2B2s

Deuteration Effects on the Gibbs Free Energy Changes in Guest Encapsulation Reactions

Importance of the Change of the Methyl Internal Rotational Barrier of Guest Molecule

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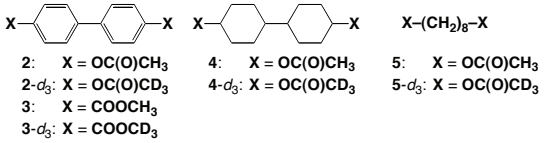
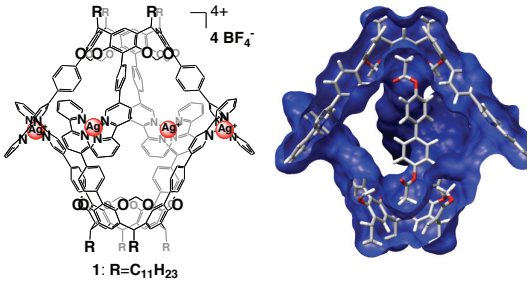
The self-assembled cage **1**•4BF_4 is known to encapsulate a variety of guest molecules and heterodimeric hydrogen-bonded pair of carboxylic acids [1]. 4,4'-Diacetoxybiphenyl, for example, is encapsulated in the confined space of **1** as shown in Figure 1. The guest is positioned along the C_4 symmetry axis of the cage, and its tumbling and free rotation are constrained due to the steric requirements of the aromatic walls. The guest is positioned along the C_4 symmetry axis of the cage, and its tumbling and free rotation are constrained due to the steric requirements of the aromatic walls. Both of the methyl groups of **2** are placed near the resorcinarene ends of the cage, creating the close contacts responsible for effective CH/π interaction. For the guest molecules shown below, the deuteration effects of the equilibrium constants and their temperature dependence were studied [2] with the competition experiments. By plotting the ratio $log(K_D/K_H)$ against the inverse of temperature $1/T$, which is called the van't Hoff plot, the change caused by the deuteration for the Gibbs free energy changes, $\Delta\Delta G_{D\text{-}H}$, in the encapsulation equilibrium were directly determined. The slop and the intercept of the plot correspond to $-\Delta\Delta H_{D\text{-}H}$ and $\Delta\Delta S_{D\text{-}H}$, respectively, if they were temperature- independent. The determined slope $-\Delta\Delta H_{D\text{-}H}^{vant'Hoff}$ ranged from 1.9 to 3.6 *kJ/mol* for guests **2** – **5**. It implies that the deuterated guest is more strongly bound inside of the capsule. The intercept also significantly differed from zero. Because the experiments were carried out at T= 250~300*K*, the low frequency motions involving the methyl groups are responsible for the observed changes. The first candidate of the motion is the methyl internal rotation. As is shown in Figure 2, a CD_3 guest molecule can be more populated at the lower quantum levels than the corresponding CH_3 guest. Figure 3 is the plot $-\{\Delta G^{ir}{}_D(V,T) - \Delta G^{ir}{}_H(V,T)\}/(RT)$, in which ΔG^{ir} is evaluated from the quantum levels, such as in Fig. 2, for various barrier height V. Outside of the capsule, V of the methyl may be nearly zero, it implies no changes in ΔG^{ir} (see the lowest line for V=5). Once the guest is inside of the capsule, because of CH/π interaction, V increases, and thus the slop becomes 1.1*kJ/mol* for V=41*kJ/mol*.



[1]Haino, Kobayashi, Fukazawa, Chem. Eur. J, 2006,12, 3310 [2]Haino, Fukuta,Iwata, Iwamoto, in preparation.

Figure 1. Drawing of Self-assembled cage **1**•4BF_4 (left) and a calculated structure of the encapsulated complex of 4,4'-diacetoxybiphenyl **2** in the cage **1** (right)



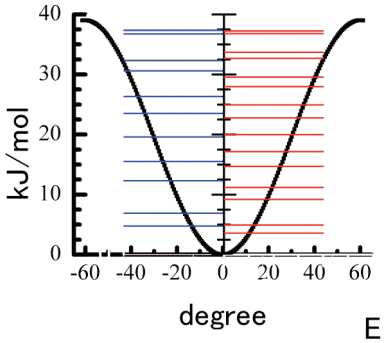


Figure 2. The energy diagrams of the methyl rotor for CD_3(red, right) and CH_3(blue, left). V=41kJ/mol.

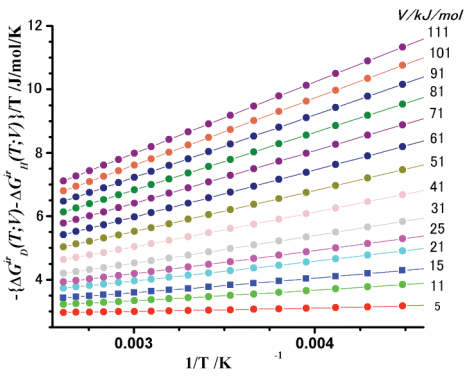


Figure 3. The plots of $-\{\Delta G^{ir}{}_D(V,T) - \Delta G^{ir}{}_D(V,T)\}/(RT)$ for various V.