Kinetic Behaviors of Solubilization of C_{60} into Water by Complexation with γ-Cyclodextrin

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Kinetic behavior of complexation of C_{60} with γ-cyclodextrin and its derivative in an aqueous solution at 50 °C was investigated. Effective solubilization of C_{60} into water, which shows first order dependency on the concentration of unsubstituted γ-cyclodextrin under present conditions, is observed. However, γ-cyclodextrin having an ammonium cation moiety on the primary site shows no sign of extraction of C_{60}.

Since C_{60} has been identified as an isolated molecule in 1990, chemistry of C_{60} and related fullerenes has been attracting much attention of many chemists over a wide range of chemical fields.[1] One of the interesting subjects of fullerene chemistry is their biochemical applications which were based on their unique shapes.[2] Recently several groups are interested in complex formation of C_{60} with γ-cyclodextrin (γ-CD) in an aqueous solution as a model system for fullerene recognition.[3] The structure of the most stable complex is expected to be a 1 : 2 adduct of C_{60} and γ-CD, in which both γ-CD's interact with C_{60} at their secondary hydroxyl (C_2- and C_3-OH of glucose) sides. Although existence of a 1 : 1 complex, which may be transformed into the 1 : 2 complex in the presence of excess amount of γ-CD, is also suggested,[3b] the detailed mechanism of the solubilization process for C_{60} is still unclear. We report here the kinetic behavior of direct solubilization of solid C_{60} with γ-CD in an aqueous phase.

The rates of solubilization of solid C_{60} in the presence of various concentrations of γ-CD at 50°C were followed by increase of absorption intensity at 260 nm of C_{60} (Figure 1a).[4] The spectrum obtained was essentially identical with that of the reported 1 : 2 complex and practically all of C_{60} used was quantitatively solubilized at the final point judging from the reported molar absorptivity of the complex. Absorption change at 260 nm observed under present conditions followed the first order kinetics as shown in Figure 1b. The first order rate constants thus obtained at various concentrations of γ-CD were summarized in Figure 2. It should be noted that the rate constants showed first order dependency on the γ-CD concentration within experimental errors. The results indicate that the rate determining step of the present complex formation is a 1 : 1 complex formation step followed by the fast process of 1 : 2 complex formation (Scheme 1).

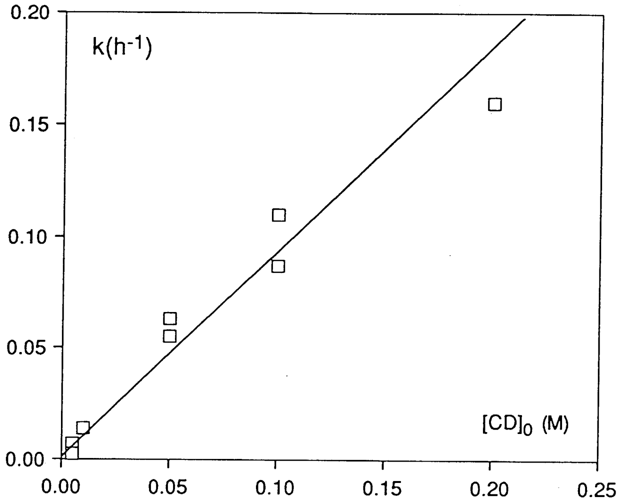


Figure 2. Plot of observed first order rate constant vs. concentration of γ-CD. All rate constants were obtained under following conditions , $[C_{60}]$ = 2.1 mM, at 50 °C in H_2O.

Finally, in order to prepare a more hydrophilic complex of C_{60} with cyclodextrins, we examined also 6-trimethylammonium-6-deoxy-γ-cyclodextrin chloride (γ-CDN^+) as a host molecule. This new host, however, showed no sign of extraction of C_{60}

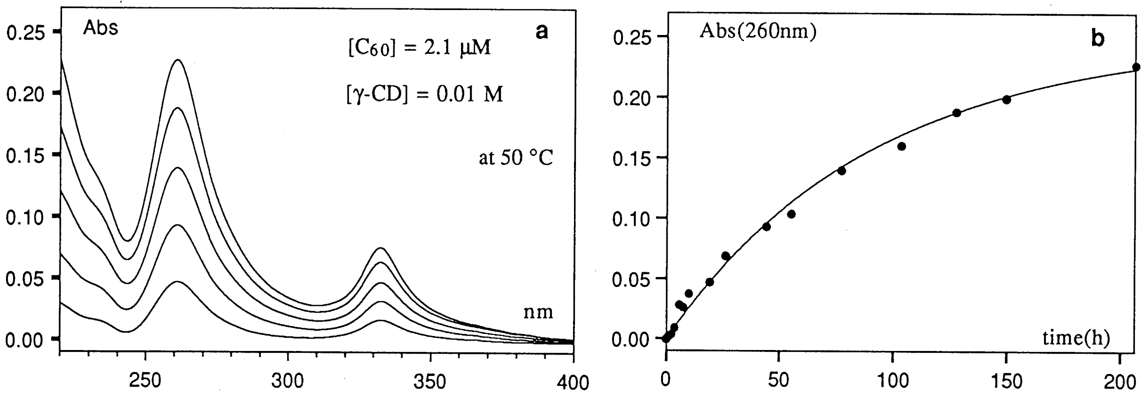
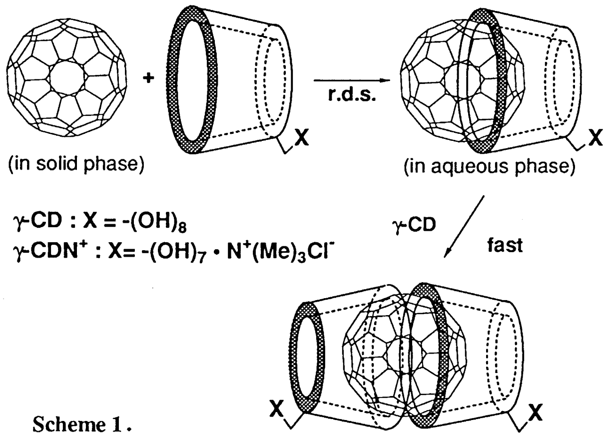


Figure 1. a) Absorption spectra obtained at 19.3, 44.3, 77.3, 127.3 and 206.5 h. after mixing. b) Plot of absorvance at 260 nm vs. time. The theoretical curve for first order kinetics is calculated by using k = 0.0107 h^{-1}.



Scheme 1.

and any spectroscopic change was not observed in the presence of 0.01 M of γ-CDN^+ even after 116 hr.[5] Since γ-CD's are expected to contact with C_{60} at their secondary sites, complete inhibition of complex formation due to modification at the primary site of γ-CD is unexpected. There may be following two possible reasons for this interesting result, i.e., a) too hydrophilic nature of γ-CDN^+ kinetically retards the rate determining adsorption on C_{60} in the solid phase to form 1 : 1 complex, b) the cationic charge on γ-CD thermodynamically destabilizes electronic interactions with C_{60} such as the charge transfer suggested by Yoshida, et al.[3c] Although it is not clear at the present stage whether complex formation between C_{60} and γ-CDN^+ is prevented kinetically or thermodynamically, the results reported here indicate a unique feature of highly specific recognition of C_{60} with cyclodextrins.

References and Notes

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4 The typical experimental procedure is as follows. A solution of C_{60} in hexane (21 µM, 0.65 mL) was carefully evaporated in a 1 cm quartz cell under nitrogen. After addition of 6.5 mL of an aqueous solution containing necessary amount of γ-CD, the cell was sealded and maintained at 50 °C in a thermostated bath. During the experiment, the solution was gently stirred with a magnetic stirring bar (300 rpm) and the electronic spectra of the resultant solution at appropriate time intervals were directly measured.

5 Preliminary attempt of preparation of the complex between C_{60} and γ-CDN^+ by the direct kneading method reported in the ref. 3b showed very weak complex formation between this host-guest pair. The efficiency, however, is estimated to be less than 1/100 of that for the γ-CD-C_{60} pair.