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The Inclusion Effects of Cyclodextrins on the Photolysis of *p*-Benzoquinone in Aqueous Solution

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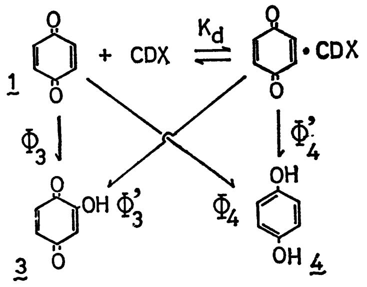
Synopsis. The additive effects of cyclodextrins on the photolysis of *p*-benzoquinone in water were investigated spectrophotometrically. By applying Michaelis-Menten keinetics, the dissociation constant of the inclusion complex was determined. The quantum yield for the formation of hydroquinone from the complex increased, while that of 2-hydroxy-1,4-benzoquinone decreased.

The cyclodextrin inclusion effects are known as a good enzymatic action model and many reports on their catalytic activities have been published.1) Cyclodextrins associate with a variety of organic substances in aqueous solution. This complexation leads to their catalytic selectivity. In the previous papers, we reported the photochemical reaction control by cyclodextrins.2) In this note, we wish to report the effects of cyclodextrins on the photolysis of *p*-benzoquinone in aqueous solution and to show that the addition of water to *p*-benzoquinone must be inhibited.

Recently several investigations of the photolysis of quinones in an aqueous solution have been reported. In the photolysis of *p*-benzoquinone (**1**) in aqueous solution, hydroquinone (**4**) has been isolated as the sole stable product in addition to the transient formation of 1,2,4-benzenetriol (**2**) and 2-hydroxy-1,4-benzoquinone (**3**)3). Kurein and Robins4) suggested in their spectrophotometric study that the primary photochemical process of this photolysis was the conversion of **1** into **2**. According to their report, **3** and **4** are formed by dark reaction between **1** and **2**, and the result is the approximately equal quantity of **3** and **4**. Kano and Matsuo5) tried this photolysis of **1** in the presence of the surfactants. The quantum yield for the disappearance of **1** was accelerated by the addition of the anionic surfactant, but was suppressed by the cationic one. Shirai and Tanaka6) suggested an electrophilic attack of the excited **1** on water.

α-Cyclodextrin (α-CDX) and β-cyclodextrin (β-CDX) were used in this work. CDX was dissolved in an aqueous solution of **1**. CDX has little absorption above 230 nm and no spectral change was observed within experimental errors after the addition of CDX. After irradiation with 254 nm light, the reacted solution was quickly converted to acidic (because **3** is not stable in the neutral pH range), and the curve resolution was carried out to determine the yield conversions of **3** and **4**. In the absence of CDX, oxidation of the reacted solution by $Ce(SO_4)_2$, the same method used by Robins, showed that products were about equal quantity of **3** and **4**, and also the curve resolution showed the same value. Scheme 1 shows the processes of the CDX catalyzed photolysis of **1**. Here, we assumed that **1** and CDX would make a 1 : 1 complex. In this scheme, K_d represents the dissociation constant of the inclusion complex, Φ_3 and Φ_4, the quantum yield for the formation of **3** and **4** from **1**, respectively, and Φ'_3 and Φ'_4, the quantum yield for the formation of **3** and **4** from the inclusion complex, respectively. The modified form of Michaelis-Menten's equation7) was applied to this system. The equation was modified by using the quantum yield instead of the first order rate constant8). This equation was used separately for the formation of **3** and **4**. The following equations were used in our calculations.



Scheme 1. The mechanism of CDX catalyzed photolysis of **1**.

$$(1-\Phi_{obs}/\Phi_3)^{-1} = (1-\Phi_3'/\Phi_3)^{-1} + K_d(1-\Phi_3'/\Phi_3)^{-1}[CDX]^{-1} \quad (1)$$

$$(\Phi_{obs}/\Phi_4-1)^{-1} = (\Phi_4'/\Phi_4-1)^{-1} + K_d(\Phi_4'/\Phi_4-1)^{-1}[CDX]^{-1} \quad (2)$$

In these equations, Φ_{obs} represents the observed quantum yields for the formation of **3** and **4** when CDX was added. Figure 1 shows the plots of the modified form of Michalis-Menten's equation in the case where α-CDX was added. The plots obtained from Eqs. 1 and 2 were strictly linear and these two lines were coincident. This means that the quantum yield for the formation of **3** from the inclusion complex decreases,

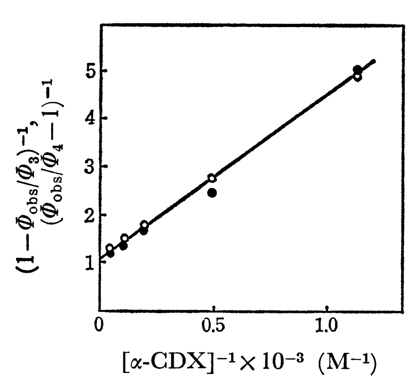


Fig. 1. The plots of Michaelis-Menten's equation.
—○—: Plots for **3** calculated from Eq. 1.
—●—: Plots for **4** calculated from Eq. 2.

Table 1. Values of the quantum yield ratios and the dissociation constants obtained from the modified form of Michaelis-Menten's equation

	α-CDX	β-CDX
Φ_3'/Φ_3	0.2 ± 0.1	0.1 ± 0.1
Φ_4'/Φ_4	1.9 ± 0.2	2.1 ± 0.4
$K_d\times10^3$ (M)	2.1 ± 0.1 [a] 1.9 ± 0.2 [b]	2.0 ± 0.1 [a] 2.3 ± 0.6 [b]

a) Obtained from Eq. 1. b) Obtained from Eq. 2.

but on the other hand that of **4** increases. This was also true when β-CDX was added and the same linear relationship was obtained. Obtained values of Φ and K_d by Eqs. 1 and 2 are showed in Table 1. In Table 1 Φ'_3/Φ_3 is nearly zero while Φ'_4/Φ_4 is nearly two and K_d obtained from Eqs. 1 and 2 quite agree with each other, in both complexes.

Next, we examined the additive effects of α-methyl D(+)-glucoside (α-MG) and poly(vinyl alcohol) (PVA, $n=500$). α-MG has only one glucopyranose unit which is contained in CDX. PVA has a helix structure and was reported to make an inclusion complex with iodine[9]. Both α-MG and PVA showed the same tendency as CDX. But this tendency is very weak for α-MG. From the above results, we conclude that CDX makes the 1 : 1 inclusion complex with **1** in aqueous solution and conformationally inhibits the addition of water to **1**, and probably the excited **1** will abstract hydrogen from CDX.

Experimental

The light source used in this work is USHIO ULO-6DQ 6 watt low pressure mercury lamp. For the counting of the photons irradiated, potassium ferrioxalate actinometry was used. Irradiations were carried out in the spectrophotometric cell (width 1 cm) according to the method proposed by Parker[10]. The light intensity at 254 nm measured in our irradiation system is $(3.54+0.57)\times10^{17}$ quanta/s·l. three ml of arerobic solution of **1** was pipeted in the spectrophotometric cell (4.4×10^{-5} M), and after the irradiation for constant time 1 ml of 2M-H_2SO_4 solution was added to the reacted solution, and UV spectrum was measured. The curve resolution was carried out at 246 nm and 256 nm to determine the yield conversions of **3** (λ_{max} 256 nm, ε 13700, ε at 246 nm is 11100) and **4** (λ_{max} 289 nm, ε at 246 nm is 180, and ε at 256 nm is 190). To ensure this curve resolution, parrallel experiment, oxidation of the reacted solution by $Ce(SO_4)_2$ was carried out. **2** is converted into **3**, and **4** is converted into **1** quantitatively by $Ce(SO_4)_2$. This oxidation gave nearly same values of conversion which obtained by the curve resolution. CDX did not disturb this oxidation. After the complete photolysis (40 min irradiation), both the curve resolution and oxidation of the reacted solution suggested that the products were about equal quantity of **3** and **4**. The quantum yield for dissaperance of **1** is 0.44 ± 0.09, and for appearance of **3** and **4** is *ca.* 0.22 without CDX.

References

1) D. W. Griffiths and M. L. Bender, *Adv. Catal.*, **23**, 209 (1973).

2) K. Yamada, J. Morimoto, and H. Iida, *J. Fac. Eng. Chiba Univ.*, **24**, 71 (1973); *ibid.*, **26**, 85 (1975).

3) S. Hashimoto, K. Kano, and H. Okamoto, *Bull. Chem. Soc. Jpn.*, **45**, 966 (1972).

4) K. C. Kurien and P. A. Robins, *J. Chem. Soc., B*, **1970**, 855.

5) K. Kano and T. Matsuo, *Chem. Lett.*, **1973**, 1127.

6) M. Shirai, T. Awatsuji, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 1329 (1975).

7) H. Lineweaver, and D. Burk, *J. Am. Chem. Soc.*, **56**, 658 (1934).

8) The modified form of Michaelis-Mentens equation.

$$\begin{tikzcd} \mathrm{S} + \mathrm{C} \arrow[r, shift left] \arrow[d, "k_1"'] & \mathrm{S\cdot C} \arrow[l, shift left, "K_d"] \arrow[r, "k_2"'] & \text{Products} \\ \text{Products} \end{tikzcd}$$

S, substrate C, CDX

The modified form of Michaelis-Mentens' equation was showed by the following form. See Refs. 1 and 7.

$$(k_{obs}-k_1)^{-1} = (k_2-k_1)^{-1} + K_d(k_2-k_1)^{-1}\,\mathrm{C}^{-1} \tag{3}$$

k_1, the uncatalyzed first order rate constants

k_2, the catalyzed first order rate constants

We can show the quantum yield by the next equation. Here, we assume that the products effect little on the absorption of photons by substrate at the irradiating wavelength.

$$\Phi = \frac{C_0\cdot V\cdot \Delta x\cdot N_A}{\int_t^{t+\Delta t} N_{pabs}\cdot V\cdot(1-x)\,dt} \tag{4}$$

C_0, the initial concentration of the substrate

V, the volume of the solution

x, the conversion of the substrate at the reaction time "t"

$x+\Delta x$, the conversion of the substrate at the reaction time "$t+\Delta t$"

N_A, Avogadro number

N_{pabs}, the number of photons absorbed at the initial concentration

Next, we assume that this photochemical reaction proceeds according to the first order rate law, following equation will be applied.

$$\ln\frac{1}{1-x} = kt \tag{5}$$

k, the first order rate constant

From Eqs. 4 and 5 we get the very simple relation between the quantum yield and the first order rate constant.

$$\Phi = \frac{C_0\cdot N_A\cdot k}{N_{pabs}} \tag{6}$$

From Eqs. 3 and 6, we obtain the Eqs. 1 and 2.

9) M. M. Zwick, *J. Appl. Polym. Sci.*, **9**, 2392 (1965).

10) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., A*, **235**, 518 (1956).