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Theoretical Study of M^+-CO_2 and OM^+CO Systems for First Transition Row Metal Atoms

M. Sodupe* and V. Branchadell

Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

M. Rosi[†] and C. W. Bauschlicher, Jr.*

NASA Ames Research Center, Moffett Field, California, 94035

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The coordination of carbon dioxide to first transition row metal cations and the insertion reaction of the metal into one CO bond of carbon dioxide have been studied theoretically. The geometry and the vibrational frequencies of the M^+-CO_2 and OM^+CO structures have been determined using the hybrid three-parameter B3LYP density functional approach. Binding energies have also been determined at the CCSD(T) level using large basis sets. The linear end-on M^+-OCO structure is the most favorable coordination for CO_2, due to the electrostatic nature of the bonding. In the inserted OM^+CO structures, the bonding arises from the electrostatic interaction between the ground state of OM^+ and CO. For the early transition metals (Sc^+, Ti^+, and V^+), the insertion reaction is exothermic and the inserted OM^+CO structure is more stable than the linear M^+-OCO isomer, because of the very strong MO^+ bond that is formed.

Introduction

Carbon dioxide is a very important natural source of carbon on our planet, and therefore the possibility of using it as a starting material for the synthesis of chemically useful compounds has received considerable attention.[1−4] Moreover, anthropogenic emissions of CO_2 are known to contribute to the greenhouse effect. Thus, recycling CO_2 through conversion to useful chemical compounds is also important from an environmental point of view. However, carbon dioxide is a thermodynamically very stable compound that needs to be activated for its utilization, for example through its interaction with transition metal complexes. For these reasons a good knowledge of the metal−CO_2 bonding is important to understand the role of the metal in the catalytic processes.

Recently, the interaction between several first transition row metal cations and CO_2 has been studied experimentally.[5−11] Although a linear M^+-OCO structure would be expected from electrostatic considerations,[12] different structures have been proposed for these systems.[9,13−14] Moreover, the experimental binding energy determined for the Fe^+-CO_2 complex (8.0 kcal/mol)[7] is unexpectedly much smaller than those determined for Ni^+-CO_2 (24.9 kcal/mol)[10] or Co^+-CO_2 (19.9 kcal/mol).[9] On the other hand, for V^+CO_2, the inserted OV^+CO isomer has been shown to be more stable than the electrostatically bound V^+-CO_2 structure.[5] As in the case of $ScCO_2^+$,[15] the larger stability of the inserted isomer is due to the fact that early transition metals form strong metal−oxide bonds,[16] and thus, a different behavior between early and late transition metals is expected. Other experimental works have studied the interaction of carbon dioxide with non-transition metal cations.[17−22]

In this paper we present the study of the interaction of first transition row metal cations with carbon dioxide. In all cases, we study both the inserted OM^+CO and the electrostatically bound M^+CO_2 structures. We determine the M^+-CO_2 and OM^+-CO binding energies and compare them with the known experimental data. The trends across the row are also discussed.

Methods

The fully optimized geometries and the vibrational frequencies have been determined using the three-parameter hybrid[23] B3LYP density functional method.[24] We have chosen this method since recent calibration calculations on transition metal compounds have shown that this hybrid functional provides accurate results for the geometries and vibrational frequencies of systems containing transitional metal atoms.[25] For many systems this hybrid functional also yields accurate binding energies. However, it is very desirable to confirm the B3LYP binding energies using highly accurate methods. Therefore, single-point calculations, at the B3LYP equilibrium geometries, have been performed using the coupled cluster singles and doubles method[26] with a perturbative estimate of the triple excitations, CCSD(T).[27] In these CCSD(T) calculations we correlate the 2s and 2p electrons of C and O, and the 4s and 3d electrons of the metal, except for Sc and Ti, for which the 3s and 3p electrons have been correlated as well. The restricted open-shell CCSD(T) approach[28,29] is used. The orbitals used in the CCSD(T) calculations are determined using the self-consistent-field (SCF) approach.

For a given electronic configuration, it is known[30] that the currently used functionals are not invariant over the set of densities associated with a degenerate atomic state, which implies that different occupancies corresponding to the same pure atomic state can lead to different energies. In the present work, the B3LYP binding energies have been referred to the orbital occupation of M^+ that leads to the lowest energy.

Two basis sets are used in the present work, a smaller one for the geometry and frequency calculations and a larger one for computing the binding energies at the CCSD(T) level. The small metal basis set is a [8s4p3d] contraction of the (14s9p5d) primitive set of Wachters[31] supplemented with two diffuse p and one diffuse d functions.[32] The final basis set is of the form (14s11p6d)/[8s6p4d]. For C and O we use the (9s5p)/[4s2p] set developed by Dunning[33] from the primitive set of Huzinaga,[34] supplemented with a set of diffuse sp functions ($\alpha = 0.0845$ for oxygen and $\alpha = 0.0438$ for carbon) and one 3d polarization function ($\alpha = 0.85$ for oxygen and $\alpha = 0.75$ for carbon). While experience has shown that basis sets of this

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[†] Permanent address: Department of Chemistry, University of Perugia, I-06100, Perugia, Italy.

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size yield good results for density functional theory based approaches, it is well-known that large basis sets are required to obtain accurate results at the CCSD(T) level of theory. The large metal basis sets are averaged atomic natural orbital (ANO)[35,36] contractions[37] that are derived from the large primitive sets optimized by Partridge,[38] supplemented with diffuse and polarization functions. For V to Cu, the final basis sets are of the form [(6+1)s(5+1)p4d3f2g]. For Sc and Ti, the basis sets are modified to allow 3s and 3p correlation; that is, the basis sets are contracted [(3+4)s(2+6)p(4+2)d3f2g]. While the uncontracted s and p functions are those with the smallest exponents, the two uncontracted d functions are those in the same region as the 3p orbital, namely those with exponents of 1.342 621 and 0.561 524 for Sc and 1.689 268 9 and 0.715 670 6 for Ti. The large O and C basis sets are the aug-cc-pVTZ sets of Dunning and co-workers.[39] Only the spherical harmonic components of the basis sets are used.

Density functional calculations were performed with the Gaussian94[40] package, while the CCSD(T) calculations were performed with the MOLPRO96 program.[41]

Results and Discussion

Carbon dioxide can behave both as a bidentate ligand (η^2-O,O or η^2-C,O) or as a monodentate ligand (η^1-O or η^1-C) when interacting with neutral metal atoms.[3,42,43] However, cationic metals are bound to CO_2 electrostatically, and since the leading term is charge−quadrupole and CO_2 has a negative quadrupole moment, the linear η^1-O (end-on) coordination is the most favorable. Test calculations on $Sc^+{-}CO_2$, $Fe^+{-}CO_2$, and $Ni^+{-}CO_2$ have confirmed this expectation. The C_{2v} symmetry structures were not found to be minima on the potential energy surface; that is, they were found to have an in-plane imaginary frequency. These T-shaped structures have the metal ion lying perpendicular to CO_2, which remains almost linear in the complex, and small displacements following the transition vector lead to the linear M^+OCO structure. Moreover, ionic $M^{2+}CO_2^-$ structures were found to lie much higher in energy than the M^+CO_2 ones. For example, the η^1-C mode in $Fe^{2+}CO_2^-$ was found to lie about 70 kcal/mol higher in energy than the linear Fe^+OCO structure. This is not surprising considering the large ionization potential of the cation, which makes the ionic bonding $M^{2+}CO_2^-$ mechanism not stabilizing enough to compensate for the electron transfer from M^+ to CO_2. The η^2-C,O mode was also not found to be a minimum on the potential energy surface. Any attempt to optimize such an structure for Fe^+ in different electronic states collapsed to the linear isomer. This is due to the fact that the repulsion between the occupied d orbitals of the metal and CO_2 is larger in this coordination mode than in the η^1-O one, while the electrostatic stabilization is smaller.[12] For Sc^+, the η^2-C,O mode was found to be a minimum only at the Hartree−Fock level, while inclusion of electron correlation lead to the inserted OSc^+CO structure.[15] On the basis of these test calculations, we have only considered the linear $M^+{-}OCO$ coordination and the inserted structure OM^+CO in the remaining systems.

TABLE 1: B3LYP Geometries (in Å) for the Linear $M^+{-}O'CO$ Systems, $M^+{-}O'CO$ Stretching Frequency (in cm^{-1}), and Relative Energies (in kcal/mol) with Respect to the Ground-State $M^+ + CO_2$ Asymptote

					ΔE	
system	$R_{MO'}$	$R_{O'C}$	R_{CO}	ω	B3LYP	CCSD(T) (ANO)
$Sc^+{-}OCO$ ($^3\Delta$)	2.206	1.189	1.151	254	−24.9	−21.4
$Ti^+{-}OCO$ ($^4\Phi$)	2.155	1.187	1.153	257	−27.9	−21.8
$Ti^+{-}OCO$ ($^4\Delta$)	2.218	1.185	1.158	230	−23.2	−17.6
$V^+{-}OCO$ ($^5\Sigma^+$)	2.144	1.185	1.155	251	−21.7	−18.9
$V^+{-}OCO$ ($^5\Delta$)	2.103	1.186	1.154	269	−23.6	−16.9
$Cr^+{-}OCO$ ($^6\Sigma^+$)	2.096	1.186	1.154	253	−20.2	−15.8
$Mn^+{-}OCO$ ($^7\Sigma^+$)	2.240	1.190	1.153	181	−14.0	−13.7
$Mn^+{-}OCO$ ($^5\Sigma^+$)	2.057	1.188	1.151	264	−2.9	
$Fe^+{-}OCO$ ($^6\Delta$)	2.141	1.192	1.151	213	−17.5	−16.6
$Fe^+{-}OCO$ ($^6\Pi$)	2.193	1.190	1.153	190	−15.3	
$Fe^+{-}OCO$ ($^4\Phi$)	2.025	1.186	1.154	268	−21.1	−15.3
$Fe^+{-}OCO$ ($^4\Sigma^-$)	2.018	1.184	1.156	271	−14.6	
$Co^+{-}OCO$ ($^3\Delta$)	1.992	1.184	1.154	277	−25.3	−22.1
$Co^+{-}OCO$ ($^3\Phi$)	1.992	1.186	1.153	273	−23.9	
$Co^+{-}OCO$ ($^3\Sigma^-$)	2.009	1.188	1.152	262	−15.0	
$Co^+{-}OCO$ ($^5\Phi$)	2.111	1.191	1.151	216	5.0	
$Ni^+{-}OCO$ ($^2\Sigma^+$)	1.953	1.185	1.153	295	−28.1	−25.0
$Cu^+{-}OCO$ ($^1\Sigma^+$)	1.950	1.186	1.153	285	−25.1	−22.2

Let us first consider the linear $M^+{-}OCO$ systems. The optimized geometrical parameters, the $M^+{-}OCO$ stretching frequency, and the relative energy with respect to the ground-state $M^+ + CO_2$ asymptote are given in Table 1. Since the bonding is mainly electrostatic, the interaction between carbon dioxide and the metal cation produces only a small asymmetry in the two CO bond lengths; the CO bond length adjacent to the metal ion increases about 0.02 Å, while the other CO bond length decreases about 0.02 Å. This variation in the CO_2 geometry remains almost constant across the row and is very similar to that found for $Mg^+{-}OCO$,[44] which indicates that no significant π back-donation from the metal ion to CO_2 is present. This is consistent with the polarization of the charge in CO_2 from the carbon atom to the oxygen atoms. The Mulliken population analysis shows about 0.3 electrons on each oxygen atom. That is, with an excess of charge on the oxygen in free CO_2, there is little energetic benefit from accepting charge from a metal cation. The metal−ligand bond distances are determined both by the size of the ion, which decreases across the row, and by the metal−ligand repulsion, which depends on the metal ion electronic configuration. That is, those electronic states that arise mainly from the metal sd^n asymptote, such as for Sc^+, Mn^+, or the sextet states of Fe^+, show larger metal−CO_2 distances than those derived from the metal d^{n+1} asymptote, to reduce the 4s−ligand repulsion.

The interaction of the five metal d orbitals with carbon dioxide is not equivalent, which also contributes to determine the optimal bonding mechanism. On the basis of the different overlap between the metal d orbitals and the occupied orbitals of CO_2, the order of repulsion is expected to be $3d\sigma > 3d\pi > 3d\delta$. This ordering has been confirmed by carrying out state-averaged SCF calculations for $Sc^+{-}OCO$, which have shown that the lowest electronic state is $^3\Delta$, derived from the $4s^1d\delta^1$ occupation, while the $^3\Pi(4s^1d\pi^1)$ and $^3\Sigma^+(4s^1d\sigma^1)$ states lie 4.2 and 14.6 kcal/mol higher in energy, respectively.

Although several factors contribute to the bonding, the ground state of each system is, in general, determined by minimizing the metal−ligand repulsion, both by 4s to 3d promotion or sdσ hybridization and by allocating the electrons into the orbitals with the lower M−CO_2 overlap. Because the promotion energy and the 3d occupation vary from one metal cation to another, the metal−CO_2 binding energy does not always increase with the decrease of the metal−ligand distance. The variation of the $M^+{-}OCO$ binding energies across the row parallels that of $M^+{-}H_2O$ systems,[45] even though the metal−ligand electrostatic interaction is weaker for the present systems because CO_2 has no permanent dipole moment. That is, first the interaction energy slightly increases from Sc^+ to Ti^+. Then, it decreases up to Mn^+, for which the binding energy is the smallest one, because the only way to reduce repulsion is by 4s4p polarization. From Fe^+ to Ni^+, the interaction energy increases again, paralleling the decrease of the ion size with Z, and finally, there is a small decrease for Cu^+ because the dσ orbital is doubly occupied, which increases the metal−ligand repulsion.

TABLE 2: B3LYP Geometries (in Å and deg) of the Inserted OM$^+$−CO Systems and Relative Energies (in kcal/mol) with Respect to the Ground-State M$^+$ + CO$_2$ Asymptote

						ΔE	
system	R_{OM}	R_{MC}	R_{CO}	∠OMC	∠MCO	B3LYP	CCSD(T) (ANO)
OSc$^+$CO ($^1A'$)	1.634	2.489	1.130	94.5	172.4	−50.3	−57.9
OSc$^+$CO ($^1\Sigma^+$)[a]	1.632	2.784	1.131	180.0	180.0	−43.1	
OTi$^+$CO ($^2A''$)	1.586	2.250	1.132	96.2	173.9	−51.8	−57.8
OTi$^+$CO ($^2A'$)	1.585	2.419	1.129	110.6	172.8	−46.0	−52.4
OTi$^+$CO ($^2\Delta$)[a]	1.588	2.639	1.130	180.0	180.0	−41.1	
OV$^+$CO ($^3A''$)	1.551	2.210	1.130	105.4	172.8	−27.6	−30.2
OV$^+$CO ($^3\Sigma^-$)[a]	1.555	2.522	1.129	180.0	180.0	−19.8	
OCr$^+$CO ($^4A'$)	1.575	2.185	1.129	112.5	175.5	26.9	30.1
OCr$^+$CO ($^4\Pi$)[a]	1.589	2.306	1.130	180.0	180.0	31.8	
OCr$^+$CO ($^6A'$)	1.839	2.136	1.129	100.2	176.0	57.6	
OMn$^+$CO ($^5\Pi$)	1.737	2.240	1.128	180.0	180.0	36.8	49.0
OMn$^+$CO ($^5A'$)	1.601	2.122	1.128	99.8	175.5	38.1	
OMn$^+$CO ($^5\Sigma^+$)	1.598	2.213	1.129	180.0	180.0	43.6	
OFe$^+$CO ($^6\Sigma^+$)	1.656	2.134	1.128	180.0	180.0	14.7	22.5
OFe$^+$CO ($^4A''$)	1.570	1.954	1.130	95.3	176.3	19.6	26.3
OFe$^+$CO ($^4\Delta$)	1.566	2.172	1.128	180.0	180.0	30.5	
OFe$^+$CO ($^4\Sigma^-$)	1.663	2.060	1.131	180.0	180.0	52.1	
OCo$^+$CO ($^5\Delta$)	1.655	2.084	1.128	180.0	180.0	25.4	30.1
OCo$^+$CO ($^3A''$)	1.685	2.015	1.128	117.9	174.5	42.2	
ONi$^+$CO ($^4\Sigma^-$)	1.661	2.037	1.127	180.0	180.0	36.1	42.1
ONi$^+$CO ($^2\Sigma^-$)	1.708	2.002	1.128	180.0	180.0	44.4	
ONi$^+$CO($^2A''$)	1.692	1.955	1.129	109.6	175.2	49.6	
OCu$^+$CO($^3\Sigma^-$)	1.798	1.969	1.128	180.0	180.0	56.3	67.4
OCu$^+$CO($^1A'$)	1.724	1.963	1.127	142.8	177.8	100.7	

[a] These systems have at least one imaginary frequency.

As found for other M$^+$−ligand systems,[25] the B3LYP interaction energies are larger than those determined at the CCSD(T) level of theory. For this system, the CCSD(T) binding energies are about 4 kcal/mol smaller than the B3LYP values. Higher levels of theory are expected to increase the CCSD(T) values slightly, so the B3LYP values are quite accurate for this system. As a test we computed the CCSD(T) binding energies using the same small basis set as used for the B3LYP calculations. Using the small basis set the CCSD(T) binding energies were on the average about 5 kcal/mol smaller than the B3LYP values, with the maximum difference being 10.2 kcal/mol in the case of Ti$^+$OCO. Thus, the B3LYP binding energies are superior to those obtained at the CCSD(T) level if the small basis set is used. For Sc$^+$−CO$_2$, the computed binding energy is about 6 kcal/mol larger than the MCPF value determined in our previous work,[15] due to the differences in the basis set and to the fact that in the previous calculations the 3s and 3p electrons of Sc were not correlated.

The Fe$^+$OCO system merits special attention since the quartet and sextet states, which arise from the ^{4}F(d^7) and ^{6}D(s^{1}d^6) electronic configurations of Fe$^+$, respectively, show a different relative stability at the B3LYP and CCSD(T) levels of calculation. That is, while at the B3LYP level, the $^4\Phi$ state of Fe$^+$-OCO is 3.6 kcal/mol more stable than the $^6\Delta$ state, the CCSD(T) calculations show that $^6\Delta$ is 1.3 kcal/mol lower in energy than $^4\Phi$. This is due to the fact that density functional calculations tend to overestimate the stability of d^{n+1} electronic configurations with respect to the s^{1}d^n ones.[25,46−48] As a consequence, the ^{4}F−^{6}D separation of Fe$^+$ is −3.6 kcal/mol at the B3LYP level, while it is 4.6 kcal/mol at the CCSD(T) level. The CCSD(T) ^{4}F−^{6}D excitation energy is in very good agreement with the experimental value of 5.8 kcal/mol. Because of that and considering that the computed value is still slightly smaller than the experimental one, our results seem to suggest that the ground state of Fe$^+$OCO is $^6\Delta$. It is also worth noting that if the B3LYP binding energy of the $^4\Phi$ state is computed with respect to the excited d^7 electronic configuration of Fe$^+$ and then corrected to the s^{1}d^6 ground state using the experimental energy separation, the obtained value of 11.7 kcal/mol is in much better agreement with the value of 15.3 kcal/mol found at the CCSD(T) level. Thus, as it has been shown in previous studies,[25] the B3LYP approach can yield much more reasonable bond energies if account is taken for errors in the metal atomic separation.

The computed vibrational frequencies for the M$^+$OCO systems also agree with the fact that the ligand is not significantly perturbed, due to the electrostatic nature of the bonding. In all cases, the vibrational frequency shifts of CO$_2$ due to complexation are very small; the largest shift is a 64 cm^{-1} increase for the asymmetric stretching of CO$_2$ in Ni$^+$−OCO. The values of the stretching M$^+$−OCO mode range from 181 to 295 cm^{-1}. The smallest value corresponds to Mn$^+$−OCO, which is consistent with the smallest binding interaction, while the largest value is found for Ni$^+$−OCO, which has the largest binding energy. It can be observed that those electronic states derived from the s^{1}d^n electronic configuration have smaller stretching frequency values than those derived from the d^{n+1} ones. See for example Fe$^+$OCO, which shows a 213 cm^{-1} value in the $^6\Delta$ state and a 268 cm^{-1} value in the $^4\Phi$ one, or Mn$^+$-OCO for which the stretchings frequencies in the $^7\Sigma^+$ and $^5\Sigma^+$ states are 181 cm^{-1} and 264 cm^{-1}, respectively. The computed B3LYP harmonic stretching frequencies for those systems with s^{1}d^n derived electronic states are in reasonable agreement with the reported experimental values of about 190 cm^{-1}.[6,9]

The optimized geometries of the inserted OM$^+$CO structures and their relative energies with respect to the ground-state M$^+$ + CO$_2$ asymptote are given in Table 2. These inserted structures can be viewed as an electrostatic interaction between MO$^+$ and CO. Therefore, to get a good understanding of these inserted structures, it is important to analyze first the electronic structure of the transition metal oxide cations. The spectroscopic parameters of MO$^+$ are given in Table 3.

The ground state of ScO$^+$ molecule is a $^1\Sigma^+$ state derived from removing the 9σ electron from neutral ScO, which results in a $8\sigma^2 3\pi^4$ electronic configuration. The 8σ orbital is the bonding combination of the metal dσ and O 2pσ orbitals, while the 3π orbitals are the bonding combinations of the M dπ and O pπ orbitals. These orbitals show more important contributions of the oxygen atom, which produces a net negative charge on oxygen. As in the neutral ScO, this system has some triple-bond character and a large dissociation energy.[16,49] For TiO$^+$

TABLE 3: Summary of the Spectroscopic Parameters for the MO^+ Systems[a]

			D_0 (kcal/mol)		
system	R_e (Å)	ω_e (cm^{-1})	B3LYP	CCSD(T) (ANO)	expt
ScO^+ ($^1\Sigma^+$)	1.621	1075	157.0	160.2	164.6
TiO^+ ($^2\Delta$)	1.577	1127	151.9	154.6	158.7
VO^+ ($^3\Sigma^-$)	1.544	1140	127.2	129.9	134.8
CrO^+ ($^4\Pi$)	1.581	904	70.3	66.1	85.8, 85
CrO^+ ($^4\Sigma^-$)	1.600	770	69.2	63.6	
MnO^+ ($^5\Pi$)	1.731	646	61.4	47.4	68.0, 57.2, 58.3
MnO^+ ($^5\Sigma^+$)	1.593	922	54.5	44.9	
FeO^+ ($^6\Sigma^+$)	1.642	829	78.9	73.0	80.1, 72.6, 69.4
FeO^+ ($^4\Phi$)	1.698	688	71.1	62.6	
FeO^+ ($^4\Delta$)	1.560	976	64.4	54.2	
CoO^+ ($^5\Delta$)	1.642	771	66.2	60.4	75.0, 63.6, 60.6
NiO^+ ($^4\Sigma^-$)	1.646	703	53.3	45.5	63.3, 45.0
CuO^+ ($^3\Sigma^-$)	1.809	494	31.2	19.4	37.4

[a] Experimental values taken from ref 54.

and VO^+ the additional electrons are placed in the nonbonding dδ orbitals, and so, the binding energies do not change significantly.

The CrO^+ ground state is $^4\Pi$, which is also derived from removing the 9σ electron of the neutral CrO. The binding energy and the vibrational frequency of CrO^+ are much smaller than those of the previous metal oxide cations, because the additional electron now occupies the antibonding 4π orbital. Thus, the bonding loses its triple character to become more like a double bond. Removing the 4π electron of the neutral CrO, instead of the 9σ, leads to a $^4\Sigma^-$ state, which is slightly less stable than the $^4\Pi$ state. The bond length is larger and the frequency smaller in the $^4\Sigma^-$ state because there is some contribution to the bonding from the Cr^+ $^6D(s^1d^4)$ excited state.

The MnO^+ ground state can be viewed as arising from that of CrO^+ by adding the next electron into the nonbonding 9σ orbital. That is, removing a 4π electron from the neutral MnO is preferred to removing one from the 9σ orbital. For FeO^+, the additional electron is added to the 4π orbital. That is, relative to FeO, an electron is removed from the 3dδ orbital. Since the remaining MO cations are formed by removing an electron from the 9σ or 4π orbitals, these states ($^4\Delta$ and $^4\Phi$) were also tested and found to be higher in energy. For CoO^+ and NiO^+ the successive electrons are placed in the dδ nonbonding orbitals. Consequently, the binding energies do no change very much. Finally, in CuO^+ the $^3\Sigma^-$ ground state arises from adding the extra electron to the 9σ orbital. That is, CuO^+ is derived from CuO by removing a 4π electron. The bond length in this metal oxide is the largest, and the vibrational frequency and binding energy are the smallest. As one moves across the row, the 3d orbitals get more compact and, so, the 8σ, 3π, and 1δ are mainly centered in the copper atom while the 4π orbitals correspond mostly to the 2p orbitals of the oxygen atom. That is, the oxygen has a $2p\sigma^2 2p\pi^2$ occupation. The 2pσ orbital is stabilized by pointing at the positively charged Cu and by donating 0.4 electrons to the Cu. The Cu 3dπ orbital donates 0.2 electrons to the O 2pπ orbital, yielding a net charge on O of about +0.2 electrons. Thus, the bonding in CuO^+ is mostly electrostatic and dative, although some covalent bonding mixes in from the Cu^0O^+ contribution to the bonding. Given this bonding mechanism, it is not surprising that CuO^+ has the smallest binding energy.

The results obtained for the metal oxide cations indicate that for all systems except Mn^+, Fe^+, and Cu^+, the ground state is obtained by removing the 9σ electron of the neutral system.[49] For FeO^+ the high-spin state ($^6\Sigma^+$) is preferred instead, while for MnO^+ and CuO^+ the electron is removed from the 4π antibonding orbital. Previous theoretical studies have provided good insight into the bonding in these metal−oxide systems.[50−52] The present results agree with those reported previously,[52] except for CrO^+, for which the $^4\Sigma^-$ was determined to be the ground state. However, as noted by Schwarz et al.[52] and found in our work both the $^4\Sigma^-$ and $^4\Pi$ states are very close in energy.

It can be observed in Tables 2 and 3 that, in all cases, the ground state of the inserted OM^+CO structure is derived from the interaction of the ground state of MO^+ with CO. However, for the early transition metals, from Sc^+ to Cr^+, the most stable OM^+CO structure is bent, while for the late transition metals the most stable structure is linear. Dative bonding is small in OM^+CO, but important for M^+CO.[53] The addition of the oxygen polarizes the metal charge away from the CO and the dative interaction becomes very small for OM^+CO. For example in ONi^+-CO there are only 0.03 electrons donated to the CO 2π* orbital. Since the OM^+-CO bonding is mainly electrostatic and the dative interaction is small, the optimal structure is determined by minimizing the OM^+-CO repulsion, especially that with the 5σ lone pair of CO. For the metals on the left side of the row, the 8σ is the highest occupied σ orbital in the metal oxide cations. This orbital is an s+dσ hybrid that increases the electron density on both sides of the metal along the M−O axis. The repulsion between this OM^+ orbital and the CO 5σ orbital is reduced by bending. As shown in Table 2, this effect is 5−11 kcal/mol. With increasing Z this 8σ orbital drops in energy, and starting at MnO^+, the nonbonding 9σ orbital becomes occupied. Therefore, the repulsive interaction with the 5σ lone pair orbital of CO is mostly due to the 9σ orbital of MO^+. Since the s−dσ hybrid orbital reduces the electron density on both sides of the metal along the MO axis, the OM^+-CO repulsion is minimized for a linear configuration, which also maximizes the charge−dipole contribution to the bonding. Consequently, the linear approach of CO is now the most favorable.

Consistent with this picture of the bonding, the bond length and stretching frequency of MO^+ and CO in OM^+CO are very similar to those of free MO^+ and CO, respectively. For all metal cations, except Cr^+ and Cu^+, the interaction with CO increases the MO^+ bond distance and decreases the stretching frequency. For Cr^+ and Cu^+, complexation produces the reverse effect, it decreases the MO^+ distance and increases the stretching frequency. For OCu^+CO, the CO and O share the cost of the sdσ hybridization, and since this reduces the charge density on both sides of the Cu atom, the presence of the CO enhances the electrostatic contribution to the O−Cu bond. The effect for OCr^+CO appears to be more subtle. For the linear configuration, the O−Cr bond is longer than in free CrO^+, as found for most other systems; it is only with bending that the O−Cr bond shortens and the frequency increases. The only noticeable change in the Mulliken populations is a transfer of 3dδ electrons to the 3dσ orbital when the CO is present in the bent configuration, which apparently strengthens the O−Cr bond. Unlike the variation in the O−M bonding, in all cases the CO distance in the complex is shorter and the CO frequency is higher than in free CO. As found for M^+-CO systems,[53] these changes are due to CO polarization by the metal ion. Due to the small π back-donation, this polarization of CO results in some CO^+ mixing in; CO^+ has a shorter bond length and higher vibrational frequency than CO. For example at the B3LYP level of theory, the bond length and vibrational frequency of CO^+ are 1.126 Å and 2264 cm^{-1} compared with 1.141 Å and 2188 cm^{-1} for CO.

The relative energies of OM^+CO computed with respect to the ground-state $M^+ + CO_2$ asymptote show that the insertion reaction is exothermic only for the first three transition metal cations. This is due to the fact that Sc^+, Ti^+, and V^+ form a

TABLE 4: Binding Energies, D_0 (in kcal/mol), for M^+-CO_2 and OM^+-CO Systems[a]

	M^+-CO_2				OM^+-CO		
	B3LYP	CCSD(T) (ANO)	expt		B3LYP	CCSD(T) (ANO)	expt
$ScCO_2^+$ ($^3\Delta$)	24.2	20.7		OSc^+CO ($^1A'$)	18.8	20.3	
$TiCO_2^+$ ($^4\Phi$)	27.2	21.1		OTi^+CO ($^2A''$)	25.5	25.5	
VCO_2^+ ($^5\Sigma^+$)	21.0	18.2	17.3	OV^+CO ($^3A''$)	26.1	22.7	24.2
$CrCO_2^+$ ($^6\Sigma^+$)	19.5	15.1		OCr^+CO ($^4A'$)	28.6	26.3	
$MnCO_2^+$ ($^7\Sigma^+$)	13.5	13.2		OMn^+CO ($^5\Pi$)	28.1	26.6	
$FeCO_2^+$ ($^6\Delta$)	17.0	16.1	8.0, 9.5	OFe^+CO ($^6\Sigma^+$)	31.8	27.1	
$CoCO_2^+$ ($^3\Delta$)	24.5	21.3	19.9	OCo^+CO ($^5\Delta$)	34.4	32.1	
$NiCO_2^+$ ($^2\Sigma^+$)	27.3	24.2	24.9	ONi^+CO ($^4\Sigma^-$)	36.6	35.1	
$CuCO_2^+$ ($^1\Sigma^+$)	24.3	21.4		OCu^+CO ($^3\Sigma^-$)	38.9	36.1	

[a] Experimental values taken from refs 9, 10, and 54.

strong metal oxide bond (see above). Although the exothermicity decreases from Sc^+ to V^+, the inserted structure is more stable than the linear M^+OCO isomer (see Table 1) for all three cations. For the remaining metals the insertion reaction is endothermic and the most stable structure is the linear M^+OCO isomer. The variation of the endothermicity of the $M^+ + CO_2 \rightarrow OM^+CO$ reaction across the row is mainly determined by the strength of the MO^+ bond. Because of that, Cu^+ shows the largest endothermicity, while Fe^+ shows the smallest. The differences between the relative energies obtained at the B3LYP and CCSD(T) (ANO) levels are now somewhat larger than for the M^+-OCO electrostatically bound systems, due to the fact that metal−oxide bonds are generally more difficult to describe. For example, in the CCSD calculations the norm of the singles' amplitudes is much larger for the OM^+CO species than for M^+-OCO.

It can be observed in Table 3 that the MO^+ computed binding energies are smaller than the reported experimental values,[16] especially for CrO^+, MnO^+, and CuO^+. However, the CCSD(T) calculations with the large basis set are expected to be quite accurate. Therefore, we feel that part of the difference between CCSD(T) and experiment is due to the experimental values being too large. Although the theoretical errors in the OM^+CO species might be larger than in M^+OCO, the inserted structures for Cr^+, Mn^+, and Cu^+ lie so high in energy compared to the electrostatically bound M^+OCO isomers (45.9, 62.7, and 89.6 kcal/mol above, respectively) that M^+OCO is clearly the most stable structure for these metal cations. For Sc^+, Ti^+, and V^+, the differences between the theoretical and experimental MO^+ binding energies are about 4 kcal/mol. Moreover, for Sc^+ and Ti^+, the inserted structure is more than 30 kcal/mol lower in energy than M^+OCO. Therefore, the most stable structure for Sc^+ and Ti^+ is clearly determined to be the inserted one. For V^+, both structures lie closer in energy; that is, at the CCSD(T) level OV^+CO is 11.3 kcal/mol more stable than V^+-OCO. Because additional improvements in the basis set and correlation treatment are expected to further increase the stability of OV^+CO with respect to V^+OCO, our calculations indicate that the ground-state structure for V^+ will also be the inserted one, in agreement with what is derived from experiments.[5]

It must be noted that the ground-state spin multiplicity in the linear M^+-OCO isomer is determined by that of the metal ion, while in the OM^+CO inserted isomer it is determined by that of the metal oxide cation. As a result, the early transition metal cations have high-spin ground states for the linear M^+-OCO isomer, while they have low-spin ground states for the inserted structure. Because the inserted structures for early metals have a lower spin multiplicity than the metal cation, the insertion reaction is not efficient unless excited low-spin states of the metal ion are present. On the contrary, the late transition metals show the reverse situation; that is, low-spin states are more stable for M^+-OCO and high-spin states for OM^+CO. Fe^+ is the only metal that has the same sextet spin multiplicity for both isomers in the lowest state. However, given that quartet states are close in energy, the insertion reaction could also take place in the quartet surface.

In Table 4 we present the M^+-OCO and OM^+-CO binding energies, D_0, and compare them to the known experimental data.[54] For both the M^+-OCO and OM^+-CO systems the agreement between the computed B3LYP and CCSD(T) (ANO) binding energies is good. The M^+-OCO binding energies are somewhat smaller than the OM^+-CO values, because CO_2 has no permanent dipole moment. Single-point calculations, using a point charge approach, confirm that the electrostatic interaction is larger in the OM^+-CO systems than in M^+-OCO. That is, replacing the Cu^+ ion by a point charge in the Cu^+-OCO complex leads to a stabilization energy of CO_2 of 25.4 kcal/mol, while replacing OCu^+ by a point charge, at the Cu^+-C distance, leads to a CO binding energy of 34.4 kcal/mol. The variation of the binding energy across the row is different in the two cases. That is, while the variation of the binding energies in M^+OCO is the result of several complex mechanisms to reduce metal−ligand repulsion, in general, the OM^+-CO binding energies increase as the OM^+-CO bond length decreases across the row.

The computed binding energies are in very good agreement with the experimental data, except for Fe^+-CO_2, for which the experimental value is significantly smaller than the theoretical one. Although a smaller binding energy is expected for Fe^+-OCO than for Ni^+-OCO or Co^+-OCO, because the bonding in Fe^+ is derived from the s^1d^n configuration while for Ni^+ and Co^+ it is derived from d^{n+1}, our calculations cannot explain the much smaller experimental value for Fe^+. Given the good agreement between theory and experiment for the other systems and considering that similar uncertainties are expected for all the systems, our results suggest that the experimental value for Fe^+-CO_2 is too small.

Conclusions

The interaction of carbon dioxide with the first row transition metal cations has been studied theoretically. Both the coordinated M^+-CO_2 and the inserted OM^+CO structures have been considered.

The most stable coordination of carbon dioxide interacting with a transition metal cation is the linear end-on M^+-OCO one, due to the electrostatic (charge−quadrupole) nature of the bonding. The ground-state and binding energies are mainly determined by several mechanisms for reducing metal−ligand repulsion.

The bonding in the inserted OM^+CO structures arises from the electrostatic interaction between the ground state of OM^+ and CO. Because of this bonding mechanism, the bonding in the transition metal oxide cations has also been analyzed. As found for the neutral systems, early transition metals (Sc^+, Ti^+, and V^+) have large MO^+ binding energies, and thus, for these metals the insertion reaction is exothermic and the inserted OM^+-CO structure is more stable than the linear M^+-OCO isomer.

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