A Method of Evaluating the Rate Constant of the Thermal Isomerization of 6-SO_3^--spiropyran by Using β-Cyclodextrin

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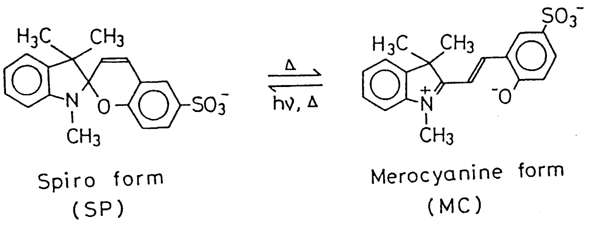
The thermal isomerizations of 1',3',3'-trimethyl-spiro[2H-1-benzopyran-2,2'-indoline]-6-sulfonic acid between its spiro (SP) and merocyanine (MC) forms were followed spectrophotometrically by using β-cyclodextrin as the control of the isomerization reaction. The rate constants of the thermal isomerizations were estimated to be 2.27×10^{-3} s^{-1} for MC ⟶ SP and 3.03×10^{-3} s^{-1} for SP ⟶ MC.

Spiropyrans are converted into a metastable form by the irradiation with light, and in the dark the thermal return to a stable form can be followed spectrophotometrically.[1] It is recognized that 1',3',3'-trimethyl-spiro[2H-1-benzopyran-2,2'-indoline]-6-sulfonic acid (6-SO_3^--SP) exists as the equilibrium mixture of the metastable colorless SP form and the stable colored MC form (Scheme 1), and kinetic studies on the thermal isomerization have been performed through a thermocoloration-photobleaching cycle.[2]



Scheme 1.

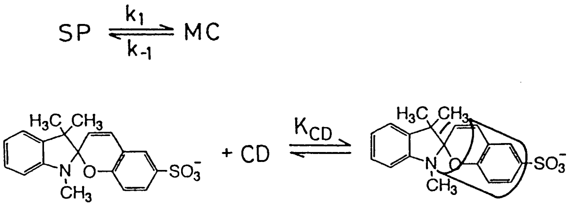
β-Cyclodextrin (β-CD) is well-known to form inclusion complexes with various kinds of molecules.[3] The thermochromism is often associated with the reversible valence isomers. In case of spiropyran, the valence isomers are the dipolar structure (MC) and the less polar structure (SP). The difference in the stabilities of inclusion complexes formed with valence isomers can be used for the control of the isomerization reaction. In this paper, we have used water-soluble 6-SO_3^--SP, and reported a method of the control of the thermal isomerization by using β-CD.

6-SO_3^--SP was prepared according to the method of Sunamoto et al.[2] β-CD was commercially purchased. Phosphate buffer (pH= 6.9) solution of 0.1 mol dm^{-3} prepared from phosphate salts was used as the solvent. A sample solution (6-SO_3^--SP: about 1×10^{-5} mol dm^{-3}) was deoxygenated by bubbling nitrogen. The thermal isomerization between SP and MC was followed by monitoring the change in the maximum absorption of the MC form by means of Union Giken 401 spectrophotometer. The first-order rate constants obtained at 313K agreed within 5% error.

In a previous paper,[4] we suggested that β-CD forms the stable 1:1 inclusion complex with the SP form of 6-SO_3^--SP, and the MC form is not included in the CD cavity on the basis of measurements of circular dichroism and uv-visible spectra. Further, we have confirmed that the isomerization reaction of 6-SO_3^--SP included in the CD cavity does not occur. The apparent rate constant (k_{obsd}) for the thermal isomerization of 6-SO_3^--SP was expressed as a function of β-CD concentration as follows,[4]

$$k_{obsd} = k_{-1} + k_1/(1+K_{CD}[CD]) \qquad (1)$$

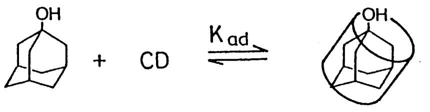
where [CD] denotes the concentration of "empty" β-CD (Scheme 2).



Scheme 2.

When the aqueous solutions of 6-SO_3^--SP and CD were mixed, the peak at 510 nm due to the MC form decreased gradually with time. Since inclusion processes of CD with various kinds of molecules are very rapid, the gradual decrease in the absorption band is due to the thermal isomerization of 6-SO_3^--SP. This suggests that the formation of the inclusion complex between the SP form and β-CD causes a shift of the equilibrium between SP and MC. Equation 1 shows that the rate constant of the isomerization in the presence of large excess β-CD corresponds to the k_{-1}-value. After mixing the solutions of 6-SO_3^--SP and large excess β-CD, the thermal MC ⟶ SP isomerization can be followed by monitoring the gradual decrease in the absorbance at 510nm, and the first-order rate constant k_{-1} has been determined as 2.27×10^{-3} s^{-1}.

Ueno et al.[5] suggested using modified β-CD that 1-adamantanol forms the most stable inclusion complex with CD among various types of alcohols.



Scheme 3.

Since the stability of the inclusion complex depends on the hydrophobicity and size of the guest molecules, β-CD itself may also form the stable inclusion complex with 1-adamantanol. We have found that upon addition of 1-adamantanol to a mixture of 6-SO_3^--SP and β-CD, the absorption band appears gradually at 510 nm due to the MC form, as shown in Figure 1. This result reveals that 6-SO_3^--SP (the SP form) included in CD is excluded from the CD cavity by 1-adamantanol, and then the SP form of excluded 6-SO_3^--SP thermally isomerizes to the MC form. Therefore, the apparent SP ⟶ MC isomerization can be followed by monitoring the change in the absorbance at 510 nm. Figure 2 shows the dependence of the 1-adamantanol concentration on the apparent rate constant k_{obsd}. The k_{obsd}-value increases with increasing the [1-adamantanol]/[β-CD] value, and a saturation curve is obtained. It may be considered that the increase in the [1-adamantanol]/[β-CD] value corresponds to the decrease in the concentration of "empty" β-CD. Therefore, under the condition [1-adamantanol]/[β-CD]>2, β-CD may exist almost as the inclusion complex with 1-adamantanol. As predicted by equation 1, the rate constant observed upon addition of excess 1-adamantanol over β-CD corresponds to $k_{obsd}=k_1+k_{-1}$. By addition of 1-adamantanol, we obtained $k_1+k_{-1}= 5.30\times10^{-3}\ s^{-1}$. Using the k_{-1}-value estimated above, the rate constant k_1 for the SP ⟶ MC isomerization can be calculated to be $3.03\times10^{-3}\ s^{-1}$, which is in agreement with the rate constant ($3.09\times10^{-3}\ s^{-1}$) estimated from the kinetic study by using the irradiation with visible light.[4]

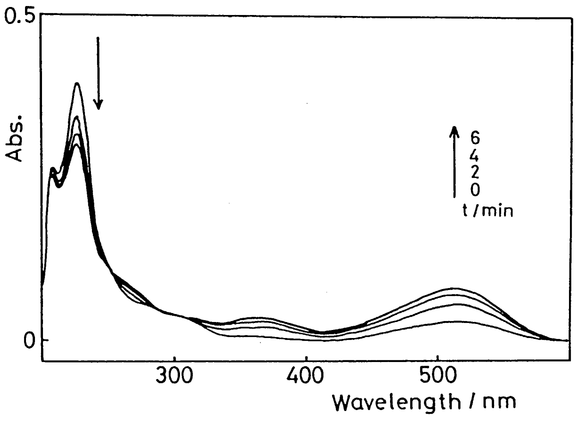


Figure 1. Absorption spectra of 6-SO_3^--SP after mixing the solutions of 1-adamantanol and inclusion complex at 313 K.

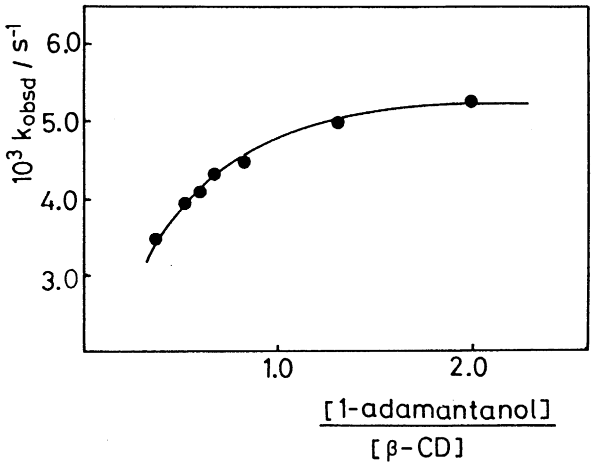


Figure 2. Effect of the 1-adamantanol concentration on the apparent rate constant for the SP ⟶ MC isomerization at 313 K.

These results for the isomerization of spiropyran demonstrate the reaction control caused by the stability of the inclusion complex with β-CD, and application for the various types of isomerization reactions is now under way.

References and Notes

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