Table II. Some Estimated $\Delta H^\circ(CH_3X)$ (kcal mol$^{-1}$)

<table>
<thead>
<tr>
<th>X</th>
<th>$V_X$</th>
<th>$\Delta H^\circ(HX)$</th>
<th>$\alpha$</th>
<th>$\Delta H^\circ(CH_3X)$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH$_3$</td>
<td>3.24</td>
<td>21.7</td>
<td>4</td>
<td>4.4 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>SnH$_3$</td>
<td>2.83</td>
<td>38.9</td>
<td>4</td>
<td>18.6 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>PH$_3$</td>
<td>4.55</td>
<td>15.9</td>
<td>3</td>
<td>-4.6 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>4.20</td>
<td>15.9</td>
<td>3</td>
<td>8.1 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>SeH$_3$</td>
<td>5.13</td>
<td>7.1</td>
<td>2</td>
<td>5.3 ± 1.0</td>
<td></td>
</tr>
</tbody>
</table>

$\Delta H^\circ(CH_3X/HX) = [0.9 - 1.5(m - 1) - 10.2p] + [1.81p - \frac{m}{0.67 + 0.21m}] V_X$ (8)

or

$\Delta H^\circ(CH_3X/HX) = [0.9 - 1.5(m - 1) - 10.2p] + [1.81p - \frac{m}{0.67 + 0.21m}] V_X + \Delta H^\circ(HX)$ (9)

Equation 9 can be used for estimating heats of formation of many kinds of compounds, such as CH$_3$CH$_2$SiH$_3$, (CH$_3$)$_2$CHGeH$_3$, (CH$_3$)$_2$CPH$_3$, (CH$_3$)$_2$CHAsH$_3$, and C$_2$H$_5$SeH.

Thermochromists have sought for a long time to find methods for the quantitative estimation of the heats of formation of chemical compounds from carefully measured data on "key" members of homologous series. The need for and the utility of such methods is well documented.6J1s12 With the discovery of $V_X$ as a measure of the electronegativity and its successful application to differences in heats of formation we seem to have found such a method. We are currently exploring its application to a variety of other elements and properties such as ionization potentials where it again seems to produce remarkably quantitative correlations. We hope to report on these efforts in the near future.

We shall also in these papers compare some of the results found by using other electronegativity scales.

\[ V_X = \frac{r_X}{r_p} \]

is proportional to the (nucleus-core) potential, $\varepsilon(Z - (\bar{r} - \bar{v}))$, experienced by a bonding electron at the covalent binding distance. It seems intuitively plausible that the strength of a covalent bond would show a dependence on $V_X$. It also seems reasonable that there will be a compensating potential in an actual compound due to the other bonding electrons, the nuclei to which they are attached, and their distances from the bond being considered. These latter influences might account in part for the appearance of $p$ and $m$ in our relationships.

**Acknowledgment.** This work has been supported by grants from The National Science Foundation (CHE-8714647) and The U.S. Army Research Office (DAAG29-85-K-0019).

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On the Electrostatic Bonding of CO to the Monocations of the First-Row Transition Elements

**A. Mavridis,† J. F. Harrison,* and J. Allison**

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**Abstract:** We have investigated the binding of a CO group to the early transition metal +1 ions Sc$^+$, Ti$^+$, V$^+$, and Cr$^+$ using ab initio electronic structure theory and find that the binding mechanism is electrostatic in nature with no more than 10% ligand-to-metal donations and practically no metal-to-ligand donation. Our calculated M$^+$ bond lengths are very long, ranging from 2.25 Å in Cr$^+$CO$^+$ (2+$^+$) to 3.38 Å in Sc$^+$CO$^+$ (2+$^+$). The calculated binding energies range from 3.4 kcal/mol in the 2+$^+$ state of Sc$^+$CO$^+$ to 21.5 kcal/mol in the 4+$^+$ state of Cr$^+$CO$^+$ and correlate with the equilibrium M–C distance.

A well-known aspect of the first-row transition metal elements is their ability to form complexes with neutral ligands, most notably the carbonyl ligand.$^{1,2}$ CO. The mechanism through which carbon monoxide binds to neutral or (formally) low oxidation states of transition metal elements is of fundamental interest in organometallic chemistry.

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Table I. Total Molecular Energies, Equilibrium Bond Lengths, and Bond Energies for Various ScCo*, TiCo*, VCo*, and CrCo* Electronic States.

<table>
<thead>
<tr>
<th>molecule</th>
<th>state</th>
<th>energy (hartrees)</th>
<th>R(M-C) (Å)</th>
<th>D_e (kcal mol⁻¹)</th>
<th>asymptotic M* products (CO always in X'Σ⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScCo*</td>
<td>3Δ (A₂)</td>
<td>-872.386.30</td>
<td>2.739</td>
<td>9.1</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td>3Δ (CI, 56039 CSFs)</td>
<td>-872.514.90</td>
<td>1.697</td>
<td>10.2</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td>2Δ (B₂)</td>
<td>-872.383.49</td>
<td>2.755</td>
<td>7.3</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td>3Σ⁺ (A₁)</td>
<td>-872.377.211</td>
<td>3.3</td>
<td>1.4</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td>3Σ⁻ (A₃)</td>
<td>-872.315.07</td>
<td>2.471</td>
<td>13.5</td>
<td>F + P</td>
</tr>
<tr>
<td>TiCo*</td>
<td>4Σ⁺ (A₅sd)</td>
<td>-961.034.85</td>
<td>2.633</td>
<td>8.7</td>
<td>2/√3[F⁺] - 1/√3[P⁻]</td>
</tr>
<tr>
<td></td>
<td>4Σ⁺ (CI, 54429 CSFs)</td>
<td>-961.191.41</td>
<td>2.663</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>VCo*</td>
<td>2Δ (A₂)</td>
<td>-1055.520.52</td>
<td>2.489</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2Δ (CI, 73877 CSFs)</td>
<td>-1055.677.02</td>
<td>2.489</td>
<td>11.4</td>
<td></td>
</tr>
<tr>
<td>CrCo*</td>
<td>6Σ⁺ (A₅)</td>
<td>-1157.978.51</td>
<td>2.479</td>
<td>13.5</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>6Σ⁺ (CI, 66338 CSFs)</td>
<td>-1156.175.74</td>
<td>2.335</td>
<td>13.9</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>4Σ⁻ (B₂)</td>
<td>-1155.850.72</td>
<td>2.250</td>
<td>21.5</td>
<td>C₃(P⁺) + C₂(P⁺) + C₁(D⁻)</td>
</tr>
</tbody>
</table>

*Results refer to GVB (4/8) calculations except where noted; the SCF energies for Sc⁺, Ti⁺, V⁺, and Cr⁺ are reported in Table I of ref 24. CI's are of SCF+1+2 type using the GVB correlated orbitals; numbers in parentheses indicate the number of configuration state functions included in the CI's. This "contaminated" state comes from the d₉dₓ²dᵧ²d₉dₓᵧ, electron distribution on Cr⁺.

The binding mechanism of CO to transition metals has often been approached within the framework of the traditional Dewar-Chatt scheme, which involves ligand-to-metal σ donation with concomitant metal-to-ligand dσ back-donation ("back-bonding"). Although early ab initio descriptions supported this picture, more recent calculations suggest a modified version of the traditional view. In particular, the bonding contribution of the CO donation to neutral metal atoms such as Cu, Ni, and Fe is far less important than the dσ back-donation to the available 2s* orbitals of the ligand.

We present calculations of the early transition metal cations, M⁺ = Sc⁺, Ti⁺, V⁺, and Cr⁺, interacting with a single carbonyl molecule forming MCO*. Our results indicate that, in this instance, a bonding mechanism other than Dewar-Chatt is operative. We find that the M⁺-CO interaction is, in essence, electrostatic in nature. The large orbital angular momentum of the transition metal ion results in many low-lying electronic states in the MCO* molecule. The selection of states studies is representative rather than complete. In all states examined we find little σ donation and practically no dσ back-donation. Similar results were reported recently for the molecules NiCo⁺ and CuCo⁺.

Computational Details
The basis set for all metals is Wachters' 10 14s9p5d basis, augmented with two additional diffuse p functions11 to represent the 4p orbitals, and an extra d function.12 The resulting 14s11p6d primitive set was contracted to 5s4p3d according to Raffenetti.13 The basis set for both C and O is the Dujneveldt14 11s7p augmented with additional s and p functions selected in an even-tempered way, and two single-component d functions on C (lₐ = 0.60, 0.20) and on O (lₐ = 0.30, 0.25). The resulting 12s8p9d2p basis was contracted to 4s4p2d according to Raffenetti.13 Occasionally, a smaller basis set for the CO moiety, 1 ls7plp augmented with additional s and p functions selected in an even-tempered way, and two single-component d functions, was used for exploratory calculations. All computations were performed using the Argonne National Laboratory collection of QUEST-164 codes.

Our basic computational ansatz is a GVB (4/8) wave function for the carbonyl ligand. Four electron pairs are correlated into a valence bond function, the four pairs being the lone pair on carbon, those in the σ bond, and those in two π bonds in the CO molecule.

References


than the ab initio calculated De, atoms: 0.15, 0.13, 0.04. We are keeping terms through 1/R4 in the model calculations of the interaction energy, and the neglected higher order terms.

Two observations are pertinent from the numerical data of Table I. (a) The M–C bond lengths are very long, ranging from 2.25 Å (CrCO, *4II*) to 3.38 Å (ScCO+, *3Σ+*). For the neutrals, the M–C bond lengths range from 1.67 Å (NiCO, *1Σ+*) to 1.98 Å (CuCO). In addition, M–C bond lengths for all ground states become progressively smaller as we move from Sc+ to Cr+ from left to right in the periodic table, correlating loosely with atomic radii of the (neutral) metals. Indeed, considering the GVB multipolar expansion are most important for these small separations.

Detailed Results

Sc+CO*. The valence electronic configuration of Sc+ is 3d1^4s^1 and gives rise to the ground-state ^3D term. As the CO molecule approaches Sc+, with its carbon end in a colinear way, three molecular states are possible according to whether the 3d electron is in a d_3 (^3Σ+), d_4 (^1II), or d_5 (^1Δ) orbital. The asymptotic GVB wave functions with i = j = 1 is given by eq 1 with the two electrons triplet-coupled. Figure 2 shows the GVB potential curves as well as the CI potential curve for the ^3Δ ground state of ScCO+. According to a Mulliken population analysis, 0.11, 0.11, and 0.03 extra electrons are associated with Sc+ in the states ^3Δ, ^3II, and ^3Σ+, respectively (at the equilibrium geometry). Note that in the ^3Δ state back-donation is forbidden by symmetry. At equilibrium the incoming lone pair of CO interacts repulsively with the 4s electron of the metal, and the orbital population is depleted by ~0.05 e. These 0.05 e and the 0.10 e due to ligand-to-metal σ-donation are equally distributed between the empty d_z and 4p^2 orbitals of the metal. Exactly the same situation prevails in the ^3II state of the system. In the ^3Σ+ state the charge density along the internuclear axis prevents the close approach of the CO, the lone pair of the latter interacting repulsively with the d_z electron density. This is reflected in a very long equilibrium Sc–C bond distance (3.38 Å) and the concomitant small interaction energy (3.4 kcal mol^-1^).

\[
\Delta E = -\mu / R^3 + \theta / R^4 - \omega / R^4 - \alpha / 2 R^4
\]

with R being the distance between the center of mass of CO and the metal atom. Using \( \mu = +0.04885 \text{ au}, \theta = -1.6019 \text{ au}, \omega = +3.9577 \text{ au}, \alpha = 16.06 \text{ au} \), all values having been calculated from the CO GVB (4/8) wave function, we obtain \( \Delta E \) as a function of the Sc–C distance. The results of this electrostatic calculation are shown in Figure 3. The ab initio electrostatic

\[\text{Figure 1.} \quad \text{The calculated dissociation energy of several metal carbonyl compounds (MCO*) versus the metal-to-carbon bond length. Points labeled (O) represent data presented here, (O) from ref 7; (A) from ref 9; (△) from ref 8. The solid line represents the electrostatic potential, from eq 2.}\]

\[\text{Figure 2.} \quad \text{Comparison of the GVB and CI potential energy curves for the ^3Δ state of the ScCO*.}\]

\[\text{Figure 3.} \quad \text{Comparison of the GVB and electrostatic interaction potential energy curves for the ^3Δ, ^3II, and ^3Σ+ states of ScCO*.}\]
CO energy curves for the second for the 3d, (311), and last for the 3d, orbital (3A) consistent between Sc+ and CO is electrostatic in nature, and that the bond expression (eq 2) tracks the "incoming" interaction energy satisfactorily, suggesting that the dominant long-range interaction between Sc+ and CO is electrostatic in nature, and that the bond energies and equilibrium M+–CO bond lengths reflect that point at which the electrostatic interaction gives way to the Pauli repulsion developed between the Sc+ 4s3d electrons and the CO lone pair. As the bond lengths and D0's of Table I show, this apparently happens first when the 3d electron is in the 3d, orbital (3Σ+), second for the 3d, (3Π), and last for the 3dΔ orbital (3Δ) consistent with their spatial extension along the internuclear axis. As mentioned, the D0's follow the order 3Δ > 3Π > 3Σ+.

Distributing the two active electrons in Sc+ as dπ,+,dπ,−, a mixture of the 3F and 3P electronic terms of the metal is obtained. At the SCF level we calculate a splitting ∆E(3F−3P) = 0.906 eV,24 in contrast to the experimental value of 0.594 eV.25 The resulting electronic state of ScCO+, with the in situ metal in a 3F state, has 3Σ+ symmetry. The potential energy curve at the GVB level is shown in Figure 4. With the active electrons of Sc+ being distributed in orbitals that lie "perpendicular" to the internuclear axis, the incoming CO can approach closer to the metal ion, and this in turn is reflected in a larger D0 value. Note that the 3Σ+ state is unbound with respect to the ground state by 8 kcal mol−1. The electrostatic expansion (eq 2) represents the interaction fairly well at large internuclear distances but not as well at short distances, owing to the interpenetration of the electron clouds of the two fragments at small separations. The population analysis of the wave function for ScCO+ predicts an additional −0.04 e on Sc+. These electrons are transferred to the empty 4s orbital on the metal, with essentially no back-donation to the ligand.

To extend our GVB (4/8) calculations we constructed the SCF+1+2 wave function for the 3Δ state of ScCO+ using the GVB orbitals. While the absolute energies dropped by 81 kcal mol−1 (Table I), the interaction energy (Figure 2) remained practically unchanged compared with that obtained using the GVB description.

The GVB (4/8) and electrostatic interaction energy of Sc+ with the oxygen end of CO is shown in Figure 5 for the 3Δ state. The electrostatic interaction once again tracks the ab initio results quite well.

TiCO+. The GVB wave function of TiCO+ is described by eq 1 with i = 1, j = 2, the three active electrons of Ti+ coupled into a quartet state. The ground state26 of Ti+ is 4F and is obtained from the electron distribution 4s14d14p1 (which in turn leads to a 3Δ (or a 3A2, state in C2v symmetry) in the molecular environment. Assuming that, in the ground state, the two d electrons are allocated in a perpendicular fashion along the internuclear (Z) axis of the molecule, away from the incoming lone pair of CO, the constructed GVB wave function is of 3Σ+ (3A2) symmetry. Therefore, the in situ metal with configuration 4s13d2 has an equilibrium Ti–C separation of 2.498 Å and is 0.3 mhartree lower in energy than the sd2 state. This is consistent with a larger electrostatic interaction permitted by the more compact charge distribution in the sd2 state. Note that in 1974 Mortola and Goddard26 reported a minimum basis set calculation on the 4Σ+ state of TiCO+ in which they assumed a Ti–C bond

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length of 1.96 Å. In contrast to our conclusions, these authors find that the CO bonds to the Ti⁺ via a σ-donating, π-accepting mechanism. We suspect the Mortola and Goddard calculation suffers from a basis set superposition error.

**VCO⁺.** The electronic ground-state configuration of the V⁺ ion is d⁶ giving rise to a 3D ground state. The first excited state is a 1F (3d⁵4s¹), 0.337 eV above the 3D. The SCF representation of V⁺ inverts the experimental ordering resulting in a 1F state that is 0.251 eV lower than the 3D state. The GVB asymptotic wave function is given by (1) with i = 1, j = 3 coupled into a quintet spin state. More specifically, the ground state of VCO⁺ should be a quintet with the d⁶ electrons distributed away from the incoming lone pair on CO. Therefore, the active electronic space separates from the traditional Dewar-Chatt view. While the latter view finds strongly suggest that the fundamental binding component, for the metal cations, is electrostatic in nature, with no more than 10% a ligand-to-metal donation and practically no metal-to-ligand donation. Our results are consistent with those of Baenschlicher et al. (NiCO⁺) and Merchan et al.'s CuCO⁺. The evidence presented here supporting dominance of electrostatic interaction is as follows.

(a) M-C bond lengths are large relative to similar neutral species as evidenced from Table I.

(b) The binding energies, Dᵣ, depend only on the bond length and the attractive component of the M-CO⁺ potential curves and are well represented by the (ab initio) electrostatic formula using

**Conclusions**

The binding mechanism of a single CO ligand to the early transition metal +1 ions, Sc⁺, Ti⁺, V⁺, and Cr⁺, is totally different from the traditional Dewar-Chatt view. While the latter view appears to have some validity for the neutral species, our findings strongly suggest that the fundamental binding component, for the metal cations, is electrostatic in nature, with no more than 10% a ligand-to-metal donation and practically no metal-to-ligand donation. Our results are consistent with those of Baenschlicher et al. (NiCO⁺) and Merchan et al.'s CuCO⁺. The evidence presented here supporting dominance of electrostatic interaction is as follows.

(a) M-C bond lengths are large relative to similar neutral species as evidenced from Table I.

(b) The binding energies, Dᵣ, depend only on the bond length and the attractive component of the M-CO⁺ potential curves and are well represented by the (ab initio) electrostatic formula using
the calculated electrostatic properties of free CO. In Figure 1 we have also included LiCO⁺ (1X+)²² and Cl₂ScHCO⁻²². In LiCO⁺ the binding clearly is electrostatic, with no opportunity for back-donation. The possibility of a donation is also very remote. In Cl₂ScHCO the Cl substituents remove electrons from Sc giving it considerable Sc⁺ character. The calculated²³ ScCO bond length and bond energy (2.406 Å and 16.4 kcal/mol) are consistent with those calculated for the transition metal monocarbonyl cations.

(c) The Mulliken population analysis results indicate that very little charge transfer takes place. Notwithstanding the well-known pitfalls of the method,²⁰ the trends are rather clear.

The question naturally arises as to why the bonding is totally different between MCO and MCO⁺? The σ-d, view is a synergistic one: the σ ligand donation assists the σ, back-donation and vice versa. If the one cannot take place, the effect of the other is also greatly diminished. For the ionic systems the σ, metal back-donation does not occur mainly for energetic reasons. Electron transfer out of the M⁺ ion is prohibitively costly in light of the values of the second IE of the metals. The second IEs's for Sc⁺, Ti⁺, V⁺, and Cr⁺ are 12.9, 13.6, 14.2, and 16.5 eV, respectively, as opposed to ~6.7 eV on the average for the first IE of the metal atoms. The gain in energy due to covalent binding, if charge is transferred from M⁺ to CO, cannot compensate for the cost of that transfer and therefore the electrostatic interaction dominates.

Acknowledgment. This work was partially supported under NSF Grants CHE8519752 (J.F.H.) and CHE 8722111 (J.A.).

Registry No. Sc⁺, 14336-91-7; Ti⁺, 14067-04-0; V⁺, 14782-33-3; Cr⁺, 14067-03-9.

Stereochemical Studies on Protonated Bridgehead Amines.

¹H NMR Determination of Cis and Trans B–C Ring-Fused Structures for Salts of Hexahydropyrrolo[2,1-a]isoquinolines and Related C Ring Homologues. Capture of Unstable Ring-Fused Structures in the Solid State†

Bruce E. Maryanoff,*,† David F. McComsey,‡ Ruth R. Inners,‡ Martin S. Mutter,† Gary P. Wooden,§ Stephen L. Mayo,§ and R. A. Olofson§


Abstract: Acid-addition salts of tricyclic isoquinolines 2a/b, 3a/b, 4a–4c, 5, 6a/b, 7, 8a/b, 9a/b, and 17a/b were studied by high-field ¹H NMR in CDC₃ solution. Cis (e.g., 14 and 15 in Figure 1) and trans (e.g., 13) B–C ring-fused structures were identified by using the vicinal 3J(CH–NH) coupling constants, which demonstrate a Karplus-like behavior. In some cases, we initially observed a trans form, which converted to a cis A form by NH proton exchange. For 4c.HBr, the exchange process was slowed by addition of trifluoroacetic acid. In many cases, cis A and cis B structures were preferred in solution. The pendant phenyl group exerted a strong influence on the preferred solution structure. Observation of the initial, unstable trans-fused structures was related to their capture in the solid state and release intact on dissolution. X-ray diffraction was performed on the HBr salts of 2a (B–C cis), 2b (B–C cis), and 4c (B–C trans). The result for 4c.HBr confirmed the connection between the initial trans form in solution and the solid state. For 17b·HCl two conformers, associated with hindered rotation about the bond connecting the 2,6-disubstituted phenyl group to the tricyclic array, were detected at ambient probe temperature; however, rotamers were not observed for either of the two forms (trans and cis A) of 17b·HBr. Two conformers were also found for 16b·HBr. Temperature-dependent behavior was recorded in the ¹H NMR spectra of 17b·HBr and 16b·HBr; the activation free energy for interconversion of conformers was estimated to be in the vicinity of 17 kcal/mol for the former and 14–15 kcal/mol for the latter. The ¹H NMR spectrum of butaclamol hydrochloride (20·HC1), a potent neuroleptic agent, is also greatly diminished. For the ionic systems the σ, metal back-donation does not occur mainly for energetic reasons. Electron transfer out of the M⁺ ion is prohibitively costly in light of the values of the second IE of the metals. The second IEs's for Sc⁺, Ti⁺, V⁺, and Cr⁺ are 12.9, 13.6, 14.2, and 16.5 eV, respectively, as opposed to ~6.7 eV on the average for the first IE of the metal atoms. The gain in energy due to covalent binding, if charge is transferred from M⁺ to CO, cannot compensate for the cost of that transfer and therefore the electrostatic interaction dominates.

Although substantial information has been acquired on the structural and conformational properties of alicyclic amines with nitrogen at the bridgehead position, such as bicyclic [m.n.0] compounds where m and n = 3 or 4, the corresponding protonated species (i.e., acid-addition salts) have been largely ignored. Since this type of molecular framework is part and parcel of a wide variety of alkaloid structures,° as well as several biologically active compounds,⁴ five further study of acid-addition salts would be useful.


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