Journal of Photochemistry, 2 (1973/74) 221–229

PHOTOPHYSICS AND PHOTOCHEMISTRY OF *o*-XYLENE SOLUTIONS
I. RADIATIVE PROCESSES OF THE $^1B_1$ STATE

R. B. CUNDALL, D. A. ROBINSON and A. J. R. VOSS
Department of Chemistry, University of Nottingham, Nottingham NG7 2RD (Gt. Britain)
(Received May 3, 1973)

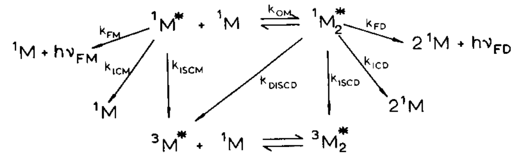
SUMMARY

The radiative decay processes of the excited monomer singlet and excimer states of *o*-xylene in solution have been examined as functions of temperature and concentration. The fluorescence rate constants for both states are independent of temperature. The values of the enthalpy (0.196 eV) and entropy (-8.8×10^{-4} eV K^{-1}) of formation of *o*-xylene excimer are less than for benzene as a result of steric influence of the methyl groups. The ground state repulsion energy ($\sim$ 0.61 eV) is greater than for benzene for similar reasons. The nature of the perturbation due to substituents is briefly discussed.

INTRODUCTION

A complete understanding of the behaviour of excited states of aromatic molecules requires that all radiative and non-radiative processes should be examined. This is a difficult task and has been partly achieved in only a few cases and only the simple aromatic hydrocarbons benzene[1], benzene-d_6[2], toluene[3], and phenylcyclohexane[4] have been studied in some detail. The effect of dimethyl substitution in the xylenes is of interest and the use of ring isomerization[5] for examining the nature of the internal conversion or the so-called "channel three" is attractive.

The work presented in this paper involves the study of the variation of the monomer and excimer fluorescence yields, and lifetimes with concentration and temperature. The general reaction scheme and rate constant terminology used is that used previously[6] and is summarized below:



Results of earlier work are summarized in Table 1.

EXPERIMENTAL

Materials

o-Xylene (Koch-Light Puriss Grade) was 99.8% pure and further purified by gas chromatography (Carbowax 20M column at 170°C). Subsequent analysis by gas chromatography (polyoxyethylene sorbitan monostearate column) failed to detect any impurity, the limit of detection being 0.5 ppm although any impurity eluting shortly after the *o*-xylene would not be detected at low concentrations. The purified samples were immediately out-gassed and stored on a vacuum line. Methylcyclohexane was acid washed and distilled over molten sodium. Several impurities were detected, probably saturated hydrocarbons, the more volatile of which were removed by prolonged vacuum refluxing of the solvent onto a cold finger at −78°C. The purified samples were transparent to light over the range 190–800 nm except for a small peak at 208 nm which gave an absorbance of 0.4 in a 1 cm cell.

Apparatus

Fluorescence spectra and quantum yields were measured using the instrument described by Cundall and Evans[7].

Fluorescence lifetimes were measured with an apparatus based on that developed by Birks and Greenleaf[8]. The lamp was of the high pressure nitrogen type similar to that described by Malmberg[9] but utilizing a higher gas pressure [20 bar (1 bar ≡ 10^5 N/m^2)] and with no synthetic switching circuit. An EHT of 30–35 kV was applied through a high resistance (400 MΩ) and the natural capacitance of the lamp resulted in a saw tooth discharge of lifetime believed to be about 1 ns and a repetition rate greater than 1 kHz. The lamp electrodes were made from pen tips, 0.1 mm in diameter for the anode and 0.05 mm for the cathode. The light from the lamp was collected by a quartz lens, filtered, and focused onto the sample. Fluorescence and scattered light were also suitably filtered and viewed by a fast response photomultiplier (Phillips 56 UVP). The output was fed to a pulse sampling oscilloscope (Hewlitt Packard 140A, 1410A, 1425A) and thence to a recorder.

The following filter systems were used. (a) Excitation: 3 mm Chance OX7, 5 cm $NiSO_4$ (100 g dm^{-3}) and 5 cm Cl_2 gas (1 bar) passing 250–285 nm; (b) emission: 3 mm Chance OX7, 2 cm of a solution of 4-methyl pyridine in n-dodecane, passing 285–320 nm.

Sample preparation was as described previously[6].

Lifetimes were calculated from the semi-logarithmic variation of intensity with time and corrected for the finite pulse lifetime by a "method of moments" calculation using:

$$\tau_M^2 = \tau_l^2 - \tau_{ex}^2$$

where τ_M is the actual fluorescence lifetime of the sample, τ_l is the observed lifetime, and τ_{ex} the lifetime of the excitation pulse. The technique is of limited accuracy due to the non-exponential character of the nitrogen lamp response after long time intervals, but was preferable to the convolution technique used previously[1], since the latter method requires very accurate matching of response and sample decay curve starting points. For example, pure *o*-xylene fluorescence at 20°C has a relatively long lived decay of about 50 ns which obeys a semi-logarithmic law at times less than 80 ns following excitation, after this time the non-exponential nature of the response function distorts the curve. The best computer produced curve, convoluting the response function of approximate lifetime 9 ns, with trial functions yielded a pure *o*-xylene emission lifetime of 38 ns. In all cases where the "method of moments" calculation was used only the first 60 ns of the decay was used in estimation of the emission lifetime.

RESULTS

Temperature had no appreciable effect on the absorption spectrum of *o*-xylene in methylcyclohexane in the range 25 to 90°C except for a small increase in

TABLE 1

PUBLISHED FLUORESCENCE PARAMETER DATA FOR *o*-XYLENE

Parameter	Value	Temp./°C	Solvent	Ref.
Φ^0_{FM}	0.15	20	n-hexane	10
	0.16	25	cyclohexane	11
	0.157	25	methylcyclohexane	13
	0.18	25	cyclohexane	14
	0.20	−78	cyclohexane	14
Φ^0_{FD}	0.029	20		10
	0.030	−78		14
E_b	0.17 eV	—	n-hexane	10
	0.20 eV	—	cyclohexane	14
τ_M	34 ns	25	cyclohexane	11
c_h	10.9 *M*	20	n-hexane	10

absorption at around 37,200 cm^{-1} with rise of temperature. Temperature reduced the intensity of fluorescence without measurably changing the shape or position of the emission band.

It was found that the shape of the fluorescence spectrum did not change when excitation occurs at any wavelength in the first absorption band and the fluorescence yield is also invariant with exciting wavelength down to 240 nm.

Fluorescence intensities for the monomer band were measured as a function of temperature between 20 and 90° C for six concentrations of *o*-xylene in methylcyclohexane (0.083 *M*, 0.83 *M*, 2.48 *M*, 4.13 *M*, 7.44 *M* and 8.29 *M*). Absolute monomer fluorescence yields were determined from a knowledge of the monomer peak intensity at 25° C as a function of concentration. The intensity at zero concentrations was put equal to a fluorescence yield, $\Phi^0{}_{FM}$, obtained from the results of Cundall and Pereira[13] (Table 1). Quantum yields for monomer emission were

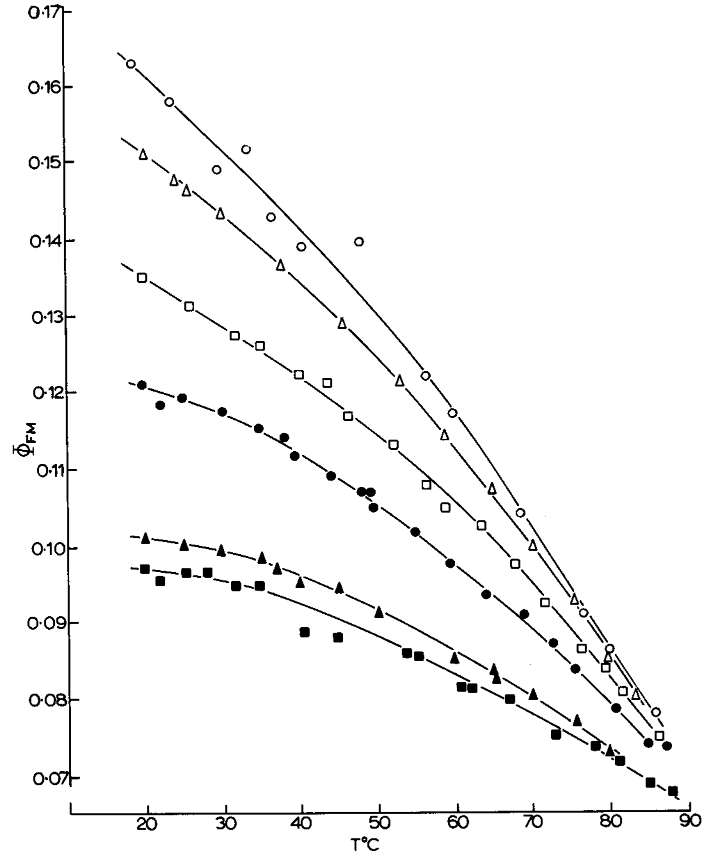


Fig. 1. Quantum yields for monomer emission at different concentrations as a function of temperature.

calculated from this value for each concentration of *o*-xylene at 25°C, and also at different temperatures from the variation of fluorescence intensity with temperature. The results are presented in Fig. 1.

Unlike benzene the only evidence of excimer fluorescence at room temperature and above is a slight "tailing" of the monomer peak of pure liquid *o*-xylene emission on the long wavelength side of the maximum although the excimer band increases markedly at lower temperatures[10]. Fully corrected spectra were recorded for a 7.5×10^{-3} *M* solution to establish the monomer spectrum and for the pure liquid (8.29 *M*) at 25°C to determine the excimer yield. The excimer yield was calculated on the basis of the ratio of peak areas, and knowledge of the monomer intensity for the pure liquid. A value of 0.011(5) was found for the excimer emission quantum yield in pure *o*-xylene at 25°C.

Fluorescence lifetime measurements were made on a 10^{-2} *M* solution of *o*-xylene in methylcyclohexane and pure *o*-xylene, as functions of temperature. The data are presented in Fig. 2.

DISCUSSION

The observed quantum yield, for excitation within the first absorption band, of *o*-xylene monomer fluorescence, Φ_{FM}, is deduced from the intrinsic fluorescence yield, $\Phi^0{}_{FM}$, in the more concentrated solutions by use of the expression[15]:

$$\Phi_{FM} = \Phi^0{}_{FM}/(1 + c/c_h) \qquad (1)$$

A similar expression for excimer fluorescence is:

$$\Phi_{FD} = \Phi^0{}_{FD}/(1 + c_h/c) \qquad (2)$$

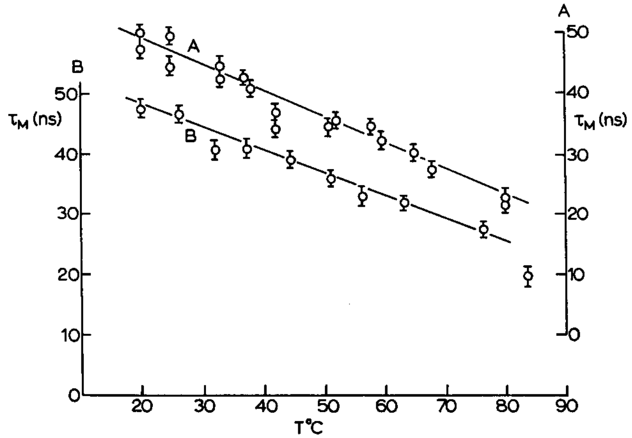


Fig. 2. Fluorescence lifetimes of *o*-xylene in 10^{-2} *M* (B) and pure *o*-xylene (A) as a function of temperature.

where $\Phi^0{}_{\mathrm{FD}}$ is the intrinsic yield of excimer fluorescence. c_{h} is the half quenching concentration, *i.e.* the concentration c when $\Phi_{\mathrm{FM}} = \frac{1}{2}\,\Phi^0{}_{\mathrm{FM}}$.

The following parameters used are defined as:

$$\Phi^0{}_{\mathrm{FM}} = k_{\mathrm{FM}}/(k_{\mathrm{FM}} + k_{\mathrm{ICM}} + k_{\mathrm{ISCM}}) \tag{3}$$

$$\tau_{\mathrm{M}} = (k_{\mathrm{FM}} + k_{\mathrm{ICM}} + k_{\mathrm{ISCM}})^{-1} \tag{4}$$

$$\Phi^0{}_{\mathrm{FM}} = k_{\mathrm{FD}}/(k_{\mathrm{FD}} + k_{\mathrm{ICD}} + k_{\mathrm{ISCD}}) \tag{5}$$

$$\tau_{\mathrm{D}} = (k_{\mathrm{FD}} + k_{\mathrm{ICD}} + k_{\mathrm{ISCD}})^{-1} \tag{6}$$

$$K_e = k_{\mathrm{DM}}/k_{\mathrm{MD}} = \tau_{\mathrm{D}}/\tau_{\mathrm{M}} c_{\mathrm{h}} \tag{7}$$

$$\Delta G^0 = -RT \ln K_e = \Delta H^0 - T\Delta S^0 \tag{8}$$

and $$E_{\mathrm{b}} = -\Delta H^0 \tag{9}$$

It is assumed that high temperature kinetics apply, *i.e.* the following inequalities are valid:

$$k_{\mathrm{MD}},\ k_{\mathrm{DM}}c \gg 1/\tau_{\mathrm{M}},\ 1/\tau_{\mathrm{D}} \tag{10}$$

Refractive index corrections

The quantum yield was corrected against the standard for environmental factors. $\Phi^0{}_{\mathrm{FM}}/\tau_{\mathrm{M}}$ under these circumstances gives k_{FM} and $k^0{}_{\mathrm{FM}}$ is evaluated from $k_{\mathrm{FM}} = k^0{}_{\mathrm{FM}}\, n^2$[16].

The effect of refractive index on the determination of the kinetic parameters governing the monomer–excimer system has been discussed previously[6]. In the *o*-xylene/methylcyclohexane system the variation of refractive index with concentration is $\leqslant 10\%$ and serious inconsistencies in the scheme arising from deviations due to refraction effects are not to be expected.

Steady luminescence data

The variation of monomer fluorescence with concentration was plotted according to eqn. (1). It was assumed that the 0.083 *M* solution approximated in behaviour to infinite dilution and the fluorescence yields for this solution at different temperatures were assigned to $\Phi^0{}_{\mathrm{FM}}$. From the slopes of these plots the temperature dependence of c_{h} was established. This is presented in Table 2. The value of Lumb and Weyl[10] of 10.9 at 20°C agrees, within 10%, with our result. The higher values for c_{h} compared with benzene agree with the trend observed for other methyl-substituted benzenes[10,15,17], and probably results from steric hindrance to excimer formation.

From the values for c_{h} at 25°C of 12.9 *M* and 0.011(5) for Φ_{FD} at 25°C, the intrinsic excimer fluorescence yield Φ_{FD} may be calculated from eqn.(2). The value of 0.029 at 25°C is in good agreement with the value of 0.029 at 20°C due to Lumb and Weyl[10].

Transient luminescence data

The measured fluorescence lifetimes of a 10^{-2} *M* *o*-xylene solution approximate to the intrinsic monomer lifetimes since, under these conditions, the fraction

TABLE 2

TEMPERATURE DEPENDENCE OF THE FLUORESCENCE PARAMETERS FOR DILUTE *o*-XYLENE SOLUTIONS (0.083 M) IN METHYLCYCLOHEXANE

Temp./°C	c_h/M	$10^{-6}\ k_{FM}/s^{-1}$	$10^{-6}\ k^0_{FM}/s^{-1}$
20	12.2	3.44	1.55
25	12.9	3.42	1.54
30	13.8	3.42	1.54
35	14.6	3.44	1.55
40	15.3	3.46	1.56
45	16.2	3.49	1.58
50	17.3	3.51	1.59
60	20.6	3.52	1.59
70	26.8	3.48	1.57
80	40.7	3.43	1.55

of excited molecules in the monomeric form is then practically unity. The radiative rate constant for the monomer, k_{FM}, is obtained from eqns. (3) and (4) and the data are presented in Table 2. Values of k^0_{FM} were calculated from refractive index data[18].

The intrinsic excimer lifetimes were calculated from eqn. (1) using knowledge of the emission lifetime of a solution of known *o*-xylene concentration, the intrinsic monomer emission lifetime, and the temperature dependence of c_h:

$$\tau_{obs}\ (c + c_h) = \tau_M c_h + \tau_D c \qquad (11)$$

The calculated values of τ_D are presented in Table 3. The values for τ_D at temperatures >60°C are affected by the cumulative errors in τ_M, τ_{obs}, and c_h which are largest in this region.

The monomer–excimer equilibrium constant is obtained from values of τ_D, τ_M and c_h by eqn. (7). The variation with temperature of K_e is shown in Table 3.

TABLE 3

EFFECT OF TEMPERATURE ON THE LIFETIME (τ_D) AND FORMATION CONSTANTS (K_e) OF THE *o*-XYLENE EXCIMER

Temp./°C	τ_D/ns	K_e/M^{-1}
20	57.3	0.099(5)
25	48.7	0.082
30	46.0	0.75
35	42.6	0.68
40	38.8	0.62
45	36.2	0.057
50	32.5	0.051
60	26.0	0.038
70	(17.0)	(0.022)
80	(7.2)	—

The variation of ln K_e with T^{-1} gives the entropy and enthalpy (binding energy) of excimer formation from eqns. (8) and (9). ΔS^0 is -8.8×10^{-4} eV K^{-1}; a comparison with the value of -12.5×10^{-4} eV K^{-1} for benzene indicates that the structure of the xylene excimer is less rigid than for benzene. The deviation from linearity of the ln K_e against T^{-1} plot above 60°C may be due to the errors in τ_D values, or breakdown of the excimer equilibrium because of a very temperature dependent internal conversion process for the monomer singlet becoming competitive with excimer formation. The linear portion of the plot indicates that $E_b =$ 0.196, with a probable accuracy of ± 15%. Lumb and Weyl[10] obtained a value of 0.17 eV from a plot of log $(\Phi_{FD}/\Phi_{FM}c)$ *vs.* K^{-1}. It has previously been shown[6] that this is $(E_b - E_{FD} + E_{FM})$. In the case of benzene[6], E_{FD} is significant and the energy difference obtained in this way does not give the binding energy. For *o*-xylene $E_{FM} = 0$ (Table 2) and since our value for E_b is similar to that of Lumb and Weyl for $(E_b - E_{FD} - E_{FM})$ it appears that E_{FD} is small, or zero in this case. The binding energy in *o*-xylene is smaller than for benzene (0.34 eV), a reduction consistent with a greater separation between the aromatic rings[19] due to steric interference of the methyl groups. The latter would be most effective in a totally eclipsed parallel plate structure, less so in the displaced structure suggested by Birks[20-22]. The activation energy for benzene excimer emission has been interpreted[6,14] as due to the necessity for displacement of one molecule with respect to the other to induce a transition moment for the otherwise dipole forbidden decay[23,24]. The methyl groups in *o*-xylene apart from increasing the separation may induce an electronic distortion which is sufficient to induce a transition moment appropriate for radiative decay of the excimer.

The ground state repulsion energy R_M may be calculated from the expression[15]:

$$\mathrm{M_D} - \mathrm{D_M} - V_M = E_b + R_M$$

The energy of the first excited singlet state of *o*-xylene is 36,900 cm^{-1} [25]. The peak in the excimer emission spectrum appears at approximately 30,400 cm^{-1} and from a knowledge of the binding energy it can be calculated that R_M is ~ 0.61 eV. This is 30% greater than the equivalent for benzene and, no doubt, is also due to methyl group effects.

General remarks

The effect of methyl substitution on the radiative transition probability for the excited monomer singlet qualitatively agrees with the trend predicted by the calculations of Petruska[26] on state mixing. It is impossible to determine if there is a similar influence in the excimer state, as methyl substitution physically perturbs the excimer to an extent which obscures the smaller changes due to inductive effects.

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