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

H.-D. Brauer, R. Schmidt, and B. Hammerich
Institute for Physical and Theoretical Chemistry, University of Frankfurt, Frankfurt (Main) 1

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The influence of temperatur and pressure on the fluorescence quantum yield of N-methylacridone (9,10-dihyдro-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, $\Delta V^{\neq}$, for the thermally activated S_1–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 $\Delta H^{\neq}$, the activation enthalpy of this process, determined at various pressures, indicates a decrease in $\Delta H^{\neq}$ at elevated pressures. Since $\Delta H^{\neq}$ can be associated with the S_1–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_f, 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_f, 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–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–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, $\Delta V^{\neq}$, to be assigned to the intersystem crossing process.

In this interpretation $\Delta V^{\neq}$ represents the difference of the partial molar volumes of the transi-

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Reprint requests to H.-D. Brauer, Institut für Physikalische und Theoretische Chemie der Universität Frankfurt, Robert-Mayer-Straße 11, D-6000 Frankfurt/M.

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tion-state in going from S_1 to T_2 and the molecule in the S_1 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 S_1-T_2 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 reresults 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 S_1 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, Q_f, of NMA in toluene for the investigated temperatures and pressures are listed in Table 1.

Since S_1-T_2 intersystem crossing is the only effective process contributing to the deactivation of S_1 apart from fluorescence emission, the fluorescence quantum yield of NMA is given by:

$$Q_f = k_f/(k_f + k_{isc})\,. \tag{1}$$

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

T (K)	Q_f* pressure (bar)						
	1	200	500	1000	1500	2000	2500
283	0.119**	0.139	0.163	0.215	0.267	0.314	0.345
293	0.098**	0.113	0.143	0.195	0.229	0.278	0.319
303	0.082**	0.095	0.120	0.159	0.203	0.242	0.286
313	0.069**	0.077	0.102	0.138	0.171	—	—

* Errors amount to ±6%.
** Values extrapolated from data reported in (1).

k_f is generally considered to be independent of pressure and temperature [5, 2]. Therefore, changes in Q_f are caused by variations in k_{isc}, the rate constant of the S_1-T_2 intersystem crossing:

$$\frac{((1/Q_f)-1)_{P,T}}{((1/Q_f)-1)_{1,298}} = \frac{(k_{isc})_{P,T}}{(k_{isc})_{1,298}} . \tag{2}$$

Using relation (2) and the values $(k_{isc})_{1,298} = 8.96 \times 10^8\ s^{-1}$ and $(Q_f)_{1,298} = 0.090$ 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):

$$k_{isc} = k^0_{isc} \exp(-E_a/RT) , \tag{3}$$

where k^0_{isc} 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}:

$$k_{isc} = \frac{k_B T}{h} \exp((\Delta S^{\neq}/R) - (\Delta H^{\neq}/RT)) , \tag{4}$$

where k_B = Boltzmann's constant, and h = Planck's constant. $\Delta S^{\neq}$ and $\Delta H^{\neq}$ 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 $\Delta H^{\neq}$ is essentially consistent with that of E_a in (3).

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

T (K)	$10^{-8} \times k_{isc}$ (s^{-1}) * pressure (bar) 1	200	500	1000	1500	2000	2500
283	6.56	5.51	4.55	3.23	2.43	1.94	1.68
293	8.15	6.96	5.31	3.66	2.98	2.30	1.89
303	9.92	8.44	6.50	4.69	3.48	2.78	2.12
313	11.95	10.62	7.80	5.53	4.30	—	—

* Errors amount to about ±6%.

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

Pressure (bar)	$\Delta H^{\neq}$ * (kJ mol^{-1})
1	12.2 **
200	13.4
500	10.9
1000	11.2
1500	11.3
2000	10.4
2500	7.4

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

$\Delta H^{\neq}$ 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 $\Delta H^{\neq}$ derived from least squares fits are given in Table 3.

To interprete 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):

$$\left(\frac{d \ln k_{isc}}{dP}\right)_T = -\frac{\Delta V^{\neq}}{RT} . \tag{5}$$

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 $\Delta V^{\neq}$ 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 4. Experimental and calculated activation volumes for the S_1-T_2 intersystem crossing of NMA in toluene.

T (K)	$\Delta V^{\neq}$ * (cm^3 mol^{-1}) experimental	calculated **
283	16.3	15.9
293	19.5	16.8
303	18.7	17.9
313	20.3	19.1

* 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 $\Delta H^{\neq}$ decreases rather than remains constant, but obviously does not increase with increasing pressure.

Since $\Delta H^{\neq}$ 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 $\Delta H^{\neq}$ and $\Delta V^{\neq}$ one can make use of the following expression describing the pressure dependence of the activation free enthalpy $\Delta G^{\neq}$:

$$\left(\frac{\mathrm{d}\Delta G^{\neq}}{\mathrm{d}P}\right)_T = (\Delta V^{\neq})_T = \left(\frac{\mathrm{d}\Delta H^{\neq}}{\mathrm{d}P}\right)_T - T\left(\frac{\mathrm{d}\Delta S^{\neq}}{\mathrm{d}P}\right)_T . \tag{6}$$

The Maxwell equation expressed in terms of activation parameters is

$$\left(\frac{\mathrm{d}\Delta S^{\neq}}{\mathrm{d}P}\right)_T = -\left(\frac{\mathrm{d}\Delta V^{\neq}}{\mathrm{d}T}\right)_P .$$

Insertion in Eq. (6) results in

$$(\Delta V^{\neq})_T = \left(\frac{\mathrm{d}\Delta H^{\neq}}{\mathrm{d}P}\right)_T + T\left(\frac{\mathrm{d}\Delta V^{\neq}}{\mathrm{d}T}\right)_P .$$

Assuming as a first approximation that $\Delta H^{\neq}$ and $\Delta V^{\neq}$ are linear functions of pressure and temperature, respectively, linear least-squares fits yield a pressure coefficient of the activation enthalpy, $(\mathrm{d}\Delta H^{\neq}/\mathrm{d}P)_T = -1.7$ J mol^{-1} bar^{-1}, and a temperature coefficient of the activation volume at 1 bar, $(\mathrm{d}\Delta V^{\neq}/\mathrm{d}T)_P = 0.11$ cm^3 mol^{-1} 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 $\Delta H^{\neq}$ and $\Delta V^{\neq}$, 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:

$$\Delta V^{\neq} = \Delta V_{\mathrm{i}}^{\neq} + \Delta V_{\mathrm{s}}^{\neq} .$$

$\Delta V_{\mathrm{i}}^{\neq}$ 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. $\Delta V_{\mathrm{s}}^{\neq}$ represents the volume change caused by recordering 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 $\Delta V_{\mathrm{s}}^{\neq}$ 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 $\Delta V_{\mathrm{s}}^{\neq}$ 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.

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[1] M. Siegmund and J. Bendig, Ber. Bunsenges. Phys. Chem. **82**, 1061 (1978).

[2] E. C. Lim, J. D. Laposa, and J. M. H. Yu, J. Molec. Spectr. **19**, 412 (1966).

[3] R. G. Bennett and P. J. McCartin, J. Chem. Phys. **44**, 1969 (1966).

[4] S. Schoof, H. Güsten, and C. von Sonntag, Ber. Bunsenges. Phys. Chem. **81**, 305 (1977).

[5] F. Tanaka and J. Osugi, Rev. Phys. Chem. Japan **42**, 85 (1972).

[6] F. Tanaka and J. Osugi, Chem. Lett. **1973**, 1279.

[7] F. Tanaka, Rev. Phys. Chem. Japan **44**, 65 (1974).

[8] W. Siebrand, J. Chem. Phys. **47**, 2411 (1967).

[9] B. Hammerich, R. Schmidt, and H.-D. Brauer, Ber. Bunsenges. Phys. Chem. **83**, 198 (1979).

[10] B. A. Baldwin and H. W. Offen, J. Chem. Phys. **48**, 5358 (1968).

[11] R. Schmidt, H. Kelm, and H.-D. Brauer, Ber. Bunsenges. Phys. Chem. **81**, 402 (1977).

[12] W. J. le Noble and O. R. Schlott, Rev. Sci. Instrum. **47**, 770 (1976).

[13] K. Vedam and P. Limsuwan, J. Chem. Phys. **69**, 4762 (1978).

[14] M. Siegmund and J. Bendig, Z. Naturforsch. **35a**, 1076 (1980).