CHEMISTRY LETTERS, pp. 53 - 56, 1984. © The Chemical Society of Japan 1984

REVERSIBLE PHOTODIMERIZATION OF WATER-SOLUBLE ANTHRACENES INCLUDED IN γ-CYCLODEXTRIN

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Anthracene-1- or 2-sulfonic and 2-carboxylic acids were found to form one host-two guest inclusion complexes with γ-cyclodextrin in aqueous solutions. The complex formation greatly enhanced the photodimerization of these anthracenes.

γ-Cyclodextrin (γ-CD) possesses eight glycopyranosides which form a daughnut-type ring with an 8.5 Å diameter and a 7 Å depth.[1)] It can include a variety of molecules and ions in the cavity. The relatively large size of the cavity of γ-CD allows two guest molecules to be included.[2)] This letter describes that some water-soluble anthracenes form two-guest inclusion complexes with γ-CD in aqueous solutions. The stoichiometry of present complexes is different from that for anthracene/γ-CD system which has been reported to form a 1:1 inclusion complex.[3)] It is of particular interest that the anthracene-type photodimerization was greatly enhanced for these 1:2 inclusion complexes and was almost quantitative even in the dilute solution ($\leq 10^{-4}$ M; M = mol dm^{-3}) of the guest molecules.

Figure 1 shows an example of the photo-response change in the absorption spectrum of potassium 2-anthracenesulfonate (2AS) in air saturated aqueous solutions at room temperature. The irradiating light was supplied by CRM photo-irradiator (JASCO) equipped with a 2 kW xenon lamp and a grating monochromator. 2AS was prepared by the reduction of 2-anthraquinonesulfonate in an aq NH_4OH by Zn dust. As shown in Fig. 1, when irradiated by the light of wavelengths longer than 300 nm, there is a significant decrease in the absorption bands in the range of 300-400 nm (Spectrum 2 → 3). This spectral change corresponds to the formation of anthracene photodimer (dianthracene). This was confirmed by NMR, IR, and the thermal decomposition of the photoproduct into the starting material.[4)] The subsequent irradiation of the absorption shoulder appearing near 280 nm with 280 ± 10 nm-light gives rise to anthracene-like absorption bands again (Spectrum 3 → 4), corresponding to the cleavage of the dianthracene. The recovery amount of anthracene did not reach the initial absorbance, but the absorbance in the photo-stationary state at the irradiating wavelength where both the photodimer and the monomer absorb the incident light. It is noteworthy that the interconversion between the spectra 3 and 4 could be repeated by selecting the irradiating wavelength. This photo-reversible reaction is in contrast with irreversible photooxidation in the absence of the host (Spectrum 1 → 5). The results imply that 2AS molecules included by γ-CD are protected from dissolved oxygen and have the configuration feasible to dimerize.

At relatively high concentration ($\geq 10^{-3}$ M) of 2AS, it could dimerize upon

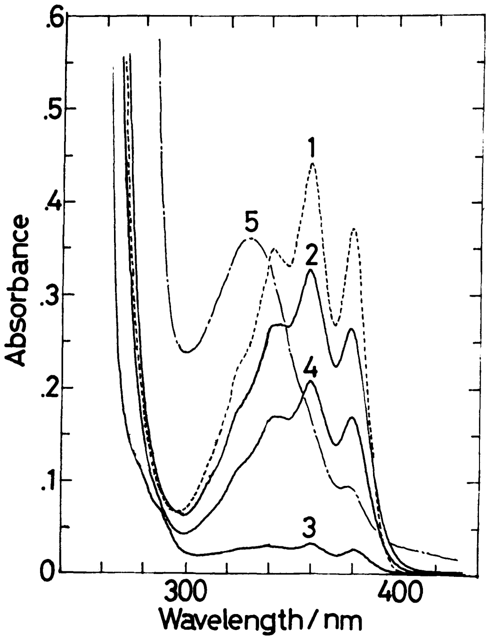

Fig. 1. Absorption spectra of 2AS (1.1×10^{-4} M): 1) in water; 2) in the presence of γ-CD; 3) after irradiation of 2 with 380-nm light; 4) after irradiation of 3 with 280-nm light; 5) after irradiation of 1.

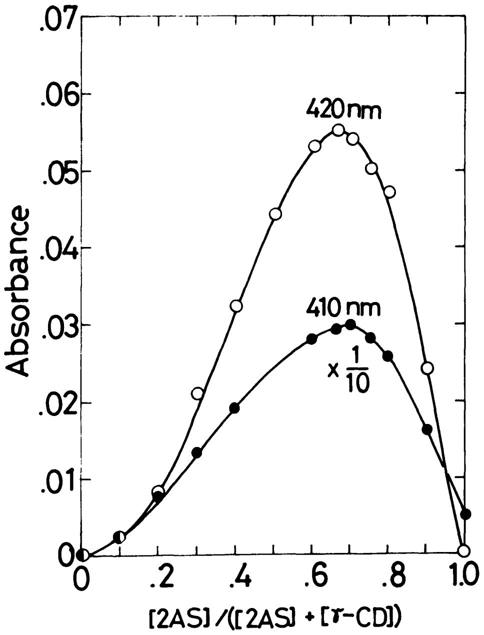

Fig. 2. Changes in absorption of 2AS monitored by the continuous variation method: [2AS] + [γ-CD] = 1.0×10^{-3} M (const)

irradiation without the aid of γ-CD. The quantum yield for the formation of dianthracene, Φ_D, was measured at 380 ± 10 nm at [2AS] = 2.8×10^{-3} M to be ca. 0.05, a value which is comparable to that reported for anthracene in benzene.[5] The efficiency of the photodimerization was strikingly enhanced by the addition of γ-CD. At [γ-CD] = 2×10^{-3} M where almost all (ca. 95% of) the guest molecules are included by the host, the value of Φ_D was evaluated to be 0.47±0.05, an order of magnitude greater than that in the absence of the host. On the other hand, the quantum yield of the reverse reaction was estimated at 280 ± 10 nm to be about 1, irrespective of the existence of the host.

The complex formation causes considerable changes in the absorption spectrum of 2AS. These are the decrease in the peak intensities, the red-shift of the peak positions from λ_{max} (log ε) = 341(3.51), 359(3.62), and 379(3.54) nm for 2AS to λ_{max} = 349, 362, and 381 nm for the inclusion complex, and the broadening of the spectrum with isosbestic points at 384 nm and 297 nm. Figure 2 shows Job's plots[6] of the new absorption appearing on the long wavelength side. The absorption measurements were done by varying the mole fraction of 2AS in the sample solutions containing constant concentration of [2AS] + [γ-CD] (= 1×10^{-3} M). These figures clearly evidence a 1:2 stoichiometry as described by Eq. 1,

$$2(2AS) + (\gamma\text{-CD}) \underset{}{\overset{K}{\rightleftharpoons}} (2AS)_2(\gamma\text{-CD}). \qquad (1)$$

This equation yields an expression,

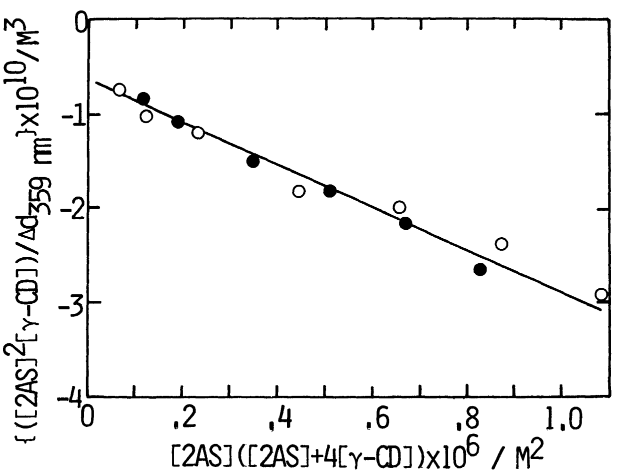

Fig. 3. Determination of the equilibrium constant by absorption method: Exp 1 (○), [γ-CD] = 2.5×10^{-3} M (const) and [2AS] ranges from 6.3×10^{-6} M to 2.1×10^{-4} M; Exp 2 (●), [2AS] = 2.0×10^{-4} M (const) and [γ-CD] ranges from 9.9×10^{-5} M to 9.9×10^{-4} M.

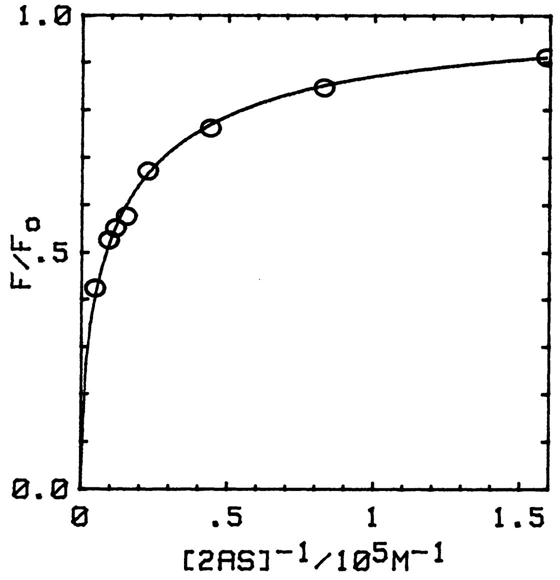

Fig. 4. Determination of the equilibrium constant by fluorescence method: the same experimental run as Exp 1 in Fig. 3.

$$K = [C]/\{([2AS] - 2[C])^2([\gamma\text{-CD}] - [C])\}, \qquad (2)$$

where [2AS] and [γ-CD] are initial concentrations of 2AS and γ-CD, respectively and [C] is the equilibrium concentration of the inclusion complex. By neglecting the terms of $[C]^2$ and $[C]^3$ by similar ways to Bender's treatment for absorption changes on complex formation,7) one can give Eq. 3 on expansion of Eq. 2,

$$[2AS]^2[\gamma\text{-CD}]/\Delta d = (1/K)/\Delta\varepsilon + [2AS]([2AS] + 4[\gamma\text{-CD}])/\Delta\varepsilon, \qquad (3)$$

where Δε (= $\varepsilon_C - 2\varepsilon_{2AS}$) is the difference of molar absorptivities and Δd (= [C] x Δε) is the absorbance change induced by complex formation. The plot for $[2AS]^2[\gamma\text{-CD}]/\Delta d$ vs. [2AS]([2AS] + 4[γ-CD]) should provide a straight line with a constant slope of 1/Δε and an intercept of (1/K)/Δε to an ordinate axes. In Fig. 3 are shown the results of two experimental runs which were done by varying [γ-CD] with constant [2AS] and vice versa. The plots obtained from the respective experiments give the same straight line with $\Delta\varepsilon_{359\ \mathrm{nm}} = -4700\ \mathrm{cm^{-1}M^{-1}}$ and $K = 3.0 \times 10^6\ \mathrm{M^{-2}}$.

The fluorescence intensity of 2AS was quenched in the presence of γ-CD. No new emission could be detected. On the assumption that the inclusion complex is non-fluorescent, one can derive Eq. 4 at sufficiently small [2AS] (< 10^{-4} M),

$$F/F_o = ([2AS] - 2[C])/[2AS], \qquad (4)$$

where F and F_o are the fluorescence intensity in the presence and absence of γ-CD, respectively. If [γ-CD] > [2AS], Eqs. 2 and 4 give Eq. 5,

$$F/F_o = -Z + (Z^2 + 2Z)^{1/2};\ Z = (1/K)/4[2AS][\gamma\text{-CD}]. \qquad (5)$$

The [2AS] dependency of F/F_o at constant [γ-CD] is shown in Fig. 4. The least squares calculation gives $K = 3.4 \times 10^6\ \mathrm{M^{-2}}$, a value which is in agreement with that obtained from the absorption measurements.

Two 2AS molecules in the hydrophobic cavity of γ-CD must be held together in close proximity. The decrease in fluorescence intensity by the complex formation may be attributed to self-quenching in the closely intimate pair. The photochemical and spectral behaviors may be explained by a sandwich dimer configuration of two anthracene rings. Chandross has first found the sandwich dimer of anthracene, which is produced by the photolytic cleavage of dianthracene in the rigid glass of methylcyclohexane at 77 K.$^{8)}$ The dimer in the rigid glass shows an excimer emission, both the hypochromicity and red-shift of the ^1L_a band, and reversible photodimerization. Except for the excimer emission, the rigid glass dimer is quite similar to the inclusion dimer studied here. It should be noted that the latter is thermodynamically stable, whereas the former is forced to maintain the configuration by the rigid matrix.

While α-CD showed no intermolecular interaction with 2AS as judged from its small cavity size, β-CD had an ability to form a complex with this aromatic compound. The latter case, however, had some dissimilarities with the case of γ-CD: 1) the absorption spectrum (^1L_a) of the complex exhibited hyperchromisty; 2) the fluorescence spectrum moved slightly to blue and had sharp structure like that in EtOH; 3) the photodimerization was enhanced, but not quantitative, competing with the photooxidation. These facts may suggest that β-CD forms the complex of a 1:1 stoichiometry with 2AS rather than of a 1:2 stoichiometry.

It is most probable that 2AS molecules are included axially in γ-CD, but not trapped with equatorial inclusion.$^{9)}$ From this point of view, the meso-substituted anthracene is not expected to be included in CD, because it is bulky in volume. Indeed, no interaction could be observed between 9-anthracenesulfonate and γ-CD. The situation was the same for 2- and 9-carboxylates. On the other hand, the 1-substituted anthracenes showed an intermediate behavior in complex formation: 1-sulfonate was able to form the inclusion complex with γ-CD, but 1-carboxylate was not. The reason for this difference is not clear at this stage of investigation.

References

1) M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry," Springer-Verlag, New York (1978).

2) A. Ueno, Y. Tomita, and T. Osa, J. Chem. Soc., Chem. Commun., 1983, 976 and references cited therein; H. Hirai, N. Toshima, and S. Uenoyama, Polymer J., 13, 607 (1981).

3) F. Cramer and F. M. Henglein, Chem. Ber., 90, 256 (1957).

4) IR(KBr) δ_{CH} 1410 and 1470 cm^{-1}. ^1H NMR(D_2O) δ_{ppm} 4.4(CH), 7.1 and 7.5 (ArH).

5) E. J. Bowen and D. W. Tanner, Trans. Faraday Soc., 51, 475 (1955); J. L. Charlton, R. Dabestani, and J. Saltiel, J. Am. Chem. Soc., 105, 3473 (1983).

6) P. Job, Compt. Rend., 180, 928 (1925); U. Shibata, S. Inoue, and U. Nakatsuka, Nippon Kagaku Zasshi, 42, 983 (1921).

7) R. L. VanEtten, J. F. Sebastian, G. A. Clowes, and M. L. Bender, J. Am. Chem. Soc., 89, 3242 (1967).

8) E. A. Chandross, J. Chem. Phys., 43, 4175 (1965).

9) K. Harata and H. Uedaira, Bull. Chem. Soc. Jpn., 48, 375 (1975).

(Received October 1, 1983)