to yield a enzyme–VO$^{2+}$–AdoMet–PPNP–Mg(II)–Tl$^+$ complex, PPNP = imidotriphosphate (O$_3$P–O–PO$_2$–NH–PO$_3$)) did not alter the coupling to Tl$^+$, whereas if either methionine or AMPPNP were omitted, coupling to Tl$^+$ was not observed.

In complexes formed with enzyme and products of the AdoMet synthetase reaction, coupling to Tl$^+$ was observed when both AdoMet and PPi were present in an enzyme–VO$^{2+}$–AdoMet–PPi–Tl$^+$ complex, with or without added Mg$^{2+}$ (Figure 2). The spectra of complexes containing PPi also exhibit superhyperfine coupling to the two $^{31}$P nuclei of the bidentate vanadyl ligand PPi, yielding the triplet structure seen in the spectrum of the K$^+$ complex.[5] Computer simulations indicate that the superhyperfine structure in the spectra of the Tl$^+$ complex is due to a 24-MHz isotropic superhyperfine coupling to a spin-$^1/_2$ nucleus, in addition to the $^{31}$P couplings of 22 MHz (additional parameters are $g_\parallel$ = 1.936, $g_\perp$ = 1.979; $A(^{51}\mathrm{V})_\parallel$ = 532 MHz, $A(^{51}\mathrm{V})_\perp$ = 198 MHz). Spectra identical with those shown in Figure 2 were obtained for the enzyme–VO$^{2+}$–ATP–methionine complexes with K$^+$ and Tl$^+$. Superhyperfine couplings to Tl$^+$ were not observed for either the enzyme–VO$^{2+}$–PPi–Mg$^{2+}$ complex, for which the VO$^{2+}$ binding site structure is extremely similar as indicated by the $g$ values, $^{51}$V and $^{31}$P hyperfine couplings,[5] nor in the enzyme–VO$^{2+}$–AdoMet complex. Apparently both substrate binding sites must be occupied in order for the thallium ion to be positioned with respect to VO$^{2+}$ in such a fashion as to allow superhyperfine coupling.

The observation of coupling between the thallium nuclear spin and the unpaired electron spin of VO$^{2+}$ at the active site of AdoMet synthetase is a rare case of superhyperfine coupling between V(IV) and another metal ion; other cases are pyruvate kinase[9] and a coupling between V(IV) and tin in SnO$_2$ doped with vanadium.[10] In the latter case vanadium couples to two types of Sn; crystallographic data show that these Sn atoms are located 3.1 and 3.7 Å from the vanadium and both lie in the plane of the vanadium orbital in which the unpaired electron is localized; the isotropic superhyperfine splittings for these Sn are 168 and 28 G, respectively. Although isotropic superhyperfine coupling is commonly mediated by a ligand that is shared between the two species involved,[11] the tin superhyperfine coupling is thought to result from direct orbital overlap between metal ion orbitals rather than being mediated by the oxygen ligands.[10] In the AdoMet synthetase complexes, the large spatial distribution of the thallium orbitals also leaves a distinct possibility that direct overlap between the Tl$^+$ and VO$^{2+}$ orbitals, rather than an intervening ligand, mediates the interaction. $^{205}$Tl NMR studies have indicated that enzyme-bound Tl$^+$ does not directly coordinate the substrates.[12]

In addition to the divalent metal ion binding site which VO$^{2+}$ has been used to probe, a second divalent metal ion is required for catalytic activity of AdoMet synthetase.[5] Magnetic coupling between Mn(II) bound to both divalent metal ion binding sites has been reported, demonstrating not only that the two divalent metal ions bind extremely closely together but that there is orbital overlap between them, consistent with formation of a metal cluster structure.[5] The finding that there is also orbital overlap between the monovalent cation and one of the divalent cations suggests that AdoMet synthetase may assemble a trimetallic cluster at the active site. Elucidation of the detailed structure of the metal ion binding sites will undoubtedly play an important role in understanding of the mechanism of catalysis.

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# Activation of Allylic Carbon–Carbon Bonds by Gas-Phase Copper(I)

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It is now established that certain gas-phase transition-metal ions activate C–C and C–H bonds of hydrocarbons,[1-8] whereas metal complexes in solution are much less reactive.[9] The first evidence that Fe$^+$, Co$^+$, and Ni$^+$ oxidatively add alkanes was reported by Ridge and co-workers.[1,2] In a later study, Armentrout and Beauchamp[4] proposed that Co$^+$ oxidatively adds allylic C–C bonds. Transfer of a $\beta$-H atom and reductive elimination produces a bis(olefin) complex. Fe$^+$ and Ni$^+$ also activate allylic C–C bonds of alkenes by the same mechanism as was reported in ref 4–8.

We wish to report here that Cu$^+$ also activates the allylic C–C bonds of alkenes. Evidence from two different experimental strategies points to a copper ion/alkene reactivity that phenomenologically mimics that of the other reactive metal ions. The first strategy is collisional activation (CA) of Cu(olefin)$^+$ adducts formed in a high-pressure mass spectrometer ion source. Copper ions were produced by electron ionization of copper(II) acetyl acetonate.[10] In the second approach, Cu$^+$ was formed by laser ionization of a metal target[11] and reacted with olefins in a FT mass spectrometer.[12]

As illustrated in Figure 1, the collisionally activated decomposition (CAD) spectrum of Cu(1-pentene)$^+$ is very similar to that of Fe(1-pentene)$^+$.[5] TiCl$^+$ was previously reported to react with 1-pentene to eliminate ethylene,[13] and the spectrum of TiCl(1-pentene)$^+$ is also similar to that of Fe(1-pentene)$^+$. All complexes decompose principally by eliminating C$_2$H$_4$.

To be certain that the CAD spectra are consistent with published results from other experimental approaches, the CAD spectra of all the first-row transition-metal ions (except Sc$^+$) complexed with 1-pentene were obtained (Table I). The results are consistent with the known reactivities of metal ions with other hydrocarbons and serve as controls to ensure there are no peculiarities with our experimental approach.

The reactivities of different M$^+$ with 1-pentene were also compared by using FTMS. Relative rate constants (Table I) for disappearance of M$^+$ were obtained. Dehydrogenation reactions of Ti$^+$ and V$^+$ are the most rapid, whereas Fe$^+$, Co$^+$, Ni$^+$, and Cu$^+$ react slightly slower with 1-pentene to give the same array of products as in Table I. As expected,[2] Cr$^+$ and Mn$^+$ do not activate, but do condense slowly to form MC$_5$H$_{10}$$^+$. Zn$^+$ charge exchanges with 1-pentene, in accord with the difference in ionization energies.[14]

The survey results demonstrate that Cu$^+$ and TiCl$^+$, in addition to Fe$^+$, Co$^+$, and Ni$^+$, activate allylic C–C bonds. The reactivity

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**Table I.** Rate Constants and CAD Spectra for Reactions of Transition-Metal Ions and 1-Pentene

| | $Ti^+$ | $V^+$ | $Cr^+$ | $Mn^+$ | $Fe^+$ | $Co^+$ | $Ni^+$ | $Cu^+$ | $Zn^+$ |
|---|---|---|---|---|---|---|---|---|---|
| rel rate[a] | 1.00 | 0.95 | 0.001 | 0.07 | 0.76 | 0.96 | 0.91 | 0.65 | 0.40 |
| CAD fragments | | | | | | | | | |
| $MC_5H_8^+$ | 64 | 63 | 1 | | 2 | 2 | 2 | 2 | |
| $MC_4H_6^+$ | 9 | 3 | 1 | | 4 | 3 | 2 | 5 | |
| $MC_3H_6^+$ | 6 | 12 | | 2 | 56 | 62 | 59 | 41 | |
| $MC_2H_4^+$ | | 1 | | | 11 | 10 | 9 | 12 | |
| $M^+$ | 6 | 5 | 76 | 82 | 11 | 9 | 9 | 18 | 24[b] |

[a] Determined by using FTMS, $p = 2 \times 10^{-7}$ torr. [b] Other ions observed: $C_5H_{10}^{\cdot+}$, 33%; $C_4H_7^+$, 9%; $C_3H_5^+$, 11%.

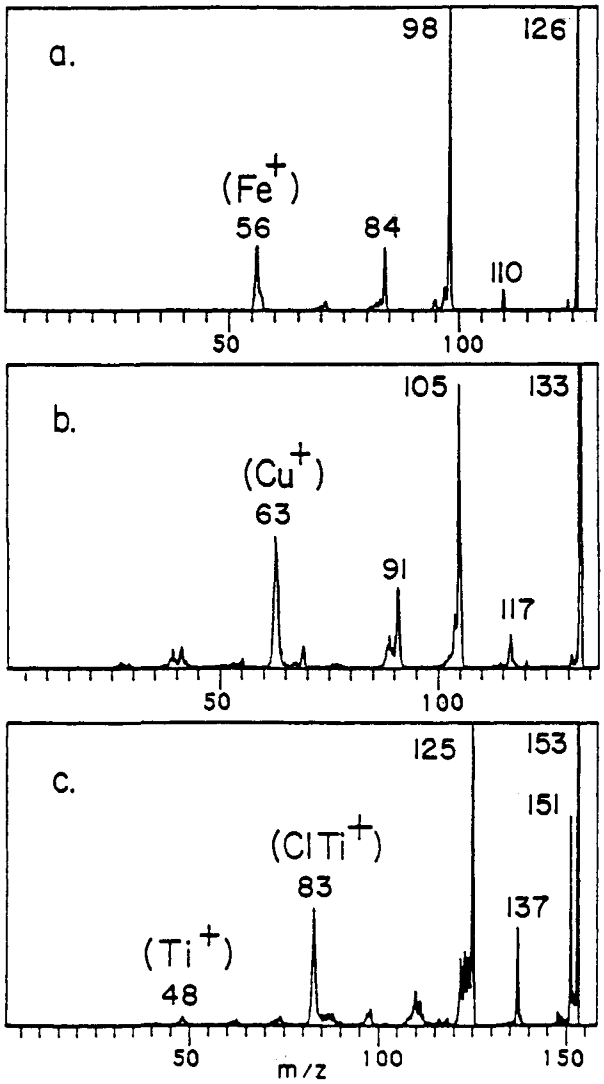

**Figure 1.** CAD spectra of 1-pentene complexes: (a) $FeC_5H_{10}^+$, *m/z* 126; $FeC_3H_6^+$, *m/z* 98. (b) $CuC_5H_{10}^+$, *m/z* 133; $CuC_3H_6^+$, *m/z* 105. (c) $Cl\text{-}TiC_5H_{10}^+$, *m/z* 153; $Cl\text{-}TiC_3H_6^+$, *m/z* 125.

of $Cu^+$ with allylic C–C bonds appears to be general: 1-pentene, 2-pentene, and hexene isomers all react. $Cu^+$ reacts with 1-hexene to form $Cu(C_3H_6)^+$ and with both 2- and 3-hexene to give $Cu(C_4H_8)^+$. This reactivity parallels exactly that of $Fe^+$.[5,7] The reactivity of $Cu^+$ and alkenes is surprising considering that $Cu^+$ ($3d^{10}$) should behave similarly to $Cr^+$ ($3d^5$) because of the stability associated with half-filled and filled 3d shells. However, there are no studies to our knowledge in which direct comparisons of $Cu^+$ and $Cr^+$ have been made.

One means for a transition metal ion to react with a hydrocarbon is oxidative addition, which has been postulated to require metal electron promotion from a 3d to 4s orbital.[15] Indeed the inertness of $Cr^+$ and its high promotion energy, ca. 34 kcal/mol, are in accord with the proposal. However, the promotion energy of $Cu^+$ is almost twice that of $Cr^+$, 63 kcal/mol,[15] and yet $Cu^+$ reacts with alkenes almost identically to $Fe^+$, $Co^+$, and $Ni^+$. Therefore, the reactivity of $Cu^+$ with alkenes is unlikely to be due to oxidative addition. Besides the high promotion energy of $Cu^+$, the $(Cu\text{–}alkyl)^+$ bond energies are undoubtedly low (15–30 kcal/mol) as estimated on the basis of the $(Cu\text{–}H)^+$ energy of 21 kcal/mol[16,17] and by the extrapolation scheme presented in ref 15. Thus, bonding between carbon and $Cu^+$ will not provide sufficient energy to compensate for the cost of severing a rather strong (>70 kcal/mol) allylic bond. The reactivity of $Cu^+$ and alkanes should be governed by the same considerations, and the recent assertion that $Cu^+$ inserts into C–C and C–H bonds of isobutane[18] may be because excited $Cu^+$ is formed by the sputtering process that was used to produce gas-phase metal ions. Oxidative addition of the O–NO bond of methyl nitrite to $Cu^+$ is more likely given the low energy of this bond (42 kcal/mol).[19]

A recent study of the endothermic reaction of gas-phase $Cu^+$ and $H_2$ may contain a hint to the reactivity of $Cu^+$ and alkenes.[20] It is postulated that $H_2$ donates its electrons to the metal ion 4s orbital to make $CuH_2^+$ having a two-electron, three-centered bond. $Cu^+$ is expected to be more reactive than $Cr^+$ in this reaction mode because of its heightened electrophilicity [IE(Cu) = 7.72 eV; IE(Cr) = 6.76 eV].[14]

Sufficient energy for reaction with alkenes may be available if $Cu^+$ is excited. Extensive numbers of excited ions are unlikely, given the large promotion energy of $Cu^+$[15] and that the kinetic curve for reaction of $Cu^+$ and 1-pentene is noncomposite. Excited $Cu^+$ formed in a spark source does react with propene,[21] but this reactivity was not observed here when $Cu^+$ was formed by laser desorption in the FTMS cell.

Another mechanism is "dissociative attachment" whereby $Cu^+$ associates with a functional group (usually a heteroatom) and causes an organic molecule to rearrange and/or cleave. The reactions of $Cu^+$ with ketones and esters,[22] alkyl chlorides,[23] and alcohols[24,25] are examples, although oxidative addition was proposed to account for dehydrogenation of alcohols.[24,25] Dissociative attachment is thought to be a trait of alkali metal ions, but they only complex with alkenes.[26,27] Moreover, if dissociative attachment applies, then one is faced with the dilemma of the inertness of $Cr^+$ and $Mn^+$ even though they should form stronger bonds with the $C_3H_6$ product from 1-pentene and afford an even

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greater driving force for the reaction.

Often in chemistry nearly identical reactivities have nearly identical underlying explanations. This apparently is not true for the reactions of alkenes with $Cu^+$ and with other transition-metal ions ($Fe^+$, $Co^+$, $Ni^+$). Research is under way to understand the unusual reactivity of $Cu^+$.

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## Equilibrium Ion Pair Acidities in Tetrahydrofuran of Benzylic Carbon Acids Stabilized by an Adjacent Cyano, Carboalkoxy, and Sulfonyl Substituent. Delocalization and Aggregation of Ion Pairs[1]

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Carbon acids containing stabilizing groups at the $\alpha$-position constitute an important class of synthetically useful reagents. Equilibrium ionic acidities are known for many of these compounds, especially in dimethyl sulfoxide solution, in large part through the work of Bordwell and his research group.[2] Nevertheless, many synthetic applications make use of ether, and particularly tetrahydrofuran (THF), solutions in which the carbanions are present wholly as ion pairs. Moreover, a number of lithium salts of such carbanions have been shown to be aggregated in THF solution.[3] Accordingly, important questions concern the relevance of ionic acidities to the effective acidities in THF solution and of the role of ion pair aggregation in such compounds. In this paper, we present results concerning equilibrium acidities and thermodynamic parameters for transmetalation reactions in THF for a related group of *benzylic carbon acids* containing a cyano, carboalkoxy, or sulfonyl substituent and draw significant conclusions regarding the state of aggregation and type of ion pairing of these carbanion systems.

The positions of transmetalation equilibria (eq 1) were determined spectroscopically by using hydrogen indicators InH of known[4,5] $pK_a$ values in THF.

$$\mathrm{RH + In^-M^+ \rightleftarrows R^-M^+ + InH} \qquad (1)$$

$$\mathrm{M^+ = Li^+, Cs^+}$$

The experimental procedure followed those published previously from this laboratory.[4-6] Results are summarized in Table I. Note that in most cases it was possible to use more than one indicator to measure the acidity of each carbonyl derivative RH. The data in Table I reveal that the $pK_a$ assignments are independent of the indicator used, and this internal consistency constitutes our best evidence that the equilibria 1 are not being perturbed by side reactions involving addition of the carbanions to substrates.

**Table I.** Acidity Data for Phenylacetonitrile (**1**), (*p*-Methoxyphenyl)acetonitrile (**2**), *tert*-Butyl Phenylacetate (**3**), and Benzyl Phenyl Sulfone (**4**), 25.0 °C in THF

| cmpd | indicator[a] | $N^b$ | $10^4[R^-M^+]^c$ | $pK_a$ |
|---|---|---|---|---|
| | | Lithium Cation | | |
| **1** | 9-PhFl | 5 | 1.05–6.40 | 18.60 ± 0.03 |
| | 1,2-BF | 4 | 6.30–22.2 | 18.66 ± 0.04 |
| **2** | 9-PhFl | 4 | 1.34–3.04 | 20.16 ± 0.05 |
| | 1,2-BF | 5 | 4.90–17.4 | 20.17 ± 0.03 |
| **3** | 9-PhFl | 10 | 0.634–9.96 | 19.61 ± 0.10 |
| **4** | Bza | 4 | 1.35–6.49 | 20.45 ± 0.03 |
| | 1,2-BF | 3 | 5.95–14.0 | 20.41 ± 0.02 |
| | | Cesium Ion[d] | | |
| **1** | 4,5-MP | 6 | 1.02–24.0 | 22.99 ± 0.06 |
| | Fl | 3 | 11.5–14.0 | 23.02 ± 0.04 |
| **2** | DBF | 5 | 0.449–2.54 | 24.82 ± 0.04 |
| | 2,3-BF | 5 | 1.71–7.74 | 24.85 ± 0.03 |
| **3** | 9-MeFl | 3 | 1.25–4.36 | 24.15 ± 0.08 |
| | 2,3-BF | 5 | 2.76–6.59 | 24.14 ± 0.05 |
| | Fl | 8 | 4.62–38.5 | 24.12 ± 0.08 |
| **4** | 4,5-MP | 3 | 6.43–14.8 | 23.33 ± 0.05 |
| | 2,3-BF | 6 | 3.05–7.94 | 23.34 ± 0.03 |

[a] Indicator anion for measurement: 9-PhFl, 9-phenylfluorene; 1,2-BF, 1,2-benzofluorene; Bza, benzanthracene; 4,5-MP, 4,5-methylenephenanthrene; Fl, fluorene; DBF, 2,3:6,7-dibenzofluorene; 2,3-BF, 2,3-benzofluorene; 9-MeFl, 9-methylfluorene. Spectral data and equilibrium acidity assignments for these indicators are contained in ref 4 and 5. $pK_a$ values are relative to an assigned value of 18.49 for 9-phenylfluorene. [b] Number of measurements. [c] Equilibrium carbanion concentration in M. [d] Results include an upward correction of 0.8 unit in the $pK_a$'s of these indicators from previously published values (ref 4); Kaufman, M. J., Gronert, S., results to be published.

**Table II.** Thermodynamic Values for Equilibrium 1[a]

| | gegenion | | | |
|---|---|---|---|---|
| | $Li^+$ | | $Cs^+$ | |
| cmpd | $\Delta H°$ | $\Delta S°$ | $\Delta H°$ | $\Delta S°$ |
| **1** | −4.1 | 8.6 | −2.7 | −4.0 |
| **2** | −1.0 | 11.3 | 0.0 | −3.2 |
| **3** | −6.1 | −2.9 | −1.6 | −5.3 |
| **4** | 0.2 | 15.0 | 1.5 | 7.8 |

[a] Units are kcal $mol^{-1}$ for $\Delta H°$ and eu for $\Delta S°$. Estimated errors are ±0.5 kcal $mol^{-1}$ for $\Delta H°$ and ±1 eu for $\Delta S°$.

It is particularly important that the substrate carbanion concentrations could be varied by factors of 10–40 without affecting the $pK_a$ values. When aggregation occurs, the additional associative equilibrium 2 has the effect of "pulling" equilibrium 1 to

$$n(\mathrm{R^-M^+}) \rightleftarrows (\mathrm{R^-M^+})_n \qquad (2)$$

the right, which results in $pK_a$ values that show a concentration dependence. It can be readily shown that $K_{\mathrm{exptl}}$ is proportional to $[\mathrm{R^-M^+}]_{\mathrm{exptl}}{}^{(n-1)/n}$. For example, if the equilibrium actually involves dimers, a 4-fold concentration change in $[\mathrm{R^-M^+}]_{\mathrm{exptl}}$ will give a 2-fold change in $K_{\mathrm{exptl}}$ or a change in apparent p$K$ of 0.3. The lack of a concentration dependence in the present examples unambiguously demonstrates that these benzylic carbanions exist exclusively as monomeric ion pairs in dilute THF solution. This result is in contrast to the behavior of more localized non-benzylic carbanion derivatives which form aggregated ion pairs in ethereal solutions.[3,6] Note particularly that the lithium salts of phenylacetonitrile[7] and benzyl phenyl sulfone[8] are dimeric in the crystal state. The present results provide a useful demonstration that the structures of organolithium compounds in solution are not necessarily the same as structures in the crystal.

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