BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2737—2738 (1978)

Temperature Effects on CD Spectra of α-Cyclodextrin Complexes with *m*- and *p*-Nitrophenol

Kazuaki HARATA

Research Institute for Polymers and Textiles, Sawatari 4, Kanagawa-ku, Yokohama 221

(Received March 17, 1977)

Synopsis. The CD spectra of α-cyclodextrin complexes with *m*- and *p*-nitrophenol were measured at 10, 30, 50, and 70 °C in aqueous solutions of various α-cyclodextrin concentrations. The CD intensity of both complexes was decreased to 14—61% of the intensity measured at 10 °C with the increase of temperature to 70 °C, but no significant change was observed in the spectral shape. The thermodynamic parameters for the complex formation were determined.

α-Cyclodextrin (α-CDx) forms inclusion complexes with *m*-nitrophenol (*m*-NP) and *p*-nitrophenol (*p*-NP). The structure of the *p*-nitrophenol complex in aqueous solutions has been investigated by CD[1,2] and NMR[3,4] spectra. Recent X-ray analyses revealed the detailed structure of the *m*-nitrophenol and *p*-nitrophenol complexes.[5,6] In the crystalline states, the *m*-nitrophenol molecule has been suggested to be more loosely bound to the α-cyclodextrin ring than the *p*-nitrophenol molecule. In the presnet study, the CD spectra of these complexes were meausred at various temperatures in order to investigate the α-cyclodextrin interaction with *m*- and *p*-nitrophenol in aqueous solutions.

Experimental

α-Cyclodextrin (G.R., Tokyo Kasei Co.) was crystallized from water and dried *in vacuo* over phosphorus pentaoxide at room temperature. *m*- and *p*-nitrophenol (G.R., Tokyo kasei Co.) were used without further purification. Solutions were prepared with deionized water, and the concentrations of *m*- and *p*-nitrophenol were adjusted to 9.66 and 8.81×10^{-4} mol, respectively. The concentration of α-cyclodextrin was varied from 0.001 to 0.054 mol. The CD spectra were recorded at 10, 30, 50, and 70 °C on a JASCO J-40A circular dichrograph with a J-DPZ data-processor by use of a 1 mm quartz cell. The temperature was regulated by using a Tokyo Rico TC-100 thermo-controller with an accuracy of ±0.5 °C inside the cell.

Results and Discussion

The CD spectra of α-cyclodextrin complexes with *m*- and *p*- nitrophenol are shown in Figs. 1 and 2. The CD intensity in these spectra decreased gradually with the increase of the temperature, although no significant change is observed in the spectral shape. The intensity changes for various molar ratios of [α-CDx]/[guest] ([C]/[G]) were measured at 280 nm for the *m*-nitrophenol complex and at 340 nm for the *p*-nitrophenol complex, as shown in Figs. 3 and 4. At 10 °C, the intensity of both complexes increased rapidly with the increase of the concentration of α-cyclodextrin up to the [C]/[G] value of 10, but only a small intensity enhancement was observed at the

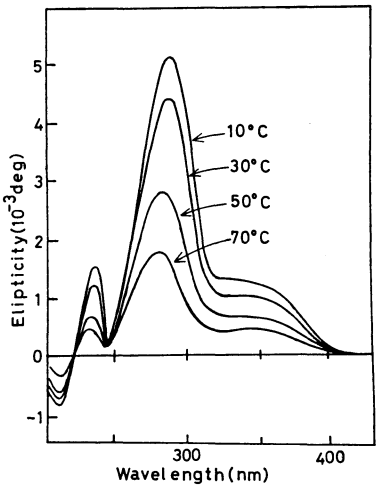

Fig. 1. The CD spectra of α-cyclodextrin–*m*-nitrophenol complex at 10, 30, 50, and 70 °C. The concentrations of α-cyclodextrin and *m*-nitrophenol are 1.8×10^{-2} and 9.66×10^{-4} mol, respectively, and a 1 mm cell was used.

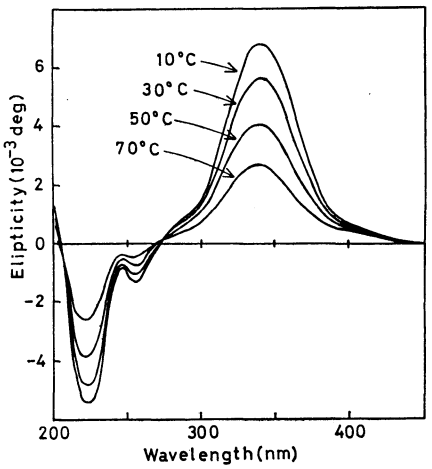

Fig. 2. The CD spectra of α-cyclodextrin–*p*-nitrophenol complex at 10, 30, 50, and 70 °C. The concentrations of α-cyclodextrin and *p*-nitrophenol are 1.8×10^{-2} and 8.81×10^{-4} mol, respectively, and a 1 mm cell was used.

[C]/[G] values greater than 20. On the other hand, at 70 °C, the CD intensity changes more slowly, and showed a gradual increase. When the temperature was raised from 10 to 70 °C, the CD intensity of the *m*-nitrophenol complex fell to 54% at the highest [C]/[G] value, while the intensity decreased to 14% at the lowest [C]/[G] value. A similar intensity change was observed in the *p*-nitrophenol complex. The in-

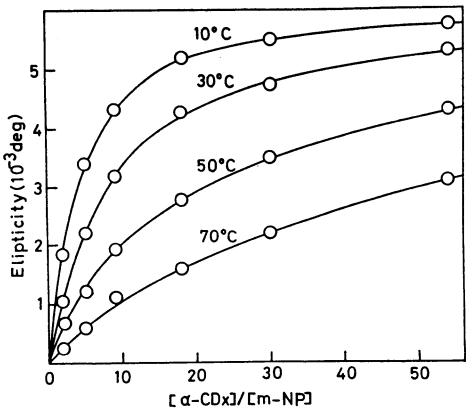

Fig. 3. Plot of the CD intensity measured at 280 nm against the [α-CDx]/[*m*-NP] ratio. The concentration of *m*-nitrophenol is 9.66×10^{-4} mol.

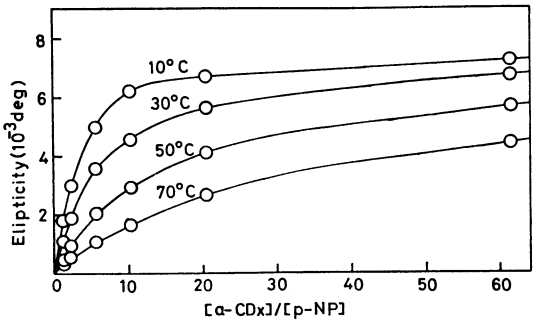

Fig. 4. Plot of the CD intensity measured at 340 nm against the [α-CDx]/[*p*-NP] ratio. The concentration of *p*-nitrophenol is 8.81×10^{-4} mol.

tensity at 340 nm fell to 61% in the solution with a [C]/[G] value of 61 and to 19% in that with a value of 1.

The dissociation constants of the complexes were determined by the Rose-Drago method,[7] on the assumption that α-cyclodextrin forms only a 1:1 complex. This assumption may be supported by the fact that no significant spectral shift or change of the spectral shape, but only an intensity decrease was found with increasing temperature or with decreasing [C]/[G] value. The observed intensity change gave a good fit to the equilibrium equation for the 1:1 stoichiometry. The results are shown in Table 1. The dissociation constants of the *m*-nitrophenol complex were 1.6—2.0 times greater than the corresponding values of the *p*-nitrophenol complex. In both complexes, about a ten-fold increase of the dissociation constants was observed when the temperature was raised from 10 to 70 °C. The enthalpy and entropy changes (ΔH and ΔS) for the complex formation were estimated: −33(1) kJ mol^{-1} and −70(4) J K^{-1} mol^{-1} for the *m*-nitrophenol complex and −30(1) kJ mol^{-1} and −56(3) J K^{-1} mol^{-1} for the *p*-nitrophenol complex, where values in parentheses are standard deviations. The ΔH and ΔS values of the *p*-nitrophenol complex are in good agreement with the values of −31 kJ mol^{-1} and −63 J·K^{-1} mol^{-1} determined by Lewis and Hansen.[8] These thermodynamic parameters indicate that *m*-nitrophenol is bound to α-cyclodextrin as strongly as *p*-nitrophenol. X-ray studies,[5,6] however, indicated that *m*-nitrophenol is more loosely bound to α-cyclodextrin than *p*-nitrophenol. In the crystalline complexes, the *p*-nitrophenol molecule deeply penetrates into the α-cyclodextrin ring and is rigidly fixed, while only a partial inclusion of the guest molecule is observed in the *m*-nitrophenol complex. On the other hand, NMR studies[2,3] have suggested that *p*-nitrophenol molecule is not deeply inserted into the α-cyclodextrin ring. In the *m*-nitrophenol complex, the deep penetration of the guest molecule is impossible because of the steric hindrance. If *m*- and *p*-nitrophenol form complexes in aqueous solutions in the same manner as found in the crystalline complexes, it seems likely that the structural difference between the two complexes will affect the enthalpy of the complex formation.[6] A possible explanation for the observed thermodynamic parameters may be that the *p*-nitrophenol molecule is only partially and loosely included in the α-cyclodextrin ring in aqueous solutions, as suggested from the NMR studies.

Table 1. Dissociation constants and free energies for the complex formation

Values in parentheses are standard deviations.

	p-NP complex		*m*-NP complex	
t °C	K_d 10^{-3} mol^{-1}	ΔG kJ mol^{-1}	K_d 10^{-3} mol^{-1}	ΔG kJ mol^{-1}
10	2.4(0.6)	−14.2(0.6)	3.5(0.4)	−13.4(0.3)
30	5.0(0.5)	−13.4(0.3)	8.1(0.7)	−12.1(0.2)
50	11.7(0.6)	−11.7(0.2)	18(3)	−10.9(0.4)
70	22(6)	−10.9(0.7)	41(9)	−9.2(0.6)

The author wishes to thank Dr. Hisashi Uedaira for supporting this study and for his helpful discussions.

References

1) K. Takeo and T. Kuge, *Staerke*, **24**, 281 (1972).
2) K. Harata and H. Uedaira, *Sen'i Kobunshi Zairyo Kenkyusho Kenkyu Hokoku*, **112**, 1 (1976).
3) R. Bergeron and R. Rowan, III, *Bioorg. Chem.*, **5**, 425 (1976).
4) D. J. Wood, F. E. Hruska, and W. Saenger, *J. Am. Chem. Soc.*, **99**, 1735 (1977).
5) K. Harata, *Bull. Chem. Soc. Jpn.*, **50**, 1416 (1977).
6) K. Harata, H. Uedaira, and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **51**, 1627 (1978).
7) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).
8) E. A. Lewis and L. H. Hansen, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 2081.