Effects of Pressure and Temperature on the Fluorescence Quantum Yield of N-Methylacridone in Solution Interpreted in Terms of the Eyring Transition-State Theory

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The influence of temperature and pressure on the fluorescence quantum yield of N-methylacridone (9,10-dihydro-9-oxo-10-methyl-acridine) in toluene in the range of 283–313 K and 1 bar to 2.5 kbar, respectively, has been investigated. Treatment of the data in terms of the Eyring transition-state theory leads to a consistent interpretation of the observed effect. The unusually large increase of the quantum yield with increasing pressure is attributed to a positive volume of activation, \( \Delta V^* \), for the thermally activated \( S_1 \rightarrow T_2 \) intersystem crossing which is known to be the only deactivation process (of the \( S_1 \)-state) competing with fluorescence. Comparison of the values for \( \Delta H^* \), the activation enthalpy of this process, determined at various pressures, indicates a decrease in \( \Delta H^* \) at elevated pressures. Since \( \Delta H^* \) can be associated with the \( S_1 \rightarrow T_2 \) energy gap involved in intersystem crossing, this result further confirms the conclusion that the change in Franck-Condon factors alone cannot account for the decrease in the intersystem crossing rate with increasing pressure.

1. Introduction

The fluorescence quantum yields, \( Q_t \), of acridone (9,10-dihydro-9-oxo-acridine) and several of its N-substituted derivates depend significantly on temperature, i.e. they decrease with increasing temperature [1]. For these compounds, \( k_t \), the rate constant of fluorescence has been shown to be insensitive to changes in temperature. Furthermore, direct radiationless deactivation of the first excited singlet state, \( S_1 \), by internal conversion to the ground state can be neglected. These results indicate that the influence of temperature on the quantum yields can be attributed to the thermally activated radiationless deactivation of \( S_1 \) by intersystem crossing (ISC) to a state of the triplet manifold, presumably \( T_2 \), which is located energetically above \( S_1 \).

The same sequence of \( S_1 \) and \( T_2 \) levels and also, as a consequence, thermally activated \( S_1 \rightarrow T_2 \) intersystem crossing have been assumed before to account for qualitatively similar results concerning the temperature dependence of the fluorescence quantum yields of meso-substituted anthracenes [2–4].

For both groups of compounds ISC has been found to be the only process to compete with fluorescence emission with respect to the deactivation of \( S_1 \). Therefore, temperature effects and also pressure effects on quantum yields are a direct indication of the respective influences on intersystem crossing.

For meso-substituted anthracenes a considerable influence of pressure on quantum yields has been detected [5—7]. The observed increase with increasing pressure has been interpreted in terms of decreasing Franck-Condon factors as the \( S_1 \rightarrow T_2 \) energy gap is considered to widen with increase in pressure [6, 7]. This interpretation, however, requires in some cases the assumption of large changes in Franck-Condon factors, by far greater than expected on the basis of the general energy gap law [8], to account for considerable changes of the transition rate associated with relatively small variations of the energy gap.

In a previous paper we proposed an alternative explanation [9]. From the point of view offered by the Eyring transition-state theory for activation controlled reactions we suggested that the observed decrease of intersystem crossing rates with increasing pressure could be attributed to a positive volume of activation, \( \Delta V^* \), to be assigned to the intersystem crossing process.

In this interpretation \( \Delta V^* \) represents the difference of the partial molar volumes of the transi-

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tion-state in going from S₁ to T₂ and the molecule in the S₁ state. Thus the assumption of drastic changes in Franck-Condon factors to be associated with the observed small or even neglectable pressure variations of the S₁−T₂ energy gap can be avoided.

The concept of activation volumes that accounts for the pressure dependence of electronic relaxation rates was suggested for the first time by Baldwin and Offen [10]. They used it in discussing the influence of pressure on singlet and triplet lifetimes of various hydrocarbons. However, in these cases no simple model explaining thermal activation of any competing deactivation process was available. Furthermore, the respective pressure dependencies could not be separated. As a consequence, the results did not lead to a consistent view of the physical meaning of the activation volumes detected.

Because of the above mentioned less complex conditions concerning the deactivation of the S₁ state of N-substituted acridones, these compounds appear to be suitable to test the perhaps more general applicability of the concept of activation volumes. In the present study we report the results on the temperature and pressure dependence of the fluorescence quantum yield of N-methylacridone (NMA) in toluene. It will be shown that the described concept of interpretation appears to be valid also in this case.

2. Experimental

NMA was purchased from EGA and recrystallized twice from ethanol. Toluene (Uvasol, spectroscopic grade, MERCK) was dried over sodium and used without further purification.

Fluorescence measurements were performed in an apparatus essentially based on an experimental arrangement described elsewhere [11]. It was modified by usage of a pressure cell which allowed for pressures up to 2.5 kbar. Fluorescence spectra were recorded at right angle to the exciting light beam using a ZEISS MM 12 double monochromator and a R 456-HAMAMATSU photomultiplier tube.

The concentration of the sample solutions was 5 × 10⁻⁵ M; the molar extinction coefficient amounts to about 3900 M⁻¹ cm⁻¹ at the excitation wavelength (365 nm). All test samples were not deaerated since it was found that oxygen did not influence the quantum yields.

The cuvettes used were of the pill-box type described by le Noble and Schlott [12] and kindly provided by these authors. For this reason no corrections of extinction values corresponding to volume changes of the compressed sample solutions had to be made. The small temperature and pressure shifts of the absorption spectrum (1.5 nm kbar⁻¹ at 293 K) observed in a ZEISS DMR 10 spectrophotometer using a thermostated pressure cell also afforded no additional corrections for changes in absorption. As the red shift of the fluorescence spectrum was less than 2 nm kbar⁻¹ in the investigated pressure range, no corrections for the sensitivity of the monochromator and photomultiplier arrangement was necessary. Changes in refraction indices up to 2.5 kbar are small and negligible [13].

The shape of the fluorescence spectrum was found to be invariable with pressure and temperature, therefore, the ratio of the fluorescence intensities at the maximum peak (409 nm, 1 bar, 293 K) could be regarded as the ratio of the respective quantum yields. Reference values at normal pressure were calculated for the investigated temperatures using data reported by Siegmund and Bendig [1].

3. Results and Discussion

The observed fluorescence quantum yields, Qt, of NMA in toluene for the investigated temperatures and pressures are listed in Table 1.

Since S₁−T₂ intersystem crossing is the only effective process contributing to the deactivation of S₁ apart from fluorescence emission, the fluorescence quantum yield of NMA is given by:

\[ Q_t = \frac{k_t}{(k_t + k_{1sc})}. \] (1)

Table 1. Pressure and temperature dependencies of the fluorescence quantum yield of NMA in toluene.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Qt*</th>
<th>pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>0.119**</td>
<td>0.139 0.163 0.215 0.267 0.314 0.345</td>
</tr>
<tr>
<td>293</td>
<td>0.098**</td>
<td>0.113 0.143 0.195 0.229 0.278 0.319</td>
</tr>
<tr>
<td>303</td>
<td>0.082**</td>
<td>0.085 0.120 0.159 0.203 0.242 0.286</td>
</tr>
<tr>
<td>313</td>
<td>0.069**</td>
<td>0.077 0.102 0.138 0.171 — —</td>
</tr>
</tbody>
</table>

* Errors amount to ± 6%.
** Values extrapolated from data reported in (1).
$k_1$ is generally considered to be independent of pressure and temperature [5, 2]. Therefore, changes in $Q_1$ are caused by variations in $k_{isc}$, the rate constant of the $S_1$-$T_2$ intersystem crossing:

\[
\frac{((1/Q_1) - 1)_{P,T}}{((1/Q_1) - 1)_{1,298}} = \frac{(k_{isc})_{P,T}}{(k_{isc})_{1,298}}.
\]  

Using relation (2) and the values $(k_{isc})_{1,298} = 8.96 \times 10^8$ s$^{-1}$ and $(Q_1)_{1,298} = 0.090$ reported in (1) we computed $(k_{isc})_{P,T}$ for the investigated temperatures and pressures. The results are given in Table 2.

The temperature dependence of $k_{isc}$ for NMA can be described in terms of the Arrhenius equation (3):

\[
k_{isc} = k_{isc}^0 \exp\left(-\frac{E_a}{RT}\right),
\]  

where $k_{isc}^0$ is the temperature independent rate constant for the isoenergetic transition between the vibrational levels of the $S_1$ and $T_2$ states which are involved in ISC, and $E_a$ is the activation energy corresponding to the energy gap separating the vibrational ground state of $S_1$ and the vibrationally excited state from which intersystem crossing occurs. Equation (3) has been experimentally verified by Siegmund and Bendig [1].

The transition-state theory leads to the following expression for the temperature dependence of $k_{isc}$:

\[
k_{isc} = \frac{k_B T}{h} \exp\left(\frac{(\Delta S^* / R) - (\Delta H^*/RT)}{T}\right),
\]  

where $k_B = \text{Boltzmann's constant}$, and $h = \text{Planck's constant}$. $\Delta S^*$ and $\Delta H^*$ are the activation entropy and activation enthalpy, respectively. These activation parameters describe the differences in the respective partial molar quantities between the initial state and the transition state of a given thermally activated rate process. With respect to the thermally activated $S_1$-$T_2$ intersystem crossing considered here, the meaning of $\Delta H^*$ is essentially consistent with that of $E_a$ in (3).

$\Delta H^*$ at constant pressure is obtained from the slope of the graph $\ln((k_{isc})_{P,T})$ versus $1/T$. The corresponding graphs showed good linearity. Values for $\Delta H^*$ derived from least squares fits are given in Table 3.

To interpret the pressure dependence of the rate constants for thermally activated processes, the transition-state theory makes use of the activation volume concept. The activation volume i.e. the difference in partial molar volumes of the initial and the transition state is given by (5):

\[
\left(\frac{d \ln k_{isc}}{d P}\right)_T = - \frac{\Delta V^*}{RT}.
\]

The graphs of $\ln k_{isc}$ versus $P$ at constant temperatures showed good linearity up to 1 kbar followed by slight curvatures. Unfortunately there is no exact expression known for the functional pressure dependence of $\ln k$. Since we are interested in values of $\Delta V^*$ at 1 bar, we used straight line fits referring to the data up to 1 kbar, which, as mentioned before, were quite satisfactory. The obtained activation volumes at 1 bar are collected in Table 4.

### Table 2. Pressure and temperature dependencies of the $S_1$-$T_2$ intersystem crossing rate constant $k_{isc}$ of NMA in toluene.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$10^{-5} \times k_{isc}$ (s$^{-1}$)</th>
<th>pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>6.56</td>
<td>1, 200, 500, 1000, 1500, 2000, 2500</td>
</tr>
<tr>
<td>293</td>
<td>6.15</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>5.92</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>11.95</td>
<td></td>
</tr>
</tbody>
</table>

* Errors amount to about ± 6%.

### Table 3. Activation enthalpies for the $S_1$-$T_2$ intersystem crossing of NMA in toluene.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.2**</td>
</tr>
<tr>
<td>200</td>
<td>13.4</td>
</tr>
<tr>
<td>500</td>
<td>10.9</td>
</tr>
<tr>
<td>1000</td>
<td>11.2</td>
</tr>
<tr>
<td>1500</td>
<td>11.3</td>
</tr>
<tr>
<td>2000</td>
<td>10.4</td>
</tr>
<tr>
<td>2500</td>
<td>7.4</td>
</tr>
</tbody>
</table>

* Errors amount to about ± 1 kJ mol$^{-1}$.
** From [1].

### Table 4. Experimental and calculated activation volumes for the $S_1$-$T_2$ intersystem crossing of NMA in toluene.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta V^*$ (cm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>15.9</td>
</tr>
<tr>
<td>293</td>
<td>16.8</td>
</tr>
<tr>
<td>303</td>
<td>17.9</td>
</tr>
<tr>
<td>313</td>
<td>19.1</td>
</tr>
</tbody>
</table>

* Errors amount to about ± 1 cm$^3$ mol$^{-1}$.
** Calculated according to Equation (7).
There is one main feature concerning the data obtained in this investigation which, to our opinion, confirms the usefulness of the activation volume concept for the interpretation of the presented results. Comparison of the values for the activation enthalpy in Table 3 reveals that $\Delta H^*$ decreases rather than remains constant, but obviously does not increase with increasing pressure.

Since $\Delta H^*$ reflects the energy gap between the respective vibrational levels of $S_1$ and $T_2$ involved in intersystem crossing, this trend indicates that in the case of NMA this gap decreases with increasing pressure. With respect to the intersystem crossing rates this narrowing of the energetic distance of $S_1$ and $T_2$ is associated with a substantial decrease (see Table 2), whereas on the basis of the energy gap law alone, one would expect an increase in transition rates. These observations are contradictory to the assumption that the pressure dependence of the intersystem crossing rate is mainly due to the relative energetic displacement of the electronic states involved.

In order to investigate the internal consistency of the derived values for $\Delta H^*$ and $\Delta V^*$ one can make use of the following expression describing the pressure dependence of the activation free enthalpy $\Delta G^*$:

$$\left(\frac{d\Delta G^*}{dP}\right)_T = \left(\frac{d\Delta H^*}{dP}\right)_T - T\left(\frac{d\Delta S^*}{dT}\right)_P.$$  \hspace{1cm} (6)

The Maxwell equation expressed in terms of activation parameters is

$$\left(\frac{d\Delta S^*}{dP}\right)_T = -\left(\frac{d\Delta V^*}{dT}\right)_P.$$  

Insertion in Eq. (6) results in

$$\left(\Delta V^*\right)_T = \left(\frac{d\Delta H^*}{dP}\right)_T - T\left(\frac{d\Delta V^*}{dT}\right)_P.$$  

Assuming as a first approximation that $\Delta H^*$ and $\Delta V^*$ are linear functions of pressure and temperature, respectively, linear least-squares fits yield a pressure coefficient of the activation enthalpy, $(d\Delta H^*/dP)_T = -1.7 \text{ J mol}^{-1} \text{ bar}^{-1}$, and a temperature coefficient of the activation volume at 1 bar, $(d\Delta V^*/dT)_P = 0.11 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$. With these coefficients values for the activation volumes at normal pressure can be calculated for the investigated temperatures, according to (7). The results are presented in Table 4. Comparison of the calculated and directly determined experimental values shows a quite satisfactory agreement.

In view of the uncertainties and scatter of the experimental values for $\Delta H^*$ and $\Delta V^*$, this result is rather of a qualitative nature. It, nevertheless, indicates that the transition state model may lead to a consistent description of the influences of pressure and temperature on intersystem crossing in NMA. However, to render this suggestion more reliable, more experimental data are required.

The experimentally determined values for the activation volumes may be separated into two terms:

$$\Delta V^* = \Delta V^*_1 + \Delta V^*_s.$$

$\Delta V^*_1$ is the intrinsic, i.e., inner structural component according to variations of bond lengths within the molecule associated with the transition process from the initial vibrational ground state of $S_1$ to the transition state. $\Delta V^*_s$ represents the volume change caused by reordering of the solvent sheaths during this process. It is interesting to note that the magnitude of the volumes of activation obtained in this investigation indicates that $\Delta V^*_s$ may dominate. If this is true, this apparently positive term further indicates that the transition state is less solvated than the $S_1$ state and $\Delta V^*_s$ may be expected to vary with solvent polarity. Actually, Siegmund and Bendig [14] attributed a negative photochromic dependence on solvent polarity to $T_2$ (in contrast $n \pi^*$-character) to $S_1$ ($\pi \pi^*$-character) which shows positive photochromism. As a consequence $T_2$ should be less polar than $S_1$. Referring to solvation Siegmund and Bendig’s suggestion may also indicate that $T_2$ is less solvated than $S_1$. This would correspond to the assumed solvation characteristics of the $S_1$–$T_2$ transition state, which according to this argument should be more similar to $T_2$ than to $S_1$. With respect to the reaction coordinate, the transition state should lie nearer to $T_2$. To obtain further information on this problem we are currently investigating the influence of various solvents on the activation volume of $S_1$–$T_2$ intersystem crossing in NMA.

Financial support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is greatly appreciated.
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