (cm^{-1})	<i>Reference</i>
<i>Naphthalene</i>				
<i>n</i> -Hexane	2.7	0.4	480	4
Ethanol	1.5	1.1	650	5
95% ethanol	—	0.55	240	6
PMMA	3.9	0.23	352	7
C_2H_6 (l)	2.7	0.062	104	8
C_3H_6 (l)	2.6	0.068	95	8
1- C_4H_8	3.0	0.072	114	8
3MP	3.25	0.088	187	This paper
<i>Pyrene</i>				
Ethanol	1.33	0.33	795	9
Liquid paraffin	1.33	0.795	1085	9
PMMA	1.94	0.069	475	10
Nonane	0	0.06	400	11
3MP	1.5	0.0595	306	This paper

The temperature-independent parameter k_0 in eqn. (1) yields the lifetimes, which are close to the experimental values measured at the lowest temperature. The experimental lifetimes at 92 K for Nph (concentration range, 10^{-5} - (7.5×10^{-3}) mol dm^{-3}) and Py (concentration range, 10^{-5} - (2.5×10^{-3}) mol dm^{-3}) in the 3MP matrix were found to be 272 ± 2 ns and

652 ± 8 ns respectively. The former value is comparable with the fluorescence lifetime of Nph in 3MP at 77 K (253 ± 12 ns) reported by Jones and Calloway [7]. In the case of Nph, $1/k_0$ is almost equal to the lifetime in the gas phase under collision-free conditions [12 - 14]. For Py the gas phase fluorescence lifetimes were found to be in the range 210 - 500 ns [14 - 17]. Since Py is a large polyatomic molecule, the density of its vibronic states can be extremely high. Under collision-free conditions its energy must be conserved throughout the internal conversion processes [15], leading to the different energy distribution between the excitation levels compared with the condensed phases. For Py the fluorescence quantum yield in the gas phase is equal to 0.14 - 0.25 [15, 17] whereas in liquid solution it was reported to be about 0.6 - 0.7 [18]. The appropriate values for Nph are in the range 0.18 - 0.23 for both phases [12, 13, 18].

The collisions with the surroundings mainly seem to influence the radiationless transition processes in the case of Py.

The temperature-independent internal quenching rate parameter k_0 is the sum of the temperature-independent rates of intersystem crossing k_0^{ISC} and internal conversion k_0^{IC} . The values of k_0^{ISC} for Nph and Py are equal to $1.5 \times 10^6 \text{ s}^{-1}$ and $3 \times 10^4 \text{ s}^{-1}$ respectively [19]. Using our data (Table 1) one may calculate the k_0^{IC} for Nph and Py. The values of k_0^{IC} obtained in this manner are almost equal for these two compounds (Nph, $1.75 \times 10^6 \text{ s}^{-1}$; Py, $1.47 \times 10^6 \text{ s}^{-1}$) but, compared with Nph, the contribution of internal conversion is predominant in the case of Py.

The low value of k_0^{ISC} for Py was attributed to the absence of any triplet state between S_1 and T_1 and the intersystem crossing should occur from S_1 into high vibrational levels of T_1 [19]. In Nph k_0^{ISC} is much higher, indicating that in this compound the intersystem crossing occurs from S_1 to an adjacent triplet state close to S_1 , rather than to vibrational levels of T_1 . Our discussion of the Arrhenius term in eqn. (1) seemed to lead us to a similar conclusion.

The second term in eqn. (1) can be attributed to collisionally induced intersystem crossing. The magnitude of α in each case (Table 1) corresponds to a spin-forbidden intersystem crossing transition, *i.e.* from a thermally activated level of S_1 to a triplet state of energy $S_1 + \Delta E$.

In Py a triplet state T_2 at $27\,200 \text{ cm}^{-1}$ corresponding to S_1 ($26\,900 \text{ cm}^{-1}$ [19]) + ΔE (Table 1, 306 cm^{-1}) has been observed [19].

In Nph the temperature-dependent intersystem crossing indicates a triplet state of energy $S_1 + \Delta E$ equal to $(32\,000 [12, 20] + 187) \text{ cm}^{-1}$. According to the theoretical calculations the second triplet state $T_2(^3B_{3u}^+)$ is nearly degenerate with S_1 . Its energy was found to be equal to $30\,800 \text{ cm}^{-1}$ [19] or $31\,700 \text{ cm}^{-1}$ [20]. The next higher triplet state $T_3(^3B_{1g}^+)$ also lies within the region of S_1 : its energy was calculated to be $33\,100 \text{ cm}^{-1}$ [20]. This suggests that in the case of Nph the two triplet states (T_2 and T_3) may be of great significance for intersystem crossing from vibronic levels in S_1 .

Finally, extrapolation of the Nph lifetime using eqn. (1) to room temperature yields a value of about 145 ns at 300 K. This lifetime is higher than

the experimental value of 110 ns obtained by us and the values typically reported for Nph fluorescence at room temperature (120 ns [18]). A similar effect was observed by Li *et al.* [8]. They attributed the lower room temperature values to an increase in the rate of intersystem crossing owing to the presence of a new crossing channel, presumably to T₃ [13].

The results presented in this communication seem to show that in certain circumstances Čerenkov radiation can be used as an effective excitation source for photochemical research. Excitation of aromatics could also be obtained with other pulsed UV light sources with a pulse width of the order of 10⁻⁸ s or less. An N₂ laser (337.1 nm), a Q-switched, frequency-doubled ruby laser (347 nm), or a frequency-quadrupled, mode locked neodymium laser (264.5 nm) could be applied but for Nph the first two lasers are less useful because the wavelengths of the light are longer than the S₀-S₁ absorption edge. The application of lasers is limited to some extent by the very narrow spectral range of the emitted light and its selectivity. The flash photolysis method (pulse width, about 10⁻⁹ s) seems to be more universal, although Čerenkov radiation used as an internal excitation source may be treated as a comparable mode of excitation.

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