ACCELERATION OF THE PHOTODIMERIZATION OF WATER-SOLUBLE ANTHRACENES INCLUDED BY β- AND γ-CYCLODEXTRINS

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ABSTRACT. The photodimerization of 2-anthracenesulfonate in water was accelerated in the presence of β- and γ-cyclodextrins (CyDs). While four configurational isomers of the photodimer were obtained in the presence of γ-CyD with similar ratio of the yields to that in the host-free solution, only one of the isomers was obtained in the presence of β-CyD. The results were explained by the formation of two guest-one host inclusion complex in the former case and of two guest-two host inclusion complex in the latter. No evidence of an inclusion complex with α-CyD was obtained. The inclusion effects of CyD on the photodimerization of other water-soluble anthracenes were also examined.

1. Introduction

The two guest-one host (2 : 1) inclusion complex has attracted increasing attention in these years. The cavity size of γ-cyclodextrin (γ-CyD) is large enough to include two homo-guest molecules (1-7) or two hetero-guest molecules (8-11). β-CyD is also known to form 2 : 1 inclusion complexes (12,13). Hamai has reported that naphthalene and β-CyD in water form a two guest-two host (2 : 2) complex generated by the association of two 1 : 1 inclusion complexes (14).

    If a bimolecular reaction occurs between two guest molecules trapped in the CyD cavity, the reaction behavior is expected to differ from that in the solution with respect to the reaction rate, selectivity, and so on. For instance, the rate of the Diels-Alder reaction between cyclopentadiene and butanone or acrylonitrile is greatly enhanced in the hydrophobic cavity of β-CyD (15).

    Recently, we have found that the photodimerization of water-soluble anthracenes is greatly accelerated in the presence of γ-CyD in water (16). It has been explained as the result of the formation of a sandwich dimer in the host cavity. This report describes the detail s of the photodimerization and of the inclusion behavior of the anthracene derivatives/CyDs systems in water.

2. Experimental

The preparation of 1- (1AS) and 2-anthracenesulfonates (2AS) was described elsewhere (16). The preparation of 1- (1AC) and 2-anthracenecarboxylates (2AC) was carried out by the haloform reaction of corresponding acetyl-anthracenes. 9-Anthracenecarboxylate (9AC) was used as commercially available.

The aqueous solutions of these anthracene derivatives (2×10^{-3} M; 1 M = 1 mole dm^{-3}) with or without CyDs (2×10^{-3} M) were exposed to the light ($\lambda \geq 340$ nm) of a 500 W Xe lamp. The configurational isomers of the photodimer obtained were separated by the HPLC technique using a NUCLEOSIL $5C_{18}$ column eluted by 0.2 M triethylamine phosphate (TEAP)/acetonitrile eluent (pH 3.0). The CyDs were eluted at first and completely separated from the photoproducts. For preparative separation of the photodimer, TEAP was replaced by a volatile eluent, ammonium acetate (0.2 M, pH 4.0), by which a part of the photodimer was eluted as included by CyDs. The identification of the configurational isomers was done by 360 MHz ^{1}H NMR spectroscopy. The circular dichroism was measured by using a JASCO J-10 spectropolarimeter.

3. Results and Discussion

3.1. Inclusion Effects on the Photodimerization

Figure 1 shows typical examples of the HPLC of the 2AS photodimer. Three configurational isomers (1, 2, and 3) were isolated as major photoproducts of oxygen-free solution in the absence of CyD. Since there was no evidence for self-association of 2AS in the solution, the photodimerization may proceed via an excimer formed between photoexcited and ground-state 2AS molecules as in the case of anthracene itself in   solution (17). The relative yields of the configurational isomers were 1 : 2 : 3 : 4 = 1 :
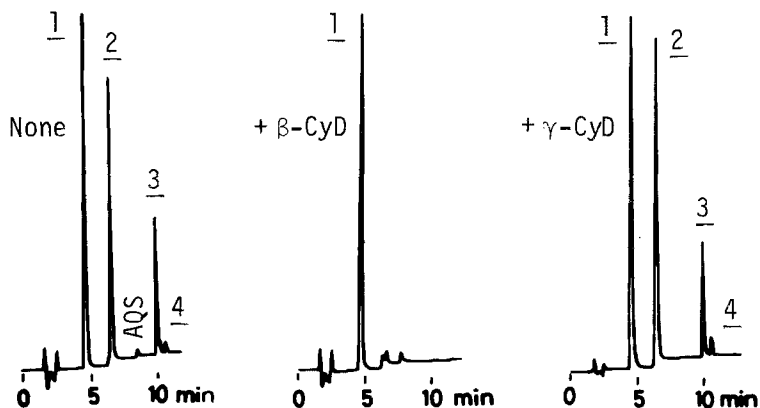

Fig. 1. The HPLC of the photodimer of 2AS. AQS; 2-anthraquinonesulfonate.

0.8 : 0.4 : 0.05. The yield of 4 was very low, which may be due to the steric hindrance and the electrostatic repulsion of adjacent sulfonate groups. The irradiation of the air-saturated solution gave a considerable amount of anthraquinonesulfonate (AQS) also. α-CyD did not modify the photoreaction at all and no inclusion complex with 2AS could be formed.

$$1 \qquad 2 \qquad 3 \qquad 4$$

$$x = SO_3^-$$
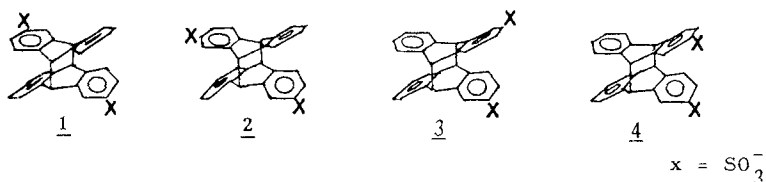
The major photoproduct in the presence of β-CyD was 1 alone, being quite in contrast with the result of the host-free solution. This prominent selectivity indicates that 2AS molecules trapped in β-CyD are forced to take a specific configuration mainly giving rise to 1.

The configurational isomers of the photodimer given in the presence of γ-CyD were identical with those in the absence of CyD. The relative yields of these isomers were quite similar in both cases. Nevertheless, the inclusion effect of γ-CyD is clear, because the quantum yield of the photodimerization was an order of magnitude greater than that in the absence of γ-CyD and because 2AS was protected from   photooxydation (16). The acceleration of the photodimerization is due to the formation of a 2 : 1 inclusion complex, in which two 2AS molecules are in a sandwich configuration. The spectrophotometric measurements gave 3×10^6 M^{-2} for the equilibrium constant (K) for the equation (16):

$$2(2AS) \quad + \quad \gamma\text{-CyD} \underset{}{\overset{K}{\rightleftharpoons}} (2AS)_2(\gamma\text{-CyD}) \qquad (1)$$
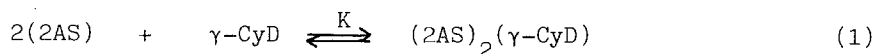
The results of the HPLC indicates that the 2AS sandwich pairs included by γ-CyD retain mutual configurations analogous to that of the excimer in the solution.

The inclusion effect of CyDs on the photodimerization of 2AC was quite similar to that in the 2AS/CyDs system. 9AC showed no complexation with CyDs and the photoreaction of this compound was little affected. These results are consistent with the Corey-Pauling-Koltun molecular model which indicates that the 2-substituted anthracenes can be included by β- and γ-CyDs   such that   the long axis of the aromatic ring is parallel to the axis of the CyD cavity (axial inclusion), and that the meso-substitution of the bulky and ionic group prevents the aromatic compounds to be effectively incorporated in the CyDs.

The inclusion complexes between 1AS and CyDs were much less stable as compared with those of 2AS. The photodimerization of 1AS in the presence of β-CyD showed little configurational selectivity, suggesting rather loose complexation. No stable complex was formed between 1AC and CyDs. This was confirmed by induced circular dichroism (i.c.d.) measurements which showed very weak or negligible i.c.d. for the complex between 1-derivatives and CyDs.
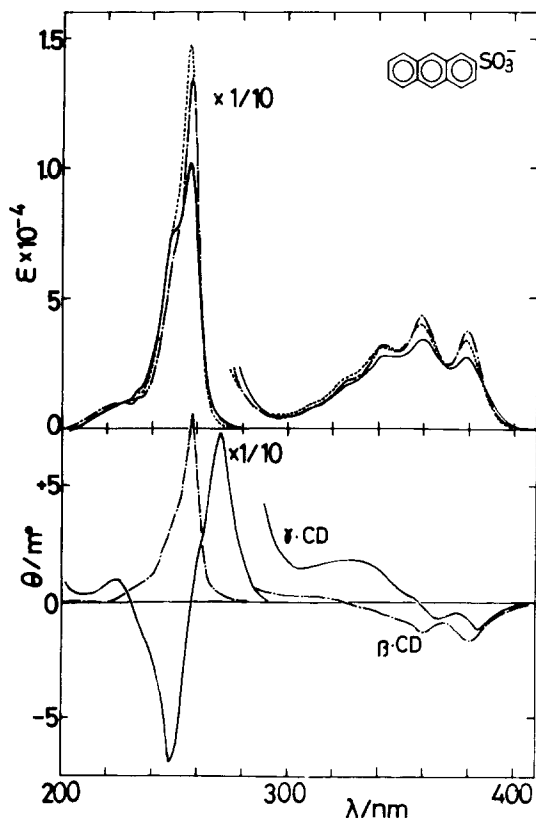
Fig. 2. The absorption (upper) and i.c.d. spectra (bottom) of 2AS (1 x 10^{-4} M) in the presence of γ-CyD (1 x 10^{-3} M, solid line), β-CyD (1 x 10^{-3} M, broken), and in the absence of the host (dotted) in water.

3.2. Inclusion Behavior

As shown in Fig. 2, the i.c.d. spectrum of 2AS in the presence of β-CyD is significantly different from that in the presence of γ-CyD. The former shows a positive i.c.d. band in 200 - 330 nm region and a negative one in 330 - 400 nm region. Since the absorption band in the short wavelength region is ascribed to the longitudinally polarized ^1B_b transition and the long-wavelength absorption band to the transversely polarized ^1L_a transition, the i.c.d. spectrum observed supports the axial inclusion (18). On the other hand, the i.c.d. spectrum in the presence of γ-CyD splits into two bands with a sign from negative (long-wavelength side) to positive (short-wavelength side) in the long wavelength region and with a sign from positive to negative in the short wavelength region, the cross points being at the wavelength of the absorption peaks. This indicates that the i.c.d. spectrum in the presence of γ-CyD arises from a dipole coupling between two 2AS molecules with R-helix configuration.

The stoichiometry of inclusion complexes was estimated by the continuous variation method. The results are shown in Fig. 3. It is clear that the inclusion complexes with β- and γ-CyDs show a 1 : 1 and 2 : 1 stoichiometry, respectively. Since the i.c.d. spectrum was unchanged in its general form at the concentration of 2AS ([2AS]) ranging from 10^{-5} M to
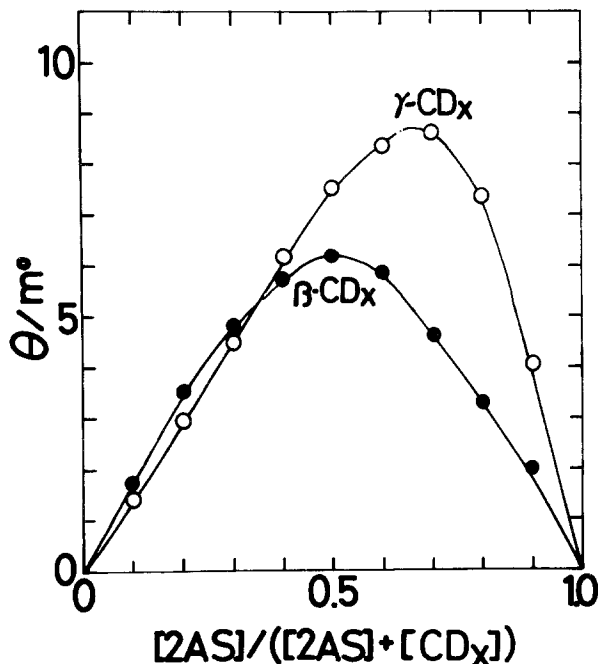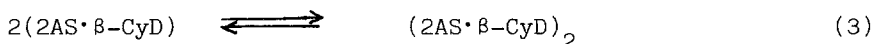
Fig. 3. Determination of the complex stoichiometry by the continuous variation method. $[2AS] + [CyD] = 1 \times 10^{-3}$ M (const). Monitored at 383 nm for the β-CyD complex and at 385 nm for the γ-CyD complex.

10^{-3} M in the presence of β-CyD (10^{-3} M – 10^{-2} M), the 1 : 1 stoichiometry is supposed to hold in the wide range of guest and host concentrations. On the other hand, the i.c.d. spectrum in the presence of γ-CyD was slightly dependent on the concentrations. At low guest (1 x 10^{-5} M) and high host (1 x 10^{-2} M) concentrations, the spectrum was the super position of both 1 : 1 and 2 : 1 inclusion complexes, while the latter complex was predominent at $[2AS] \geq 10^{-4}$ M.

There was also significant difference between effects of β- and γ-CyDs on the absorption spectra of 2AS. The peak absorption decreased monotonically with increasing [γ-CyD], being attributable to the formation of the 2 : 1 inclusion complex. The trend of the absorption change was fundamentally identical even at the low values of [2AS] where the 1 : 1 inclusion complex is significant.

The change in the absorption spectrum of 2AS in the presence of β-CyD was complex. The absorption bands increased and sharpened at lower values of [2AS] (< 10^{-4} M) with increasing [β-CyD], while they decreased and broadened at higher values of [2AS] ($\geq 10^{-3}$ M) as [β-CyD] increased. This implies that the complexation with β-CyD involves at least a di-step equilibrium which induces opposite absorption changes. Since no change in the inclusion stoichiometry could be observed from the i.c.d. measurement under the conditions, the results can be explain by the following equilibria;

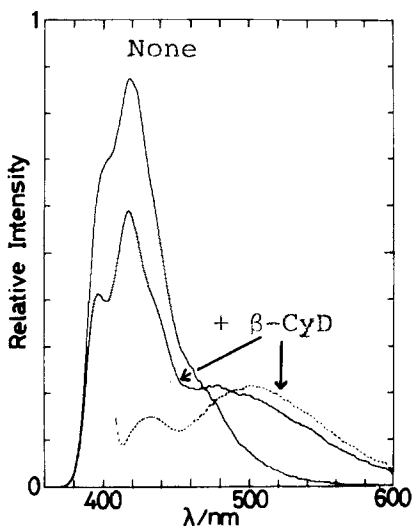$$2AS \; + \; β\text{-}CyD \; \rightleftharpoons \; 2AS \cdot β\text{-}CyD \tag{2}$$

$$2(2AS \cdot β\text{-}CyD) \; \rightleftharpoons \; (2AS \cdot β\text{-}CyD)_2 \tag{3}$$

Fig. 4. Fluorescence spectra of 2AS (1 x 10^{-4} M) in the presence and absence of β-CyD in water at room temperature. Excited at 360 nm (solid) and at 410 nm (dotted).

where (2AS·β-CyD)$_2$ represents a 2 : 2 inclusion complex which is formed by the association of two 1 : 1 inclusion complexes (2AS·β-CyD) as in the case of naphthalene/β-CyD system (14).

The 2AS/β-CyD system exhibits an excimer emission with the maximum at λ_f = 500 nm with concomitant decrease of a monomer fluorescence, as shown in Fig. 4. The excitation spectrum of the excimer emission was different from that of the monomer fluorescence, supporting the formation of a static dimer. Although the fluorescence of 2AS was largely quenched in the presence of γ-CyD, no excimer emission could be detected. The mutual configuration of adjacent anthracene nuclei in the complex may be responsible for the emissive behavior. In this respect, it has been reported that there are a variety of excimer states corresponding to the magnitude of the overlap between two covalently-linked anthracene nuclei like those in anthracenophane or 1,2-dianthrylethane (19). The excimer state of the 2AS/β-CyD system is an intermediate between those of 1,2-di(1-anthryl)-ethane (λ_f = 460 nm) in   solution at room temperature and of the photo-cleavage product (λ_f = 530 nm) of its photodimer in a rigid glass at 77 K. The sandwich pair of 2AS included by γ-CyD is related to [2.2](9,10)-anthracenophane which emits no excimer emission and undergoes rapid photocycloaddition without any need of large structural change.

As shown in Fig. 5, the close proximity of the aromatic nuclei in γ-CyD is confirmed by tremendous upfield shifts (∿ 0.6 ppm) of their protons in the NMR spectrum. The protons of γ-CyD were also affected by the presence of the guest. The interior H_3 and H_5 showed large upfield, shifts (∿ 0.25 ppm) due to anisotropic shielding of the aromatic moiety, while the exterior H_2 and H_4 showed a smallar shift (∿ 0.09 ppm). In the case of the 2AS/β-CyD complex, the shifts of the aromatic protons are quite small   or negligible. The H_5 of β-CyD showed major shifts (∿ 0.25 ppm) with H_3 showing a somewhat smaller upfield shift (∿ 0.13 ppm) and with H_2 and H_4 showing negligible shift (∿ 0.03 ppm).
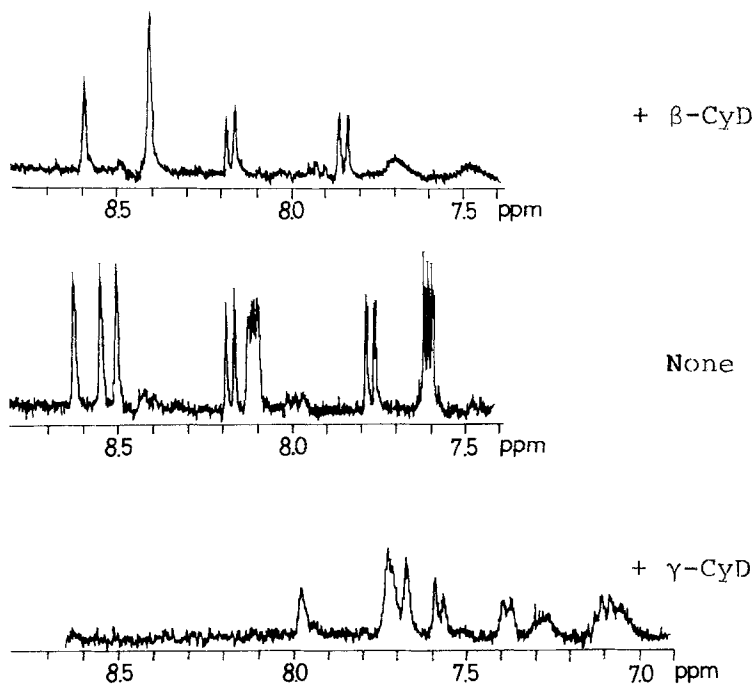
Fig. 5. ^{1}H NMR spectra of 2AS (2×10^{-3} M) in the presence and absence of CyD (1×10^{-2} M) in D_2O.

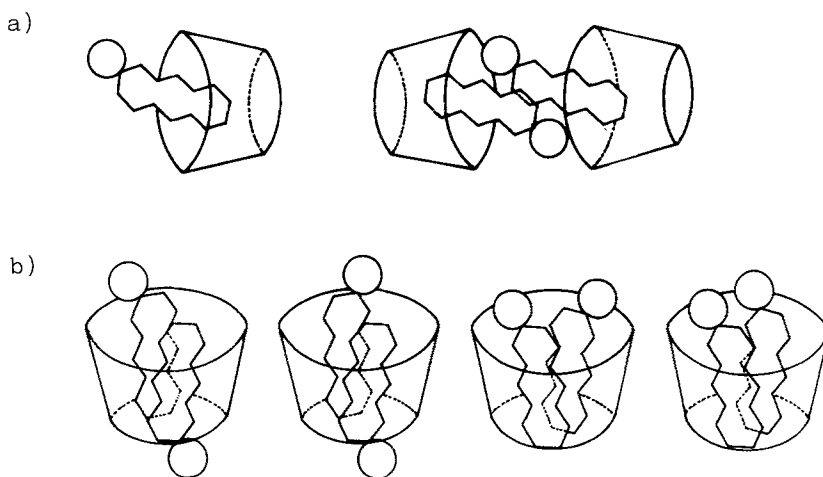Fig. 6. The model of the inclusion complexes of a) β-CyD and b) γ-CyD with 2AS or 2AC.

The models of the inclusion complexes of β- and γ-CyDs with 2AS or 2AC are shown in Fig. 6a and 6b, respectively. From the results of photo-dimerization, it is likely that four possible configurations of the guest molecules must exist in the inclusion complex with γ-CyD. The C_2 molecular symmetry of the guest configuration with R-helicity is responsible for the Davidov splitting of the i.c.d. spectrum observed. The 1 : 1 inclusion complex of β- or γ-CyD, which is important at low concentrations, may take a configuration in which the aromatic nucleus is in the hydrophobic CyD cavity, leaving the sulfonate group in an outer aqueous phase. The 2 : 2 inclusion complex of β-CyD may be formed by the head-to-head association of two β-CyDs to include two guest molecules in the cylindrical cavity. The distance of two aromatic nuclei included by β-CyD may be comparable with that (∿ 3.5 Å) of the excimer (19), but larger than that of the sandwich dimer in γ-CyD.

References

(1) A. Ueno, K. Takahashi, and T. Osa, J. Chem. Soc., Chem. Commun., 1980, 921.

(2) J. Emert, D. Kodali, and R. Catena, J. Chem. Soc., Chem. Commun., 1981, 758.

(3) H. Hirai, N. Toshima, and S. Uenoyama, Polymer J., 13, 607 (1981).

(4) K. Kano, I. Takenoshita, and T. Ogawa, Chem, Lett., 1982, 321.

(5) A. Harada and S. Nozakura, Polymer Bulletin, 8, 141 (1982).

(6) T. Yorozu, M. Hoshino, and M. Imamura, J. Phys. Chem., 86, 4426 (1982).

(7) K. Takamura, S. Inoue, and F. Kusu, Chem. Lett., 1983, 233.

(8) K. Kano, I. Takenoshita, and T. Ogawa, Chem. Lett., 1980, 1035; J. Phys. Chem., 86, 1833 (1982).

(9) A. Ueno, K. Takahashi, Y. Hino, and T. Osa, J. Chem. Soc., Chem. Commun., 1981, 194.

(10) N. Kobayashi, A. Ueno, and T. Osa, J. Chem. Soc., Chem. Commun., 1981, 340.

(11) H. Kobashi, M. Takahashi, Y. Muramatsu, and T. Morita, Bull. Chem. Soc. Jpn., 54, 2815 (1981).

(12) H. Takeshita, M. Kumamoto, and I. Kouno, Bull. Chem. Soc. Jpn., 53, 1006 (1980).

(13) G. S. Cox, N. J. Turro, N. C. Yang, and M. Chen, J. Am. Chem. Soc., 106, 422 (1984).

(14) S. Hamai, Bull. Chem. Soc. Jpn., 55, 2721 (1982).

(15) D. C. Rideout and R. Breslow, J. Am. Chem. Soc., 102, 7816 (1980).

(16) T. Tamaki, Chem. Lett., 1984, 53.

(17) J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley-Inter-science, London (1970).

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

(19) T. Hayashi, N. Mataga, Y. Sakata, S. Misumi, M. Morita, and J. Tanaka J. Am. Chem. Soc., 98, 5910 (1976).