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Temperature Dependence of the Fluorescence Intensity of 1-Benzyloxy-2-pyridone and Related Compounds

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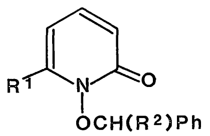
Synopsis. A quantitative analysis of the temperature dependence of fluorescence intensity of the title compounds in saturated hydrocarbon solvents has revealed that the relevant thermally-activated radiationless process from singlet manifold involves a rotation about the N–O bond in these compounds.

Variable-temperature dynamic NMR spectroscopy is undoubtedly one of the most powerful tools for the analysis of conformational interconversion in hydroxylamines, although molecular orbital calculations have also contributed to shedding considerable light on conformational problems of these molecules.[1] It has been shown by the dynamic NMR technique that the rate-determining rotation about the N–O bond in cyclic and acyclic hydroxamic acid derivatives possesses an appreciable energy barrier.[2,3]

In the course of our systematic study on the photolysis of 1-benzyloxy-2-pyridone (**1**), 1-(α-methylbenzyloxy)-2-pyridone (**2**), and 1-benzyloxy-6-methyl-2-pyridone (**3**), we have found that the fluorescence of these cyclic hydroxamic acid derivatives exhibits a pronounced temperature dependence in methylcyclohexane.[4] This dependence has been suggested to be due to some thermally-activated nonradiative decay process competing with some radiative (fluorescence) decay one. In this paper we present a quantitave analysis of temperature dependence of the fluorescence intensity, which allows an estimation of energy barriers to the rotation about the N–O bond in **1**—**3**.



1: $R^1 = R^2 = H$
2: $R^1 = H$, $R^2 = Me$
3: $R^1 = Me$, $R^2 = H$

Results and Discussion

Temperature effects on the fluorescence of **1**—**3** ([**1**—**3**]=10^{-4} mol dm^{-3}, excitation wavelength=313 nm) were examined in hexane (HX), methylcyclohexane (MCH), and decahydronaphthalene (DHN) over the range of 283 to 318 K. In this temperature range the decomposition of all the compounds was found to be negligible during the fluorescence measurements in these solvents. The fluorescence maxima and band shapes, as well as the UV absorption spectra, were not subject to temperature effects. Since the overlap of the fluorescence and absorption spectra is fairly small under our experimental conditions, the fluorescence intensity ratio at temperatures T_1 and T K, $I_f(T_1)/I_f(T)$, can be taken as the fluorescence quantum yield ratio, $\Phi_f(T_1)/\Phi_f(T)$. Then we obtain

$$I_f(T_1)/I_f(T) = [k_f + k_d(T)]/[k_f + k_d(T_1)], \tag{1}$$

where $k_d(T)$ and $k_d(T_1)$ are the radiationless rate constants at temperatures T and T_1 K, respectively, and k_f is the radiative rate constant which is generally temperature independent.[5] The fluorescence quantum yields of **1**—**3** were determined to be 2×10^{-3}, 2×10^{-3}, and 3×10^{-3} in methylcyclohexane at 298 K, respectively. These values indicate the validity of the assumption that $k_d(T)$ and $k_d(T_1)$ are much larger than k_f, i.e., $k_d(T), k_d(T_1) \gg k_f$. Thus Eq. 1 is simplified to

$$I_f(T_1)/I_f(T) = k_d(T)/k_d(T_1). \tag{2}$$

By using the Arrhenius relationship $k_d(T)=A\exp(-E_a/RT)$, we can rewrite Eq. 2 to

$$\log[I_f(T_1)/I_f(T)] = (E_a/2.303R)(1/T_1 - 1/T). \tag{3}$$

We can use Eq. 3 to estimate activation energies (E_a) for thermally-activated radiationless processes if, in addition to the viscosity and refractive index of the solvents, the quantum yield (Φ_{S_1}) for the formation of the fluorescent state of **1**—**3** remains constant over the temperature range examined. Figure 1 illustrates a typical linear plot of $\log[I_f(T_1)/I_f(T)]$ against $(1/T_1 - 1/T)$, the slope of which gives the E_a value. The existence of the linear relationship between these two

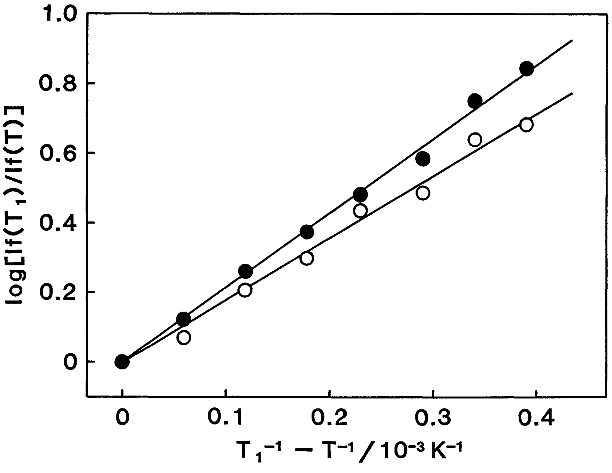


Fig. 1. Plot of $\log[I_f(T_1)/I_f(T)]$ vs. $T_1^{-1} - T^{-1}$ for the temperature dependence of the fluorescence intensity of **1** (10^{-4} mol dm^{-3}) in hexane (○) and decahydronaphthalene (●). Excitation wavelength= 313 nm. T_1=283 K.

quantities demonstrates that the assumptions made for the derivation of Eq. 3 are reasonable and also that the temperature-independent radiationless rate constant becomes very small relative to $A\exp(-E_a/RT)$, i.e., the overall radiationless rate constant $k_d(T)\approx A\exp(-E_a/RT)$ in the temperature range investigated.

The viscosity of HX, MCH, and DHN is decreased by a factor of 1.4, 1.4, and 1.8, respectively, with increasing temperature from 283 (T_1) to 318 K, although variation in the refractive index of these hydrocarbon solvents is considered negligible in this temperature range.[6] On the other hand, a linear relationship with the same slope of 0.44±0.02 for all the compounds holds between the ratio of the fluorescence intensity of a given compound in HX, MCH, and DHN to that in HX and the viscosity ratio of HX, MCH, and DHN to HX at 283, 298, and 318 K, as typically shown in Fig. 2. This finding makes it possible to correct the apparent E_a values for the temperature dependence of solvent viscosity. It has previously been found that the quantum yield (Φ_D) for the disappearance of **1**—**3** in MCH, the photolysis of which takes place from higher vibrational states of the first excited singlet state of these compounds in competition with vibrational relaxation to the fluorescent state, increases almost linearly in proportion to reaction temperature.[4] Based on this observation we can determine the extent to which the Φ_D value increases with increasing temperature from 283 to 318 K: 17% increase for **1**, 39% increase for **2**, and 29% increase for **3**. An increase in Φ_D may cause a decrease in Φ_{S_1} to the same extent, which should be reflected in a reduction in the fluorescence intensity observed at a given temperature. Thus we are allowed to have the E_a values corrected for the temperature dependence of both solvent viscosity and Φ_{S_1} with a high degree of confidence as shown in Table 1.[7]

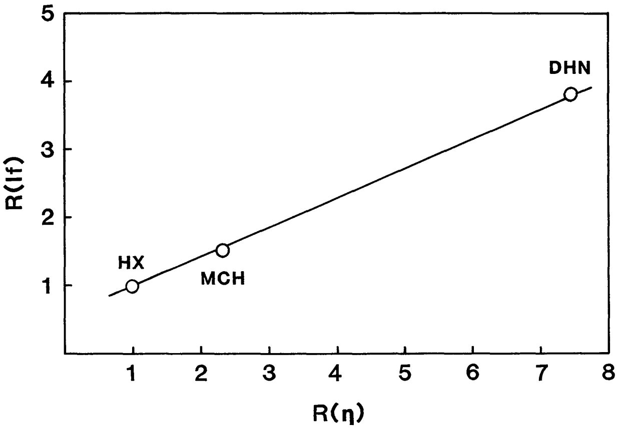


Fig. 2. Fluorescence intensity ratio ($R(I_f)$) of **1** versus viscosity ratio ($R(\eta)$) of solvents used at 298 K. Here, $R(I_f)=I_f$ of **1** in a given solvent relative to I_f of **1** in hexane and $R(\eta)=\eta$ of a given solvent relative to η of hexane. HX, MCH, and DHN represent hexane, methylcyclohexane, and decahydronaphthalene, respectively.

An examination of Table 1 reveals that the E_a values of **1**—**3** increase with increasing solvent viscosity. This result suggests some involvement of rotation about the N–O bond in thermally-activated nonradiative decay processes of these compounds. If so, then the introduction of a methyl group into **1** is expected to give an E_a value larger than that of **1** owing to the steric hindrance of this group. However, the result obtained with **2** is not consistent with our expectation. Although we cannot provide a good explanation for the unexpected E_a value of **2**, it may imply that in our previous study[4] we have estimated a somewhat larger temperature dependence of Φ_D for **2**. Raban and Kost[3] have obtained barriers ($\Delta G^{\ddagger}$) of about 9 and 10 kcal mol⁻¹ to the rotation about the N–O bond in 1-isopropoxy-2-pyridone (**4**) and 1-isopropoxy-6-chloro-2-pyridone, respectively, the structure of which is similar to that of **1**—**3**, by means of the dynamic NMR method. Their results indicate that the introduction of a bulky group at the 6-position of the pyridone skeleton in **4** increases the barrier, in consistency with our observation that the E_a value of **3** has a tendency to become larger than that of **1** in any solvents used. Additionally on the basis of the calculated values of the viscosity of solvent (toluene-d_8) they employed at 298 and 187 K,[6] we may estimate the barrier (E_a) of **4** as about 8 kcal mol⁻¹ near ambient temperature[8] the value of which is comparable to the E_a value of 7.5 kcal mol⁻¹ obtained for **4** ($\Phi_f=10^{-4}$) by means of our fluorescence method. This finding coupled with the results of solvent viscosity and steric effects on the barrier permits us to conclude that the rotation about the N–O bond in **1**—**3** is the

Table 1. Activation Energies (E_a) for Thermally-Activated Radiationless Processes of **1**—**4**

Solvent (η/cP)[a,f]	E_a[b]/kcal mol^{-1}[c]			
	1	**2**	**3**	**4**
Hexane (0.361)	6.6±0.5 (8.2±0.6)[d]	5.2±0.5 (8.5±0.9)[d]	6.7±0.4 (9.0±0.5)[d]	
Methylcyclohexane (0.841)	6.9±0.2 (8.6±0.3)[d]	5.9±0.3 (9.0±0.5)[d]	7.4±0.6 (9.9±0.8)[d]	7.5±0.7[e] (9.2±0.9)[d]
Decahydronaphthalene (3.039)	7.8±0.6 (9.9±0.7)[d]	7.1±0.3 (10.7±0.4)[d]	8.8±0.6 (11.9±0.8)[d]	

a) Calculated viscosity at 283 K (see Ref. 6). b) Average and standard deviation of more than five determinations. c) 1 kcal mol⁻¹=4.184 kJ mol⁻¹. d) Uncorrected value. e) Calculated by using the f value for **1**. f) 1 cP=10^{-3} Pa s.

origin of thermally-activated nonradiative decay from the first excited singlet state of these compounds and hence plays a key role in this nonradiative decay process near room temperature.

Experimental

Materials and Solvents. 1-Benzyloxy-2-pyridone (**1**), 1-(α-methylbenzyloxy)-2-pyridone (**2**), and 1-benzyloxy-6-methyl-2-pyridone (**3**) were the same as used in our previous study.[4] 1-Isopropoxy-2-pyridone (**4**) was prepared and purified according to the method of Raban and Kost,[3] bp 110 °C (733 Pa). The structure of this compound was also established by IR and ^{1}H NMR spectroscopy. 2-Naphthol was recrystallized twice from aqueous ethanol. Hexane was of spectroscopic grade and used as received. Methylcyclohexane and decahydronaphthalene (mixture of *cis* and *trans*) were purified by column chromatography over silica gel (28—200 mesh, Wakogel Q-12) followed by fractional distillation over sodium.

Measurements. UV absorption and fluorescence spectra were recorded on a Shimadzu Model UV-210A spectrophotometer and a Shimadzu Model RF-5000 spectrophotofluorimeter, respectively. The temperature of a solution for measuring UV and fluorescence spectra was controlled by circulating water of a given temperature through a jacketed cell holder. 2-Naphthol in 0.05 mol dm^{-3} borate buffer (pH=10, Φ_f=0.21 at 313 nm) was used as a reference in the determination of fluorescence quantum yields which were corrected for the difference in refractive index between the reference and sample solutions at 298 K.[9] The absorbances of 2-naphthol and **1**—**4** at 313 nm were both adjusted to 0.1 for the Φ_f determination. A large difference in emission-band area between the reference and the sample made it difficult to obtain accurate fluorescence quantum yields of **1**—**4**, but even the order estimation of these yields is sufficient to show that k_f is negligibly small compared to k_d under our experimental conditions.

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7) As a typical example we present below how to correct the viscosity dependence of the fluorescence intensity and the temperature dependence of Φ_{S_1} of **1** in MCH. Based on the calculated value of viscosity we obtain 28% decrease in viscosity with increasing temperature from 283 to 318 K. This decrease corresponds to 28×0.44=12% decrease in the fluorescence intensity, so that we get the corrected log $[I_f(T_1)/I_f(T)]$ (=0.64) at 318 K by adding log 0.88=−0.06 to the observed log $[I_f(T_1)/I_f(T)]$ (=0.70) at this temperature. Then a correction factor (f') is determined to be f'=0.64/0.70=0.91. Next we correct the temperature dependence of Φ_{S_1}. With increasing temperature from 283 to 318 K Φ_D increases by a factor of 1.17. Because this incease corresponds to 17% decrease in Φ_{S_1}, that is, the fluorescence intensity, we can have the newly corrected log $[I_f(T_1)/I_f(T)]$ (=0.56) at 318 K in a similar manner as above. Then a new correction factor (f) is calculated to be f=(0.56/0.64)f'=0.80. The same procedure at different temperatures gave the same f values and thus we may correct the apparent E_a value by multiplying it by this f value. For this correction procedure with the other solvents we assumed that Φ_{S_1} has the same magnitude of temperature dependence in any solvents employed.

8) For this estimation we assumed activation entropy $\Delta S^{\ddagger}$=0.

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