

Preliminary Note

Simple relation between Arrhenius activation parameters for non-radiative processes from proton-transferred forms of intramolecularly hydrogen-bonded molecules

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1. Introduction

Proton transfer in the excited states of intramolecularly hydrogen-bonded molecules is a topic of current interest [1 - 7]. It is a chemically very simple process, and is of great interest in view of the possibilities of making a proton transfer laser [8] and an information storage device at a molecular level [9]. Nagaoka and coworkers have investigated the dynamic processes of the excited states of *o*-hydroxybenzaldehyde and its derivatives in detail [1 - 4].

There remains, however, an important problem concerning the dynamic processes in the excited states of intramolecularly hydrogen-bonded molecules. These molecules generally exhibit fluorescence emissions with unusually large Stokes shifts. The fluorescence-decay rate constants of these molecules in solvents were found to be temperature dependent [1, 2, 10 - 12]. The exact mechanism for the temperature-dependent decay process, however, has not been fully established. In view of the wide occurrence of such a process in the excited states of intramolecularly hydrogen-bonded molecules [1, 2, 10 - 12], it is necessary to clarify the mechanism of this process.

Saltiel and D'Agostino have analysed in detail the non-radiative processes of several systems by measuring their fluorescence intensities at different viscosities and various temperatures [13]. They found a simple relation between the Arrhenius activation parameters for the processes. Using this relation, Nakashima *et al.* analysed the fluorescence properties of ergosterol [14]. The existence of a simple relation suggests that the same mechanism operates for the related series of compounds.

In the present work, it is shown that the same relation as that found by Saltiel and D'Agostino can be discerned between the Arrhenius parameters for the non-radiative processes from the proton-transferred forms of several intramolecularly hydrogen-bonded molecules. It is considered that a con-

stant mechanism operates throughout these processes as in the case of those studied by Saltiel and D'Agostino.

2. Relation between the Arrhenius parameters

For each of the molecules studied by Saltiel and D'Agostino, as well as for intramolecularly hydrogen-bonded molecules, the fluorescence-decay rate constant $k_f(T)$ is given by the sum of the temperature-dependent non-radiative-decay rate constant $k_f^{nr}(T)$ and the temperature-independent decay rate constant k_f^0

$$k_f(T) = k_f^0 + k_f^{nr}(T) \quad (1)$$

$k_f^{nr}(T)$ is given by

$$k_f^{nr}(T) = k^0 \exp(-E_a/RT) \quad (2)$$

where E_a denotes an activation energy. $k_f^{nr}(T)$ can be expressed as the product of an inherent thermal rate constant k_t and a viscosity-dependent rate constant k_v

$$k_f^{nr}(T) = k_t k_v \quad (3)$$

k_t and k_v are given by

$$k_t = k_t^0 \exp(-E_t/RT) \quad (4)$$

$$k_v = k_v^0 \exp(-E_v/RT) \quad (5)$$

where E_t and E_v denote inherent thermal and viscosity-dependent activation energies respectively.

Saltiel and D'Agostino noted that there is a good linear relation between E_v and $\log k^0$ ($\log(k_t^0 k_v^0)$). The relation may be expressed mathematically by

$$\log k^0 = \log(k_t^0 k_v^0) = \log k_t^0 + CE_v \quad (6)$$

where C is a constant determined to be 0.71. From the good linear relation, it was considered that the $\log k_t^0$ values for the processes studied by Saltiel and D'Agostino are close to one another. Equation (6) then reduces to

$$\log k_v^0 = CE_v \quad (7)$$

This relation between E_v and $\log k_v^0$ illustrates the existence of an isokinetic relationship for viscosity-dependent parameters. Equation (7) is a specific example of the more general isokinetic relationship.

3. Application to intramolecularly hydrogen-bonded molecules

A relation similar to that found by Saltiel and D'Agostino can be discerned between the Arrhenius parameters for non-radiative processes from proton-transferred forms of several intramolecularly hydrogen-bonded molecules [1, 2, 10, 11]. In each of these molecules, the individual values of E_v and E_t have not been estimated, but the sum of the two values ($E_v + E_t$)

has been obtained. Thus, $\log k^0$ vs. $E_v + E_t$ for these molecules is plotted in Fig. 1. This plot is found to give a good linear fit with a slope of $0.75 \text{ mol kcal}^{-1}$ and an intercept of 9.5.

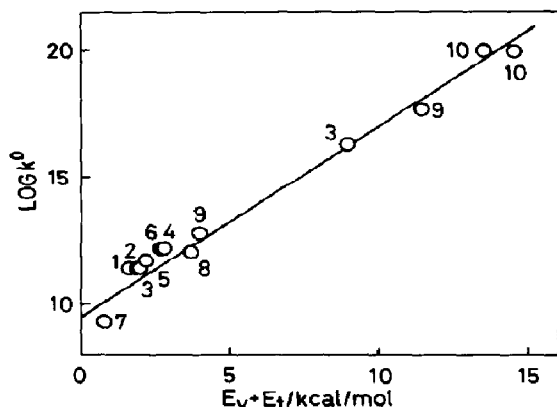


Fig. 1. Plot of $\log k^0$ vs. $E_v + E_t$ for the following solutions: *o*-hydroxybenzaldehyde in 3-methylpentane (1), in a 1:1 mixture of decalin and methylcyclohexane (2) and in ethanol (3); *o*-hydroxyacetophenone in 3-methylpentane (4) and in ethanol (5); *o*-hydroxypropiophenone in 3-methylpentane (6); 7-hydroxy-1-indanone in 3-methylpentane (7); methyl salicylate in methylcyclohexane (8); 2-(2-hydroxyphenyl)benzothiazole in isopentane (9) and in triacetin (10). *o*-Hydroxybenzaldehyde in ethanol and 2-(2-hydroxyphenyl)benzothiazole in isopentane and in triacetin show two different fluorescence emissions with different decay times.

The straight-line relationship may be expressed mathematically by

$$\log k^0 = A + B(E_v + E_t) \quad (8)$$

where A and B are constants. It is probably more than coincidental that for several intramolecularly hydrogen-bonded molecules the Arrhenius activation parameters cluster in the vicinity of the straight line. Furthermore, the value of B determined from Fig. 1 (0.75) agrees well with that of C estimated by Saltiel and D'Agostino (0.71). From these facts, it is considered that eqn. (6) is also true for the non-radiative processes from the proton-transferred forms of the intramolecularly hydrogen-bonded molecules. A and B are then given by

$$A = \log k_t^0 - CE_t \quad (9)$$

$$B = C \quad (10)$$

From the good linear relation for the plot of Fig. 1, it is considered that the E_t values as well as the $\log k_t^0$ values for the processes in question are close to one another. It is speculated that the inherent thermal processes from the proton-transferred forms of the intramolecularly hydrogen-bonded molecules are quite similar. The inherent thermal process may involve out-of-plane bending and/or torsional motion involving the C=O or C=N group [2, 10]. Equation (7) is likely to also be true for the non-radiative processes

from the proton-transferred forms of the intramolecularly hydrogen-bonded molecules, and an isokinetic relationship for viscosity-dependent parameters exists for these processes. The viscosity appears to affect the kinetics of these processes in the same way.

From the foregoing discussion, one may suppose that a constant mechanism exists in the non-radiative processes from the proton-transferred forms of intramolecularly hydrogen-bonded molecules in solvents.

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