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

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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 ($\Phi_T$) and of fluorescence ($\Phi_F$) is close to unity (see, e.g., a compilation by Birks ¹), which means that other paths from the lowest excited singlet state are usually of minor importance. Recently presented results from this laboratory ² 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 $\Phi_F$ ³ and of the fluorescence lifetime ⁴ 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 $\Phi_F$ has been analyzed for benzene, benzene-$d_6$, and toluene using the values of $\Phi_F$ and $\Phi_T$ at 20°C. The value of $\Phi_T$ for benzene has also been determined at 7°C.

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EXPERIMENTAL

Relative fluorescence quantum yields were measured with an Aminco Bowman spectrophotofluorometer 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. 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.\(^6\)

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\(^{-5}\) M) used are large enough\(^6\) to allow the consideration of only the monomer properties. Retaining the notations used in the previous paper, 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:

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

or

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

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 \(\Phi_F\) values in cyclohexane solution given by Berlman\(^7\) should be multiplied.

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

<table>
<thead>
<tr>
<th>Solute</th>
<th>(\Phi_F)</th>
<th>(\Phi_T)</th>
<th>(\alpha = \frac{\Phi_F + \Phi_T}{\Phi_F})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.058</td>
<td>0.252</td>
<td>5.34</td>
</tr>
<tr>
<td>Benzene-(d_8)</td>
<td>0.066</td>
<td>0.240</td>
<td>4.64</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.141</td>
<td>0.530</td>
<td>4.76</td>
</tr>
</tbody>
</table>

Table 2. Results from measurements of sensitized biacetyl luminescence.

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Temp. °C</th>
<th>$k_s/k_3$ M⁻¹ $\times 10^{-3}$</th>
<th>$k_s/k_4$ M⁻¹ $\times 10^{-3}$</th>
<th>$k_s/k_5=\Phi_T$</th>
<th>$k_s/k_4$ M⁻¹ $\times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>7</td>
<td>1.34</td>
<td>0.452</td>
<td>0.337</td>
<td>9</td>
</tr>
<tr>
<td>Benzene</td>
<td>20</td>
<td>1.81</td>
<td>0.457</td>
<td>0.252</td>
<td>10</td>
</tr>
<tr>
<td>Benzene-$d_6$</td>
<td>20</td>
<td>1.92</td>
<td>0.460</td>
<td>0.240</td>
<td>10</td>
</tr>
</tbody>
</table>

by a factor of 0.83.* Table 1 gives corrected values of $\Phi_F$, values of $\Phi_T$ from Ref. 2 and from this work (cf. Table 2), and also the corresponding values of $x$.

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 $\Phi_T$ cause marked deviations from linearity. These facts seem to support the assumptions made and indicate that the values of $\Phi_T$ 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 $\log[(1/\Phi_F)-x]$ vs. $1/T$. Solutes: 0.011 M benzene (O), 0.006 M benzene-$d_6$ (□), and 0.006 M toluene (Δ).](image)

Cundall and Davies ⁸ 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 $5 \times 10^6$ 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 $\Phi_F$ values given in Table 5 in Ref. 2, none of the $(\Phi_T+\Phi_F)$ values exceed unity.

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From the values of $\Phi_F$, $\Phi_T$, the fluorescent state lifetime, and of $E_A$, the following values of $\log k_a'$ 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\(^\circ\)C) are presented in Table 2, where $k_s$ and $k_g$ denote the singlet and triplet energy transfer rate constants, $k_4$ the triplet decay rate constant of the sensitizer, and $k_a = k_1 + k_2 + k_3$.

The data from solutions with benzene as sensitizer will first be discussed. The ratio between the values of $\Phi_T$ at 20\(^\circ\)C and at 7\(^\circ\)C is 0.75, a value which, within limits of error, is equal to the ratio between the corresponding $\Phi_F$ 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 $\Phi_F$ with increasing temperature is accompanied by an increase in $\Phi_T$.\(^9\) The ratio $k_6/k_4$ is found to be proportional to $T/\eta$, where $\eta$ is the viscosity of the solvent, as expected if $k_6$ is temperature-independent and if the value of $k_4$ 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 formation\(^10\) 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 $k_6/k_4$ for benzene and benzene-$d_6$, together with the values of $k_4$ at 20\(^\circ\)C ($32 \times 10^8$ and $29 \times 10^8$ sec\(^{-1}\), respectively) a ratio of 1.16 between the intersystem crossing rates is obtained. Helman\(^4\) 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 deuterium effect on the intersystem crossing rate even though the present results indicate that the rate constant ratio is less than 1.5.

Adopting a $k_6$ value\(^8\) of $5 \times 10^9$ M\(^{-1}\) sec\(^{-1}\), the value of $k_4$ may be estimated at $5 \times 10^8$ sec\(^{-1}\) for both benzene and benzene-$d_6$. In the gas phase a benzene triplet decay rate constant of $4 \times 10^4$ sec\(^{-1}\) at 300\(^\circ\)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 deuterium effect on the triplet lifetime is observed in cyclohexane solution at 20\(^\circ\)C.

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REFERENCES


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