Enthalpy of the Gas-Phase CO_2 + Mg Reaction from ab Initio Total Energies

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Various highly accurate ab initio composite methods of Gaussian-n (G1, G2, G3), their variations (G2-(MP2), G3(MP2), G3//B3LYP, G3(MP2)//B3LYP), and complete basis set (CBS-Q, CBS-Q//B3LYP) series of models were applied to compute reaction enthalpies of the ground-state reaction of CO_2 with Mg. All model chemistries predict highly endothermic reactions, with $\Delta H_{298} = 63.6-69.7$ kcal mol^{-1}. The difference between the calculated reaction enthalpies and the experimental value, evaluated with recommended experimental standard enthalpies of formation for products and reactants, is more than 20 kcal mol^{-1} for all methods. This difference originates in the incorrect experimental enthalpy of formation of gaseous MgO given in thermochemical databases. When the theoretical formation enthalpy for MgO calculated by a particular method is used, the deviation is reduced to 1.3 kcal mol^{-1}. The performance of the methodologies used to calculate the heat of this particular reaction and the enthalpy of formation of MgO are discussed.

I. INTRODUCTION

Carbon dioxide is an inert species due to the high C−O bond energy, 191.1 kcal mol^{-1}, which can be broken only under extreme conditions. On the other hand, when it is heated with metal atoms, carbon monoxide is produced. The reactions of the main group metal atoms with small molecules are of particular interest because of their relevance in the crossover point between inorganic and organic chemistry as well as in atmospheric and environmental chemistry.

The CO_2 + Mg reaction has already been studied. Laser-assisted experiments have shown that ground-state MgO-$(X^1\Sigma^+)$ is formed mainly from Mg(^{1}P),[1] whereas the excited-state MgO(B$^1\Sigma^+$) is produced from the Mg(^{1}S) state.[2] Theoretically, kinetic isotope effects have been interpreted in detail on the basis of conventional transition state theory according to the Bigeleisen formalism, and a transition state structure for the isotope-fractionation governing step of the reaction mechanism has been proposed.[3] Jeung[4] has studied the singlet and triplet reaction potential surface of Mg−CO_2 with CI calculations considering the neutral and ionic components and clearly showed that collision between linear CO_2 and Mg leads to a purely repulsive interaction and that only a bent CO_2 molecule can lead to bound interaction potential. Quite recently, the ab initio calculation of reaction pathways has been reported.[5] The structures of intermediates and transition states have been provided at the MP2 level with a double-ζ basis set including polarization and diffusion functions. The relative energies have been calculated at the QCISD(T)/6-311+G(3df)//MP2/6-31+G(d) level.

High level ab initio methods allow most thermodynamic properties to be predicted with high accuracy. In recent years,

two families of model chemistries have been developed with the goal of calculating molecular energies leading to chemical accuracy. The formalism common to all these models is designed to overcome uncertainties in electron energy calculations arising from the influence of basis set size and electron correlation. Both the Gaussian-n (Gn) series models and the complete basis set (CBS) methods are a composite procedure on a sequence of well-defined ab initio calculations. The total energy is obtained by combining the results of different level calculations. The methods differ in the choice of geometry, zero-point vibrational energy (ZPE), high level electron correlation treatment, and basis set size. Importantly, the declared accuracy for a particular method is related to the calculations of enthalpy of formation, ionization energies, and electron or proton affinities, but there is no agreed conclusion concerning the accuracy for calculating the reaction energetics.

In this work, we present a systematic study employing several composite ab initio methods for determining the enthalpy of the ground-state reaction

$$Mg(^1S) + CO_2(X^1\Sigma_g^+) \rightarrow MgO(X^1\Sigma^+) + CO(X^1\Sigma^+)$$
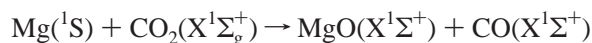
and the formation enthalpy, $\Delta_f H_{298}$, of ground state MgO. In the next section, the computational methods used in the present study are briefly reviewed. The following section contains our results and discussion. A summary is given in the final section.

II. COMPUTATIONAL METHODS

Particular compound methods for calculating accurate energies have been discussed in detail in the original references cited, so only a brief summary of the steps will be given. The G1,[6,7] G2,[8] and G3[9] models use structure optimized at the MP2(full)/6-31G(d) level and the HF/6-31G(d) scaled ZPE. G1 theory involves approximating the

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Table 1. Total Energies[a] (hartree) for Reactants (CO_2, Mg) and Products (CO and MgO) and Atomic Oxygen

method	E_{CO_2}	E_{Mg}	E_{CO}	E_{MgO}	E_O
G1(0 K)	−188.361076	−199.646132	−113.177224	−274.726373	−74.982049
G1	−188.357508	−199.643772	−113.173919	−274.722950	−74.979688
G2(0 K)	−188.361320	−199.645150	−113.177497	−274.721518	−74.982030
G2	−188.357752	−199.642790	−113.174192	−274.718095	−74.979669
G2(MP2)(0 K)	−188.356616	−199.646202	−113.175409	−274.726937	−74.978678
G2(MP2)	−188.353048	−199.643842	−113.172104	−274.723514	−74.976317
G3(0 K)	−188.500298	−199.907424	−113.267368	−275.030099	−75.030991
G3	−188.496730	−199.905064	−113.264063	−275.026676	−75.028630
G3(MP2)(0 K)	−188.378833	−199.650845	−113.188874	−274.739530	−74.989774
G3(MP2)	−188.375265	−199.648484	−113.185569	−274.736107	−74.987414
G3//B3LYP(0 K)	−188.504351	−199.907991	−113.269569	−275.032279	−75.032293
G3//B3LYP	−188.500731	−199.905631	−113.266664	−275.028894	−75.029932
G3(MP2)//B3LYP(0 K)	−188.385798	−199.651688	−113.193288	−274.742909	−74.992064
G3(MP2)//B3LYP	−188.382178	−199.649327	−113.189983	−274.739523	−74.989704
CBS-Q(0 K)	−188.371220	−199.642906	−113.181485	−274.729045	−74.987067
CBS-Q	−188.367673	−199.640545	−113.178180	−274.725623	−74.984707
CBS-Q//B3LYP(0 K)	−188.372013	−199.642990	−113.181966	−274.728382	−74.987627
CBS-Q//B3LYP	−188.368440	−199.640630	−113.178661	−274.725005	−74.985267

[a] (0 K) = sum of electronic and ZPE energies. The ab initio computed energies are at 298 K and 1 atm.

QCISD(T)/6-311+(2df,p) energy using the MP4 and QCISD-(T) energies calculated with the 6-311G(d,p) basis set and the MP4 energies calculated with the 6-311+G(d,p) and 6−311(2df,2p) basis sets. The remaining deficiencies in the basis set are included by an empirically estimated term, which depends on the number of paired as well as unpaired electrons. The G2 model approximates the QCISD(T)/6-311+(3df,2p) calculations by combining the MP4 and MP2 energies calculated with the 6-311G(d,p), 6-311+G(d,p), and 6-311G(2df,p) basis sets and MP2/6-311+G(3df,2p) and QCISD(T)/6-311G(d,p) energies. A higher level correction, based on the number of pairs of valence electrons, is used to account for residual basis set errors. G3 theory achieves significantly improved accuracy and requires less computational time relative to G2 theory. The MP4 and QCISD(T) single point calculations in G3 theory are based on the 6-31G(d) basis set, instead of the 6-311G(d,p) basis set as in G2 theory. The MP2 single point calculations use the G3 large basis set, which is a modification of the 6-311+G-(3df,2p) basis set used in G2 theory. A spin−orbit correction is added to the energies of atomic species and a correction for core correlation is added. The higher level correction for molecules and for atoms is separated. G2(MP2)[10] and G3-(MP2)[11] methods are modifications of G2 and G3, respectively, which use MP2 basis set extensions at the second-order Møller−Plesset level, thus eliminating the MP4 calculations. In the G3//B3LYP[12] variant of G3 and the G3-(MP2)//B3LYP[12] variant of G3(MP2) methods, the B3LYP/6-31G(d) geometry and the scaled ZPE value replaced the MP2(full)/6-31G(d) geometry and the HF/6-31G(d) scaled ZPE. The CBS-Q model[13] uses geometry derived from the second-order Møller−Plesset (MP2/6-31G(d)) theory[14] and the zero-point energy computed by the Hartree−Fock (HF/6-31G(d)) theory.[14] The MP2 calculation with larger basis set and a CBS extrapolation ensure the energy corrections through second-order, and the two additional calculations at the QCISD(T)/6-31+G(d) and the MP4(SDQ)/6-31+G(d,p) levels are used to approximate higher orders of contributions. There is an empirical correction for spin contamination as well as a size-consistent higher-order correction. The CBS-QB3[15] method is a modified CBS-Q model which uses B3LYP hybrid density functional geometries and frequencies.

Table 2. Calculated Reaction Enthalpies for $CO_{2(g)} + Mg_{(g)} \rightarrow CO_{(g)} + MgO_{(g)}$ at 0 K, ΔH_0, and 298 K, ΔH_{298} and Their Deviations from the Experimental Value, Dev (kcal mol^{-1})

method	ΔH_0	ΔH_{298}	dev$_{298}$[a]	ΔH_{298}^{expI} [b]	devI_{298}[c]
G1	65.02	65.52	−1.85	64.75	0.77
G2	67.43	67.93	0.56	67.17	0.76
G2(MP2)	63.05	63.55	−3.82	62.32	1.22
G3	69.18	69.69	2.32	68.83	0.85
G3(MP2)	63.55	64.05	−3.32	64.30	−0.25
G3//B3LYP	69.08	69.53	2.16	68.65	0.91
G3(MP2)//B3LYP	63.56	64.00	−3.36	64.12	−0.12
CBS-Q	65.01	65.52	−1.85	64.20	1.32
CBS-Q//B3LYP	65.67	66.14	−1.23	64.99	1.15

[a] dev$_{298}$ = ΔH_{298} − ΔH_{298}^{exp}, where ΔH_{298}^{exp} = 67.37 (see Table 3.). [b] ΔH_{298}^{expI} calculated by using experimental enthalpies of formation at 298 K for CO_2, CO, and Mg from JANAF Tables (see Table 3.) and the theoretical formation enthalpy for MgO as provided by particular theoretical methods (see Table 4.). [c] devI_{298} = ΔH_{298} − ΔH_{298}^{expI}.

All calculations in this paper were performed with the GAUSSIAN 98 program.[16]

III. RESULTS AND DISCUSSION

Reaction Enthalpies. The total energies of reactants and products presented in Table 1 have been calculated using seven Gaussian-n ab initio approaches, G1, G2, G2(MP2), G3, G3(MP2), G3//B3LYP, and G3(MP2)//B3LYP, as well as two complete basis set approaches, CBS-Q and CBS-Q//B3LYP. The reaction enthalpies, ΔH_0 and ΔH_{298}, calculated as the difference in total energies between the products and the reactants at 0 and 298 K, respectively, are given in Table 2. All the model chemistries employed predict highly endothermic reactions, 63.1−69.2 and 63.6−69.7 kcal mol^{-1} for ΔH_0 and ΔH_{298}, respectively. The highest value is provided by the G3 and G3//B3LYP methods, while the G2 result is about 2 kcal mol^{-1} lower. Next is the CBS-Q/B3LYP method with 66.1 kcal mol^{-1}, while the CBS-Q is equivalent to G1 with 65.5 kcal mol^{-1}. Also, G3(MP2) and G3(MP2)//B3LYP produce nearly the same value, which is about 1.5 kcal mol^{-1} lower compared to the later. The G2(MP2) reaction enthalpy is the lowest one.

An experimental enthalpy of reaction was derived from the recommended experimental standard enthalpies of forma-

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Table 3. Summary of Experimental Formation Enthalpies, $\Delta_f H$, at 0 and 298 K for Reactants (CO_2, Mg), Products (CO and MgO), and Atomic Oxygen, with Evaluated Reaction Enthalpies, ΔH^{exp} (kcal mol^{-1})

| | JANAF^a | | | others | |
species	0 K	298 K	I-TERMO^b 298 K	0 K	298 K
CO_2(g)	−93.965	−94.054	−94.051		
CO(g)	−27.200	−26.417	−26.417		
Mg(g)	34.871	35.158	35.158		
MgO(g)	14.003	13.900	7.712	36 ± 5^c	34.9 ± 5^d
O(g)	58.984	59.554	59.555		
ΔH^{exp}		46.38	40.19		67.37

^{a} Reference 17. ^{b} Reference 18. ^{c} Reference 20. ^{d} Reference 19.
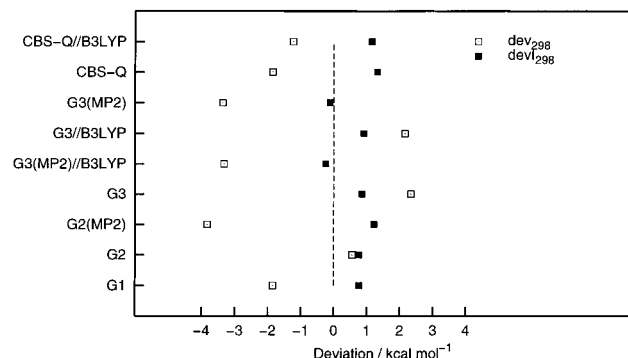
Figure 1. Deviations of reaction enthalpies for $CO_{2(g)}$ + $Mg_{(g)}$ → $CO_{(g)}$ + $MgO_{(g)}$ calculated using selected theories from experiment.

tion for products and reactants. Table 3 summarizes the experimental enthalpies of formation from different sources for reactants and products at 0 and 298 K, and the evaluated experimental enthalpies of reaction are included. It is evident that the reaction enthalpies based on values from the JANAF Thermochemical Tables cited on the NIST Webbook page[17] and from the IVTANTERMO Database[18] are on the average 20 and 26 kcal mol^{-1}, respectively, lower than the results from theoretical calculations. But the calculated reaction enthalpies are close to $\Delta H^{exp}_{298} = 67.4$ kcal mol^{-1}, which is obtained using $\Delta_f H_{298} = 34.9$ kcal mol^{-1}[19] for MgO. The formation enthalpy of MgO will be discussed further below. The deviation between the calculated and experimental reaction enthalpies at 298 K, dev$_{298}$, are included in Table 2 and are illustrated in Figure 1 by open squares. The G2 reaction enthalpy approaches the experimental value quite closely, being only 0.6 kcal mol^{-1} higher. Next is CBS-Q// B3LYP, being 1.3 kcal mol^{-1} lower than the experimental value. The G3 and G3//B3LYP methods overestimate, while the G1 and CBS-Q methods underestimate the experimental one by about 2 kcal mol^{-1}. The underestimation of the G3-(MP2)//B3LYP and G3(MP2) results increases to 3.3 kcal mol^{-1}, while that of G2(MP2) approaches 3.8 kcal mol^{-1}.

Comparing the G3, G3(MP2), and CBS-Q with the G3// B3LYP, G3(MP2)//B3LYP, and CBS-Q//B3LYP calculations, one can observe a negligible influence on reaction enthalpy of substituting the levels of calculated geometry used in subsequent single point calculations. On the other hand, replacing the basis set extensions at the MP4 level in the G2, G3, and G3//B3LYP methods with that of at the MP2 level in the G2(MP2), G3(MP2), and G3(MP2)//B3LYP methods results in a decrease of reaction enthalpy by 4.4, 5.6, and 5.5 kcal mol^{-1}, respectively. The significant discrepancy between the Gn and the simpler Gn(MP2)

Table 4. Calculated Formation Enthalpy for Gaseous MgO, $\Delta_f H$ at 0 and 298 K, and Deviations from the Experimental Value, Dev (kcal mol^{-1})

method	$-\Delta_{at}H_0{}^a$	$-\Delta_{at}H_{298}$	$\Delta_f H_0{}^b$	$\Delta_f H_{298}$	dev^c	CPU ratio^d
G1	−61.62	−62.43	32.24	32.29	−2.60	1.0
G2	−59.20	−60.01	34.66	34.71	−0.18	1.6
G2(MP2)	−64.04	−64.85	29.82	29.86	−5.02	1.2
G3	−57.53	−58.35	36.33	36.37	1.48	2.4
G3(MP2)	−62.07	−62.88	31.79	31.84	−3.05	1.4
G3//B3LYP	−57.73	−58.56	36.13	36.15	1.26	2.3
G3(MP2)//B3LYP	−62.22	−63.06	31.64	31.66	−3.23	1.3
CBS-Q	−62.17	−62.98	31.69	31.74	−3.15	1.6
CBS-Q/B3LYP	−61.35	−62.19	32.51	32.53	−2.36	1.5

^{a} Atomization reaction: MgO(g) → Mg(g) + O(g), $-\Delta_{at}H =$ E(MgO) − E(Mg) − E(O) (For total energies see Table 1.). ^{b} $\Delta_f H =$ $-\Delta_{at}H + \Delta_f H^{exp}(Mg_{(g)}) + \Delta_f H^{exp}(O_{(g)})$, experimental enthalpies of formation for $Mg_{(g)}$ and $O_{(g)}$ from JANAF Tables (See Table 3.). ^{c} dev $= \Delta_f H_{298} - \Delta_f H^{exp}_{298}$, where $\Delta_f H^{exp}_{298} = 34.9$ (See Table 3.). ^{d} The CPU timing ratios are presented in the last column.

enthalpies of reaction suggests a need for caution in replacing the MP4 corrections of Gn theories with the less expensive MP2 counterparts when energies of this type of reactions are calculated.

It could be concluded that, for the ground-state Mg + CO_2 reaction, the G2 method performs best from among all the methods applied in predicting the enthalpy of this reaction. Hwang et al.[5] reported a reaction endothermicity of 66.1 kcal mol^{-1} obtained at the QCISD(T)/6-311+G(3df)//MP2/6-31+G(d) level of calculation. Having in mind that the G2 theory, as a composite method, approximates the energy at the former level, it may be expected that these two methods will predict similar endothermicity. Actually, the value from the G2 theory is higher by 1.8 kcal mol^{-1} and is in good agreement with the reference experimental data evaluated above. Finally, the mean value of reaction enthalpy calculated with the nine composite methods is 66.2 ± 2.3 kcal mol^{-1}. This value is not significantly different from that of 66.1 kcal mol^{-1} obtained by Hwang et al.

Formation Enthalpy of MgO($X^1\Sigma^+$). Theoretical methods are becoming more and more efficient for estimating of thermochemical quantities and are very desirable in situations where the experimental results are either unavailable or suspicious. In the previous subsection it is clearly demonstrated that the formation enthalpy of gaseous MgO cited in the JANAF Thermochemical Tables and in the IVTANTERMO Database is incorrect. A more reliable experimental value is $\Delta_f H = 36 \pm 5$ kcal mol^{-1}, derived from a charge-transfer reaction with Fourier transform mass spectrometry.[20] Schultz et al.[19] have modified the latter value to $\Delta_f H_{298} = 34.9 \pm 5$ kcal mol^{-1}.

In this study we applied nine composite models for the calculation of formation enthalpy of gaseous MgO. Of the two principal approaches available for predicting heats of formation, we have used the one based on the atomization reaction.[21] Total energies of MgO, Mg, and O, calculated for various composite ab initio methods, are given in Table 1. Table 4 presents calculated enthalpies of formation at 0 and 298 K. $\Delta_f H_0$ and $\Delta_f H_{298}$ vary within 29.8−36.3 and 29.9−36.4 kcal mol^{-1}, respectively. The ordering of the methods used in predicting the formation enthalpy is as follows: G2(MP2) > G3(MP2)//B3LYP > CBS-Q > G3-
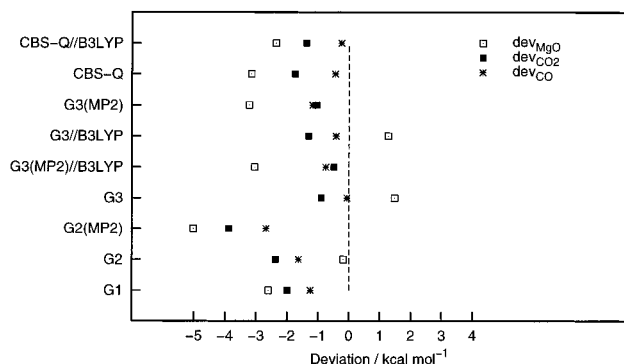
Figure 2. Deviations of formation enthalpies for MgO calculated using selected theories from experiment; those for CO_2 and CO are included for comparison.

(MP2) > G1 > CBS-Q//B3LYP > G2 > G3//B3LYP > G3. The deviations between calculated formation enthalpies and formation enthalpy derived from experimental data of 34.9 kcal mol^{-1} [19] (later denoted as experimental value) are included in Table 4 and illustrated in Figure 2 by open squares. The formation enthalpy provided by the G2 method is in excellent agreement with this experimental value, being only 0.2 kcal mol^{-1} lower. Higher values result from the G3 method and its variant G3//B3LYP, the deviation amounting to about 1.6 kcal mol^{-1}. The underestimation of the G1, G3(MP2), G3(MP2)//B3LYP, CBS-Q, and CBS-Q//B3LYP methods is, on the average, 2.9 kcal mol^{-1}. The mean value of the formation enthalpy calculated by the nine composite methods is 33.0 ± 2.2 kcal mol^{-1}. Considering the performance of particular composite methods for predicting the gas-phase MgO formation enthalpy, similar conclusions can be drawn as those in the previous subsection for the case of reaction enthalpy.

To illustrate the performance of selected methods in predicting formation enthalpies, we include in Figure 2 the deviations of calculated and experimental values for CO_2 and for CO. Here, the JANAF experimental values of both molecules quoted in Table 3 were used. One can see that the discrepancy between the Gn and Gn(MP2) formation enthalpies is more pronounced for MgO than that of CO_2 and CO.

Finally, we evaluated the enthalpy of reaction using experimental standard enthalpies of formation for CO_2, CO, and Mg from the JANAF Tables and the theoretical formation enthalpy for MgO provided by the particular theoretical methods. These enthalpies, referred to as ΔH_{298}^{expI}, are included in Table 2 as well as their deviations, devI_{298}, from the theoretical enthalpies of reaction. The deviations are presented in Figure 1. The maximum absolute deviation is 1.3 kcal mol^{-1}, which is significantly lower than that of 3.8 kcal mol^{-1} obtained for the deviation where the experimental enthalpy of formation for MgO was used.

IV. SUMMARY

In the course of this study we have assessed the performance of a series of theoretical models for calculating of heats of the gas-phase CO2 + Mg reaction, the energy differences being computed using nine highly accurate ab initio correlation calculations. The calculated reaction energies decrease in the following order: G2(MP2) > G3(MP2)// B3LYP > G3(MP2) > CBS-Q > G1 > CBS-Q//B3LYP >

G2 > G3//B3LYP > G3. ΔH_{298} computed with G2 is 67.9 kcal mol^{-1}, which in good agreement with the experimental value of 67.4 kcal mol^{-1}, which is obtained with $\Delta_f H_{298} = 34.9$ kcal mol^{-1} [19] It should be stressed that the experimental reaction enthalpy derived from standard enthalpy of formation given in the thermochemical database is more than 20 kcal mol^{-1} too low. Further, all nine composite models were applied in calculating the formation enthalpies of gaseous MgO. The G2 method, which predicts $\Delta_f H_{298} = 34.7$ kcal mol^{-1} with a deviation of 0.2 kcal mol^{-1}, again most closely approaches the experimental value.

Of the methods examined, we recommend G2 as a practical means of obtaining a reliable reaction enthalpy as well as the formation enthalpy of gaseous MgO. Replacing the basis set extensions at the MP4 level in the Gn methods with those at the MP2 level in the Gn(MP2) methods results in a significant decrease of reaction enthalpy and formation enthalpy of MgO. The present systematic study of reaction enthalpy and MgO formation enthalpy together with some recent theoretical work on the reaction mechanism[5] and MgO dissociation energy[22,23] strongly suggests the new experimental determinations of thermochemical properties for gaseous MgO.

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