above-mentioned K_d values.[11] This result indicates that noncovalently bound species can be detected directly in a complex mixture without chromatographic separation.

Other macromolecular complexes may be detectable under conditions which are compatible with ion-spray MS.[12] In the negative-ion mode, this technique might be appropriate for highly acidic proteins or oligonucleotides. The use of MS to detect and identify complexes of charged macromolecules with their specific molecular ligands (or vice versa) may also find application in exploring signal transduction,[13] cellular adhesiveness,[14] and other multicellular processes.[15] Antibody-antigen recognition and aggregation phenomena may likewise be amenable to study with antibody Fab fragments,[16] single chain V_L/V_H and V_H antigen-binding proteins[17,18] as well as other, lower MW immunoglobulins.[19] Ongoing research in our laboratories will address these issues.

Acknowledgment. This research was supported by a grant from the Cornell Biotechnology Program, which is sponsored by the New York State Science and Technology Foundation, a consortium of industries, the U.S. Army Research Office, and the National Science Foundation. We thank Professor Stuart Schreiber (Harvard University) for providing generous samples of FKBP, FK506, rapamycin, and cyclosporin A. We also acknowledge helpful technical assistance from Messrs. James Conboy (Cornell) and Robert Standaert (Harvard).

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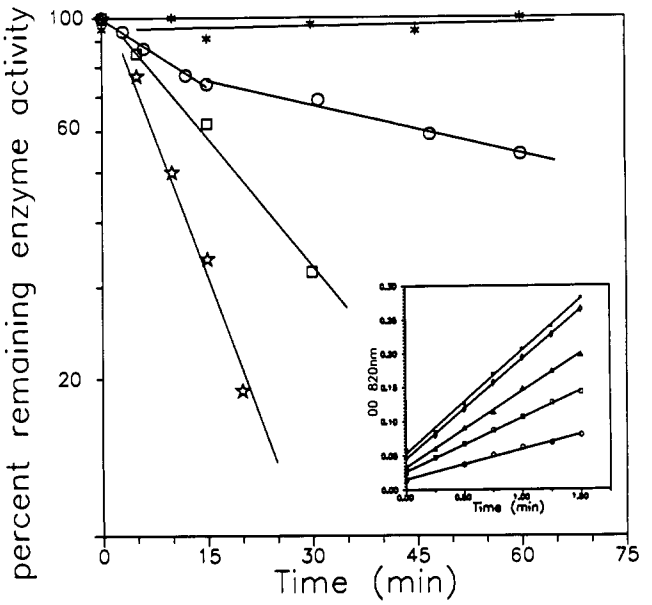
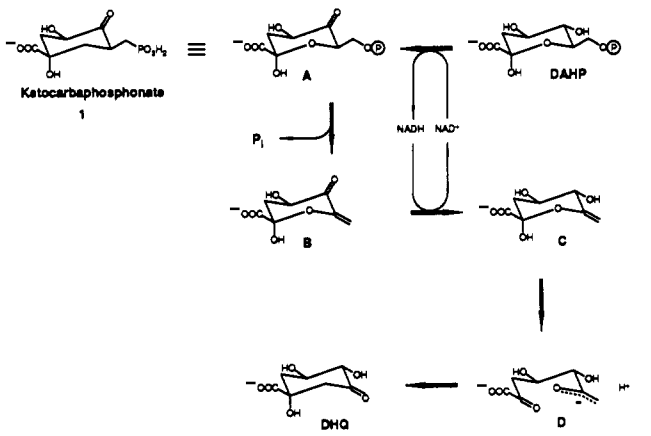


Figure 1. Time-dependent inhibition of DHQ synthase by ketocarbaphosphonate **1**. Enzyme (0.2 μM) was incubated at 15 °C in MOPS buffer (50 mM, pH 7.5) containing NAD (0.25 mM), $CoCl_2$ (0.25 mM), and one of the following: (*) 800 μM DAHP and 0 μM **1**; (○) 0 μM DAHP and 8 μM **1**; (□) 800 μM DAHP and 8 μM **1**; (★) 800 μM DAHP and 160 μM **1**. Aliquots were removed at timed intervals and diluted. Enzyme activity was then determined by colorimetric quantitation (OD_{820}) of product inorganic phosphate.[10] Grade V-C NAD (Sigma) was used for all experiments. All lines are based on linear regression analysis of each set of data points. Insert: Steadily increasing concentrations of DAHP (50, 100, 200, 500, and 800 μM) restore enzyme activity when DHQ synthase (0.025 μM) is incubated for a relatively short time (1.5 min) with a reduced concentration (2 μM) of ketocarbaphosphonate **1**.

Scheme I



Irreversible Inhibition of 3-Dehydroquinate Synthase

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An analogue[1] (**1**, Scheme I) of a reactive intermediate (A, Scheme I) formed during 3-dehydroquinate synthase (DHQ synthase) catalyzed[2] conversion of 3-deoxy-D-*arabino*-heptulosonic acid 7-phosphate (DAHP) to 3-dehydroquinate (DHQ) has been discovered to be an irreversible inhibitor. Ketocarbaphosphonate **1** is the first reported irreversible inhibitor of DHQ synthase and one of the few examples[3] of irreversible inhibition of an enzyme in the common pathway of aromatic amino acid biosynthesis.[4] The unique enzymology associated with ketocarbaphosphonate's inhibition of DHQ synthase also suggests a general strategy for irreversibly inhibiting enzymes that exploit nicotinamide adenine dinucleotide (NAD) as a catalyst rather than a cosubstrate.[5]

Ketocarbaphosphonate **1** was synthesized (Scheme II) from quinic acid in 12 steps with an 8% overall yield.[6] Incubation of

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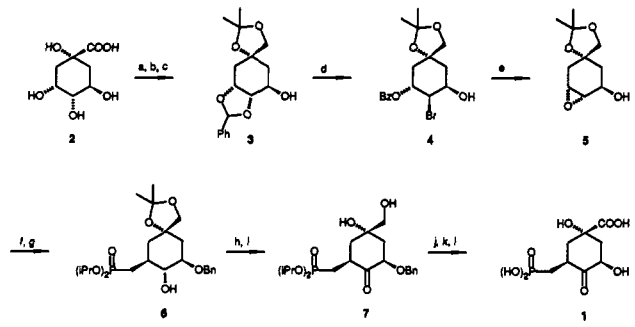
Scheme II[a]



[a] (a) PhCHO, *p*-TsOH, C_6H_6, reflux, 85%; (b) $NaBH_4$, EtOH, 0 °C, 76%; (c) 2-methoxypropene, *p*-TsOH, DMF, room temperature, 79%; (d) NBS, C_6H_6, room temperature, 79%; (e) MeONa, MeOH/THF (1:2), 0 °C, 87%; (f) NaH, *n*-Bu_4NI, BnBr, THF, 0 °C, 96%; (g) $(i\text{-PrO})_2P(O)CH_2Li\cdot BF_3$, THF, −78 °C, 79%; (h) $(COCl)_2$, DMSO, TEA, CH_2Cl_2, −78 °C, 95%; (i) $AcOH/H_2O$/THF (2:2:1), 65 °C, 80%; (j) H_2, 10% Pd on C, MeOH, 100%; (k) (i) TMSBr, Pyr, CH_2Cl_2, room temperature, (ii) H_2O, 100%; (l) O_2, Pt, $NaHCO_3$, H_2O, 55 °C, 42%.

DHQ synthase with ketocarbaphosphonate resulted in enzyme inhibition that was time-dependent in nature. At relatively short incubation times (Figure 1, insert), ketocarbaphosphonate was found to be a competitive inhibitor with $K_i = 0.15\ \mu M$. Incubation of DHQ synthase with ketocarbaphosphonate and DAHP for longer time intervals (Figure 1) resulted in pseudo-first-order loss of enzyme activity, which was not recovered even after dialysis of the enzyme.[7] Such enzymology is reminiscent of the irreversible inhibition observed with suicide inactivators.[8] An important difference is the ability of substrate to protect against suicide inactivation. Substrate DAHP does not protect DHQ synthase from irreversible inhibition by ketocarbaphosphonate. In fact, the presence of substrate DAHP accelerates the rate of irreversible inhibition (Figure 1).

Slow-binding inhibition[9] of DHQ synthase has been reported to lead to formation of enzyme-bound NADH along with oxidation of the inhibitors. The enzyme-generated carbonyl-containing forms of the inhibitors are reduced before release of the inhibitor from the enzyme active site. Such a reduction would not be possible if ketocarbaphosphonate **1** bound to DHQ synthase containing NAD. A resulting inability to clear ketocarbaphosphonate **1** from its active site might account for irreversible inhibition of the enzyme. A related situation could arise if ketocarbaphosphonate bound to DHQ synthase which lacked NAD. Bound NAD is released from DHQ synthase during active turnover of substrate to product.[2c] The required presence of DAHP for such release of NAD may also be an explanation for the more rapid irreversible inhibition of the enzyme by ketocarbaphosphonate in the presence of DAHP. Alternatively, substrate DAHP bound to DHQ synthase could induce an enzyme conformational change. Release of bound DAHP prior to its oxidation to intermediate A (Scheme I) may leave DHQ synthase conformationally disposed for more rapid binding by ketocarbaphosphonate.

DHQ synthase is a premier example of the steady evolution of strategies directed toward inhibition of an enzyme. Micromolar, competitive inhibition of the enzyme was first achieved with a nonisosteric organophosphonate analogue of substrate DAHP.[11] Inhibition of DHQ synthase was then moved to nanomolar levels with slow-binding, carbacyclic analogues of DAHP.[2b,d,j] Ketocarbaphosphonate constitutes the next step in inhibitory potency with its irreversible inhibition of the enzyme.

The importance of ketocarbaphosphonate's irreversible inhibition becomes apparent when regulatory responses to disruption of biosynthetic pathways are considered. Plants, for instance, respond to inhibition of an enzyme in the common pathway of aromatic amino acid biosynthesis by increasing the flow of carbon into the common pathway.[12] Resulting buildup of the inhibited enzyme's substrate can readily override competitive inhibition of the enzyme.[2i] Metabolic override of enzyme inhibition can be circumvented if the rate of release of the inhibitor from the enzyme is sufficiently slow. The apparent irreversible inhibition of DHQ synthase by ketocarbaphosphonate and the acceleration of this inactivation by DAHP would be ideal for maintaining in vivo enzyme inhibition.

Beyond DHQ synthase, carbonyl-containing analogues of reaction intermediates might irreversibly inhibit *S*-adenosylhomocysteinase[13] and *myo*-inositol-1-phosphate[14] synthase, which also use NAD as a catalyst.[5] These enzymes play critical roles during methylations involving *S*-adenosylmethionine and maintenance of *myo*-inositol levels in brain tissue. Disruption of *S*-adenosylmethionine methylation is associated with antiviral activity[15] while diminished levels of *myo*-inositol in brain tissue characterize control of manic depression with Li^+ treatment.[16] Ketocarbaphosphonate **1** may thus point the way to a sizable class of reaction-intermediate analogues whose irreversible inhibition

(6) Spectral data for ketocarbaphosphonate **1**: ^1H NMR (500 MHz, D_2O, internal sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$ $\delta = 0$) δ 4.7 (dd, J = 7, 13 Hz, 1 H), 3.2 (m, 1 H), 2.4–2.5 (m, 2 H), 2.2 (ddd, J = 16, 5, 5 Hz, 1 H), 2.1 (dd, J = 14, 14 Hz, 1 H), 1.4 (ddd, J = 16, 16, 8 Hz, 1 H); ^{13}C NMR (50 MHz, D_2O, internal CH_3CN $\delta = 3.69$) δ 217 (J_{PCCC} = 12 Hz), 184, 77.7, 74.7, 47.3, 46.5 (J_{PCC} = 5 Hz), 42.9, 28.8 (J_{PC} = 134 Hz); high-resolution FAB MS calcd 269.0426, found 269.0420. Organophosphonate **6** can also be converted into the slow-binding inhibitor, (1*S*)-(1α,3β,4α,5β)-5-(phosphonomethyl)-1,3,4-trihydroxycyclohexane-1-carboxylic acid.[2d] Inhibitor synthesized from organophosphonate **6** is identical with the same inhibitor synthesized by an independent, published route.[2d]

(7) Inhibited-enzyme-containing solution (0.5 mL) was dialyzed at 4 °C against a solution (500 mL) of MOPS buffer (50 mM, pH 7.5), NAD (0.25 mM), and $CoCl_2$ (0.25 mM). The dialysis solution (500 mL) was changed after 3 h, and dialysis continued for an additional 21 h.

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of enzymes is of considerable agricultural and medicinal importance.

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Evidence for an Externally Bound Fe^+–Buckminsterfullerene Complex, FeC_{60}^+, in the Gas Phase

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One of the most intriguing aspects of C_{60}[1] is its ≃7-Å-diameter cavity, which may be impregnated by other elements and perhaps even by small molecules, thus altering its chemical and physical properties. Even before a macroscopic synthesis of C_{60}[2] was available, Smalley and co-workers demonstrated that metal-included species could be generated in the gas phase by growing them in a supersonic expansion source following laser desorption from a graphite target dosed with various metals, M = La, K, and Cs.[3,4] Also formed are a variety of less symmetrical MC_n complexes. These species, in particular MC_{60} and its singly charged counterpart, are highly stable. In all cases the complexes were predicted to have the metal atom either wholly or partially surrounded by a shell of carbons. Supporting this hypothesis was the fact that the MC_{60}^+ ions fragmented only under the extreme activation conditions of multiphoton absorption at high ArF excimer laser fluence and, then, only by sequential C_2 loss.[4] Further loss of C_2 ceased at some critical even number of carbon atoms depending on the metal, such as $C_{44}La^+$ (possibly $C_{42}La^+$), $C_{44}K^+$, and $C_{48}Cs^+$. Again, these results are in accord with expectations of a central metal enclosed in an inert carbon cage. While these MC_{60} species were grown in situ in the supersonic expansion, the question arises as to whether a metal ion interacting with a preformed fullerene will attach externally or internally. Looking at a space-filling model for CsC_{60} and KC_{60},[5] for example, one would predict external attachment. Recently, potassium-doped C_{60} has shown a superconducting transition; the metal ions are externally bound.[6]

Although our initial attempts to generate a LaC_{60}^+ species failed due to the rapid reaction of La^+ with background gas to form LaO^+,[7] FeC_{60}^+ was formed in our Nicolet FTMS-2000 Fourier transform mass spectrometer via the following multistep sequence:[8] (1) Fe^+ was generated by laser desorption from an Fe target in a source external to the solenoid magnet;[9] (2) the Fe^+ was permitted to react with pentane at 1×10^{-6} Torr, generating $Fe(C_nH_{2n})^+$ (n = 2–5); (3) these ions then underwent ligand-exchange reactions with preformed C_{60} and C_{70} heated at 350 °C off a solids probe to generate FeC_{60}^+ and FeC_{70}^+; and (4) after a total reaction time of 300 ms, C_{60}^+, C_{70}^+, and other, lower mass ions were ejected by double-resonance techniques,[10] Figure 1A. The FeC_{60}^+ and FeC_{70}^+ were not observed to react further with background pentane.

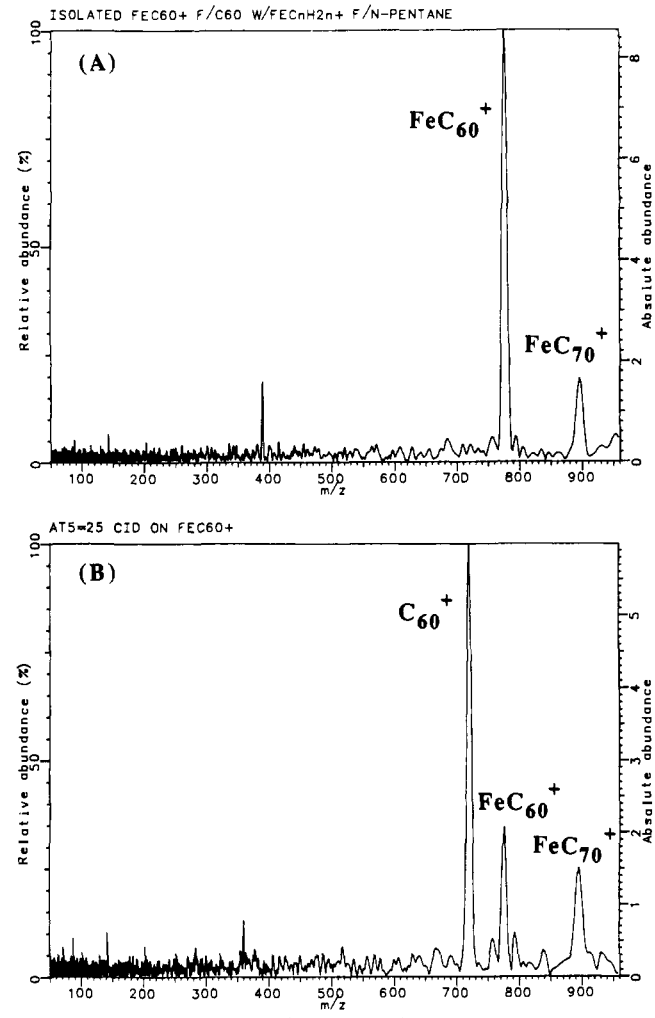

Figure 1. (A) Isolated FeC_{60}^+ and FeC_{70}^+. The peak at m/z 388 is attributed to a harmonic. (B) Collision-induced dissociation of FeC_{60}^+ at 76 eV in laboratory energy, and 3.7 eV in center-of-mass energy. Both spectra were obtained using 16K data points.

Collision-induced dissociation of FeC_{60}^+ was performed by rf irradiation of the ion at its resonant frequency in the presence of Ar at a pressure of 3×10^{-6} Torr. As shown in Figure 1B, C_{60}^+ is the sole product ion observed. This result is consistent with IP(Fe) =7.9024 eV[11] > IP(C_{60}) =7.61 eV[12] and contrasts with the results of the earlier studies on MC_{60}^+ species in requiring relatively little activation energy (12–241 eV in laboratory energy and 0.6–11.8 eV in center-of-mass energy[13]) and in generating the intact C_{60}^+ rather than losing C_2 molecules. Thus, either the

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