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NMR Observation of Inclusion Complex between C60 and cyclodextrin

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It was found by the NMR analyses that C60 forms inclusion complex with γ–CD in aqueous solution at high temperatures and does not form the complex with α–CD and β–CD. The ^{1}H NMR spectral analyses indicate that in the complex, C60 molecule intrudes into the hydrophobic cavity of γ–CD.

Introduction

Recently, fullerenes have many interests in organic chemistry and material sciences[1]. It is well known that fullerene is insoluble in water, because it is composed of only carbon atoms and is a non-polar molecule. On the other hand, cyclodextrins (hereafter abbreviated as CD) are soluble in water, and form various kinds of complexes with many non-polar molecules. Therefore, it is expected that fullerene can be soluble in water by forming a complex with cyclodextrin.

In this paper, we report the results of the analyses of the complex of fullerene with cyclodextrins by NMR spectroscopy.

Experimental

Fullerene used in this study was C60 commercially available from Science Laboratories Co. (The purity is 99.5%). It is pure in ^{1}H NMR spectral level.

^{1}H and ^{13}C NMR spectra were measured with a JEOL α–500 NMR spectrometer (499.45 MHz for ^{1}H nucleus and 120.22 MHz for ^{13}C nucleus) with the data point of 65536.

In the NMR measurements, 5 mg of C60 and 15 mg of cyclodextrin were added to 0.5 ml D_2O solution in 5 mm sample tube, but only very small portion of C60 seemed to be soluble. The measurements were done in the heterogeneous states.

Results and Discussion

^{1}H NMR spectrum of the sample of the mixture of γ–cyclodextrin and C60 at room temperature (24.0 °C) is almost same as that of γ–CD only. However, it was found that, after heating the mixture at 95 °C during one

Table 1. ^{1}H NMR Chemical Shifts and Chemical Shift Differences of γ-CD and C60 Mixture at 95℃

Proton No.	δ(γ-CD)	δ(γ-CD+C60)	△δ(ppm)
1	5.112	5.111	-0.001
2	3.660	3.659	-0.001
3	3.920	3.918	-0.002
4	3.579	3.579	0.000
5	3.844	3.838	-0.006
6	3.857	3.857	0.000

hour, the spectral pattern of the mixture at the room temperature is a very little changed. Moreover, at 95 °C, the spectrum of the mixture changed considerably comparing with the spectrum of γ–CD only. In Table 1, ^{1}H NMR chemical shifts(δ) and chemical shift differences(δΔ) of γ–CD only and the mixture of CD and C60 at 95 °C are shown. The signals of H1, H2, H4, and H6 of the glucose ring in CD show no change (The experimental error in the ^{1}H NMR chemical shifts in this study is ±0.001 ppm). However, the chemical shift of H5 proton of the glucose ring in the cyclodextrin moves to some extent (0.006 ppm higher field shift) changing from CD only to the mixture of CD and C60, and the signal of H3 changes a little (0.002ppm).

In the case of α–CD and β–CD, the spectra of the mixture of C60 and CD after one hour heating at 95 °C are completely same as the spectra of the corresponding CD only (The chemical shift differences are within 0.001 in all protons.). Thus, it is obvious that the influence on the ^{1}H NMR chemical shifts by mixing C60 to the γ-CD solution is observed. However, it is relatively small effect.

Therefore, in order to recognize these interesting experimental results in ^{1}H NMR, ^{13}CNMR spectra were measured at various conditions. ^{13}C NMR chemical shifts of γ–CD only and the mixture of γ–CD and C60 (heating at 95 °C during one hour) are given in Table 2. The signals of C1, C2, C3, and C5 of γ–CD move to the higher field by adding C60 to CD, but that of C6 moves to the lower field. The signal of C4 is unchanged. In the cases of α–CD and β–CD, the chemical shift changes were negligibly small by heating the mixture with C60 at 95 °C during one hour (The chemical shift differences are within 0.01 ppm.). These interesting chemical shift changes found only in the mixture of γ–CD and C60

Table 2. ^{13}C NMR Chemical Shifts and Chemical Shift Differences of γ-CD and C60 Mixture at 95℃

Carbon No.	δ(γ-CD)	δ(γ-CD+C60)	△δ(ppm)
1	104.28	104.18	-0.10
2	75.73	75.69	-0.04
3	75.16	75.08	-0.08
4	83.19	83.20	+0.01
5	74.79	74.68	-0.11
6	63.04	63.14	+0.10

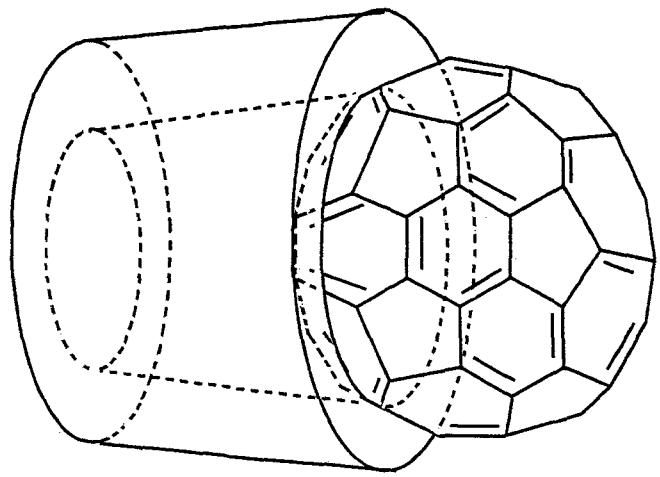
indicate the formation between γ–CD and C60 molecules.

Concerning the ^{13}C NMR spectrum of C60 molecule, ^{13}C signal could not be detected in a number of accumulation in the sample of C60 and D_2O, even after 120 hours heating at 100 °C, probably because of the insolubility of C60 in water.

Unfortunately, ^{13}C NMR signal of C60 in the mixture in water at 95 °C could not be detected, despite of many tries in the measurements with longer pulse delay time. The reason of non-detection of ^{13}C NMR signal of C60 of the complex may be a very small portion of the complex in the NMR sample tube after one or several hours heating.

These interesting chemical shift changes by mixing the C60 to γ-CD aqueous solution, found in ^{1}H and ^{13}C NMR spectra of cyclodextrin, can be reasonably explained by considering the complex formation between C60 and cyclodextrin. The obtained chemical shift defferences(δΔ) between the mixture and the CD only are relatively small as shown in Table 1 and 2. This is due to the NMR observation of the equilibrium system among the complex and free C60 and large excess of γ-CD.

Concerning the complex between C60 and CD, Andersson et. al. reported the results of UV-VIS spectra and computer calculations[2]. However, the detailed steric structure of the complex seems not completely clear. Our NMR results clearly indicate the formation of the complex between C60 and γ–CD. It is already known that hydrogen atoms at 5 and 3 positions of the glucose ring of CD are in the inner hydrophobic space of CD ring[3]. The diameter of the cavity of γ–CD ring is 10Å On the other hand, it was reported [4] that the largeness of C60 molecule is 10Å. Therefore, it is reasonable to consider that



C60 molecule intrudes into the cavity of γ–cyclodextrin. However, the diameters of the inner cavities of α–CD and β–CD are 6Å and 8Å, respectively, and are too small to form the inclusion complex with C60.

These facts obtained in this NMR work indicate that C60 is insoluble in water even after heating at high temperature during long hours, but that it becomes soluble in water to some extent by forming the inclusion complex with γ-CD molecule.

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