$\Delta V^{\ddagger}_{\mathrm{TST}}$ and solvent, the assumption remains valid.

V. Summary

We observe that ring inversion in cyclohexane is accelerated as pressure is applied. This pressure dependence which is nonlinear is more pronounced in acetone-d_6 and carbon disulfide than in the more viscous methylcyclohexane-d_{14} solvent. The experimental data are interpreted in terms of the stochastic model of isomerization reactions. The observed activation volume is strongly pressure and solvent dependent as is the collisional contribution to the activation volume. $\Delta V^{\ddagger}_{\mathrm{OBS}}$ and the transmission coefficient correlate extremely well with the solvent viscosity, which is proportional to the collision frequency. Thus we conclude that the reaction coordinate is coupled via collisions to the surrounding medium. To the best of our knowledge these results represent the first experimental proof of the predictions of stochastic models[16,17] for isomerization reactions in condensed phases.

The main result is our observation of a large collisional contribution to the activation volume, $\Delta V^{\ddagger}_{\mathrm{COLL}}$, which is strongly pressure dependent. The experimental data also indicate nonmonotonic transition between the inertial and diffusive regimes of isomerization reactions.

Acknowledgment. We express our thanks to Drs. D. Chandler and Peter Wolynes for helpful discussions. This research was supported partly by the National Science Foundation under grant No. NSF CHE79-12-8011420 and by the Department of Energy under contract No. DE-AC02-76ER01198 55. Detailed tables of experimental data are available on request from the corresponding auther (J.J.).

Registry No. Cyclohexane, 110-82-7.

Relative Bond Dissociation Energies for Two-Ligand Complexes of Cu^+ with Organic Molecules in the Gas Phase

Roger W. Jones and Ralph H. Staley*[1]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received June 15, 1981*

Abstract: Relative two-ligand dissociation enthalpies, $\delta D(Cu^+{-}2L)$, for Cu^+ with 43 organic molecules are determined. A pulsed-laser volatilization/ionization source is used to generate Cu^+ which reacts with EtCl and/or other molecules to give $Cu(ligand)_2^+$ species. Equilibrium constants are measured for the ligand-exchange reactions which occur when pairs of ligand molecules are present. Free energies for two-ligand exchange are obtained from the equilibrium constant for the reaction $Cu(A)_2^+ + 2B \rightleftarrows Cu(B)_2^+ + 2A$. The free-energy differences are added to give a scale of relative free energies for ligand exchange. These are converted to enthalpies to give the $\delta D(Cu^+{-}2L)$ scale with the assumption that entropy changes are small and can be neglected except for symmetry corrections which are made in appropriate cases. Dependence of $\delta D(Cu^+{-}2L)$ on functional group and substituent effects is analyzed. The results for Cu^+ are compared to available results for other reference acids: H^+, Al^+, Mn^+, Li^+, and $CpNi^+$. These comparisons show that Cu^+ is a softer acid than the other reference acids. This is apparent from the relative preference of Cu^+ for mercaptans and HCN compared to alcohols and other oxygen bases.

Relative gas-phase ligand binding energies, $D(M^+{-}L)$, for Al^+ and Mn^+ have recently been obtained by use of ion cyclotron resonance (ICR) spectroscopy with a pulsed-laser volatilization/ionization source of atomic-metal cations.[2,3] Such binding energies are useful in evaluating the energetics of reaction processes and in developing models for understanding molecular interactions. Recent work in our laboratory has also shown that complexes of Cu^+ with two ligands can be readily produced and do not react further with a variety of organic molecules except by ligand-exchange reactions.[4,5] Determination of relative binding energies of organic molecules in two-ligand complexes of Cu^+ is therefore possible. These two-ligand binding energies should reveal bonding effects due to the presence of a second ligand when compared to the one-ligand binding energies that have been previously obtained. Also, Cu^+ is a classic example of a soft acid,[6] and thus should show a preference for soft bases such as nitriles and sulfur bases. Data obtained in gas-phase ligand binding energy studies can provide a quantitative measure for hard and soft acid–base concepts unencumbered by solvation and other complicating effects. In the present paper we report determinations of relative binding energies of 43 organic molecules in two-ligand complexes with Cu^+. The results are compared to available gas-phase basicity scales for other reference acids: H^+, Li^+, Al^+, Mn^+, and $CpNi^+$ ($Cp \equiv \eta^5\text{-}C_5H_5$).

Experimental Section

Experiments were carried out with ICR instrumentation and techniques which have been previously described.[2-5,7,8] The output of a pulsed YAG laser is focused onto a copper wire target at the end of the ICR cell to produce atomic-copper cations. The mass spectrum for this source with no added gases shows 69% ^{63}Cu and 31% ^{65}Cu in their natural ratio. No Cu^{2+} or Cu_2^+ are observed. HCN was obtained by mixing NaCN and H_2SO_4 under vacuum. Chemicals were from commercial sources and were degassed by repeated freeze–pump–thaw cycles before use. Gas mixtures were prepared in the cell and partial pressures measured by difference as has been previously described.[2] Accuracy of pressure ratios is limited to about ±30% because the ion gauge is not individually calibrated for each gas.

Results

Ethyl chloride was used as a reagent for prepartion of the two-ligand complex $Cu(EtCl)_2^+$ which is formed in a rapid biomolecular reaction sequence as has been previously described.[4] Other molecules studied as ligands in this work readily displace EtCl to give $Cu(ligand)_2^+$ complexes. With many of the more

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[1] Address correspondence to this author at the Central Research Department, Experimental Station, DuPont Company, E356, Wilmington, DE 19898.

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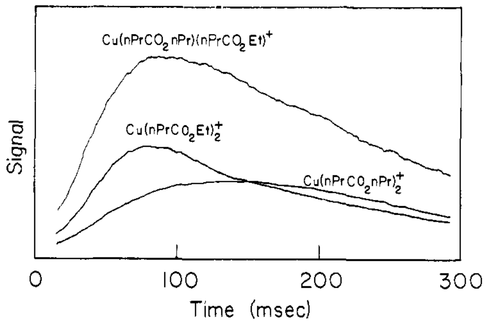


Figure 1. Variation of ion abundances with time for the Cu^+ source with a 5:3 mixture of n-$PrCO_2Et$ and n-$PrCO_2$-n-Pr at a total pressure of 9 × 10^{-6} torr. Initial reactions (not shown) during the first 70 ms yield $Cu(n\text{-}PrCO_2\text{-}n\text{-}Pr)_2^+$, $Cu(n\text{-}PrCO_2\text{-}n\text{-}Pr)(n\text{-}PrCO_2Et)^+$, and $Cu(n\text{-}PrCO_2Et)_2^+$ as the final product ions in this system. Ligand-exchange reactions of these ions with the n-$PrCO_2Et$ and n-$PrCO_2$-n-Pr neutrals are shown by double-resonance experiments to be rapid and approach equilibrium after about 200 ms. The equilibrium constants for these exchange reactions are calculated from the ratios of ion abundances at long times and the measured partial pressures of n-$PrCO_2Et$ and n-$PrCO_2$-n-Pr. The slow decrease in total ion abundance in this figure results from ion loss by diffusion to the walls of the ICR cell.

strongly bound ligands such complexes can be formed by direct condensation of the neutral molecule with Cu^+ and then Cu(ligand)$^+$. Where these condensation reactions proceed rapidly under the experimental conditions of interest, use of EtCl was omitted. In all cases examined in this work, initial reactions proceeded rapidly to give two-ligand complexes of Cu^+ and stopped without further addition of ligands.

With two ligand molecules A and B present, initial reactions forming Cu(ligand)$_2^+$ complexes are followed by ligand-exchange reactions 1 and 2, M = Cu. The enthalpy expressions for these

$$AMA^+ + B \overset{K_1}{\rightleftharpoons} AMB^+ + A \qquad \Delta H°_1 = D(AM^+\text{–}A) - D(AM^+\text{–}B) \tag{1}$$

$$AMB^+ + B \overset{K_2}{\rightleftharpoons} BMB^+ + A \qquad \Delta H°_2 = D(BM^+\text{–}A) - D(BM^+\text{–}B) \tag{2}$$

reactions follow from the definition of the heterolytic bond-dissociation energy for a single ligand in a two-ligand complex, eq 3. Overall, reactions 1 and 2 together result in the exchange of both ligands, reaction 4, where $D(M^+\text{–}2L)$ is the enthalpy for dissociation of both ligands in a two-ligand complex, eq 5.

$$AMB^+ \rightarrow AM^+ + B \qquad \Delta H° \equiv D(AM^+\text{–}B) \tag{3}$$

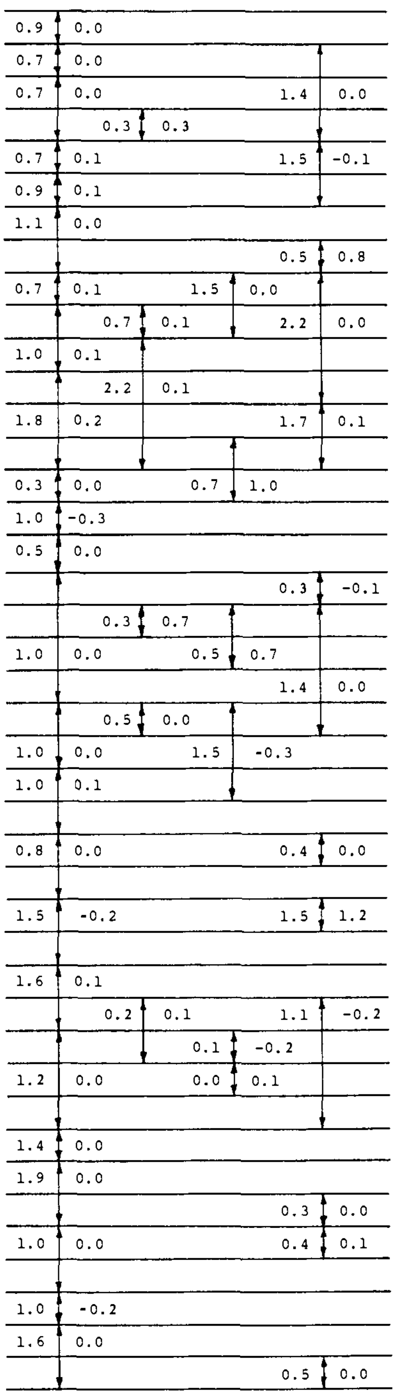
$$AMA^+ + 2B \rightleftharpoons BMB^+ + 2A \qquad \Delta H°_4 = D(M^+\text{–}2A) - D(M^+\text{–}2B) \tag{4}$$

$$LML^+ \rightarrow M^+ + 2L \qquad \Delta H \equiv D(M^+\text{–}2L) \tag{5}$$

Figure 1 shows the variation of ion abundances with time for the Cu^+ source in a mixture of n-$PrCO_2Et$ and n-$PrCO_2$-n-Pr. Initial reactions yield $Cu(n\text{-}PrCO_2\text{-}n\text{-}Pr)_2^+$, $Cu(n\text{-}PrCO_2\text{-}n\text{-}Pr)(n\text{-}PrCO_2Et)^+$, and $Cu(n\text{-}PrCO_2Et)_2^+$ as the final-product ions in this system. Ligand-exchange reactions 1 and 2 for these ions with the n-$PrCO_2Et$ and n-$PrCO_2$-n-Pr neutrals are shown by double-resonance experiments to be rapid and to approach equilibrium. The equilibrium constants for reactions 1, 2, and 4 can be calculated from the ratios of ion abundances at long times and the measured partial pressures of n-$PrCO_2Et$ and n-$PrCO_2$-n-Pr. The equilibrium constants are conveniently expressed as free energies with the relation $-\Delta G° = RT \ln K$.

Equilibria were measured for various pairwise combinations of 43 organic molecules as ligands. Values for the free-energy difference for exchange of both ligands, $\Delta G_{\text{exchange}}$, calculated from the measured equilibrium constants from reaction 4 are given in Table I. Each value represents the average of at least three determinations at different pressures. The results are combined

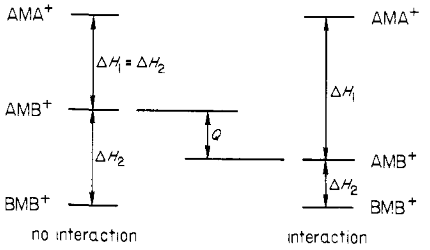
Table I. Measured Free Energies for Exchange of Both Ligands, ΔG_{exch}, Measured Enthalpies of Stabilization of the Mixed-Ligand Species, Q, and Relative Two-Ligand Dissociation Enthalpies, $\delta D(Cu^+\text{–}2L)$, for Two-Ligand Complexes of Cu^+ in the Gas Phase[a]



Ligand(L)	$D(Cu^+\text{-}2L)$[b]
i-Pr_2CO	25.4
n-$PrCO_2n$-Pr	24.5
n-$PrCO_2Et$	23.8
MeNCS	23.5
Et_2CO	23.2
$EtCO_2Et$	22.5
MeCOEt	21.7
EtSH	21.1
Me_2CO	20.6
THF[c]	19.8
$MeCO_2Me$	19.0
Et_2O	18.8
t-BuOH	18.6
MeSH	17.3
HCO_2n-Bu	16.9
t-BuCHO	16.6
i-PrCHO	15.5
i-PrOH	15.0
n-PrCHO	14.8
HCN	14.4
$Me_2C{=}CH_2$	13.4[d]
n-BuOH	14.0
EtCHO	13.5
n-PrOH	12.9
HCO_2Me	12.5
MeCHO	12.0
EtOH	11.6
Me_2O	11.1
$MeCH{=}CH_2$	9.7
s-BuBr	9.6
Oxirane	8.0
i-PrBr	8.0
MeOH	7.9
$MeNO_2$	7.9
i-BuBr	6.9
n-PrBr	5.5
i-PrCl	3.9
EtBr	3.6
MeNCO	3.1
i-BuCl	2.6
n-PrCl	1.6
CH_2O	0.5
EtCl	0.0

[a] All data in kcal/mol. [b] Values are relative to $\delta D(Cu^+\text{-}2EtCl) = 0$. Free-energy differences from the second column are added to give relative free energies which are converted to relative enthalpies, $\delta D(Cu^+\text{–}2L)$, by assuming that entropy changes are small and can be neglected except for corrections for symmetry number changes. [c] Tetrahydrofuran. [d] In converting the relative free energy to relative enthalpy, a correction of $T\Delta S = -0.82$ kcal/mol is made for isobutylene to correct for a decrease in symmetry number by a factor of 2 for each isobutylene on formation of the Cu(ligand)$_2^+$ complex.

Scheme I



into a ladder to give a scale of relative free energies for ligand, binding, $\delta\Delta G_{\text{exchange}}$. The zero of this scale is arbitrarily chosen by setting the value for EtCl, the weakest ligand measured, equal to zero. Redundant determinations in this scale provide an internal consistency check on the results. Agreement is found to within about ±0.2 kcal/mol. This corresponds to the variation expected from inaccuracies in the pressure measurements and is thought to arise principally from this source.

The measured equilibria for reaction 4 take no account of the relative abundance of the mixed-ligand species AMB^+. This abundance may be used to establish the values of the separate equilibria for reactions 1 and 2. This is conveniently expressed as an energy difference, Scheme I. If there were no interaction between the two ligand sites on the metal, then the enthalpies for reactions 1 and 2 would be equal, $\Delta H_1 = \Delta H_2$, defining a relative value for the enthalpy of the mixed species AMB^+ as the average of the enthalpies for the species AMA^+ and BMB^+. The actual relative enthalpy for AMB^+ is conveniently expressed as the deviation Q from this average value, where $Q = (\Delta H_2 - \Delta H_1)/2 = [D(AM^+\text{–}B) + D(BM^+\text{–}A) - D(AM^+\text{–}A) - D(BM^+\text{–}B)]/2$, Scheme I. In terms of the equilibrium constants, Q is given as $Q = (1/2)RT \ln (K_1/4K_2)$; the factor of a quarter is a statistical correlation arising because the mixed species can be formed in two ways as AMB^+ or BMA^+. Other entropy corrections cancel or are small and can be neglected;[9] see Discussion. Values of Q calculated from the measured equilibria among the 43 ligands studied are given in Table I.

Several additional molecules were studied as ligands but quantitative results were not obtained. The relative order of binding energies for these molecules was established, however, by observing the preferred direction of reaction 4 as follows: Me_3N, $HCO_2NH_2 > Me_2NH > MeNH_2 > MeCN > NH_3 > Me_2S > i\text{-}Pr_2CO$, which is the molecule with the highest binding energy in Table I.

Discussion

Relative enthalpies for dissociation of both ligands from $Cu(ligand)_2^+$ complexes, $\delta D(Cu^+\text{–}2L)$, are given in Table I for the 43 molecules studied. These are given relative to $\delta D(Cu^+\text{–}2EtCl) = 0$, which is chosen arbitrarily. The absolute zero of this enthalpy scale cannot be determined from the present work. The enthalpy scale is obtained from the free-energy scale by the assumption that entropy changes are small and tend to cancel so that they may be neglected except for corrections for symmetry changes.[10] This assumption has been made in analyzing the results of ICR studies of proton-transfer equilibria to obtain proton affinities.[11] Comparison to results with other techniques, which include temperature studies so that entropies can be experimentally determined, supports the use of this assumption for protons.[11] For metal cations, corrections for changes in moments of inertia as well as for symmetry changes may also be necessary.[12]

The symmetry correction is necessasry when a ligand which has a symmetry number greater than 1 as a free molecule binds in the $Cu(ligand)_2^+$ complex so as to reduce its symmetry.[10] This is clearly the case for isobutylene, which must bind to Cu^+ on one side of the double bond losing its twofold symmetry axis. The relative free energy, $\delta\Delta G°_{\text{exchange}}$, for isobutylene is therefore corrected by adding $T\Delta S° = -2RT \ln 2 = -0.82$ kcal/mol in calculating the relative enthalpy, $\delta D(Cu^+\text{-}2\text{-isobutylene})$, Table I. No such symmetry correction is made for any of the other molecules studied as ligands in this work.[13]

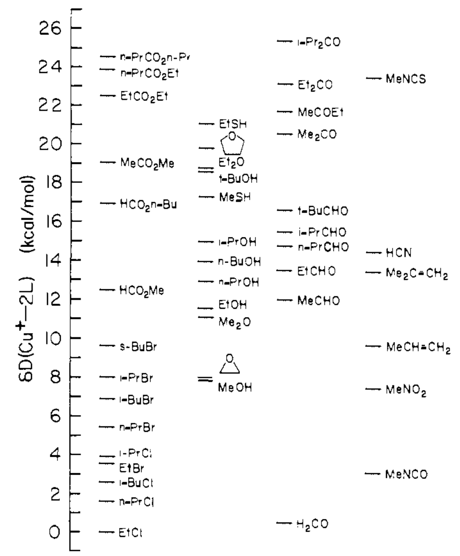


Figure 2. Relative two-ligand dissociation enthalpies, $\delta D(Cu^+\text{–}2L)$, for the 43 molecules studied, arranged by functional group, relative to $\delta D(Cu^+\text{–}2EtCl) = 0$.

Changes in moments of inertia could also make a significant contribution to ΔS for reaction 4. This contribution has been analyzed in detail for one-ligand complexes of Li^+ by Woodin and Beauchamp.[12] Accurate treatment of this contribution requires knowledge of the geometries of the species involved. Geometries are not available for the $Cu(ligand)_2^+$ species. However, this effect seems likely to be unimportant in the present work. Moment-of-inertia changes are important when the metal–ligand bonding distance and the ligand mass are significantly different for the two ligands. The ligands studied with Cu^+ are generally similar in mass and can be expected to bond similarly. Neglect of entropy changes, except for the symmetry number correction, thus appears to be an acceptable, although not desirable, assumption in the present work. Quantitative treatment of the entropy term would be a desirable correction to the present data if accurate geometries for the $Cu(ligand)_2^+$ species become available.

A simple, ideal model of the bonding in the two-ligand complexes studied in this work would assume that the bonding at each site is independent. It would follow that the dissociation energies for the first and second ligands would be equal: $D(LM^+\text{–}L) = D(M^+\text{–}L)$. For the real complexes, however, the dissociation energy for the second ligand should be significantly less than that for the first: $D(LM^+\text{–}L) < D(M^+\text{–}L)$. This arises because interaction of the partial charges on the ligands increases the total bond energy of the $L\text{–}M^+\text{–}L$ complex compared to twice the bond energy of the $M^+\text{–}L$ complex. This interaction also favors a linear geometry for the $L\text{–}M^+\text{–}L$ species. Covalent effects will further complicate the bonding in the two-ligand complexes. The relative two-ligand dissociation energies, $\Delta D(Cu^+\text{–}2L)$, measured in the present work are therefore not expected to be simply related to the one-ligand dissociation energies, $D(Cu^+\text{–}L)$.

Evidence for a particular kind of nonideal behavior in the bond enthalpies is contained in the measured enthalpies of stabilization of the mixed-ligand species, Q, listed in Table I for all the ligand-pair combinations examined in this work. Pairs of oxygen

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[9] Corrections for symmetry number changes cancel because Q is a difference.

[10] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976; p 76.

[11] Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417–5429.

[12] Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.

[13] Symmetric ethers and ketones (Me_2O, Me_2CO, etc.), which have twofold axes as free molecules, are assumed to form $Cu(ligand)_2^+$ complexes with the Cu^+ on the symmetry axis of the ligand so that this symmetry is retained.

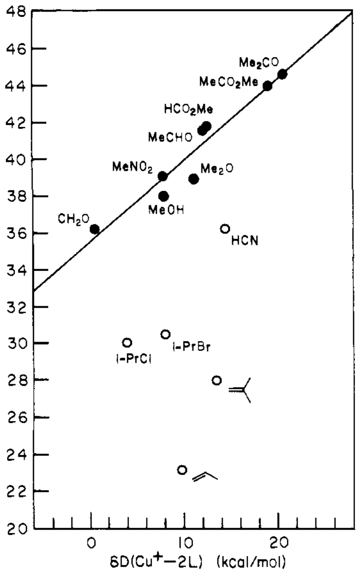

Figure 3. Comparison of ligand dissociation enthalpies for Li^+ to relative two-ligand dissociation enthalpies for Cu^+. The solid line is a least-squares fit to the data for the eight oxygen bases (solid circles); $D(Li^+–L) = 0.443[\delta D(Cu^+–2L)] + 35.5$ kcal/mol (correlation coefficient, $r = 0.96$).

bases together show no stabilization of the mixed species. For pairs of oxygen bases with alkenes, however, the mixed species are stabilized by about 0.9 kcal/mol. A similar effect is observed for pairs of oxygen and sulfur bases. These effects have been reported in a separate paper where they are analyzed in detail.[14]

Relative two-ligand dissociation enthalpies for the 43 molecules studied in this work, arranged by functional group, are plotted in Figure 2. Within each functional group series, substitution of a larger alkyl group for a smaller one is seen to lead to a systematic increase in $\Delta D(Cu^+–2L)$. The results are consistent with and illustrate an increase in basicity in the sequence H < Me < Et < *n*-Pr < *n*-Bu < *i*-Bu < *i*-Pr < *sec*-Bu < *t*-Bu. Similar systematic alkyl substituent effects have been observed for proton affinities,[11] $PA(B) \equiv D(B–H^+)$, and for one-ligand binding energies to Li^+,[15] and Mn^+.[3] Evidently, differences in bonding in the two-ligand complexes compared to the one-ligand complexes do not affect the qualitative behavior of these substituent effects.

Atomic-copper cation, Cu^+, has a ^1S ground state corresponding to an $[Ar](3d)^{10}$ configuration.[16] The next higher states, $[Ar](3d)^9(4s)$ ^3D at 2.7 eV and $[Ar](3d)^9(4s)$ ^1D at 3.3 eV, should not be involved in ligand bonding. Some evidence was observed in studies of the initial reactions of Cu^+ with neutrals that a fraction of electronically excited species might be present.[4] The ^3D state might likely be the state involved if the observed phenomena indeed involve internal excitation. It seems unlikely that this excitation, if present, whatever its form, would affect the ligand-exchange equilibria examined in the present work. Several-dozen reactive and nonreactive collisions with various neutrals intervene between the production of Cu^+ and the point at which the equilibrium ratios of $Cu(ligand)_2^+$ species are measured.

The bonding interaction of Cu^+ with ligand molecules may be expected to reflect both ionic and covalent factors. In bonding to Cu^+, ligands are attracted by interaction of intrinsic and induced-ligand dipoles with the charge on Cu^+. Covalent bonding can occur by delocalization of electrons from occupied ligand orbitals into the empty 4s and 4p orbitals on Cu^+. This delocalization will be limited by repulsion by the electrons in the filled 3d and core orbitals. Covalent bonding can also occur by delocalization of 3d electrons on Cu^+ into unoccupied π^* or d orbitals, π-back-bonding. This can occur only for ligand molecules with suitable orbitals available.

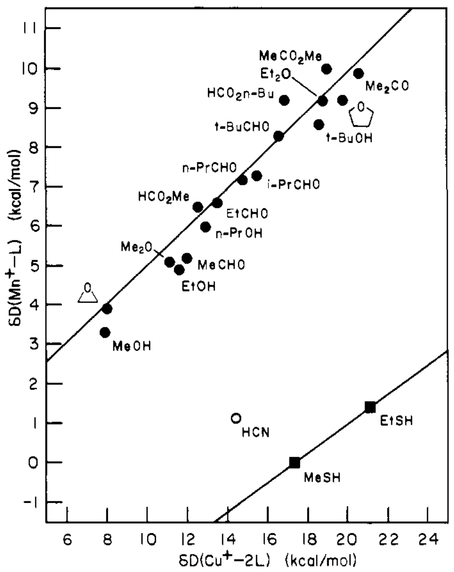

Figure 4. Comparison of relative ligand dissociation enthalpies for Mn^+ to relative two-ligand dissociation enthalpies for Cu^+. The upper solid line is a least-squares fit to the data for the 17 oxygen bases; $\delta D(Mn^+–L) = 0.524[\delta D(Cu^+–2L)] - 0.631$ kcal/mol ($r = 0.98$). The line through the two mercaptans is given by $\delta D(Mn^+–L) = 0.368[\delta D(Cu^+–2L)] -6.374$ kcal/mol.

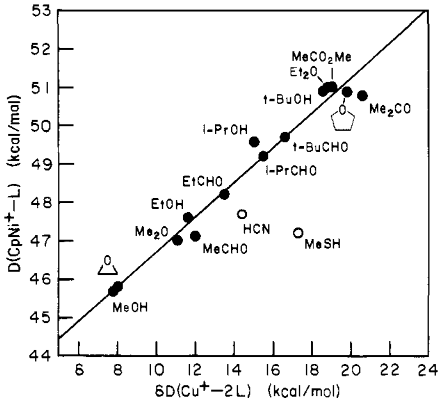

Figure 5. Comparison of relative ligand dissociation enthalpies for $CpNi^+$ to relative two-ligand dissociation enthalpies for Cu^+. The solid line is a least-squares fit to the data for the 14 oxygen bases; $D(CpNi^+–L) = 0.454[\delta D(Cu^+–2L)] + 42.1$ kcal/mol ($r = 0.99$)

Comparisons of Basicity Scales for Other Reference Acids. Comparison of the relatively two-ligand dissociation enthalpies for Cu^+ with available results for other reference acids reveals some interesting points about the nature of the metal–ligand bonding interaction. Figure 3 shows a plot of ligand binding energies to Li^+,[15] $D(Li^+–L)$, vs. the results for Cu^+, $\delta D(Cu^+–2L)$. The eight oxygen bases show a good linear correlation. A least-squares fit to these data gives $D(Li^+–L) = 0.443$ $[\delta D(Cu^+–2L)] + 35.5$ kcal/mol (correlation coefficient, $r = 0.96$). A similar plot of Al^{+2} vs. Cu^+ results for 18 oxygen bases gives $\delta D(Al^+–L) = 0.770[\delta D(Cu^+–2L)] - 8.72$ kcal/mol ($r = 0.97$). The zero of the $\delta D(Al^+–L)$ scale is arbitrarily chosen to be $D(Al^+–EtOH) = 0$. The oxygen bases include alkyl alcohols, ethers, aldehydes, ketones, and esters. In the Li^+ vs. Cu^+ comparison, Figure 3, *i*-PrCl, *i*-PrBr, HCN, and two alkenes, all soft bases, are seen to fall off the line for oxygen bases, bonding relatively more strongly to Cu^+. This is consistent with the expectation that the soft acid Cu^+ should bond relatively more strongly to soft bases compared to the hard acid Li^+. Comparison of results for Mn^+[3] with those for Cu^+, Figure 4, shows similar effects. Seventeen oxygen bases fall around a line given by $\delta D(Mn^+–L) = 0.524$-

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[14] Kappes, M. M.; Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 888.

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[16] Moore, C. E. "Atomic Energy Levels" *Natl. Bur. Stand. (U.S.) Circ.* **1952**, No. 467.

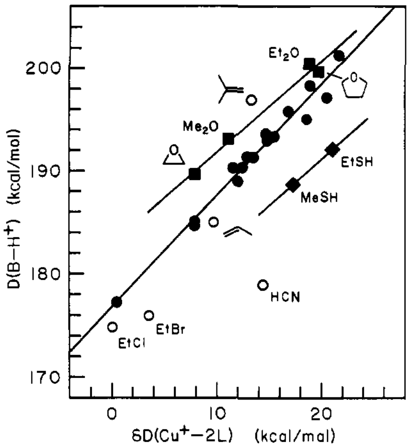

Figure 6. Comparison of proton affinities PA(B) ≡ $D(\text{B–H}^+)$ to relative two-ligand dissociation enthalpies for Cu^+. The upper solid line is a least-squares fit for the four ethers; PA(L) = $0.890[\delta D(\text{Cu}^+\text{–2L})] + 182.8$ kcal/mol ($r = 0.99$). The middle solid line is a least-squares fit for 16 other oxygen bases (solid circles); PA(L) = $1.074[\delta D(\text{Cu}^+\text{–2L})] + 176.9$ kcal/mol ($r = 0.99$). The lower solid line through the two mercaptans is given by PA(L) = $0.895[\delta D(\text{Cu}^+\text{–2L})] + 173.121$ kcal/mol.

$[\delta D(\text{Cu}^+\text{–2L})] - 0.631$ kcal/mol. Cu^+ is clearly also a softer acid than Mn^+ as HCN and the two mercaptans show a strong preference toward binding to Cu^+, Figure 4. The offset of HCN from the line for the oxygen bases is 11.0 kcal/mol on the $\Delta D(\text{Cu}^+\text{–2L})$ axis. The offset of the line for the two mercaptans is 16.4 kcal/mol. Note that there is actually a reversal of binding energies for MeSH compared to MeOH and EtSH compared to EtOH on the Cu^+ scale compared to the Mn^+ scale, Figure 4. There is only a slight perference of HCN and MeSH for Cu^+ when compared to CpNi^+,[17] Figure 5. The line for the 14 oxygen bases is given by $D(\text{CpNi}^+\text{–L}) = 0.454[\delta D(\text{Cu}^+\text{–2L})] - 42.1$ kcal/mol. HCN is offset by 2.2 kcal/mol and MeSH by 6.1 kcal/mol on the $\delta D(\text{Cu}^+\text{–2L})$ axis.

Comparison of the Cu^+ results to proton affinities,[11,18] PA(B) ≡ $D(\text{B–H}^+)$, reveals two separate lines for oxygen bases. Sixteen oxygen bases fall on a line given by PA(L) = $1.074[\delta D(\text{Cu}^+\text{–2L})] + 176.9$ kcal/mol ($r = 0.99$). These bases include alkyl alcohols, aldehydes, ketones, and esters. Four ethers fall along a separate line given by PA(L) = $0.890[\delta D(\text{Cu}^+\text{–2L})] + 182.8$ kcal/mol ($r = 0.99$). A number of soft bases fall off the oxygen lines toward stronger binding to Cu^+; these include EtCl, EtBr, MeSH, EtSH, and MeNCS, Figure 6, indicating as expected that Cu^+ is a softer acid than H^+. The two alkenes behave erratically, one falling above and the other below the lines for the oxygen bases. Bonding of the proton to alkenes is unlike complex formation of alkenes with metals, however. Protonation of isobutylene yields *tert*-butyl cation, for example. A simple correlation of proton affinities of alkenes with alkene–metal cation binding energies is therefore not expected.

The slopes of the correlation plots of the other reference acids vs. Cu^+ for oxygen bases vary in the order H^+ (1.074), Al^+, (0.770), Mn^+ (0.524), and Li^+ (0.443). This same order has been seen for correlation plots for these reference acids with one another.[3] It likely reflects the relative metal–ligand bond distance, H^+ having the shortest bond distance and Li^+ the longest. With a shorter bond distance the effect of a larger alkyl substituent is greater since it is closer to the charge center. The slope of the line thus favors the metal with the shorter bond distance as basicity increases with increasing alkyl substitution. With division of the $\delta D(\text{Cu}^+\text{–2L})$ scale by two to give the relative dissociation enthalpy per ligand for Cu^+, the slopes become H^+ (2.15), Al^+ (1.54), Mn^+ (1.05), and Li^+ (0.89). The ligand bonding distance to Cu^+ is thus seen to be shorter than that to Li^+ since the slope for Cu^+ vs. itself is 1.00. Actually, the one-ligand dissociation enthalpies are not known from the average dissociation energy available from the present work and may well be higher as discussed above. This would give a higher effective slope for comparison of Cu^+ to H^+, Mn^+, and Al^+. It is thus not clear whether bonding distance to Cu^+ may be shorter than that to these reference acids or not. The significance of the slope in the correlation of CpNi^+ to Cu^+ is also not clear since two-ligand effects are present in both data sets in this comparison in different ways.

In conclusion, the relative gas-phase two-ligand dissociation enthalpies for Cu^+, $\delta D(\text{Cu}^+\text{–2L})$, measured in this work do show, as expected, that Cu^+ is a softer acid than H^+, Al^+, Mn^+, and Li^+. This is apparent from the relative preference of Cu^+ for mercaptans and HCN compared to alcohols and other oxygen bases. Comparison of Cu^+ and Mn^+ results shows a clear reversal of binding energies of mercaptans and the corresponding alcohols. Slopes of the correlation plots for oxygen bases imply that the ligand bonding distance to Cu^+ is less than to Li^+. Furthere analysis and comparison of the Cu^+ results to results for H^+, Al^+, Mn^+, CpNi^+, and Li^+ are limited by uncertainties about possible differences between two-ligand dissociation energies, or average bond energies, measured for Cu^+ and the one-ligand bond dissociation energies available for the other reference acids. Studies underway in our laboratory to measure two-ligand dissociation enthalpies for Co^+, Ni^+, and FeBr^+ should provide useful comparisons to the Cu^+ results.

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Registry No. $\text{Cu}(i\text{-Pr}_2\text{CO})_2^+$, 80975-97-9; $\text{Cu}(n\text{-PrCO}_2n\text{-Pr})_2^+$, 80975-98-0; $\text{Cu}(n\text{-PrCO}_2\text{Et})_2^+$, 80975-99-1; Cu(MeNCS)_2^+, 80976-00-7; $\text{Cu(Et}_2\text{CO)}_2^+$, 80976-01-8; $\text{Cu(EtCO}_2\text{Et)}_2^+$, 80976-02-9; Cu(MeCOEt)_2^+, 80976-03-0; Cu(EtSH)_2^+, 80976-04-1; $\text{Cu(Me}_2\text{CO)}_2^+$, 80976-05-2; Cu(THF)_2^+, 80976-06-3; $\text{Cu(MeCO}_2\text{Me)}_2^+$, 80976-07-4; $\text{Cu(Et}_2\text{O)}_2^+$, 80976-08-5; $\text{Cu}(t\text{-BuOH})_2^+$, 80976-09-6; Cu(MeSH)_2^+, 80976-10-9; $\text{Cu(HCO}_2n\text{-Bu)}_2^+$, 80976-11-0; $\text{Cu}(t\text{-BuCHO})_2^+$, 80976-12-1; $\text{Cu}(i\text{-PrCHO})_2^+$, 80976-13-2; $\text{Cu}(i\text{-PrOH})_2^+$, 80976-14-3; $\text{Cu}(n\text{-PrCHO})_2^+$, 80976-15-4; Cu(HCN)_2^+, 80976-16-5; $\text{Cu(Me}_2\text{C{=}CH}_2)_2^+$, 80976-17-6; $\text{Cu}(n\text{-BuOH})_2^+$, 80976-18-7; Cu(EtCHO)_2^+, 80976-19-8; $\text{Cu}(n\text{-PrOH})_2^+$, 80997-15-5; $\text{Cu(HCO}_2\text{Me)}_2^+$, 80976-20-1; Cu(MeCHO)_2^+, 80976-21-2; Cu(EtOH)_2^+, 80976-22-3; $\text{Cu(Me}_2\text{O)}_2^+$, 80976-23-4; $\text{Cu(MeCH{=}CH}_2)_2^+$, 72267-45-9; $\text{Cu}(s\text{-BuBr})_2^+$, 80976-24-5; Cu(oxirane)_2^+, 80976-25-6; $\text{Cu}(i\text{-PrBr})_2^+$, 80976-26-7; Cu(MeOH)_2^+, 80976-27-8; $\text{Cu(MeNO}_2)_2^+$, 80976-28-9; $\text{Cu}(i\text{-BuBr})_2^+$, 80976-29-0; $\text{Cu}(n\text{-PrBr})_2^+$, 80976-30-3; $\text{Cu}(i\text{-PrCl})_2^+$, 80976-31-4; Cu(EtBr)_2^+, 80976-32-5; Cu(MeNCO)_2^+, 80976-33-6; $\text{Cu}(i\text{-BuCl})_2^+$, 80976-34-7; $\text{Cu}(n\text{-PrCl})_2^+$, 80976-35-8; $\text{Cu(CH}_2\text{O)}_2^+$, 80976-36-9; Cu(EtCl)_2^+, 80976-37-0.

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