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# Unexpected Displacement of Alkenes by Alkanes in the Reactions of $Y(alkene)^{2+}$. An Experimental and Theoretical Study

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**Abstract:** Ligand-displacement reactions in the gas phase using Fourier transform mass spectrometry yield the following metal-ligand bond energy order for $Y^{2+}$: $CH_4$, $C_2H_6$ < $C_2H_2$, $C_2H_4$ < $C_3H_8$ < $C_3H_6$ < $C_4H_{10}$ < $C_4H_6$. The unexpected displacement of alkenes by alkanes in the reactions of $Y(alkene)^{2+}$ is explained by a detailed theoretical treatment, which indicates that $Y^{2+}$ binds primarily by electrostatic interactions. As an aid to the discussion, $Sc^{2+}$ and $Cu^+$ are also considered.

An intensive effort has been underway over the past ten years to obtain qualitative and quantitative information on metal-ligand bond energies. The investigation has been broad in scope, including measurements in the gas phase, in solution, and on surfaces.[1] This effort is testimony to the importance of metal-ligand bond energies in postulating and testing reaction mechanisms and in understanding fundamental features about metal-ligand bonding. The increasing number of theoretical studies has been particularly important in this latter regard.

Specifically, gas-phase studies have provided a wealth of thermodynamic data on the binding energies of ligands to bare atomic metal atoms, cations, and anions.[2] The absence of complicating effects due to solvent and other coordinated ligands yields "intrinsic" metal-ligand bond energies ideally suited for comparison to theory. Of the many mass spectrometric methods developed for this purpose, the determination of endothermic reaction thresholds by the ion beam approach[3] and the determination of photodissociation thresholds using Fourier transform mass spectrometry[4] have been particularly successful at yielding absolute metal cation-ligand bond energies, i.e., $D°(M^+-L)$.

While a fairly extensive data base on singly charged metal bond energies is now available, only a handful of studies have been performed on doubly charged metal ions. On the basis of an earlier study of $Ti^{2+}$ by Tonkyn and Weisshaar,[5] we have begun to focus on several doubly charged early-transition-metal ions including $Nb^{2+}$,[6] $La^{2+}$,[7] $Zr^{2+}$,[8] $Ta^{2+}$,[8] and $Y^{2+}$.[9] These metals have relatively low second ionization potentials and are observed to undergo interesting reactions with small organic molecules in competition with simple charge transfer. These reactions can result in the formation of ligated doubly charged metal ions, $M^{2+}-L$, whose physical and chemical properties can then be investigated.

Two of the more interesting results from these studies, thus far, both involving $La^{2+}$, have been the observation of a stable $LaFe^{2+}$[10] and the finding that $La^+$ binds acetylene more strongly than $La^{2+}$.[7] Both of these results have been supported by theoretical calculations.[11] In this paper the relative metal-ligand bond energy ordering for a series of small hydrocarbons to $Y^{2+}$ is determined by ligand-displacement reactions, and the unexpected observation that alkanes can displace alkenes from $Y^{2+}$ is explained by a detailed theoretical treatment. As an aid in the discussion, $Sc^{2+}$ and $Cu^+$ are also considered.

## Experimental Section

**Experimental Methods.** The experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer.[12] The instrument is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The metal ions were generated by focusing the fundamental frequency (1064 nm) of a Quanta Ray Nd:YAG laser onto a thin high-purity metal target.[13] The doubly charged ions were then isolated by ejecting the singly charged ions. Intensities of $Sc^{2+}$ and $Y^{2+}$ were enhanced by focusing the laser near the edge of the metal target.

The chemicals were obtained from commercial sources. They were either leaked into the cell through Varian leak valves in order to maintain a constant background pressure or pulsed[14] into the cell in order to form a metal-ligand species, which further reacts with the other gas samples leaked into the cell. Pressures were measured with an uncalibrated (Bayard-Alpert) ionization gauge and were usually around $5 \times 10^{-7}$ Torr for the sample gases and $5 \times 10^{-5}$ Torr for Ar used for CID experiments. To ensure that all of the ions studied were thermally cool, they were allowed to collide with background neutral gas for at least 1 s.

**Computational Methods.** The geometry of each of the systems was fully optimized at the self-consistent-field (SCF) level by analytic first- and second-derivative methods. The vibrational frequencies, evaluated by using the second derivatives, confirmed that the geometry corresponds to a minimum. In order to account for any metal to ligand donation, it is important to include electron correlation. Therefore, the metal ion-ligand binding energies were computed by using the SCF-based modified coupled pair functional[15] (MCPF) method at the SCF equilibrium geometries. Previous work[16] has shown that this procedure yields metal-ligand binding energies that agree to within 1 kcal/mol with those obtained with the equilibrium geometries obtained at the MCPF level, but at a fraction of the computational expense. All of the valence electrons were correlated including the C 2s and 2p, H 1s, and metal $(n - 1)$d and ns electrons.

The Sc and Cu basis sets were of the form (14s 11p 6d)/[8s 6p 4d]. They were derived from the primitive sets of Wacthers[17] plus two diffuse

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**Table I.** Reactions Used To Generate $M^{n+}$–L

| | | |
|---|---|---|
| $Y^{2+} + C_2H_6$ | $\rightarrow$ | $YC_2H_6^{2+}$ |
| $Y^{2+} + C_2H_6$ | $\rightarrow$ | $YC_2H_4^{2+} + H_2$ |
| $Y^{2+} + C_3H_8$ | $\rightarrow$ | $YC_3H_6^{2+} + H_2$ |
| $YC_2H_4^{2+} + C_3H_8$ | $\rightarrow$ | $YC_3H_8^{2+} + C_2H_4$ |
| $Y^{2+} + C_4H_{10}$ | $\rightarrow$ | $YC_4H_6^{2+} + 2H_2$ |
| $YC_2H_4^{2+} + C_4H_{10}$ | $\rightarrow$ | $YC_4H_{10}^{2+} + C_2H_4$ |
| $Cu^+ + C_3H_8$ | $\rightarrow$ | $CuC_3H_8^+$ |
| $Cu^+ + C_3H_6$ | $\rightarrow$ | $CuC_3H_6^+$ |
| $Cu^+ + C_2H_4$ | $\rightarrow$ | $CuC_2H_4^+$ |
| $Sc^{2+} + C_2H_6$ | $\rightarrow$ | $ScH^+ + C_2H_5^+$ |
| | $\rightarrow$ | $Sc^+ + C_2H_6^+$ |
| $Sc^{2+} + C_3H_8$ | $\rightarrow$ | $ScCH_3^+ + C_2H_5^+$ |
| | $\rightarrow$ | $ScH^+ + C_3H_7^+$ |
| | $\rightarrow$ | $Sc^+ + C_3H_8^+$ |

p functions and diffuse d function.[18] For Y, the relativistic effective core potential (RECP) developed by Hay and Wadt[19] was used. In this RECP, the outermost core orbitals, the 4s and 4p, are in the valence shell. The valence electrons can thus be correlated, since the valence orbitals have the correct nodal structure.[20] The supplemented valence basis set described in ref 21 was employed, yielding a Y basis set of the form (6s 5p 5d)/[5s 4p 4d]. For C and H, a valence double $\zeta$, VDZ, basis set was used. The C and H VDZ basis sets were the (9s 5p)/[3s 2p] and (4s)/[2s] sets developed by Dunning and Hay[22] from the primitive sets of Huzinaga.[23] In the MCPF calculations the 3s combinations of the 3d basis functions were eliminated. The calculations were carried out using the MOLECULE-SWEDEN[24] and GRADSCF[25] program systems at the NASA Ames Research Center central computing facility.

## Results and Discussion

**Determination of Relative Metal–Ligand Bond Energies.** Relative metal–ligand bond energies were determined by noting the occurrence or nonoccurrence of reaction 1. In favorable cases,

$$M^{n+}\text{–}L + L' \rightarrow M^{n+}\text{–}L' + L \qquad (n = 1, 2) \qquad (1)$$

both the forward and reverse reactions were monitored. Such tests hopefully minimize the possibility of being mislead by these experiments. In particular the absence of a reaction does not always indicate that it is endothermic, and conversely, the occurrence of a reaction does not always indicate that it is exothermic.

The reactions used to generate the primary $M^{n+}$–L species are listed in Table I, and the ligand-displacement reactions tested are given in Table II. Competing reactions were observed but are not listed, with the exception of $Sc^{2+}$ in Table I. Unfortunately, in contrast to $Y^{2+}$, attempts to generate any $Sc^{2+}$–L species proved unsuccessful with only charge-splitting reactions observed.

From the results in Table II the following metal–ligand bond energy orders are assigned:

for $Y^{2+}$

$$CH_4, C_2H_6 < C_2H_2, C_2H_4 < C_3H_8 < C_3H_6 < C_4H_{10} < C_4H_6$$

for $Cu^+$

$$C_3H_8 < C_2H_4 < C_3H_6$$

The most striking feature of these results is the observation that $C_n$ alkanes are bound more strongly to $Y^{2+}$ than are $C_{n-1}$ alkenes.

**Table II.** Ligand Displacement Reactions[a]

| | | | |
|---|---|---|---|
| $YC_2H_4^{2+} + CH_4$ | $\nrightarrow$ | $YCH_4^{2+} + C_2H_4$ | |
| $YC_2H_4^{2+} + C_2H_6$ | $\nrightarrow$ | $YC_2H_6^{2+} + C_2H_4$ | |
| $YC_2H_4^{2+} + C_2H_2$ | $\nrightarrow$ | $YC_2H_2^{2+} + C_2H_4$ | |
| $YC_2H_2^{2+} + C_2H_4$ | $\nrightarrow$ | $YC_2H_4^{2+} + C_2H_2$ | |
| $YC_2H_4^{2+} + C_3H_8$ | $\rightarrow$ | $YC_3H_8^{2+} + C_2H_4$ | |
| $YC_2H_4^{2+} + C_4H_{10}$ | $\rightarrow$ | $YC_4H_{10}^{2+} + C_2H_4$ | |
| $YC_2H_4^{2+} + C_3H_6{}^{b}$ | $\rightarrow$ | $YC_3H_6^{2+} + C_2H_4$ | |
| $YC_2H_6^{2+} + C_2H_2$ | $\rightarrow$ | $YC_2H_2^{2+} + C_2H_6$ | |
| $YC_3H_6^{2+} + C_2H_4$ | $\nrightarrow$ | $YC_2H_4^{2+} + C_3H_6$ | |
| $YC_3H_6^{2+} + C_2H_6$ | $\nrightarrow$ | $YC_2H_6^{2+} + C_3H_6$ | |
| $YC_3H_6^{2+} + C_3H_8$ | $\nrightarrow$ | $YC_3H_8^{2+} + C_3H_6$ | |
| $YC_3H_6^{2+} + C_4H_{10}$ | $\rightarrow$ | $YC_4H_{10}^{2+} + C_3H_6$ | |
| $YC_4H_6^{2+} + C_2H_6$ | $\nrightarrow$ | $YC_2H_6^{2+} + C_4H_6$ | |
| $YC_4H_6^{2+} + C_3H_6$ | $\nrightarrow$ | $YC_3H_6^{2+} + C_4H_6$ | |
| $YC_4H_6^{2+} + C_3H_8$ | $\nrightarrow$ | $YC_3H_8^{2+} + C_4H_6$ | |
| $YC_4H_6^{2+} + C_4H_{10}$ | $\nrightarrow$ | $YC_4H_{10}^{2+} + C_4H_6$ | |
| $YC_3H_8^{2+} + C_2H_4$ | $\nrightarrow$ | $YC_2H_4^{2+} + C_3H_8$ | |
| $YC_3H_8^{2+} + C_3H_6$ | $\rightarrow$ | $YC_3H_6^{2+} + C_3H_8$ | |
| | $\rightarrow$ | $YC_6H_{14}^{2+}$ | |
| $YC_6H_{14}^{2+}$ | $\xrightarrow{\text{CID}}$ | $YC_3H_6^{2+} + C_3H_8$ | 72%[c] |
| | $\rightarrow$ | $YC_3H_8^{2+} + C_3H_6$ | 11% |
| | $\rightarrow$ | $YC_4H_6^{2+} + C_2H_6 + H_2$ | 17% |
| $YC_3H_8^{2+} + C_4H_{10}$ | $\rightarrow$ | $YC_4H_{10}^{2+} + C_3H_8$ | |
| $YC_4H_{10}^{2+} + C_3H_6$ | $\nrightarrow$ | $YC_3H_6^{2+} + C_4H_{10}$ | |
| $YC_4H_{10}^{2+} + C_3H_8$ | $\nrightarrow$ | $YC_3H_8^{2+} + C_4H_{10}$ | |
| $YC_4H_{10}^{2+} + C_4H_6$ | $\rightarrow$ | $YC_4H_6^{2+} + C_4H_{10}$ | |
| $CuC_3H_8^+ + C_2H_4$ | $\rightarrow$ | $CuC_2H_4^+ + C_3H_8$ | |
| $CuC_2H_4^+ + C_3H_8$ | $\rightarrow$ | $CuC_3H_6^+ + C_2H_6$ | |
| $CuC_3H_6^+ + C_2H_4$ | $\nrightarrow$ | $CuC_2H_4^+ + C_3H_6$ | |
| $CuC_2H_4^+ + C_3H_6$ | $\rightarrow$ | $CuC_3H_6^+ + C_2H_4$ | |
| $CuC_3H_6^+ + C_3H_8$ | $\nrightarrow$ | $CuC_3H_8^+ + C_3H_6$ | |
| $CuC_3H_8^+ + C_3H_6$ | $\rightarrow$ | $CuC_3H_6^+ + C_3H_8$ | |

[a] Other reactions are observed that compete effectively with ligand displacement. Absence of ligand displacement implies a rate constant for the reaction of $<1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. [b] $C_3H_6$ is propene in these reactions. [c] Favorable signal intensity of $YC_6H_{14}^{2+}$ permitted a CID study in this case. Greater loss of $C_3H_8$ relative to $C_3H_6$ is in accordance with the ligand-displacement results.

The limited $Cu^+$ data, however, follow the more expected ordering. The results are supported and explained by the theoretical calculations discussed below.

**Theory: The Explanation for the Unexpected Displacement Reactions of $Y^{2+}$–L.** The optimal structures for $Sc^{2+}$ interacting with a series of hydrocarbons are shown in Figure 1. The molecular systems are ordered by the $Sc^{2+}$ ligand binding energies, also given on the figure. Similar optimal structures for $Y^{2+}$ and $Cu^+$ interacting with these hydrocarbons are found and their binding energies are also given on the figure. On the basis of previous work,[16] we suspect that these binding energies are ~5 kcal/mol too small due to limitations in both the basis set and the treatment of correlation. However, the relative binding energies for the various ligands should be more accurate.

One notable difference in geometry occurs for $C_2H_2$ and $C_2H_4$ where the $Sc^{2+}$ adopts an asymmetric structure, shown in the figure, while both $Y^{2+}$ and $Cu^+$ sit at the bond midpoint yielding structures with $C_{2v}$ symmetry. For $Sc^{2+}$ the asymmetric structure is 0.4 kcal/mol more stable than the symmetric one. For $Y^{2+}$ the asymmetric structure is slightly lower at the SCF level, but the symmetric structure becomes slightly favored at the MCPF level. Given these small energy differences, we cannot unambiguously determine whether the asymmetric or symmetric structure is the more stable. However, as the binding energies are very similar, it will not introduce any serious error in the computed trends in the ligand binding energy.

The bonding is dominantly electrostatic in origin. There is some charge donation between the metal ion and ligand, but the largest change is a polarization of the charge on the metal and ligand. Therefore, it is not surprising to find that there is only a small change from the free ligand geometry. For example, the C–H bonds change by only ~0.01 Å when the metal is present. The C–C distances show only a slightly larger change with the metal ion; the C–C bond in $C_2H_4$ increases by only 0.025 Å. Given the small changes in the ligands, we do not report the geometries.

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(25) GRADSCF is a vectorized SCF first- and second-derivative code written by A. Komornicki and H. King.

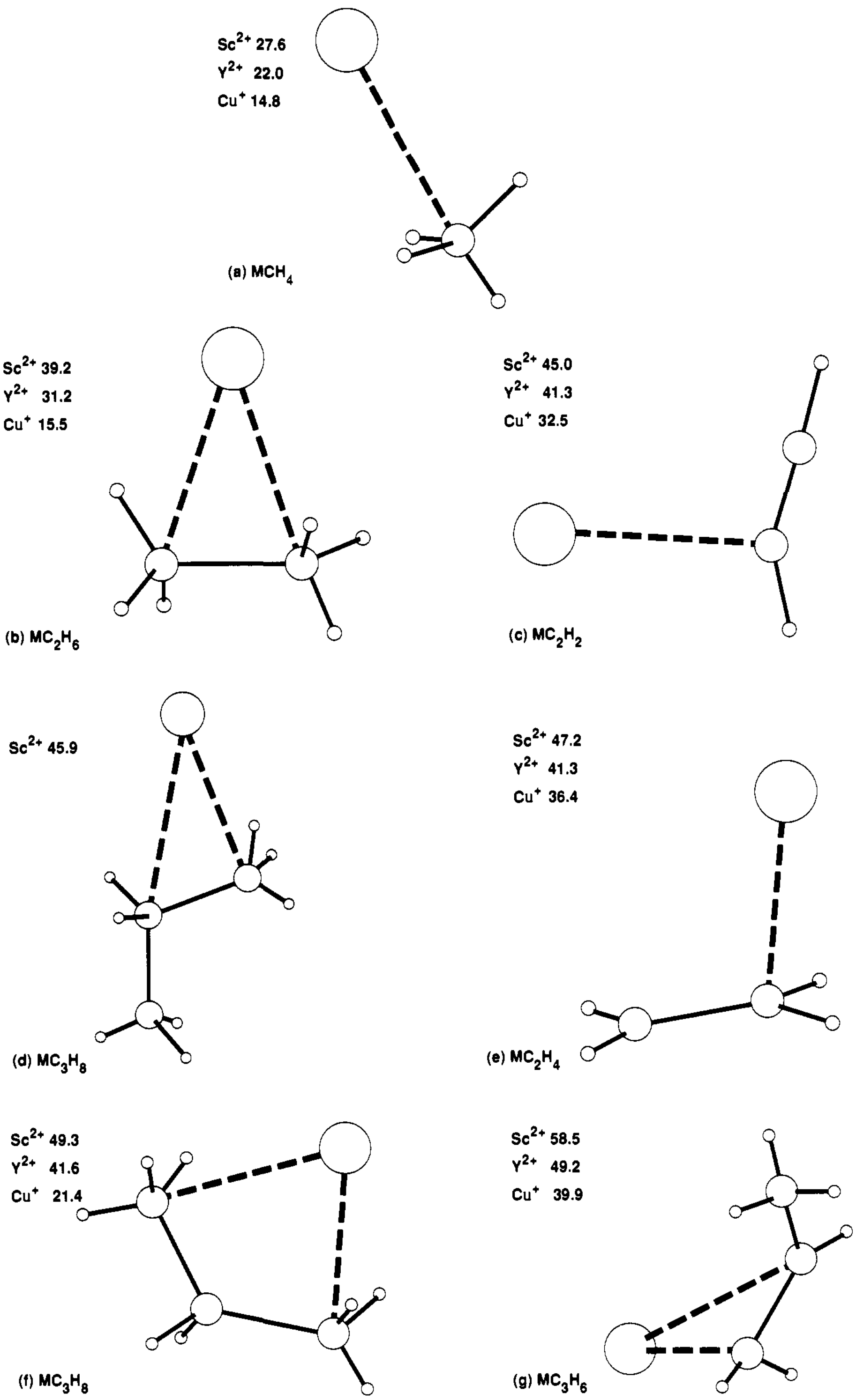

**Figure 1.** Optimal structures for $Sc^{2+}$ interacting with a series of hydrocarbons. The structures are drawn to scale for $Sc^{2+}$. The MCPF binding energies (kcal/mol) are reported for all three metal ions. The structures for $Cu^+$ and $Y^{2+}$ are similar to those pictured for $Sc^{2+}$ except for $C_2H_2$ and $C_2H_4$, where the $Cu^+$ and $Y^{2+}$ sit at the bond midpoint.

However, both the geometrical information and vibrational frequencies can be obtained by writing to C.W.B.

If the bonding were completely electrostatic, we would expect the same order for the ligand bond energies for both the singly and doubly charged ions. This order might be expected to then follow the ligand ionization potential (IP) or polarizability. Inspection of Figure 1 shows that the trends in the metal–ligand bond energies are not the same for the three metal ions. Furthermore, none of the metals follow the trends in the IPs

$$CH_4 < C_2H_6 < C_2H_2 < C_3H_8 < C_2H_4 < C_3H_6$$

However, the difference between the metal ions can be understood in terms of the difference in importance of metal to $\pi^*$ donation, the size of the metal ions, and the size of the ligands.

$Cu^+$ binds more strongly to unsaturated hydrocarbons than to saturated hydrocarbons. The unsaturated hydrocarbons bond more strongly since the metal can donate charge into the $\pi^*$ orbital of the ligand. The binding energy of both the saturated and unsaturated hydrocarbons increases with the size of the hydrocarbon due to larger relaxation and polarization effects.

The binding energies of $Sc^{2+}$ and $Y^{2+}$ are significantly larger than those for $Cu^+$ due to the increased electrostatic interaction. The enhanced binding of the unsaturated hydrocarbons that was observed in $Cu^+$ is much reduced in $Sc^{2+}$ and $Y^{2+}$. For ligands with the same number of carbon atoms, the unsaturated one is more strongly bound; for example, $C_2H_2$ and $C_2H_4$ are more strongly bound than $C_2H_6$, but enhanced stabilization with hydrocarbon size is the same magnitude as the binding due to metal to $\pi^*$ donation so that larger saturated hydrocarbons can be more stable than smaller unsaturated ones. In addition to enhanced stabilization due to large polarization, bigger ligands can interact with the metal ion at more than one site. For example in $C_3H_8$, if $Sc^{2+}$ approaches the bond midpoint of one C–C bond, the binding energy is 6.7 kcal/mol larger than for $C_2H_6$, but if the $Sc^{2+}$ interacts with both terminal $CH_3$ groups at the same time, the binding energy is increased by an additional 3.4 kcal/mol—compare Figure 1d and 1f. It is interesting to note that the $Sc^{2+}$ binding energies would follow the order suggested by the IPs if the $Sc^{2+}$ approached the C–C midpoint (i.e., that shown in Figure 1d). Thus, the ligand size effects are only a few kilocalories per mole, but this is sufficient to change the order from that expected based on electrostatic arguments.

The smaller metal to $\pi^*$ binding for the dipositive ion is not unexpected since a dipositive ion is much less able to donate charge than a singly charged ion. This reduced metal to $\pi^*$ donation is also responsible for the asymmetric and symmetric forms of $MC_2H_2^{2+}$ and $MC_2H_4^{2+}$ for Sc and Y having similar energies; a large metal to $\pi^*$ donation naturally favors a symmetric structure.

While some of the changes in the binding energies arise from the difference in the size of the metal ions, we feel that the difference in the ligand bonding order between the singly charged $Cu^+$ and doubly charged $Sc^{2+}$ or $Y^{2+}$ arises from the metal to $\pi^*$ donation for the singly charged ion. We are able to test our hypothesis by comparing the bonding of $Sc^{2+}$ and $Sc^+$ in its first excited triplet state to $C_2H_2$ and $C_2H_6$. We should note that the $Sc^+$ is constrained to be electrostatically bound to the ligands and, therefore, does not represent the lowest triplet excited state of a $ScC_2H_n^+$ ion; this type of bonding is, therefore, analogous to that in $Cu^+$. If the bonding was only electrostatic, the ratio of the ligand binding energies would be similar for $Sc^+$ and $Sc^{2+}$. However, if the importance of metal to $\pi^*$ donation increased as expected for the singly charged ion, the ratio will change. The binding energies for $ScC_2H_2^+$ and $ScC_2H_6^+$ are 17.8 and 9.2 kcal/mol, respectively. This is smaller than half that found for $Sc^{2+}$, since $Sc^+$, with an occupied 4s orbital, is larger in size, so that the metal–ligand bond distance is larger than for the dipositive ion. The difference in the metal $C_2H_2$ and $C_2H_6$ binding energies is larger for $Sc^+$ than $Sc^{2+}$, which is a clear indication of enhanced metal to $\pi^*$ donation in the singly charged ion relative to the dipositive ion. The ratio of the binding energies ($C_2H_2/C_2H_6$) is 1.9 for $Sc^+$, compared to 2.1 for $Cu^+$. This is quite different from 1.2 and 1.3 for $Sc^{2+}$ and $Y^{2+}$, respectively. Therefore, we conclude that the differences in ligand binding energies between $Sc^{2+}$ and $Cu^+$ are due both to the charge and to the degree of metal to $\pi^*$ donation. Thus, the order of ligand binding energies is expected to be quite different for singly charged and dipositive ions in general. These results are in excellent agreement with the experimental observations described in this study.

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# Estimate of the Iodine–Iodine Two-Center Three-Electron Bond Energy in $[CH_3\text{-}I\text{-}I\text{-}CH_3]^+$

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**Abstract:** The gas-phase ion–molecule association reaction $CH_3I^+ + CH_3I \rightleftarrows [CH_3\text{-}I\text{-}I\text{-}CH_3]^+$ in various bath gases was studied at 503 K. The iodine–iodine bond in the association product is an example of a two-center three-electron (2c-3e) or a $2\sigma/1\sigma^*$ bond. The bond energy was estimated from $\Delta G°$ of reaction, which was in turn determined from equilibrium experiments. Assuming a value for $\Delta S°$ of reaction of −20 to −25 cal/(mol K), a bond strength of 23–26 kcal/mol is estimated. This is the first experimental gas-phase binding energy estimate for a 2c-3e bond in an organic molecule involving an iodine–iodine interaction and one of only a few experimental studies of well-characterized gas-phase 2c-3e bonding interactions between heteroatoms in organic molecules. A study of the ion–molecule reactions occurring at low ionizing energies leading to $(CH_3)_2I^+$, $[C_2H_5I_2]^+$, and $[CH_3\text{-}I\text{-}I\text{-}CH_3]^+$ is discussed.

## Introduction

Two-center three-electron (2c-3e) bonding or $2\sigma/1\sigma^*$ bonding was first described by Linus Pauling in 1931.[1] More recently Clark[2a] and Radom[2b] have published theoretical descriptions of these bonds. Asmus[3] has published extensive experimental results for molecules containing 2c-3e bonds formed in solution by pulse radiolysis, and we reported what we believe is the best experimental gas-phase binding estimate for a 2c-3e bond, namely, the sulfur–sulfur interaction in $[(CH_3)_2\text{-}S\text{-}S\text{-}(CH_3)_2]^+$.[4] Yet in spite of the early description by Pauling and the flurry of recent interest in these bonds, gas-phase experimental data on 2c-3e bonding involving organic molecules are extremely sparse.[5]

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[1] Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 3225.

[2] For leading references to theoretical work on 2c-3e bonding, see: (a) Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672. (b) Gill, P. M. W.; Weatherall, P.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 2783.

[3] For recent leading references, see: (a) Anklam, E.; Mohan, H.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1297. (b) Kishore, K.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2079. (c) Drewello, T.; Lebrilla, C. B.; Asmus, K.-D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1275. (d) Anklam, E.; Asmus, K.-D.; Mohan, H. *J. Phys. Org. Chem.* **1990**, *3*, 17.

[4] Illies, A. J.; Livant, P.; McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 7980.

[5] The bonding in many diatomic cations, including $He_2^+$, $Ne_2^+$, $Kr_2^+$, and $Xe_2^+$, is of course well-characterized and involves 2c-3e electron bonds. These simple systems will not be considered here; rather, the present focus is on 2c-3e bonding through heteroatoms in organic molecules. Additionally, though the binding energies for a great number of gas-phase ion–molecule association complexes have been reported (see ref 17), in most cases the nature of the binding interaction and even the atomic connectivity is unknown; hence, these systems are not well-characterized and will also not be further considered.

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