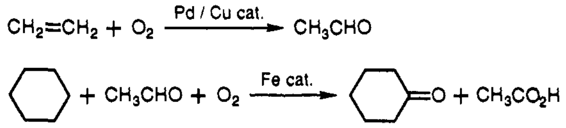
responding ketones and alcohols highly efficiently (entries 1–6). The oxidation of methylcyclohexane shows that the tertiary/secondary C–H bond selectivity on a per bond basis is 11 and that no oxidation occurs at the primary C–H bond. Poorly reactive linear alkanes also can be oxidized readily under the present reaction conditions (entry 7). Alkylated arenes are oxidized at the benzylic position selectively (entry 8). The aldehydes used are converted into the corresponding carboxylic acids.

In order to gain insight into the mechanism of the present oxidation of alkanes, the relative reaction rates of the iron-catalyzed oxidation of four substituted toluenes ($XC_6H_4CH_3$, X = *p*-CH_3, H, *p*-Cl, and *p*-NO_2) with molecular oxygen in the presence of heptanal in CH_2Cl_2 were determined by the GLC analysis of the oxygenated products. The rate data correlate well ($\gamma = 0.999$) with the Hammett linear free energy relationship with use of σ^+ values. The ρ value (−1.69) thus obtained is consistent with that observed for the oxidation of substituted toluenes by oxoiron porphyrin (−1.69).[7] The intramolecular deuterium isotope effect of the iron-catalyzed oxygenation of 1,1-dideuterio-1,3-diphenylpropane was determined to be 5.0 by GC–MS analysis of the product ketones. This value is smaller than that observed with cytochrome P-450 (11).[8] Furthermore, the intermolecular isotope effect of the oxygenation of cyclohexanes was determined to be 5.5 by GLC analysis of the oxygenated products obtained from the competitive reaction of cyclohexane and cyclohexane-d_{12}. The value 5.5 is quite similar to the value of 5.4[31] obtained for the oxidation with non-porphyrin oxoiron species. The observed intra- and intermolecular isotope effects indicate that C–H bond breaking is a crucial step. Intermediacy of alkyl radicals is supported by both these data and detection of cyclohexyl chloride from the oxidation of cyclohexane in CH_2Cl_2. Although it is premature to discuss the precise mechanism at the present stage, the reaction can be rationalized by assuming the following pathways. The reaction of aldehydes with molecular oxygen[9] in the presence of either ruthenium complexes or iron complexes derived from iron powder and acetic acid would give peracids,[10] which subsequently react with the metal complexes to afford oxometal species[5,6,11] along with carboxylic acids. Hydrogen abstraction of alkanes with oxometal species, followed by hydroxy ligand transfer to the resulting radical, would give alcohols. Alcohols can be converted into ketones under the same reaction conditions. Iron- and ruthenium-catalyzed oxidations of alkenes under the same reaction conditions give epoxides selectively,[12] indicating the presence of oxometal species. The oxidation of *cis*-stilbene gives the corresponding epoxides nonstereospecifically (trans/cis = 83/17), indicating that the present epoxidation is not due to the reaction with peracids formed in situ. It is noteworthy that the present catalytic system is quite different from the Gif^{IV} system (Fe^{II} catalyst/O_2/Zn^0).[3f,4b,c] That is, tertiary/secondary C–H bond selectivity on a per bond basis for the oxidation of adamantane is 20 for our system and 0.25 for the Gif^{IV} system, and the ratio of cyclohexene oxide/(2-cyclohexen-1-one + 2-cyclohexen-1-ol) for the oxidation of cyclohexene is 95/5 for our system and 0 for the Gif^{IV} system.

Oxidative transformation of cyclohexane to cyclohexanone is of importance from an industrial point of view. Cobalt-catalyzed aerobic oxidation of cyclohexane has been used commercially; however, the total yield of cyclohexanone and cyclohexanol is quite low.[13] Our oxidation reaction provides a powerful industrial strategy for the synthesis of cyclohexanone by combination of Wacker oxidation of ethylene with the present iron-catalyzed oxidation of cyclohexane. Practically, the oxidation of cyclohexane can be performed without a solvent under slightly modified reaction conditions. Actually, the oxidation of cyclohexane without a solvent in the presence of iron powder catalyst (0.025 mol %), acetic acid (0.025 mol %), and acetaldehyde (10 mol %) at 70 °C under 8 atm of O_2 gave cyclohexanone (60%) and cyclohexanol (40%) with a high turnover number (146) along with acetic acid. The combined yield of cyclohexanone and cyclohexanol is almost 100%. Cyclohexanol can be converted into cyclohexanone readily under the same reaction conditions.



Work is in progress to provide definitive mechanistic information and to apply the present new method to other systems.

Acknowledgment. This work was supported by the Shorai Foundation for Science and Technology and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

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(7) Khanna, R. K.; Pauling, T. M.; Vajpayee, D. *Tetrahedron Lett.* **1991**, *32*, 3759.

(8) Hjelmeland, L. M.; Aronow, L.; Trudell, J. R. *Biochem. Biophys. Res. Commun.* **1977**, *76*, 541.

(9) (a) Phillips, B.; Frostick, F. C., Jr.; Starcher, P. S. *J. Am. Chem. Soc.* **1957**, *79*, 5982. (b) Also, see: ref 2a; pp 359–363.

(10) The formation of peracetic acid in $RuCl_3 \cdot nH_2O$-catalyzed oxidation of adamantane in the presence of acetaldehyde was confirmed by ^1H NMR analysis.

(11) (a) Sugimoto, H.; Tung, H.-C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 2465. (b) Leising, R. A.; Brennan, B. A.; Que, L., Jr. *Ibid.* **1991**, *113*, 3988.

(12) The iron-catalyzed oxidation of cyclohexene proceeds readily to give cyclohexene oxide (71%), 2-cyclohexen-1-ol (1%), and 2-cyclohexen-1-one (3%).

(13) (a) Steeman, J. W. M.; Kaarsemaker, S.; Hoftyzer, P. J. *Chem. Eng. Sci.* **1961**, *14*, 139. (b) Miller, S. A. *Chem. Process Eng.* (*London*) **1969**, *50* (6), 63.

Novel Ion–Molecule Reactions of C_{60}^{2+} with NH_3

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With the recent discovery of a new class of carbon molecules, named fullerenes,[1-3] a new area of chemical endeavor has been opened. Since Kratschmer and co-workers[4] have shown that C_{60} can be obtained in relatively large amounts by pyrolyzing graphite in a helium environment, an intense study of the physical and chemical properties of this intriguing class of carbon molecules has begun. In addition, a wide range of theoretical[5-8] calculations have been carried out.

The solution-phase chemistry of C_{60} with oxygen[9] and various amines[10] has shown some insight into its unique reactivity. Cox and co-workers[9] have reported the production and isolation of a fullerene monoepoxide, $C_{60}O$, produced by dissolving C_{60} in oxygen-rich benzene. C_{60}, when dissolved in propylamines,[10] undergoes addition of as many as 12 solvent molecules to the C_{60}

[†] Alfred P. Sloan Foundation Fellow 1991–1993.

(1) Kroto, H. W.; Heath, J. R.; O'Brien S. C.; Curl, R. F.; Smalley, R. E. *Nature* (*London*) **1985**, *318*, 162–163.

(2) Heath, J. R.; Zhang, Q.; O'Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Am. Chem. Soc.* **1987**, *109*, 359–356.

(3) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Astrophys. J.* **1987**, *314*, 352–355.

(4) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354–358.

(5) Dias, J. R. *J. Chem. Educ.* **1989**, *66*, 1012–1015.

(6) Wastberg, B.; Rosen, A. *J. Am. Chem. Soc.* **1988**, *110*, 8701–8703.

(7) Brendsdal, E.; Cyvin, B. N.; Brunvoll, J.; Cyvin, S. J. *Spectrosc. Lett.* **1988**, *21*, 313–318.

(8) Fowler, P. W.; Cremona, J. E.; Steer, J. I. *Theor. Chim. Acta* **1988**, *73*, 1–26.

(9) Creegan, K. M.; Robbens, J. L.; Robbens, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T.; Smith, A. B., III. *J. Am. Chem. Soc.* **1992**, *114*, 1103–1105.

(10) Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P. M. Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. *Fullerenes*; *ACS Symposium Series* 481; American Chemical Society: Washington, DC, 1991.

0002-7863/92/1514-7914$03.00/0

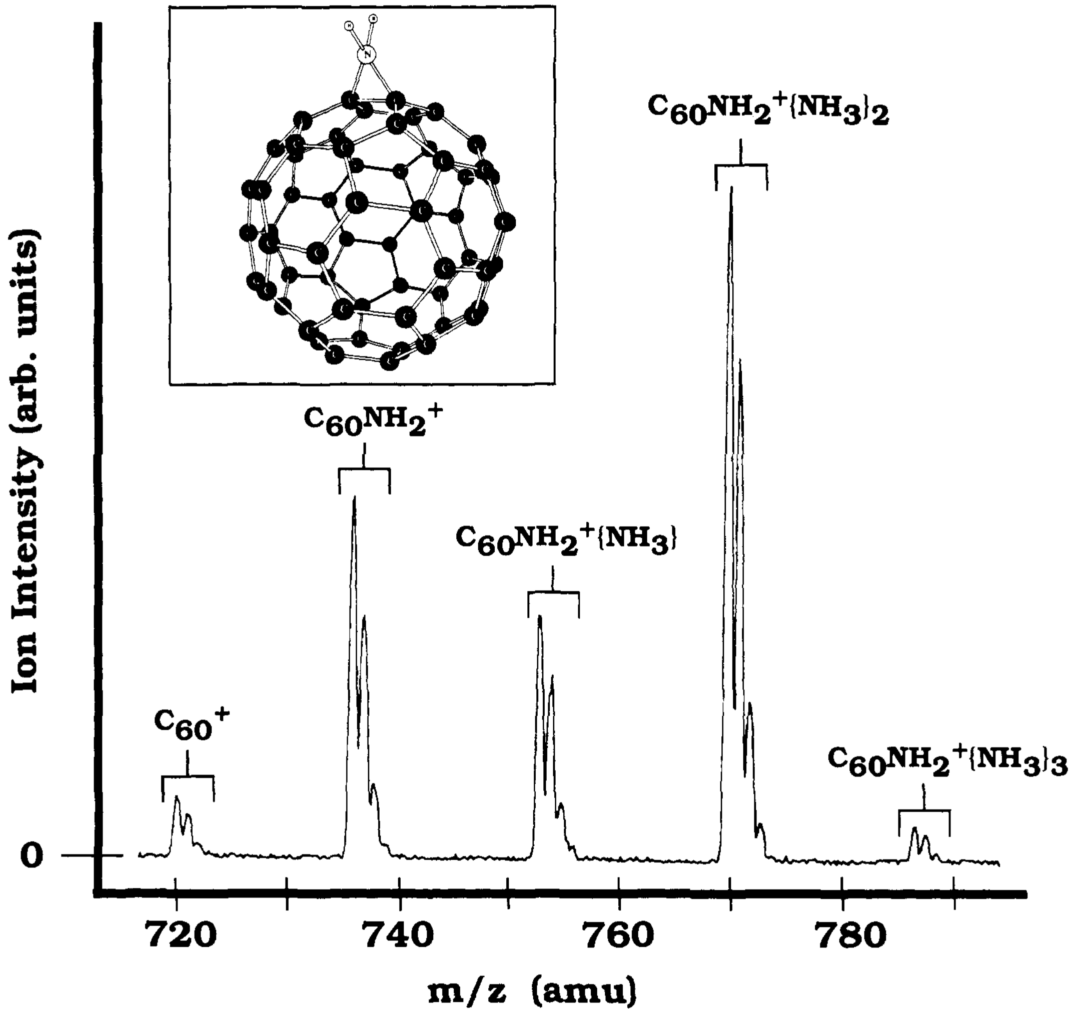

Figure 1. Product ions produced from the reaction of C_{60}^{2+} + NH_3. The pressure of ammonia in the collision cell is 7.4 mTorr, and the collision energy E_{LaB} is 2.0 eV. Note that the multiple peaks for each species result from the natural abundances of ^{13}C. The inset figure shows a proposed structure for the $C_{60}NH_2^+$ ion.

framework. A stepwise mechanism has been proposed for this, involving electron transfer from the amine to C_{60} followed by covalent bond formation between the resulting ions. This reactivity of C_{60}, along with its large electron affinity (2.6–2.8 eV[11]), strongly suggests that it can behave as a good electrophile[10] in reactions with heteronucleophiles.

In this communication we report the gas-phase associative charge transfer reactions of C_{60}^{2+} with ammonia. All experiments reported in this study were performed on a triple-quadrupole mass spectrometer (VGTRIO-3). The fullerene extract (obtained by extracting fullerene-rich soot, provided by the Texas Fullerene Corporation, with toluene)[12] was introduced into the ion source of the mass spectrometer via a heated solid probe inlet (570 °C). Following electron impact ionization (70-eV electron impact energy), the first quadrupole was employed to mass select the C_{60}^{2+} cation (i.e., the mass window employed was *m/z* 355–365). These ions were then directed, via a second quadrupole filter, into a collision cell containing neutral molecules of either NH_3 (Linde, anhydrous grade) or ND_3 (Isotec, 99.1 atom % deuterium) at pressures ranging from 0.1 to 10 mTorr. The third quadrupole filter was mass scanned to analyze the ions exiting the collision cell, including any new species that had been produced via ion–molecule reactions occurring within the cell.

When C_{60}^{2+} was passed through 2–10 mTorr of NH_3 at collision energies of 0.01–0.30 eV (E_{cm}), the ions detected were C_{60}^+ (720 amu), $C_{60}NH_2^+$ (736 amu), $C_{60}NH_2NH_3^+$ (753 amu), $C_{60}NH_2(NH_3)_2^+$ (770 amu), and $C_{60}NH_2(NH_3)_3^+$ (787 amu), which are shown in Figure 1. Other ions also observed include NH_4^+, $NH_4NH_3^+$, and the unreacted C_{60}^{2+}. The mass assignments of these product ions were confirmed through the use of ND_3 as a target gas. We note that the $C_{60}NH_3^{2+}$ ion is not observed under any conditions. A possible mechanism for the reaction with ammonia is as follows (the ions which we directly observe are shown in italics):

$$C_{60}^{2+} + NH_3 \rightleftarrows \{C_{60}^{+}\text{-}NH_3^{+}\} \tag{1}$$

$$\{C_{60}^{+}\text{-}NH_3^{+}\} + NH_3 \rightarrow C_{60}^{+} + NH_4^{+} + NH_2 \tag{2a}$$

$$\rightarrow C_{60}NH_2^{+} + NH_4^{+} \tag{2b}$$

$$C_{60}NH_2^{+} + nNH_3 \rightarrow C_{60}NH_2^{+}(NH_3)_{1-3} \tag{3}$$

$$NH_4^{+} + NH_3 \rightarrow NH_3NH_4^{+} \tag{4}$$

The relative abundances of all product ions are highly dependent on the ammonia gas pressure and collision energy, as shown in Figure 2. The inverse dependence of product ion abundance on collision energy may indicate that an exothermic reaction is taking place.[13,14] We feel that the NH_2 addition to the cationic fullerene (reaction 2b) indicates the production of either a fullerene amine or a protonated fullerene aziridine. On the previous character-

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(11) Yang, S. H.; Pettiette, C. L.; Conceicao, J.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233.

(12) Shinohara, H.; Sato, H.; Saito, Y.; Takayama, M.; Izuoka, A.; Sugawara, T. *J. Phys. Chem.* **1991**, *95*, 8449–8451.

(13) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University Press: New York, 1987; Chapter 2.

(14) Orlando, R.; Fenselau, C.; Cotter, R. J. *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 189–197.

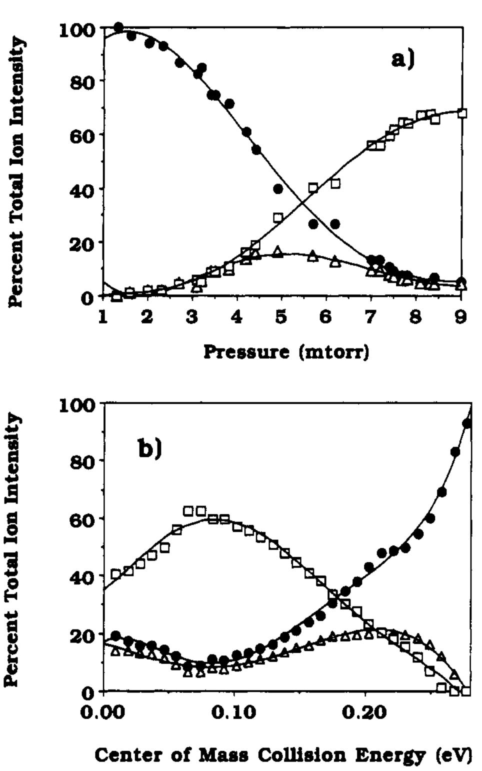

Figure 2. The key to the symbols used in this figure is as follows: ●, C_{60}^{2+}; △, $C_{60}NH_2^{+}$; □, $C_{60}NH_2(NH_3)_2^{+}$. (a) Percent total ion intensity of product ions produced from $C_{60}^{2+} + NH_3$ reactions as a function of ammonia pressure in the target cell. The collision energy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

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

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.

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(15) *Handbook of Chemistry and Physics*, 65th ed.; CRC Press, Inc.: Boca Raton, FL, 1984-1985; pp E72-E74.

(16) Huffman, D. R. *Phys. Today* 1991, November, 22-29.

(17) The second ionization energy of C_{60} has been the subject of numerous investigations. A range of values, depending on the method of analysis, have been reported: 12.25 ± 0.5 eV,[18] 11.9 ± 0.5 eV,[19] 9.7 ± 0.5 eV,[20] and <11.8 eV.[21] The reactivity observed in our lab for C_{60}^{2+} with NH_3 and O_2, as well as its relative inertness with the other gasses in Table I, leads us to conclude that the IE of C_{60}^{2+} lies between 12.0 and 12.6 eV.

(18) Lifshitz, C.; Iraqi, M.; Peres, T.; Fisher, J. E. *Rapid Commun. Mass Spectrom.* 1991, 238.

(19) Cadwell, K. A.; Giblin, D. E.; Gross, M. L. *J. Am. Chem. Soc.* **1992**, *114*, 3743.

(20) McElvany, S. W.; Ross, M. M.; Callahan, J. W. *Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 697.

(21) Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. *J. Phys. Chem.*, in press.

(22) Stry, J. J.; Coolbaugh, M. T.; Garvey, J. F. In preparation.

(23) Zimmerman, J. A.; Eyler, J. R.; Bach, S. B. H.; McElvany, S. W. *J. Chem. Phys.* **1991**, *94*, 3556.

(24) Rohlfing, E. A. *J. Chem. Phys.* **1990**, *93*, 7851.

(25) Lias, S. G.; Bartness, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas Phase Ion and Neutral Thermochemistry*; American Chemical Society and American Institute of Physics: New York, 1988; Vol. 17, Suppl. 1.

(26) In Figure 2 we note that due to the multiple bimolecular collisions occurring in the collision cell, the E_{cm} listed pertains only to the initial collision of the selected fullerene ion with a neutral ammonia molecule.

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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(1) Klotz, I. M. In *Enzyme Mechanisms*; Page, M. I., Williams, A., Eds.; Royal Society of Chemistry: London, 1987; Chapter 2.

(2) Suh, J.; Cho, Y.; Lee, K. J. *J. Am. Chem. Soc.* **1991**, *113*, 4198.

(3) Suh, J. *Acc. Chem. Res.* **1992**, *25*, 273.

(4) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66.

(5) Bender, M. L. In *Enzyme Mechanisms*; Page, M. I., Williams, A., Eds.; Royal Society of Chemistry: London, 1987; Chapter 4.

(6) Breslow, R.; Chung, S. *J. Am. Chem. Soc.* **1990**, *112*, 9659.