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Theoretical Study on the Reaction Mechanism of CO_2 with Mg

Der-Yan Hwang*,[†] and Alexander M. Mebel*,[‡]

Department of Chemistry, Tamkang University, Tamsui 25137, Taiwan, and Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 10764, Taiwan

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Ab initio QCISD(T)/6-311+G(3df)//MP2/6-31+G(d) calculations of potential energy surface for the reaction of Mg atoms with CO_2 show that re-forming of carbon dioxide to carbon monoxide can be significantly enhanced in the presence of Mg atoms. The overall endothermicity of the $Mg + CO_2 \rightarrow MgO + CO$ reaction is calculated to be about 66 kcal/mol, almost twice lower than the energy needed for spin-forbidden unimolecular decomposition of CO_2 to $CO + O(^3P)$. The $Mg + CO_2$ reaction is spin-allowed and the barrier, 68.8 kcal/mol, is greatly reduced as compared to the barrier for the unimolecular decomposition, 131 kcal/mol. The reaction proceeds via the MgOCO cyclic intermediate which lies 14.3 kcal/mol higher in energy than the reactants and stabilized with respect to $Mg + CO_2$ by a barrier of 5.9 kcal/mol. The catalytic role of Mg atoms for re-forming of CO_2 to CO is discussed. The reverse $MgO + CO \rightarrow Mg + CO_2$ reaction is highly exothermic and has a barrier of 2.8 kcal/mol indicating that magnesium oxide can be rapidly reduced by carbon monoxide producing Mg atoms and carbon dioxide. Highly accurate full valence active space MRCI calculations with extrapolation to the complete basis set allowed us to propose a new value for the standard heat of formation of MgO in the gas phase, 31.4−31.9 and 33.5−34.0 kcal/mol for $\Delta H_f°(0\ K)$ and $\Delta H_f°(298\ K)$, respectively. The result is 20 kcal/mol higher than the present recommended value and new experimental measurements of thermochemical data for gaseous MgO are suggested.

Introduction

Reducing of CO_2 on surfaces or in solution are important topics in catalytic chemistry. Catalytic properties of metal oxides are thought to be related to acid−base properties[1] and structural defects.[2] Many structural investigations of the active sites have been made.[3] Calculations on cluster models of the MgO surface have confirmed certain qualitative notions on the reactivity of defect sites.[4] The coordination of the carbon dioxide molecule to the metal center has been considered as a key step to reduce this molecule to useful organic substances. The naked metal−carbon dioxide molecules were only recently studied.[5] The interaction mechanism between metal atoms and small molecules has become an attractive subject of experimental and theoretical studies. A small number of metal-CO_2 complexes involving one, two or three metal centers have been isolated and their structures were characterized by X-ray diffraction. There is a plenty of IR and NMR spectroscopic evidences for the existence of various M-CO_2 intermediates.[5−15] Some quantum chemical calculations for the M-CO_2 molecules with alkali metal atoms,[16] and transition metal atoms[14,17] have also been reported.

The ab initio calculation reported in this paper is intended to study the reaction pathways of carbon dioxide with magnesium including reliable structures of the reactants, products, intermediates, and transition states as well as their accurate energies. The $Mg + CO_2$ reaction will be compared with unimolecular decomposition of CO_2 and the differences in energy barriers and the heats of reaction will be discussed. The reason for significant decrease of the reaction barrier for re-forming of CO_2 into CO in the presence of Mg will be demonstrated.

Computational Details

Since the low-temperature reduction of carbon dioxide by Mg atoms is expected to follow the minimum energy pathway from the singlet ground state of CO_2 and Mg, we mostly consider the singlet ground electronic state potential energy surface of the title reaction. On this surface, full geometry optimizations were run to locate all the stationary points at the MP2/6-31G(d), MP2/6-31+G(d), MP2/6-311+G(d) (in some cases), and QCISD/6-31G(d) levels of theory.[18,19] The harmonic vibration frequencies were obtained at the MP2/6-31G(d) and MP2/6-31+G(d) levels in order to characterize the stationary points as minima or first-order saddle points, to obtain zero-point vibration energy corrections (ZPE) and to generate force constant data needed in the IRC calculation. To predict more reliable ZPE, the raw calculated ZPE values were scaled by 0.967 at the MP2/6-31+G(d) levels to account for their average overestimation.[20] The intrinsic reaction coordinate IRC method[21] was used to track minimum energy paths from transition structures to the corresponding minimum. A step size of 0.1 $amu^{-1/2}$ bohr was used in the IRC procedure. The relative energies were refined using the QCISD(T)/6-311+G(3df) theory[19] with MP2/6-31G(d) or MP2/6-31+G(d) optimized geometry. All the ab initio calculations described here were performed employing the Gaussian 94 programs.[22]

Results and Discussion

The total and ZPE corrected relative energies of various compounds in the reaction of $CO_2 + Mg$ calculated at the MP2/6-31+G(d), QCISD/6-31G(d) and QCISD(T)/6-311+G(3df) levels of theory are listed in Table 1. Table 2 presents calculated vibrational frequencies. The energy diagram along the reaction path computed at QCISD(T)/6-311+G(3df)//MP2/6-31+G(d)

[†] Tamkang University.

[‡] Academia Sinica.

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TABLE 1: Total Energies E_{tot} (hartree), ZPE (kcal/mol), and Relative Energies E_{rel} (kcal/mol) of Various Compounds in the Reaction of Mg + CO_2

	MP2/6-31+G(d)		QCISD(T)/6-311+G(3df)//MP2/6-31+G(d)	
species	ZPE	E_{tot}	E_{tot}	E_{rel}
Mg		−199.61772	−199.64016	
CO_2	7.15	−188.11796	−188.33146	
Mg + CO_2	7.15	−387.73568	−387.97162	0.00
CO_2−Mg A	7.19	−387.73619	−387.97222	−0.34
CO_2−Mg B	7.19	−387.73615	−387.97207	−0.25
TS1	6.10	−387.70570	−387.93785	20.17
MgOCO	7.14	−387.71772	−387.94880	14.31
TS2	4.82	−387.63104	−387.85834	68.83
MgO	1.42	−274.60434	−274.70524	
CO	3.01	−113.02913	−113.15689	
MgO + CO	4.43	−387.63347	−387.86213	66.07

	QCISD/6-31G(d)		QCISD(T)/6-311+G(3df)//QCISD/6-31G(d)	
species	ZPE[a]	E_{tot}	E_{tot}	E_{rel}
Mg		−199.62917	−199.64016	
CO_2	7.15	−188.10637	−188.33211	
Mg + CO_2	7.15	−387.73554	−387.97227	0.00
CO_2−Mg B	7.19	−387.73612	−387.97280	−0.29
TS2	4.82	−387.62183	−387.86589	64.51

[a] At the MP2/6-31+G(d) level.

TABLE 2: Vibrational Frequencies (cm^{-1}) of Various Compounds in the Mg + CO_2 Reaction Calculated at the MP2/6-31+G(d) Level

species	frequencies
TS1	516i, 41, 443, 455, 1211, 2119
cyclic MgOCO	264, 385, 432, 818, 1377, 1723
TS2	138i, 130, 141, 286, 834, 1978
MgO	997 (744)[a]

[a] In parentheses: the frequency calculated at the CCSD(T)/6-311G(d) level which gives a better agreement with the experimental value of 785 cm^{-1} (ref 26).

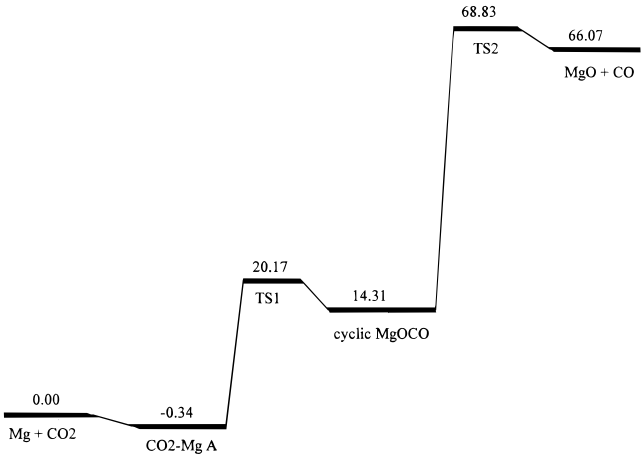

Figure 1. Potential energy diagram for the Mg + $CO_2 \rightarrow$ MgO + CO reaction calculated at the QCISD(T)/6-311+G(3df)//MP2/6-31+G(d) + ZPE level.

is shown in Figure 1. The optimized geometry of various compounds along the predicted pathway of the CO_2 + Mg reaction are depicted in Figure 2.

A. Reaction Mechanism. For studying the reaction mechanism of CO_2 + Mg, the MP2/6-31+G(d) or higher levels optimization calculations are required to map out a reasonable reaction pathway. As seen in Figure 1 and Figure 2, at the first stage, the CO_2 molecule attaches to magnesium atom to form a week triangle complex of C_{2v} geometry, CO_2−Mg A. At MP2/6-31+G(d) and MP2/6-311+G(d), the complex CO_2−Mg A conserved the structure of linear singlet carbon dioxide and both of its two oxygen atoms have equal distances from the magnesium atom, about 4.6 Å. The QCISD(T)/6-311+G(3df)//MP2/6-31+G(d) calculated exothermicity of the CO_2 + Mg $\rightarrow$ CO_2−Mg A reaction step is only −0.34 kcal/mol. The structure of CO_2−Mg A, shown in Figure 2, is planar and corresponds to a minimum on the MP2/6-31+G(d) and MP2/6-311+G(d) potential energy surfaces. The structure of CO_2−Mg B is linear and corresponds to a minimum at the MP2/6-31+G(d) potential energy surface. Only one of the oxygen atoms of CO_2 is oriented toward the magnesium atom with a distance between them of about 4.14 Å, and CO_2−Mg B is only 0.09 kcal/mol higher energy than CO_2−Mg A at QCISD(T)/6-311+G(3df)//MP2/6-31+G(d). Without diffuse functions added, a bent structure of CO_2−Mg B corresponds to a minimum at the MP2/6-31G(d) and QCISD/6-31G(d) potential energy surfaces. Both structures A and B can be characterized as very weak coordination complexes of Mg with CO_2.

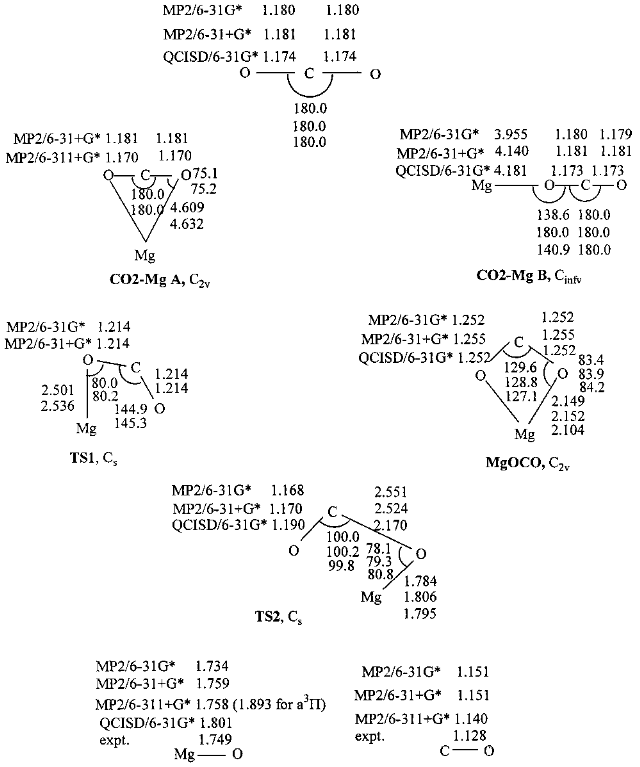

Figure 2. Geometries of the reactants, products, intermediates, and transition states of the Mg + $CO_2 \rightarrow$ MgO + CO reaction, optimized at various levels of theory. (Bond lengths are in Å and bond angles are in degrees).

At MP2/6-31+G(d), from the triangular CO_2−Mg A the reaction proceeds via transition state TS1 to a planar cyclic MgOCO intermediate of C_{2v} geometry. The OCO angle in TS1 is bent to 145.3° and the Mg−O bond length is shortened to 2.536 Å, so the transition state is late in accord with the high endothermicity of the process. The QCISD(T)/6-311+G(3df)//MP2/6-31+G(d) calculated activation energy is 20.51 kcal/mol and the endothermicity of the CO_2−Mg A $\rightarrow$ cyclic MgOCO reaction step is 14.65 kcal/mol. The transition state optimization was followed by the frequency and IRC calculations at the MP2/6-31+G(d) level of theory which confirmed that TS1 does connect CO_2−Mg A and a planar cyclic MgOCO. The structure of MgOCO obtained at MP2/6-31+G(d) is similar to the η^3_{OCO} form optimized at a CI level by Jeung.[23] At QCISD(T)/6-311+G(3df)//MP2/6-31+G(d), the potential energy of cyclic MgOCO is 14.65 kcal/mol higher than CO_2−Mg A. Our result disagrees with the finding by Jeung[23] whose CI calculations with a large but nonstandard basis set gave the MgOCO molecule 2.3 kcal/mol lower in energy than isolated Mg and CO_2. We investigated the influence of the basis set on the relative energy of MgOCO at the QCISD(T) level. With the 6-31G(d) basis set the energy is 16.2 kcal/mol and it decreases to 14.9 kcal/mol when diffuse functions are added [6-31+G(d)]. With the 6-311G(d) basis set the energy increases to 20.2 kcal/mol and again decreases to 14.3 kcal/mol with 6-311+G(3df). Similar trends are also found at the MP2 level. CCSD(T)/6-311G(d) calculations gave a result very close to that at QCISD(T)/6-311G(d). With different basis sets, the relative energy of MgOCO varies within 5−6 kcal/mol, so the difference in the basis sets alone cannot account for ∼17 kcal/mol difference between the present result and that of Jeung.[23] The origin of the difference apparently lies in the treatment of electronic correlation. Jeung[23] used the single-reference CI method with all excitations only for two electrons and with single excitations for other 10 valence electrons. This approach is inferior to CISD which in turn is less accurate than QCISD(T). The QCISD(T)/6-311+G(3df) calculations are expected to provide chemical accuracy for the energies of the first and second row compounds,[24] and we believe that the cyclic MgOCO structure is higher in energy than the reactants and stabilized with respect to Mg + CO_2 only due to the barrier of ∼6 kcal/mol at TS1.

Bonding in MgOCO was characterized by Jeung as a mixture of neutral (covalent) and ionic ($Mg^+(CO_2)^-$) components. The weakening of CO bonds in the CO_2 fragment, where the bond lengths increase by 0.07 Å as compared to isolated CO_2, and significant bending distortion of carbon dioxide are compensated by the newly formed Mg−CO_2 bonds. The energy required for deformation of isolated CO_2 to the bent geometry of the OCO fragment in MgOCO is 54.7 kcal/mol. This means that the reaction of Mg atom with deformed CO_2 is exothermic by 40.4 kcal/mol, so that MgOCO is 14.3 kcal/mol higher in energy than Mg + CO_2.

From the cyclic MgOCO the reaction proceeds to produce carbon monoxide and magnesium oxide via transition state TS2. At MP2/6-31+G(d), the MgO and CO (1.806 and 1.170 Å) terminal bonds in TS2 become stronger and the central C−O bond (2.524 Å) is weakened. This finding is in accord with the fact that the next step leading to formation of MgO + CO involves a cleavage of the central C−O bond. The calculated QCISD(T)/6-311+G(3df)//MP2/6-31+G(d) energies place the TS2 transition state 54.5 kcal/mol higher than cyclic MgOCO and the MgO + CO at 51.76 kcal/mol higher than cyclic MgOCO in good agreement with 49.9 kcal/mol calculated by Ortiz et al. at MP2/6-31+G*//HF/6-31G* level.[25] The MP2/6-31G(d) IRC calculation confirmed that the first-order saddle point TS2 does connect the cyclic MgOCO and MgO + CO. Since the calculated energy difference between TS2 and MgO + CO is small and can be sensitive to the level of theory used, the presence of the barrier at TS2 is not certain; it may not exist. It is worth mentioning that the QCISD/6-31G(d) geometry optimization for TS2 gave a much shorter C−O distance for the breaking bond, 2.170 Å. However, the potential energy surface along this geometric parameter is quite flat; the QCISD(T)/6-311+G(3df) energies computed at the MP2/6-31+G(d) and QCISD/6-31G(d) optimized geometries differ only by ∼4 kcal/mol (Table 1).

Triplet electronic state is not expected to play a significant role in the reaction. According to experimental data,[26] the lowest triplet state of the Mg atom lies ∼62 kcal/mol above the singlet ground state. For the products, the $a^3\Pi$ state of MgO is 9.1 ± 3.0 kcal/mol higher in energy than the $X^1\Sigma^+$ state.[26] Thus, the triplet products lie above TS2 and intersystem crossing from the singlet to triplet electronic state is much less likely to occur on the course of the reaction than the formation of singlet products.

B. Catalytic Role of Mg in Re-forming Carbon Dioxide. From the potential energy diagram for the Mg + CO reaction shown in Figure 1, we can conclude that re-forming of carbon dioxide to carbon monoxide can be greatly enhanced in the presence of metal atoms, such as Mg. For instance, the unimolecular $CO_2 \rightarrow CO + O(^3P)$ reaction is endothermic by 125.7 kcal/mol.[27] Our recent calculations showed this spin-forbidden reaction has to overcome a barrier of at least 131 kcal/mol.[28] In the presence of Mg, re-forming of CO_2 to CO becomes spin-allowed, its endothermicity decreases by almost two times and the reaction barrier is reduced to 68.8 kcal/mol.

The interaction between magnesium atom and carbon dioxide illustrates an important catalytic role played by metals. When a metal or its derivative is bonded to a substrate, the energy required for the endothermic process of deformation or even decomposition of the substrate decreases due to the bonding between the metal and substrate. At the next reaction step, the bond between metal and a fragment of the substrate (oxygen atom for the case of MgOCO) strengthens and the metal-substrate complex dissociates yielding two fragments of the initial substrate (CO + O), one of those is bonded to the metal. The decrease of endothermicity for the substrate (CO_2) decomposition in the presence of metal (Mg) is due to the energy income from the formation of chemical bond between metal and substrate fragment (oxygen atom).

C. Reduction of MgO by Carbon Monoxide. The reverse $MgO + CO \rightarrow Mg + CO_2$ reaction is highly exothermic and calculated to have a barrier of only 2.8 kcal/mol. This means that the reaction of magnesium oxide with carbon monoxide should be fast. Thus, MgO can efficiently remove CO transforming it into CO_2. The MgO + CO reaction can be, in principle, used for the production of magnesium. One of the methods of Mg production existing now includes formation of $Mg(OH)_2$ from the seawater,

$$Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+}$$

The magnesium hydroxide is removed by filtration and then neutralized with hydrochloric acid to form $MgCl_2$. This is followed by electrolysis of molten magnesium chloride. In another industrial method, magnesium hydroxide is decomposed to magnesium oxide and water by heating. MgO is then reduced with ferrosilicon to obtain metallic magnesium. Our calculations showed that the reaction of MgO with CO in the gas phase should be very efficient. Hence, another reducing agent to reduce magnesium oxide to Mg could be carbon monoxide.

D. Heat of Reaction $MgO + CO \rightarrow Mg + CO_2$ and Enthalpy of Formation of MgO in the Gas Phase. If one takes recommended standard enthalpies of formation for Mg (35.16 kcal/mol), CO_2 (−94.05 kcal/mol), CO (−26.42 kcal/mol), and MgO (13.9 kcal/mol) from the NIST Chemistry Webbook,[26] the experimental heat of the $Mg + CO_2 \rightarrow MgO + CO$ reaction is 46.37 kcal/mol. However, the QCISD(T)/6-311+G(3df) calculated reaction endothermicity is 66.1 kcal/mol. Thus, the discrepancy between theory and experiment is 20 kcal/mol. The major source of the deviation is the bond strength in MgO. At the QCISD(T)/6-311+G(3df) level with scaled MP2/6-31+G(D) zero-point energy correction the strength of the Mg−O bond in magnesium oxide is 57.0 kcal/mol, while based on the NIST

TABLE 3: Bond Strength and Heat of Formation of MgO (kcal/mol)

	cc-pvdz		cc-pvtz		cc-pvqz		cc-pv5z	
	MRCI	MRCI+D	MRCI	MRCI+D	MRCI	MRCI+D	MRCI	MRCI+D
ΔE (w/o ZPE)	42.20	42.51	54.29	54.64	58.97	59.37	60.94	61.36

	MRCI/∞	MRCI+D/∞
ΔE (w/o ZPE)	61.95	62.42
D (0 K)	60.83	61.30
D (298 K)	60.73	61.20
$\Delta H_f°$ (0 K)[a]	31.85	31.38
$\Delta H_f°$ (298 K)[b]	33.98	33.51

[a] Computed based on D (0 K) and experimental $\Delta H_f°$ (0 K) for Mg and O, 33.58 and 59.00 kcal/mol, respectively. [b] Computed based on D (298 K) and experimental $\Delta H_f°$ (298 K) for Mg and O, 35.16 and 59.55 kcal/mol, respectively.

recommended enthalpies of formation for Mg, O (59.55 kcal/mol)[26] and MgO one obtains the value of 80.8 kcal/mol. Looking into another source of thermochemical data, *CRC Handbook of Chemistry and Physics*,[29] we find the value of 86.8 ± 3.0 kcal/mol for the bond strength in MgO. Earlier ab initio calculations by Bauschlicher and co-workers[30] resulted in 63.4 kcal/mol which is much closer to the QCISD(T)/6-311+G(3df) value than to the experimental results. The existing uncertainty concerning the bond strength and standard heat of formation for MgO prompted us to reinvestigate energetics of this molecule using highly accurate multireference configuration (MRCI) method.[31]

The full valence active space including 8 electrons distributed on 8 orbitals was chosen for the MRCI calculations using the MOLPRO-96 program.[32] We employed the series of Dunning's correlation consistent basis sets,[33] cc-pvdz, cc-pvtz, cc-pvqz, and cc-pv5z, to estimate the MRCI energy with the complete basis set. The results are shown in Table 3. With the basis set change from cc-pvdz to cc-pv5z the energy ΔE (MgO → Mg + O) which does not include ZPE increases from 42.2 to 60.9 kcal/mol at the MRCI level and from 42.5 to 61.4 kcal/mol when Davidson's correction for quadruple excitations is taken into account. Now we use the extrapolation scheme suggested by Dunning and co-workers,[34]

$$A(x) = A(\infty) + B \exp(-Cx)$$

Where x is the cardinal number of the basis set, 2, 3, 4, and 5 for cc-opvdz, cc-pvtz, cc-pvqz, and cc-pv5z, respectively, and $A(\infty)$ is the bond strength estimated for the complete basis set. Then we obtained the ΔE values as 61.95 and 62.42 kcal/mol at MRCI and MRCI+D. At the next step we add ZPE correction computed from the experimental vibrational frequency of 785 cm^{-1} for MgO[26] to compute the bond strength at 0 K, D(0 K). It is worth mentioning that at the MP2/6-31+G(d) level this frequency, 997 cm^{-1}, is significantly overestimated. However, more accurate CCSD(T)/6-311G(d) calculations give the value of 744 cm^{-1}, in satisfactory agreement with experiment. When ZPE is taken into account, the calculated bond strength, ~61 kcal/mol, is 2 kcal/mol lower than the number reported by Bauschlicher and co-workers[30] and 4 kcal/mol higher than the QCISD(T)/6-311+G(3df) value. Thermal corrections are included to get the D(298 K) value. D(0 K) and D(298 K) together with experimental $\Delta H_f°$(0 K) and $\Delta H_f°$(298 K) for the Mg and O atoms are used to predict $\Delta H_f°$(0 K) and $\Delta H_f°$(298 K) for MgO. The results indicate the standard heat of formation of gaseous magnesium oxide at 298 K is expected to be in the range of 33.5−34.0 kcal/mol, i.e., about 20 kcal/mol higher than previous experimental estimations. New experimental studies of the standard heat of formation of gaseous magnesium oxide at room temperature are encouraged.

Using our estimate for $\Delta H_f°$ of MgO (33.5 kcal/mol at the MRCI+D level) and experimental heats of formation for Mg, CO_2, and CO we predict that the Mg + CO_2 → MgO + CO reaction should be endothermic by 66.0 kcal/mol. This result is very close to the value of 66.1 kcal/mol obtained from the QCISD(T)/6-311+G(3df) calculations reported in the previous section. Therefore, we believe that the energies for the intermediates and transition states of the Mg + CO_2 reaction computed at this level should possess a chemical accuracy.

Note also that the adiabatic singlet−triplet energy gap between the $X^1\Sigma^+$ and $a^3\Pi$ electronic states of MgO is calculated to be 2510 cm^{-1} at the MRCI+D/cc-pv5z level with ZPE corrections using experimental vibrational frequencies of 785 and 650 cm^{-1} for the singlet and triplet, respectively.[26] This value agrees well with the experimental data which have a significant uncertainty, 3200 ± 1000 cm^{-1}.[26]

Conclusions

Re-forming of CO_2 to CO can be significantly enhanced in the presence of Mg atoms due to catalytic role of the metal. The reaction of Mg with carbon dioxide is shown to proceed by formation of the MgOCO four-member ring molecule which lies 14.3 kcal/mol higher in energy than the reactants. MgOCO is stabilized with respect to Mg + CO_2 by a barrier of 5.9 kcal/mol at TS1. The barrier in the forward direction is 20.2 kcal/mol. Weakly bound intermediates CO_2−Mg A and B could also play some role in the reaction but their binding energies relative to Mg + CO_2 are only 0.2−0.3 kcal/mol. From the cyclic MgOCO structure the reaction continues by the cleavage of one C−O and one Mg−O bonds to produce the MgO + CO products via transition state TS2. The energy of TS2 corresponding to the highest barrier the system has to overcome is 68.8 relative to the reactants that is much lower than the energy barrier for the CO_2 → CO + O(^3P) reaction, 131 kcal/mol. The overall endothermicity of the Mg + CO_2 → MgO + CO reaction is calculated to be about 66 kcal/mol ca. with 125 kcal/mol for unimolecular decomposition of carbon dioxide.

High exothermicity and low barrier (2.8 kcal/mol) for the reverse MgO + CO → Mg + CO_2 reaction mean that magnesium oxide can be rapidly reduced by carbon monoxide producing Mg atoms and carbon dioxide.

A new value is suggested for the standard heat of formation of MgO in the gas phase. Highly accurate MRCI calculations with full valence active space gave 31.4−31.9 and 33.5−34.0 kcal/mol for $\Delta H_f°$(0 K) and $\Delta H_f°$(298 K), respectively. The present result is ~20 kcal/mol higher than the value recommended earlier. New experimental measurements of the ambient temperature thermochemical data for magnesium oxide are strongly appealed for.

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Supporting Information Available: Reaction path tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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