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Theoretical Calculations on the Interaction of CO with MgO and CaO

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Abstract: Ab initio calculations have been performed on linear and cyclic structures resulting from the interaction of CO with MgO and CaO. For the MgO case, linear carbonyl (OC–MgO) and isocarbonyl (CO–MgO) minima are higher in energy than a four-membered ring geometry with C_{2v} symmetry. Linear carbonyl and isocarbonyl structures spontaneously rearrange to two cyclic minima in the CaO case. The first of these resembles the Mg cyclic structure, but the second has a Ca–O–C three-membered ring. All of the cyclic structures contain a metal dication coordinated to a bent CO_2^{2-} ligand.

Metal oxides serve as catalysts for a host of important reactions.¹ Reducing CO on surfaces or in solution is a prominent topic in catalytic chemistry.² Catalytic properties of metal oxides are thought to be related to acid–base properties³ and structural defects.⁴ Carbon monoxide, capable of acting as Lewis acid or base, exhibits a rich chemistry with metal oxides. Adsorption of CO onto thermally activated MgO or CaO leads to the formation of a variety of anionic (CO)_x species.⁵ Cyclic, planar species generated in this way have been analyzed with electron spin resonance techniques.^{5,6} Active sites of high basicity may effect electron transfer and subsequent CO reduction and telomerization.⁷ Inhibition of these reactions takes place by blocking normal or defect sites, implying that adsorption on normal sites may be followed by migration to more reactive defect sites. Many structural investigations of the active sites have been made.⁸ Calculations on cluster models of the MgO surface have confirmed certain qualitative notions on the reactivity of defect sites.⁹ Trends in various indices of electronic structure suggest that the coordination environment about a surface atom or vacancy has a pronounced effect on donating or accepting reactivity. The more oxygens about a metal atom, the more its empty levels are destabilized; increasing metal coordination about an oxygen lowers the lone pair energy levels. Precise calculations on species relevant

to this problem have been restricted to diatomics.¹⁰ There is a need for calculations that go beyond the identification of qualitative

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trends. This ab initio study is intended to provide reliable structural and energetic information on the interaction of CO with MgO and CaO. We first choose to consider single molecules of the oxides. After gaining understanding of these simple systems, later theoretical work will probe small cluster ((MgO)_x and (CaO)_x) interactions with CO. Modes of coordination, rearrangements to different structures, energies accompanying these transformations, and vibrational frequencies, which may become useful in future matrix isolation studies, are the focus of this work.

Computational Details

Hartree-Fock (HF) geometry optimizations¹¹ and second-order perturbation theory¹² calculations (MP2) are performed with Gaussian82¹³ plus program links modified for effective core potential¹⁴ calculations on the University of New Mexico's VAX 8650. Standard basis sets¹⁵ are used for Mg, C, and O atoms. For Ca, the effective core potentials of ref 16 (ECP II) are found to give superior CaO geometries to those of ref 17 (ECP I) and are used in all subsequent calculations. The ECP II model includes the 3s and 3p electrons in the valence space. The three s and p gaussian basis functions with the largest exponents are combined according to the prescribed contraction scheme¹⁶ to describe these electrons. A 4-1 decontraction of five gaussians for the 4s region and a 1-1 decontraction of the two most diffuse gaussians for the 4p are employed.¹⁸ Six d gaussians¹⁸ are decontracted to 5-1 to describe the 3d region. The Ca ECP basis contraction notation is (5s,5p,6d/3s,3p,2d).

Results and Discussion

I. Linear Carbonyl-MgO Complexes. According to simple bonding notions, Mg in MgO is a Lewis acidic center that can accept electron density from CO. Back-bonding is hardly a consideration, as Mg in a +2 oxidation state has no electrons to donate to CO. These guiding concepts are easily stated with the vocabulary of qualitative molecular orbital theory. MgO has low empty orbitals with predominantly metal 3s or 3p character that can stabilize filled orbitals on CO, especially the HOMO, 5σ. MgO's filled orbitals are concentrated on O, a very electronegative atom, and are therefore very low. Energy differences with CO's empty π* orbitals are too great to lead to effective donation from MgO to CO. Overlap between CO's HOMO and MgO's LUMO, a σ orbital whose largest lobe points away from O, is maximized

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Table I. MgCO₂ Complexes^a

	HF/ 6-31G*	HF/ 6-31+G**/ HF/6-31G*	MP2/ 6-31+G**/ HF/6-31G*	expt ²⁰
Separated Molecules: CO and MgO				
CO ^b	1.114			1.128 Å
MgO ^b	1.738			1.749
COMgO: Linear Isocarbonyl Structure				
CO ^b	1.123			
MgO ^b	1.707			
OMg ^b	2.239			
binding energy ^c	7.3	7.0	-1.3	
OCMgO: Linear Carbonyl Structure				
CO ^b	1.104			
MgO ^b	1.705			
CMg ^b	2.484			
binding energy ^c	7.8	6.9	3.6	
Mg(OCO): C _{2v} Cyclic Structure				
CO ^b	1.254			
MgO ^b	1.972			
CMg ^b	2.268			
O-C-O ^d	120.4			
binding energy ^c	54.3	51.1	49.9	

^aThe second and third columns employ the geometries optimized in the first column. ^bÅ. ^ckcal/mol. ^dDegrees.

Table II. Vibrational Frequencies (cm⁻¹)

	HF/6-31G*	expt ²⁰
Separated Molecules: CO and MgO		
CO	2438.84	2143.0
MgO	769.40	785.1
COMgO: Linear Isocarbonyl Structure		
CO str	2349.20	
MgO str	938.10	
OC-MgO str	182.31	
CO bend	129.11	
MgO bend	29.38	
OCMgO: Linear Carbonyl Structure		
CO str	2531.37	
MgO str	952.52	
CO bend	230.41	
OC-MgO str	169.08	
MgO bend	29.19	
Mg(OCO): C _{2v} Cyclic Structure		
a ₁	1222.27	
	793.81	
	285.63	
b ₂	1565.20	
	444.83	
b ₁	439.83	

in a linear structure where C is next to Mg. The most stable orientation of the diatomics' dipoles¹⁹ also favors such a geometry. CO's dipole moment is much smaller than MgO's, but the negative charge resides on the C side.

Linear O-C-Mg-O (carbonyl) and C-O-Mg-O (isocarbonyl) linkages are optimized at the HF/6-31G* level. This treatment produces reasonable bond lengths²⁰ for MgO and CO. To check the assumption of linear geometries, both linear and nonlinear initial guess structures are tested. Linear minima in the potential energy surface are obtained, i.e., at the geometries where the energy gradients vanish, the energy second derivative matrices

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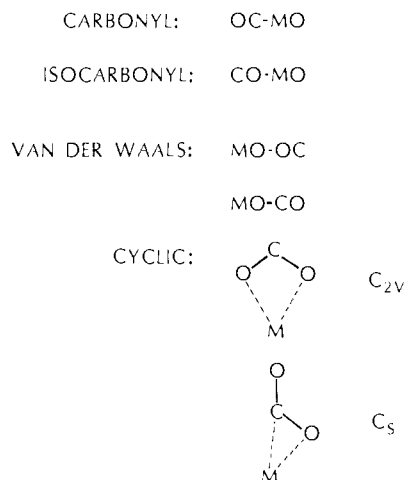


Figure 1. Structures of complexes studied, M = Mg, Ca.

are positive definite. Harmonic force constants are obtained as eigenvalues of the energy second derivative matrix.¹¹

In both isomers, the MgO distance decreases from the free molecule and the MgO vibrational frequency is higher (Tables I and II). Bonding between Mg and O has been strengthened. This can be explained on the grounds that the carbonyl provokes hybridization of the Mg 3s and 3p_z so as to create a lobe that points toward the oxygen dianion. The CO distances change little with respect to free CO.

Energy differences between the linkage isomers are calculated several ways. In addition to HF/6-31G* total energy differences, the geometry optimized with the latter basis is used in calculations with the 6-31+G* basis, which introduces diffuse s and p functions on each atom. Correlation improvements through second order in perturbation theory are also added. The best calculation favors the carbonyl structure by 4.9 kcal/mol. One can safely say that the two isomers are separated by a small amount of energy. (6-31G* Mg-C overlap population in the carbonyl case is about four times larger than Mg-O overlap population in the isocarbonyl case.) Binding energies can be deduced from CO and MgO total energies calculated with 6-31+G* at the HF/6-31G* geometries. HF and second-order correlation results are in close agreement, with the latter giving the carbonyl complex a binding energy of 3.6 kcal/mol. This implies that the isocarbonyl species is higher than the separated limit by 1.3 kcal/mol. Weakly directional bonding between CO and MgO is indicated by the low frequencies associated with the MgO bending modes. It costs little energy for the MgO axis to oscillate about the $C_{\infty v}$ symmetry axis of MgCO₂.

Two other linear possibilities exist, though they depend on van der Waals interactions. CO could bind to the O atom of MgO. When CO is pressed against MgO through the C atom, dissociation into Mg and CO₂ takes place in HF/3-21G optimizations. When the two O atoms are brought into close contact, the interaction is repulsive, and dissociation into CO and MgO takes place.

II. Linear Carbonyl-CaO Complexes. Optimization with the 3-21G basis on the CO atoms, 3-21+G on the oxygen dianion, and the ECP II Ca basis are attempted for carbonyl and isocarbonyl complexes of CaO. These basis sets produce good bond lengths for CO and CaO.²⁰ In spite of several attempts to find propitious starting bond lengths for linear complexes, the optimizations repeatedly diverge from such structures. Long initial separations between CO and CaO also fail to yield a stable, linear minimum. With a carbonyl linkage initial guess, the molecule gradually rearranges to a C_s structure (Figure 1) in which Ca bridges between C and the O that originates with CaO, forming a three-membered ring. At the same time, the Ca-O bond length increases. An isocarbonyl initial guess converges toward a C_{2v} structure in which a four-membered ring is formed. The two O atoms are at opposite ends of this ring. In each rearrangement, the atom of CO nearer to Ca in the linear guess geometry forms

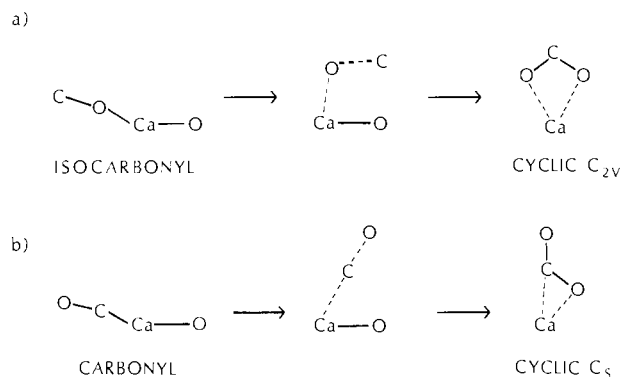


Figure 2. Spontaneous rearrangement of the carbonyl and isocarbonyl CaCO₂ complexes.

Table III. CaCO₂ Complexes^a

	HF/I	MP2/I	HF/II	MP2/II	expt ²⁰
Separated Molecules: CO and CaO					
CO ^b	1.134				1.128 Å
CaO ^b	1.865				1.822
Ca(OCO): C_{2v} Cyclic Structure					
CO ^b	1.380				
CaO ^b	2.609				
CaC ^b	2.101				
O-C-O ^c	106.7				
binding energy ^d	44.5	22.7	38.4	33.5	
Ca(OCO): C_s Cyclic Structure					
CO(exo) ^b	1.211				
CaO ^b	2.034				
CaC ^b	2.321				
CO(ring) ^b	1.409				
O-C-O ^c	124.9				
binding energy ^d	30.3	21.9	31.2	33.9	

^aBasis I: Ca ECP II (5s,5p,5d/3s,3p,2d); C, O, Mg 3-21+G. Basis II: Same except C and O basis is now 3-21+G plus d functions. All MP2 and basis II calculations use HF/I optimized geometries. ^bÅ. ^cDegrees. ^dkcal/mol.

a smaller and smaller bond angle with the CaO axis. The other atom in the migrating CO tilts over the Ca-O bond as the O-Ca-X (X = C or O) bond angle nears 90° (Figure 2, a and b). No stable linear or almost linear minima are found in the potential energy surface. Cyclic structures for the Mg and Ca cases must therefore be investigated.

III. Cyclic MgCO₂. Both of the cyclic structures observed in the previous section contain a metal ion coordinated to a bent CO₂ unit, in which the two C-O distances are similar. These complexes roughly consist of a metal dication bound to a CO₂²⁻ ligand. HF/6-31+G optimizations on C_{2v} CO₂²⁻ yield a C-O bond length of 1.287 Å and an O-C-O angle of 123.5°. One can readily understand the electronic structure of the dianion by recalling that it is isoelectronic with CF₂, a carbene.

HF/6-31G* optimizations are carried out on cyclic complexes with Mg. Optimization of the C_s three-membered ring structure follows a path that more or less reverses that of the previous section. The CO, linked to MgO through C, slowly migrates (before the calculation is terminated) toward a geometry that resembles that of the linear carbonyl minimum. This result is qualitatively opposite to the OC-CaO optimization. The C_{2v} four-membered ring optimization converges to a geometry that preserves much of the initial structure of the CO₂²⁻ fragment. In the C_{2v} structure, the C-O bond lengths and the O-C-O angle are close to the values of the free dianion (Table I). A correlated total energy at this geometry with the 6-31+G* basis is then calculated. At all levels of theory, this isomer has the lowest energy by about 45 kcal/mol. The best calculated binding energy with respect to separated CO and MgO is 49.9 kcal/mol. Vibrational frequencies are calculated at the HF/6-31G* level, in order to provide comparisons with future experiments (Table II). Because the anion is understood to be a carbene, a third structure is tried

in which the metal is coordinated to the carbene lone pair of CO_2^{2-} . This optimization leads to a rearrangement toward the C_{2v} structure.

IV. Cyclic CaCO_2 . Final refinements of the preliminary results of section II are performed with the 3-21+G basis on all non-metal atoms (Table III). Both the C_s and C_{2v} optimizations converge to stable geometries. In the former structure, the O-C-O angle remains about the same as in the isolated anion calculation, but there is a considerable difference between the CO bond lengths. In the C_{2v} isomer, the O-C-O angle is narrower and the CO distances are longer. These results, plus those for the Mg-containing C_{2v} isomer, indicate that the anionic fragment has considerable flexibility in binding to the metal ions. Further perturbations are applied to these structures to see if breaking symmetry, e.g., destroying planarity, leads to lower energy. None of these perturbations has any effect on the final optimized structures. Total energy calculations on the two isomers are improved by adding second-order correlation corrections. A final improvement adds d functions^{15b} to O and C atoms as well as correlation. The correlated calculations yield energies that are quite close.

Conclusions

The present study shows that the interaction of MgO with CO results in stable linear and C_{2v} four-membered ring structures.²¹ The binding energy associated with the cyclic structure is much larger than those of the linear systems. The interaction of CaO with CO yields stable C_s three-membered ring and C_{2v} four-membered ring CaCO_2 complexes with nearly equivalent binding energy values. The cyclic structures resemble coordination of a CO_2^{2-} anion with an M^{2+} cation, and the anion has considerable flexibility in binding.

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Registry No. CO, 630-08-0; MgO, 1309-48-4; CaO, 1305-78-8.

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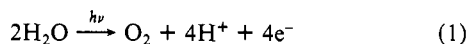
Photoactivation of H_2O by *p*-Benzoquinone and the Role of Mn^{III} Complexes in O_2 Evolution: Molecular Orbital Theory

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Abstract: A mechanistic quantum chemical study is made of the photogeneration of O_2 from H_2O coordinated to active Mn^{III} complexes in the presence of *p*-benzoquinone, as studied experimentally by Ashmawy and co-workers. The abstraction of H from H_2O by $\pi^* \leftarrow n$ optically excited *p*-benzoquinone is explained, using molecular orbital theory, as being caused by the H accepting ability of the O^* in the excited quinone. In the absence of active Mn complexes, hydroquinone and 2-hydroxy-*p*-benzoquinone are the photoproducts. In the presence of active Mn complexes, and in acidic solution to prevent these reactions, H_2O coordinated to Mn^{III} is photoactivated, leading to hydroquinone and OH strongly bound to Mn^{IV} . Following deprotonation, stable di- μ -oxo Mn^{IV} dimers form which disproportionate via a 4Mn complex (reminiscent of proposed photosystem II processes by plants) to O_2 and a stable O-bridged Mn^{III} dimer. According to the calculations, this last step is rate limiting. It is shown that dimerization of the Mn complexes is the key to O_2 generation in the active systems, and this is controlled by the ligand structure.

In plant photosynthesis, dioxygen is evolved from the catalyzed photodecomposition of water. The generation of one molecule of oxygen from two molecules of water requires the transfer of four electrons:



It is generally believed that four atoms of Mn in the reaction center are essential for oxygen evolution in biological photosystem II (PSII) activity.¹ At least two of these Mn atoms occur in a binuclear species with a Mn-Mn separation of ca. 2.7 Å.²

Kambara et al.³ devised a model for photosynthetic water oxidation to provide a possible mechanistic explanation. In this model the four Mn^{III} cations are divided into two groups, [Mn] complexes in a hydrophobic cavity and (Mn) complexes on a hydrophilic surface. Following oxidation to Mn^{IV} , caused by electron transfer to light-absorbing centers, each of the two hydrophobic Mn complexes oxidizes a coordinated H_2O and the protons transfer to the hydrophilic Mn complexes along the hy-

drogen bonds between their respective ligand H_2O molecules. It is proposed that the O_2 molecule in a complex of the form $\text{Mn}^{\text{III}}-\text{O}_2-\text{Mn}^{\text{III}}$ is replaced by two H_2O molecules, which complete the cycle.

An alternative mechanism has been given by Brudvig and Crabtree⁴ for photosynthetic oxygen evolution based on a structural conversion of an Mn_4O_6 complex to an Mn_4O_4 complex. They proposed that Mn_4O_4 undergoes a series of photoactivated oxidation steps and structural rearrangements to the Mn_4O_6 form which has two O^{2-} or OH^- coordinated in it. The formation of an O-O bond and the loss of O_2 and the recreation of the starting Mn_4O_4 cluster completes the cycle.

Several other models have been devised in attempts to explain the role of manganese and the mechanism of oxygen evolution in the photosynthetic process.⁵⁻⁷ However, the true mechanism or mechanisms for oxygen evolution remain unproved.

Recently there has been an interest in the photogeneration of O_2 from H_2O using soluble Mn^{III} complexes.^{8a} The photolysis

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