A New Method for the Determination of Thermochromic Equilibrium Constant of Indoline Spiropyran

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Since the first observation of Fischer and Hirshberg^[1], the thermochromism and photochromism of spiropyran (SP) and related compounds has continue to attract strong interests in connection with their applications in various fields^[2]. In solution, there is a

Scheme 1

thermochromic equilibrium between the closed colorless form (C.F.) and the open colored form (O.F.) of SP. The equilibrium position and the $\lambda_{\max}$ of O.F. absorptoin are very sensitive to the polarity of solvents and had been used as a model system to study solvent effect^[3]. For the determination of the equilibrium constants, spectroscopic method was introduced by Flannery^[4]. By this method, equilibrium constants of thermochromic reaction can be obtained from equation (1).

$$S_T = A_e \left[\frac{1}{\epsilon} \left(1 + \frac{1}{K_e} \right) \right] \quad (1)$$

where ϵ is the molar extinction coefficient of the visible absorbing species (O.F.), S_T is the total concentration of C.F. and O.F., and A_e is the equilibrium absorbance at the visible absorption maximum. But in calculating of K_e from the slope of the plot of S_T with A_e , the molar extinction coefficient, ϵ is necessary. However which is known only for a limited number of solvents and spiropyrans. In Flannery's work, arbitrarily estimated

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ϵ values should be used for most solvents and usually up to 30% relative deviation to K_e values were unavoidable. Since the work of Flannery, no improved method has been developed. In this work, a new method with higher reliability for the determination of K_e is proposed. By this method k_f and k_r in scheme 1 are measured independently, and K_e can be obtained by using equation(2).

$$K_e = \frac{k_f}{k_r} \quad (2)$$

Decoloration kinetic measurements of O.F.

In polar solvents, the decay of the photoinduced (Ultraviolet) colored open form (O.F.) obeys first-order kinetics^[4]. The kinetic equation of decoloration for O.F. after exposure to ultraviolet is

$$(k_f + k_r) = \frac{1}{t} \ln \frac{A_t - A_e}{A_0 - A_e} \quad (3)$$

where A_0 , A_t and A_e are visible absorbance at time 0, t and ∞ , after UV irradiation respectively.

Fig.1 a. Visible spectra of $1.5 \times 10^4 \text{ mol} \cdot \text{L}^{-1}$ SP-1 after UV irradiation at different time, $t(\text{s})$: 0, 5, 10, 15, 20, 25, 30, 35, ∞ . The dashed line shows the visible spectrum of $1.45 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ SP-1 without UV irradiation;
b. The rate constant plot for the first-order decoloration kinetics.

Fig.1a shows the changes of the visible spectra of SP-1 ($R_1 = \text{Me}$, $R_2 = \text{OMe}$) with time after UV irradiation, by fitting the data from Fig.1a into equation (3), Fig.1b is obtained, then we have $k_f + k_r = 9.8 \times 10^{-2} \text{ s}^{-1}$. By assuming ϵ value to be $3.5 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ as Flannery did^[4], the K_e obtained should be 7.76×10^{-3} from the dashed line.

Determination of k_f

Apart from the absorption spectra, another distinct difference between C.F. and O.F. is the complexation of the later to certain metal ions^[2]. Fig.2a gives the visible spectra of SP-1 in acetone solution in the presence of $\text{Cu}(\text{II})$ ($5.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) at different time in the dark. In the presence of $\text{Cu}(\text{II})$, a new band corresponding to the formation of

complex at 400nm appears. Since C.F. can't form complexes with Cu(II), the complex formation process has to be:

By treating the process under steady-state assumption, we have:

$$-\frac{d[\text{C.F.}]}{dt} = \frac{d[\text{O.F.} - \text{Cu(II)}]}{dt} = \frac{k_f K_c [\text{Cu(II)}]}{k_r + K_c [\text{Cu}]} [\text{C.F.}] \quad (4)$$

$$\ln \frac{A_0^{\text{C.F.}} - A_t^{\text{C.F.}}}{A_0^{\text{C.F.}} - A_\infty^{\text{C.F.}}} = \ln \frac{A_t - A_0}{A_\infty - A_0} = \frac{k_f k_c [\text{Cu(II)}]}{k_r + K_c [\text{Cu}]} t \quad (5)$$

where $A_0^{\text{C.F.}}$ (or A_0), $A_t^{\text{C.F.}}$ (or A_t), $A_\infty^{\text{C.F.}}$ (or A_∞) are the absorbance of C.F. (or O.F.) at $t = 0, t, \infty$ respectively.

or

$$\ln \frac{A_t - A_0}{A_\infty - A_0} = k_{\text{ob}} t \quad (6)$$

in which

$$k_{\text{ob}} = \frac{k_f k_c [\text{Cu(II)}]}{k_r + k_c [\text{Cu(II)}]} \quad (7)$$

or

$$\frac{1}{k_{\text{ob}}} = \frac{1}{k_f} + \frac{k_r}{k_f k_c [\text{Cu(II)}]} \quad (8)$$

By fitting the data from Fig.2a to equation (6), we have $k_{\text{ob}} = 4.93 \times 10^{-4} \text{s}^{-1}$ (Fig.2b). In the similar way, when the concentrations of Cu(II) are $1.0 \times 10^{-3} \text{mol} \cdot \text{L}^{-1}$ and $2.0 \times 10^{-3} \text{mol} \cdot \text{L}^{-1}$, k_{ob} 's are $4.89 \times 10^{-4} \text{s}^{-1}$ and $5.01 \times 10^{-4} \text{s}^{-1}$, respectively.

Fig.2 a. Visible spectra of $6.0 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$ SP-1 in acetone with $5.0 \times 10^{-4} \text{mol} \cdot \text{L}^{-1}$ CuCl_2 at different time. Time (min): 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, ∞ ;
b. Rate plot for the first-order chelation of SP at different concentration of Cu(II): $5.0 \times 10^{-4} \text{mol} \cdot \text{L}^{-1}$ (o), $1.0 \times 10^{-3} \text{mol} \cdot \text{L}^{-1}$ (Δ), $2.0 \times 10^{-3} \text{mol} \cdot \text{L}^{-1}$ ($\square$)

Obviously, the concentration of Cu(II) has no manifest effect on the rates of complexation. Comparing these results with equation (8), we have

$$k_f = 4.94 \times 10^{-4} \text{ s}^{-1} \quad \text{and} \quad k_r/k_f k_c \approx 0.$$

Then

$$k_r = (k_f + k_r) - k_f = 9.8 \times 10^{-2} \text{ s}^{-1} - 4.94 \times 10^{-4} \text{ s}^{-1} \approx 9.8 \times 10^{-2} \text{ s}^{-1},$$

so that

$$K_e = k_f/k_r = 5.0 \times 10^{-3}$$

There are significant differences between K_e values obtained by Flannery's method and ours. We believe the later method is more reliable, since no arbitrary estimation data should be done in determination of K_e .

Another conclusion from these results is that the chelation process between O.F. and Cu(II) is the faster step and the ring open step is the rate determination step in the complex formation process. And this is in consistent with the result reported by Atabekyan and Chibasov^[5].

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吡啶螺吡喃热致变色平衡常数的新测定法

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摘要 报导了一种吡啶螺吡喃(SP)在丙酮溶液中热致变色平衡常数的新测定方法. 通过分别检测紫外光照射SP后生成有色体的褪色过程和避光条件下其开环异构体与Cu(II)的配合物形成过程, 求得闭环无色体的开环速度常数 k_f 和开环有色体的闭环褪色速度常数(k_r)分别为 $4.94 \times 10^{-4} \text{ s}^{-1}$ 和 $9.8 \times 10^{-2} \text{ s}^{-1}$. 利用 $K_e = k_f/k_r$, 可求得 K_e 为 5.0×10^{-3} . 此方法有助于解决Flannery等人方法中对不同溶剂 ϵ 估值所带来误差的问题.

关键词: 吡啶螺吡喃, 光致变色, 配位作用, 热致变色平衡