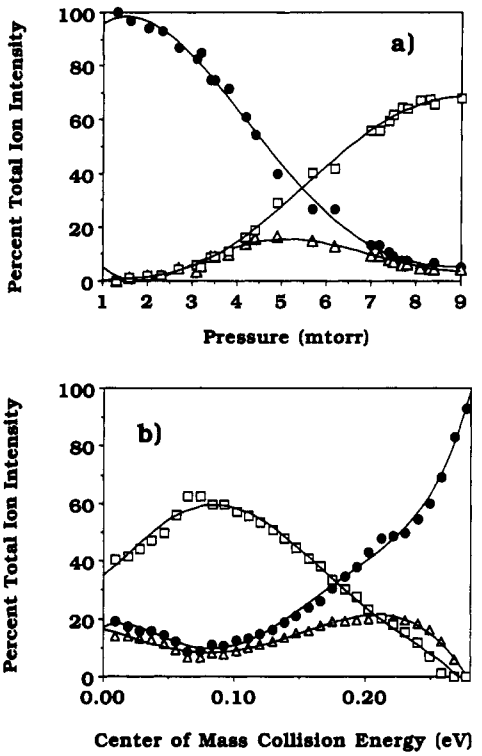

Figure 2. The key to the symbols used in this figure is as follows: ●, C_{60}^{2+}; △, $C_{60}NH_2^+$; □, $C_{60}NH_2(NH_3)_2^+$. (a) Percent total ion intensity of product ions produced from C_{60}^{2+} + NH_3 reactions as a function of ammonia pressure in the target cell. The collision energy E_{LaB} is 2.0 eV. (b) Percent total ion intensity of product ions produced from C_{60}^{2+} + NH_3 reactions as a function of collision energy.[26] The pressure of ammonia in the collision cell is 7.3 mTorr.

Table I. Ionization Energies for Molecules Used in This Study

molecule	IE (eV)	molecule	IE (eV)
NH_3	10.2[a]	N_2	15.6[a]
O_2	12.0[a]	Ar	15.7[c]
C_{60}^+	>12.0[b]	He	24.6[c]
CH_4	12.6[a]		

[a] Reference 15. [b] Reference 17. [c] Reference 25.

ization of the $C_{60}O$ species as an epoxide,[9] we feel that the $C_{60}NH_2^+$ species corresponds to the formation of a protonated aziridine whose structure is shown as an inset in Figure 1.

For both the amine and aziridine structures, the two projecting hydrogens from $C_{60}NH_2^+$ should be highly susceptible to hydrogen bonding, therefore favoring a doubly coordinated species. Indeed we do observe the preference for the formation of $C_{60}NH_2(NH_3)_2^+$ at high ammonia pressures. Further support for this effect comes from the collision energy regime required for removal of the two bound NH_3 molecules. The collision energy dependence for the production of $C_{60}NH_2^+$ appears to be quite distinct from that for the production of $C_{60}NH_2^+\{NH_3\}_{1-3}$ ions (Figure 2b), suggesting that the NH_3's are indeed more weakly associated than the NH_2.

The reactivity of ammonia with C_{60}^{2+} correlates with the low ionization energies (IEs) of this molecule,[15] as shown in Table I. The IEs for C_{60} and C_{60}^+ are 7.6 eV[16] and >12.0 eV,[17] respectively. One would expect that a charge-transfer reaction will only occur if the IE of the target molecule is below the second IF and C_{60}, as illustrated in reaction 5. While the recombination

$$C_{60}^{2+} + M \rightleftarrows \{C_{60}^+ - M^+\} \qquad IE(M) < 12.0 \text{ eV} \qquad (5)$$

energy is sufficient to ionize ammonia, other gases having a larger IE should not react with C_{60}^{2+}. Indeed, we have found that the passage of C_{60}^{2+} through such gases (He, Ar, N_2, and CH_4) at low collision energy exhibits no reactivity. However, passage through oxygen does exhibit reactivity, which we will report in a later paper.

In conclusion, we have observed an associative charge exchange reaction for C_{60}^{2+} with ammonia which does not occur for C_{60}^+ under identical experimental conditions. We believe that this is indicative of a new family of charge-exchange reactions for C_{60}^{2+} which will occur for any molecule whose IE lies below the IE of C_{60}^+. This line of reasoning suggests that the inertness of C_{60}^+ is due to the relatively low IE of C_{60}, which prevents direct charge-transfer reactions from occurring.[23,24] Our work also suggests that C_{60}^+ may undergo similar charge-exchange reactions with molecules whose IE lies below 7.6 eV. We are now in the process of examining this as well as gas-phase chemistry for other C_n^{m+} ions.

Acknowledgment. We gratefully acknowledge the financial support of this work by the Office of Naval Research and the Alfred P. Sloan Foundation. We also acknowledge the assistance of Prof. Jiali Gao in generating the proposed structure of $C_{60}NH_2^+$.

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A Novel Host Containing Both Binding Site and Nucleophile Prepared by Attachment of β-Cyclodextrin to Poly(ethylenimine)

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Enzymatic catalysis is characterized by complex formation with substrates and very fast chemical conversion within the complexes. Many attempts have been made to design artificial enzymes capable of both complexation and catalysis. Both poly(ethylenimine) (PEI)[1-3] and cyclodextrin (CD)[4-6] derivatives have been extensively exploited in the design of biomimetic catalysts. Several functional groups were attached to PEI, and hydrophobic microenvironments were created on PEI by alkylation or acylation of the nitrogen

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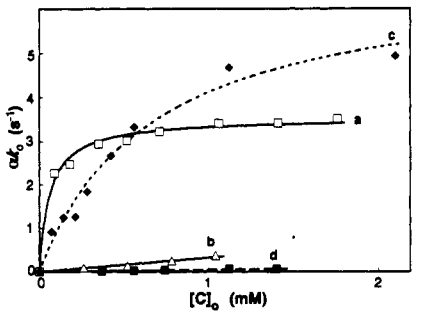
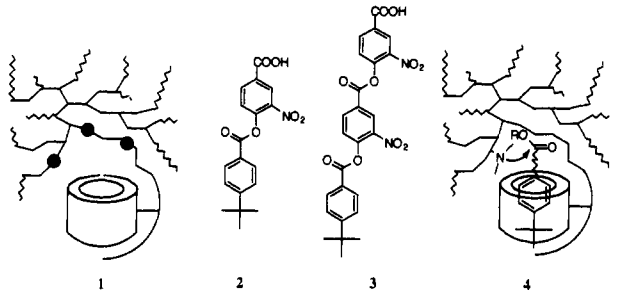


Figure 1. Plot of the pseudo-first-order rate constant against $[C]_0$ for deacylation of **2** (α = 1000) by CD-PEI (a) or PEI (b) and of **3** (α = 100) by CD-PEI (c) or PEI (d). Different α values were used for **2** and **3** in order to put their kinetic data on the same graphical scale. $[C]_0$ represents the total concentration of CD moiety of CD-PEI or CD. $[C]_0$ for PEI is taken as 1.4% of the residue molar concentration of PEI, so that it corresponds to the concentration of PEI moiety of CD-PEI. For b and d, k_0 is proportional to $[C]_0$. When $[C]_0$ = 0.3 mM, deacylation of **2** by CD-PEI was 30 or 600 times faster than that by PEI or CD, respectively. When $[C]_0$ = 0.6 mM, deacylation of **3** by CD-PEI was 160 or 900 times faster than that by PEI or CD, respectively.

atoms of PEI. Although several PEI derivatives manifest catalytic activity in various organic reactions, creation of specific binding sites on PEI is needed in order to mimic enzymes better. Many derivatives of CD have been prepared as enzyme mimics. Since CD is much smaller than enzymes, introduction of several catalytic groups on CD in positions suitable for high catalytic efficiency is not easy. Combination of PEI with CD may lead to a cavity-containing molecular skeleton suitable for incorporation of multiple catalytic elements. This is schematically illustrated in **1** where filled circles indicate possible catalytic functional groups.



In the present study, β-CD was covalently linked to PEI by the reaction of PEI (0.55 monomeric residue mol) with mono-6-(*p*-tolylsulfonyl)-β-CD (7.7 mmol) in 200 mL of DMSO at 60 °C for 6 h followed by purification through dialysis, leading to a β-CD-containing PEI (CD-PEI). The content of CD in CD-PEI was estimated as 1.3% of the monomeric residues of PEI on the basis of initial burst kinetic studies (see below) and as 1.6% on the basis of elemental analysis. On the average, a PEI (MW 60000) molecule contains 1400 monomeric residues, and therefore, CD-PEI contains 18-22 CDs.

Kinetics of the deacylation of esters **2** and **3** was studied in the presence of CD, PEI, or CD-PEI with $[C]_0 > [S]_0$ ($[C]_0$ is the initially added concentration of hosts and $[S]_0$ that of **2** or **3**; $[S]_0$ was ca. 5×10^{-5} M). Rate measurements were performed at pH 7.65 (0.5 M NaCl and 0.02 M phosphate buffer) and 25 °C in the presence of 1% (v/v) acetonitrile (used as the solvent for the stock solutions of **2** and **3**). Kinetic data are illustrated in Figure 1. Analysis of the saturation kinetic data of CD-PEI led to $k_{cat} = (3.53 \pm 0.08) \times 10^{-3}$ s^{-1} and $K_m = (6.00 \pm 0.88) \times 10^{-5}$ M for **2** and $k_{cat} = (6.81 \pm 0.58) \times 10^{-2}$ s^{-1} and $K_m = (6.52 \pm 1.24) \times 10^{-4}$ M for **3**. It appears that **2** is bound by CD-PEI more strongly than **3** and the carboxylate of **2** provides an extra binding interaction with the ammonium ion of CD-PEI.

The kinetics of deacylation of **2** or **3** was also examined in the presence of CD-PEI with $[C]_0 < [S]_0$. Biphasic kinetics was observed, and the amount of the phenol released during the initial burst stage corresponded to the amount of CD, indicating that acylation of the nucleophilic amine by the substrate inactivates CD-PEI. It is possible that the *tert*-butylbenzoyl group of the acylated polymer occupies the CD cavity.[7]

The efficient binding of **2** and **3** by CD-PEI, in contrast to the weak binding by PEI as reflected by the linear rate data of Figure 1, is achieved by the interaction of the *tert*-butylphenyl ring of the substrate with the CD ring. The greater reactivity of CD-PEI compared with PEI is due to efficient complexation of the esters by CD-PEI and effective nucleophilic attack within the complexes. The much faster rate of CD-PEI compared with CD indicates that the amino groups present on the PEI portion, instead of the hydroxyl group on the CD rim, act as the nucleophile (**4**). The amino groups on the PEI backbone may have better access to the ester linkage of the bound substrate.[8,9]

CD-PEI may be regarded as either a derivative of CD with a convergent nucleophile located above the CD cavity or a PEI derivative containing specific binding sites. The next step toward obtaining better artificial enzymes containing both PEI and CD is to introduce a second catalytic functional group in a planned position near the CD cavity.

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Registry No. Mono-6-(*p*-tolylsulfonyl)-β-CD, 67217-55-4.

(7) HPLC analysis of reaction products indicated that only 1 equiv of 4-carboxy-2-nitrophenol and no *tert*-butylbenzoate is released after deacylation of both **2** and **3** by CD-PEI.

(8) The k_{cat} value for CD-PEI-promoted deacylation of **3** is 19 times greater than that of **2**, whereas **3** is more reactive toward PEI than is **2** by only 40%. It is not clear which of the two ester groups of **3** is initially attacked by the amine of CD-PEI, although the greater k_{cat} for **3** compared with **2** indicates more effective attack at **3**.

(9) The average pK_a of the primary amine of PEI was reported to be 9.5, which is considerably smaller than that (10.6) of methylamine.[10] This may be attributed to the unfavorable electrostatic interactions among ammonium cations of the polymer, resulting in suppression of additional protonation. The electrostatic effect becomes more significant as more amines of PEI are protonated at lower pHs. For example, the amount of unprotonated amine was reduced by only 2 times when the pH was lowered from 8.5 to 7.5 in the case of PEI derivatives containing macrocyclic metal centers.[2] The fraction of the neutral amine at the pH (7.65) of the kinetic measurements, therefore, would be considerably greater than 1.4%, which is the value expected for a simple amine with the same pK_a value.

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Purification of Gram Quantities of C_{60}. A New Inexpensive and Facile Method

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Buckminsterfullerene (C_{60}), the newly discovered spherical allotrope of carbon, has precipitated a flurry of recent research endeavors.[1] A severe limitation to this research is the difficulty in producing gram quantities of C_{60} free of the higher molecular

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