

## THE TEMPERATURE DEPENDENCE OF COMPETING PHOTO-ISOMERIZATION AND FLUORESCENCE DECAY\*

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### Summary

The quantum yield for the photoisomerization of bicyclo [2.2.1]-heptene-2,3-dione (I) to bicyclo [3.2.0]heptene-6,7-dione (II) was found to be temperature dependent. This reaction competes (with a rate of  $1.3 \times 10^{10} \exp(-775/T) \text{ s}^{-1}$ ) with the fluorescence decay which is, in addition, vibronically coupled to the ground state resulting in a non-radiative decay rate of  $2.7 \times 10^{10} \exp(-550/T) \text{ s}^{-1}$ .

### 1. Introduction

The photoisomerization of bicyclo [2.2.1]heptene-2,3-dione (I) to bicyclo [3.2.0]heptene-6,7-dione (II) (Fig. 1) has recently been reported [1] and the solvent independent quantum yield for this reaction at 298 K was found to be  $0.021 \pm 0.002$ . A number of observations suggest that reaction (1) proceeds from the  $(n, \pi^*)^1$  excited state of I: (1) both quantum yield and product composition are not affected by the presence of oxygen; (2) the reaction was not quenched by anthracene ( $E_T \approx 42 \text{ kcal mol}^{-1}$ ) but could be sensitized by singlet sensitizers; (3) triplet sensitization produced cyclopentadiene with quantum yields close to unity.

We now report the temperature dependence of both the photoisomerization and fluorescence quantum yields. It was anticipated that the fluorescence quantum yield would exhibit a temperature dependence due to quenching of the  $(n, \pi^*)^1$  state of I by the reaction  $I \rightarrow II$ . Moreover, for a forbidden transition, such as  $n \rightarrow \pi^*$ , it might be expected that temperature dependent vibronic coupling of the  $(n, \pi^*)^1$  manifold would affect the observed fluorescence yield [2, 3].

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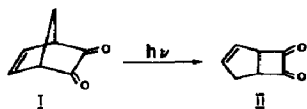


Fig. 1. The photoisomerization of bicyclo [2.2.1]heptene-2,3-dione (I) to bicyclo [3.2.0]heptene-6,7-dione (II).

## 2. Experimental

Fluorescence spectra of I were recorded using a dye laser based fluorimeter [4]. Relative fluorescence quantum yields were obtained from measurement of the integrated fluorescence spectrum. (Spectral range 470 - 670 nm,  $\lambda_{\text{max}} = 552$  nm). Lifetime measurements were carried out using a PAR 163 boxcar.

The absolute values of the quantum yield for the reaction I  $\rightarrow$  II at temperatures lower than 298 K were determined by monitoring the absorption decrease at  $\lambda_{\text{max}}$  (462 nm) over the initial 25% of reaction relative to a sample at 298 K using a specially constructed Dewar-type vessel [5] which fitted into the sample compartment of a Cary 15 spectrophotometer and allowed irradiation at 436 nm and measurement of the absorption spectra.

## 3. Results and discussion

Both quantum yields for photoisomerization ( $\phi_r(T)$ ) and relative quantum yields of fluorescence ( $\phi_f(T)$ ) were measured over the range 77 - 310 K. Identical values of  $\phi_f(T)$  were obtained in 2-methyltetrahydrofuran solutions and in polymethyl methacrylate matrices. The results are presented in Table 1 and show that  $\phi_r$  decreases with decreasing temperature while  $\phi_f$  increases. The simplest mechanism that can account for these results is a competition between a thermally activated reaction of the excited state and a fluorescence decay process. However, we note that  $\phi_r + \phi_f$  is a decreasing function of temperature at low temperatures which requires that a temperature dependent non-radiative decay route for the excited state of I must also be considered. It is well known that radiative and non-radiative vibronic coupling of excited vibrational states to the ground state results in temperature dependent values of  $\phi_f$  [2, 3]. This phenomenon is more pronounced for forbidden transitions, such as the  $n \rightarrow \pi^*$  transition involved in the present study. The appropriate kinetic scheme to account for the observations is

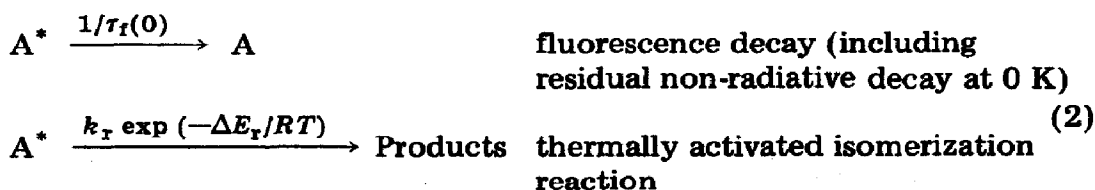
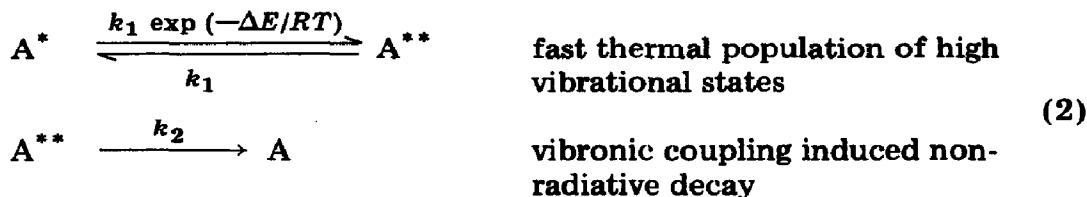


TABLE 1

Temperature dependent absolute reaction quantum yield  $\phi_r$  for the photochemical rearrangement of I together with the relative experimental fluorescence quantum yield  $\phi_f(T)$  and the normalized fluorescence quantum yield  $\phi_f/\phi_0$

T(K)	$\phi_r^a$	$\phi_f(T)$	$\phi_f/\phi_0$
310	0.22	0.040	0.060
288	0.21	0.062	0.094
265	0.19 <sub>5</sub>	0.070	0.105
230	0.15 <sub>4</sub>	0.112	0.168
198	0.10 <sub>7</sub>	0.126	0.189
153	0.06 <sub>1</sub>	0.161	0.242
130	—	0.485	0.727
100	—	0.575	0.863
77	0.01 <sub>6</sub>	0.641	0.962

<sup>a</sup>Values of  $\phi_r$  between liquid nitrogen temperature (77 K) and 153 K could not be determined with sufficient precision because of temperature variation in the experimental set-up over the long irradiation times required for measurement of low quantum yields.



where  $A^*$  denotes an excited molecule having a fluorescent lifetime  $\tau_f(0)$  at 0 K in its ground vibrational level,  $\Delta E_r$  is the activation energy required for the rearrangement reaction,  $\Delta E$  is the average vibrational energy of the vibrational mode contributing to the vibronic coupling and  $A^{**}$  is the vibronically excited molecule. Applying the steady state condition for the concentration of the species  $A^{**}$  we obtain

$$\phi_r = \tau_f(0)k_r\beta^{-1} \exp(-\Delta E_r/RT) \quad (3)$$

$$\phi_f/\phi_0 = \beta^{-1} \quad (4)$$

where

$$\beta = 1 + \tau_f(0)k_2 \exp(-\Delta E/RT) + \tau_f(0)k_r \exp(-\Delta E_r/RT) \quad (5)$$

and  $\phi_0$  is the fluorescence quantum yield at 0 K. From eqns. (3) - (5) we can obtain two Arrhenius-type plots as follows:

$$\ln(\phi_r\phi_0/\phi_f) = \ln\{\tau_f(0)k_r\} - \Delta E_r/RT \quad (6)$$

$$\ln\{\phi_0(1 - \phi_r)/\phi_f - 1\} = \ln\{\tau_f(0)k_2\} - \Delta E/RT \quad (7)$$

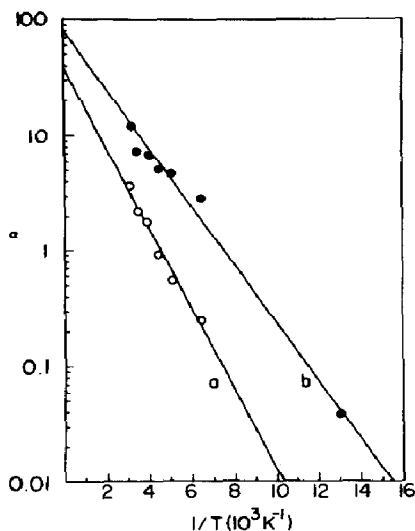


Fig. 2. Arrhenius plots of  $\ln \alpha$  vs.  $1/T$ : (a)  $\alpha = \phi_r \phi_0 / \phi_f$ ; (b)  $\alpha = \phi_0(1 - \phi_r) / \phi_f - 1$ .

The results of applying eqns. (6) and (7) to the experimental data (Table 1) are shown in Fig. 2. The best fit parameters obtained are

$$\Delta E_r = 1.55 \pm 0.25 \text{ kcal mol}^{-1}$$

$$\Delta E = 1.10 \pm 0.15 \text{ kcal mol}^{-1}$$

$$\tau_f(0)k_r = 38$$

$$\tau_f(0)k_2 = 80$$

The numerical values of the term  $\phi_0/\phi_f$  were evaluated from the experimentally determined values of  $\phi_f(T)$  and the value of  $\phi_0$  obtained by extrapolating to  $0 \text{ K}^\dagger$ . No arbitrary assumption of the absolute value  $\phi_f(0)$  of the fluorescence quantum yield at  $0 \text{ K}$  was necessary for the subsequent calculations. Within the overall time resolution of our experimental set-up  $\tau_f$  at  $77 \text{ K}$  was determined to be  $2 \text{ ns}$ . This yields  $\phi_f(77) = 0.89$  using the rate data obtained. The discrepancy between this value and the data of Table 1 is due to the non-radiative decay rate which determines  $\tau_f$ . Estimating  $\tau_f(0)$  to be  $3 \text{ ns}$ , we obtain  $k_r = 1.3 \times 10^{10} \text{ s}^{-1}$  and  $k_2 = 2.7 \times 10^{10} \text{ s}^{-1}$ ; these values are reasonable for a unimolecular reaction rate and non-radiative decay rate respectively. Moreover,  $\Delta E_r$  is within the expected range for this kind of rearrangement and may be associated with some normal mode which is coupled to the dissociative continuum. The value obtained for  $\Delta E$  is  $300 \text{ cm}^{-1}$  which is indicative of vibronic coupling [6, 7]. It should be noted that  $\tau_f(0)$  is typical of singlet state lifetimes; at room temperature we can estimate the lifetime, using the relation  $\tau_f(T) = \tau_f(0)/\beta$ , to be about  $60 \text{ ps}$ . In our set-

<sup>†</sup>The extrapolated value of  $\phi_0 = 0.66$  is accurate to within  $\pm 15\%$ .

up we can only observe that the fluorescence decay follows the laser pulse (5 ns width).

In conclusion we note that the present study provides an example of a thermally activated photochemical rearrangement, a process which acts as an additional quenching mechanism of the fluorescence of the excited state. The main features of these temperature dependent phenomena are in agreement with those of other reported temperature dependent photophysical processes [3, 7] and of the competing photochemical reaction and fluorescence decay [8].

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