

Fluorescence and Triplet Yields of Benzene and Toluene in Cyclohexane Solutions. Temperature and Deuteration Effects

KJELL SANDROS

Institutionen för fysikalisk kemi, Chalmers Tekniska Högskola, S-402 20 Göteborg 5, Sweden

Relative fluorescence yields of benzene, benzene- d_6 , and toluene in dilute cyclohexane solutions have been measured in the temperature range 7–50°C. Triplet yields of these compounds at 20°C have been obtained from measurements of sensitized biacetyl luminescence. The triplet yield of benzene has also been determined at 7°C. The results are compatible with a reaction scheme involving, *inter alia*, a thermally activated nonradiative process from the fluorescent state with the following activation energies: 0.288 eV (benzene), 0.292 eV (benzene- d_6), and 0.318 eV (toluene), together with a temperature-independent intersystem crossing process. A small, but significant, deuteration effect on the rate of the last process was observed.

For most aromatic molecules hitherto studied in dilute solution at room temperature, the sum of the quantum yields of triplet formation (Φ_T) and of fluorescence (Φ_F) is close to unity (see, *e.g.*, a compilation by Birks¹), which means that other paths from the lowest excited singlet state are usually of minor importance. Recently presented results from this laboratory² indicate, however, that for benzene and toluene in cyclohexane solutions at 20°C the values of $\Phi_T + \Phi_F$ are only 0.3 and 0.7, respectively. The temperature dependences of Φ_F ³ and of the fluorescence lifetime⁴ for benzene in dilute solution are compatible with a mechanism involving a radiationless process with an activation energy which is solvent-dependent and amounts to 0.28 eV in cyclohexane solution, in addition to temperature-independent processes. In both papers cited, it is suggested that the thermally activated process might be an indirect internal conversion *via* an isomeric state and that intersystem crossing to the triplet manifold is temperature-independent. It seemed to be of interest to examine whether this interpretation is in agreement with triplet yield data. In the present work the temperature-dependence of Φ_F has been analyzed for benzene, benzene- d_6 , and toluene using the values of Φ_F and Φ_T at 20°C. The value of Φ_T for benzene has also been determined at 7°C.

EXPERIMENTAL

Relative fluorescence quantum yields were measured with an Aminco Bowman spectrofluorometer fitted with a mercury-xenon lamp. The cyclohexane solutions used were of such concentrations that the fraction of the exciting light absorbed in the observed part of the cell was almost temperature-independent. (With the experimental arrangement used, this condition is fulfilled at an absorbance of about 1 per cm.) The deaerated solution contained under nitrogen in a rectangular quartz cell was brought to the desired temperature (7–50°C). The fluorescence intensity at an emission maximum on irradiation by 254 nm light was measured with an identical sample at 20°C as reference. Corrections were applied for the geometrical refractive index effect.⁵ The corrected intensities were assumed to be proportional to the fluorescence quantum yields, which means that the effects of spectral changes with temperature were neglected. These were judged to be insignificant particularly as the detector part was set at a low spectral resolution.

Triplet quantum yields were determined as described previously.²

RESULTS AND DISCUSSION

Temperature-dependence of the fluorescence quantum yields. The steady state ratios between the concentrations of singlet excited monomers and excimers at the temperatures and solute concentrations (about 10⁻² M) used are large enough⁶ to allow the consideration of only the monomer properties. Retaining the notations used in the previous paper,² the depopulation of the lowest excited state of the aromatic monomer may be described by the following rate constants: k_1 (fluorescence), k_2 (radiationless deactivation processes to the ground state), and k_3 (intersystem crossing). Tentatively assuming k_1 and k_3 to be temperature-independent, and k_2 to be dominantly determined by a process having an activation energy of E_A , one obtains:

$$\frac{1}{\Phi_F} = \frac{k_1 + k_3}{k_1} + \frac{k_2'}{k_1} \exp(-E_A/kT) \quad (\text{I})$$

or

$$\log\left(\frac{1}{\Phi_F} - \alpha\right) = \text{const} - \frac{E_A}{kT \ln 10} \quad (\text{II})$$

where k_2' denotes a frequency factor, k Boltzmann's constant, and $\alpha = (k_1 + k_3)/k_1 = (\Phi_F + \Phi_T)/\Phi_F$.

Birks (Ref. 1, p. 103) has presented strong arguments for the view that the Φ_F values in cyclohexane solution given by Berlman⁷ should be multiplied

Table 1. Fluorescence and triplet formation yields in dilute cyclohexane solutions at 20°C.

Solute	Φ_F	Φ_T	$\alpha = \frac{\Phi_F + \Phi_T}{\Phi_F}$
Benzene	0.058	0.252	5.34
Benzene- <i>d</i> ₆	0.066	0.240	4.64
Toluene	0.141	0.530	4.76

Table 2. Results from measurements of sensitized biacetyl luminescence.

Sensitizer	Temp. °C	$k_6/k_3 \text{ M}^{-1}$ $\times 10^{-3}$	$k_6/k_3 \text{ M}^{-1}$ $\times 10^{-3}$	$k_3/k_5 = \Phi_T$	$k_6/k_4 \text{ M}^{-1}$ $\times 10^{-3}$
Benzene	7	1.34	0.452	0.337	9
Benzene	20	1.81	0.457	0.252	10
Benzene- d_6	20	1.92	0.460	0.240	10

by a factor of 0.83.* Table 1 gives corrected values of Φ_F , values of Φ_T from Ref. 2 and from this work (cf. Table 2), and also the corresponding values of α .

Plots according to eqn. (II) are presented in Fig. 1. It should be noted that the points can be fitted remarkably well to straight lines, and that rather small changes in the applied values of Φ_T cause marked deviations from linearity. These facts seem to support the assumptions made and indicate that the values of Φ_T used are fairly accurate. The slopes of the lines correspond to the following values of E_A : 0.288 eV (benzene), 0.292 eV (benzene- d_6), and 0.318 eV (toluene).

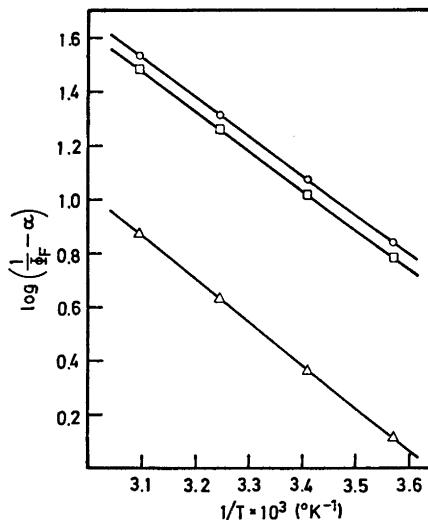


Fig. 1. Plots of $\log[(1/\Phi_F) - \alpha]$ vs. $1/T$. Solutes: 0.011 M benzene (O), 0.006 M benzene- d_6 (□), and 0.006 M toluene (△).

Cundall and Davies⁸ conclude, that for benzene in the gas phase, a deuteration sensitive internal conversion process with only a small activation energy is operative. If such a process operates in cyclohexane solution with a rate constant equal to that in the gas phase (about $5 \times 10^5 \text{ sec}^{-1}$), it will be too slow to affect the analysis of the temperature-dependence of the fluorescence significantly.

* It may be noted that with this correction applied to the Φ_F values given in Table 5 in Ref. 2, none of the $(\Phi_F + \Phi_T)$ values exceed unity.

From the values of Φ_F , Φ_T , the fluorescent state lifetime,^{4,7} and of E_A , the following values of $\log k_2'$ are obtained: 12.3 (benzene and benzene- d_6), and 12.4 (toluene). The high, and within limits of error identical, values of the pre-exponential factor indicate that the fluorescent states have great probabilities for decay once the activation barriers are mounted.³

Triplet yields. The results of measurements of sensitized biacetyl luminescence from this work and from Ref. 2 (benzene at 20°C) are presented in Table 2, where k_5 and k_6 denote the singlet and triplet energy transfer rate constants, k_4 the triplet decay rate constant of the sensitizer, and $k_s = k_1 + k_2 + k_3$.

The data from solutions with benzene as sensitizer will first be discussed. The ratio between the values of Φ_T at 20°C and at 7°C is 0.75, a value which, within limits of error, is equal to the ratio between the corresponding Φ_F values (0.72). This fact provides further evidence that the intersystem crossing rate is not very temperature-dependent, contrary to what applies to some substituted anthracenes, where the decrease in Φ_F with increasing temperature is accompanied by an increase in Φ_T .⁹ The ratio k_5/k_3 is found to be proportional to T/η , where η is the viscosity of the solvent, as expected if k_3 is temperature-independent and if the value of k_5 is diffusion-controlled. The values of k_6/k_4 are rather uncertain, but they show no strong temperature-dependence. To test whether triplet excimer formation¹⁰ might influence the triplet lifetime of benzene at the low concentrations used (about 0.01 M), the value of k_6/k_4 was determined at some benzene concentrations in the range 0.01–0.5 M. The ratio was constant, within the wide limits of error, at benzene concentrations < 0.1 M, whereas at the highest benzene concentrations lower values indicate excimer effects.

From the values of k_3/k_s for benzene and benzene- d_6 , together with the values of k_s at 20°C (32×10^6 and 29×10^6 sec⁻¹, respectively⁴) a ratio of 1.16 between the intersystem crossing rates is obtained. Helman⁴ concludes from his data that this ratio is at least 1.2 and the best fit to the data in Arrhenius plots gives a rate constant ratio of 1.5. Evidently, there is a significant deuteration effect on the intersystem crossing rate even though the present results indicate that the rate constant ratio is less than 1.5.

Adopting a k_6 value² of 5×10^9 M⁻¹ sec⁻¹, the value of k_4 may be estimated at 5×10^5 sec⁻¹ for both benzene and benzene- d_6 . In the gas phase a benzene triplet decay rate constant of 4×10^4 sec⁻¹ at 300°K has been reported.¹¹ It is possible that solvent impurities deactivate triplet benzene by energy transfer, favoured by the high triplet energy of benzene. The difference between the gas phase and cyclohexane solution triplet lifetimes of benzene may, of course, also be a medium effect. Measurements on benzene and benzene- d_6 in solid matrices at lower temperatures show large temperature and solvent effects, "which are not explained by the current theories of radiationless transitions".¹² It is therefore not surprising that no deuteration effect on the triplet lifetime is observed in cyclohexane solution at 20°C.

Acknowledgements. I am indebted to Professor Hans L. J. Bäckström for comments and suggestions on the manuscript. My thanks are also due to Dr. Mats Almgren for many helpful discussions, and to Mrs. I.-L. Samuelsson for experimental assistance.

REFERENCES

1. Birks, J. B. *Photophysics of Aromatic Molecules*, Wiley-Interscience, London 1970, p. 251.
2. Sandros, K. *Acta Chem. Scand.* **23** (1969) 2815.
3. Eastman, J. W. *J. Chem. Phys.* **49** (1968) 4617.
4. Helman, W. P. *J. Chem. Phys.* **51** (1969) 354.
5. Hermans, J. J. and Levinsson, S. *J. Opt. Soc. Amer.* **41** (1951) 460.
6. Hirayama, F. and Lipsky, S. *J. Chem. Phys.* **51** (1969) 1939.
7. Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic, New York and London 1965.
8. Cundall, R. B. and Davies, A. S. *Trans. Faraday Soc.* **62** (1966) 1151.
9. Lim, E. C., Laposa, J. D. and Yu, J. M. H. *J. Mol. Spectr.* **19** (1966) 412.
10. Cundall, R. B. and Voss, A. J. R. *Chem. Commun.* **1969** 116.
11. Parmenter, C. S. and Ring, B. L. *J. Chem. Phys.* **46** (1967) 1998.
12. Hatch, G. F., Erelitz, M. D. and Nieman, G. C. *Molecular Luminescence*, Benjamin, New York 1969, p. 21.

Received March 23, 1971.