J. Phys. Chem. A **2001,** 105, 10433−10438

Conversion of CO to Formaldehyde Catalyzed by BeO: A Theoretical Study

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Received: June 12, 2001; In Final Form: August 21, 2001

Ab initio calculations at the G2M(MP2)//MP2/6-31G** level have been performed to investigate the potential energy surface for various reaction mechanisms in the BeO/CO/H_2 system. The results show that the conversion of carbon monoxide to formaldehyde can be catalyzed by beryllium oxide in the gas phase. Two different reaction mechanisms have been suggested. In the first one, BeO + CO + H_2 → OBeOC + H_2 → $OBeOCH_2$ → BeO + H_2CO, BeO first reacts with CO to form the OBeOC complex (bound by 20.2 kcal/mol), which interacts with H_2 to give the complex between BeO and H_2CO via a barrier of 53.1 kcal/mol relative to the initial reactants, and $OBeOCH_2$ decomposes to BeO + formaldehyde without an exit barrier but with endothermicity of 44.9 kcal/mol. In the second mechanism, BeO + H_2 + CO → HBeOH + CO → *t*-HCOBeOH → $OBeOCH_2$ → BeO + H_2CO, the initial step is the reaction of BeO with molecular hydrogen exothermic by 88.3 kcal/mol. Then, CO inserts into the Be−H bond of HBeOH to form the HCOBeOH intermediate, 80.2 kcal/mol below the reactants, which undergoes a 1,3-hydrogen shift from carbon to oxygen yielding the $OBeOCH_2$ complex and the latter decomposes to the final products. On this pathway, the highest barrier is found for the *t*-HCOBeOH → $OBeOCH_2$ hydrogen shift step with a transition state lying only 5.4 kcal/mol above BeO + H_2 + CO, thus making the gas-phase reaction possible even at low temperatures. The reverse reaction of the H_2CO decomposition to H_2 + CO can be also catalyzed by BeO in the gas phase, since the barrier decreases from ~80 kcal/mol for the unimolecular dissociation to only 2.0 kcal/mol for the reaction in the presence of BeO.

Introduction

The utilization of methane, one of the world's abundant resources, to produce basic chemicals is one of the desirable goals of the current chemical industry. The conversion of methane to useful chemicals has attracted attention in recent years. Although the direct conversion of methane to valuable chemicals such as ethylene, methanol, and formaldehyde is a most fascinating route, no viable process or catalyst has yet been developed,[1] and indirect transformation of methane via synthesis gas is still the most competitive process.[2]

$$CH_4 + {}^1/_2O_2 \rightarrow CO + 2H_2$$

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

$$CO + H_2 \rightarrow H_2CO$$

$$CO + 2H_2 \rightarrow CH_3OH$$

Metals and their compounds can catalyze many important chemical reactions, either homogeneously or heterogeneously. The coordination of the carbon dioxide to the metal center has been considered a key step to reduce this molecule to useful organic substances.[3−5] Carbon monoxide also exhibits a rich chemistry with metal oxides. For example, adsorption of CO onto thermally activated CaO or MgO leads to the formation of various anionic $(CO)_x$ species[6] and is therefore related to the catalytic properties of metal oxides and to oxidizing CO on surfaces and solution. Experimental studies of Andrews and coworkers[7] have shown that pulsed-laser-evaporated Be atoms react with CO_2 during condensation in excess argon to form CO, ArBeO, BeOBe, OC−BeO, and CO−BeO. Our ab initio calculations[8] of the potential energy surface (PES) for Be + CO_2 → BeO + CO revealed the reaction mechanism and showed that the reaction proceeds by formation of the cyclic BeOCO intermediate, which can isomerize to the linear OBeOC complex, and the latter decomposes to BeO + CO without an exit barrier. Beryllium oxide is a strong Lewis acid and is capable of forming stable donor−acceptor complexes with very poor Lewis bases, such as He, Ar, N_2, and CO,[7,9−11]as well as formaldehyde.[12] The unusually strong acceptor ability of BeO was attributed to its strong dipole moment in combination with a large positive partial charge at Be and a rather low-lying empty orbital.[9] The reactions of BeO with carbon monoxide to produce the OBeOC and OBeCO complexes are exothermic by 21.6 and 36.9 kcal/mol, respectively, and occur without a barrier.[8]

On the other hand, BeO can readily react with molecular hydrogen. According to our ab initio calculations,[13] the BeO + H_2 reaction proceeds by barrier-less formation of the $OBeH_2$ molecular complex bound by 15.6 kcal/mol with respect to the reactants. Then, the complex rearranges to HBeOH with a low barrier of 3.7 kcal/mol and the corresponding transition state lies lower in energy than the reactants. The BeO + H_2 → HBeOH reaction was calculated to be highly exothermic.

Since beryllium oxide easily reacts both with CO and H_2 and can form a strongly bound complex with formaldehyde, a reasonable question to ask is whether BeO can assist the

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10.1021/jp0122171 CCC: \$20.00

TABLE 1: Total Energies E_{tot} (hartree), ZPE (kcal/mol), and ZPE-Corrected Relative Energies E_{rel} of Various Species in the $CO/H_2/BeO$ System Calculated at the MP2/6-31G, MP2/6-311G**, CCSD(T)/6-311G**, MP2/6-311+G(3df,2p), and G2M(MP2) Levels of Theory with MP2/6-31G** Optimized Geometries**

	MP2/6-31G**			MP2/6-311G**		CCSD(T)/6-311G**		MP2/6-311+G(3df,2p)		G2M(MP2)
species	E_{tot}	ZPE	E_{rel}	E_{tot}	E_{rel}	E_{tot}	E_{rel}	E_{tot}	E_{rel}	E_{rel}
					CO/H_2					
CO	−113.02122	3.01		−113.07443		−113.09253		−113.13623		
H_2	−1.15766	6.59		−1.16026		−1.16828		−1.16276		
$CO + H_2$	−114.17888	9.60	0	−114.23469	0	−114.26081	0	−114.29899	0	0
TS1	−114.03259	11.99	94.10	−114.09140	92.22	−114.12177	89.55	−114.16216	88.17	85.50
H_2CO	−114.18350	17.19	4.43	−114.23501	7.13	−114.26033	7.63	−114.30616	2.83	3.34
					$CO/H_2/BeO$					
BeO	−89.64760	1.99		−89.68845		−89.69332		−89.74312		
$BeO + CO + H_2$	−203.82648	11.59	0	−203.92314	0	−203.95413	0	−204.04211	0	0
OBeOC	−202.70221	6.75		−202.79508		−202.82232		−202.90991		
$OBeOC + H_2$	−203.85987	13.34	−19.26	−203.95534	−18.51	−203.99060	−21.19	−204.07267	−17.48	−20.16
TS2	−203.73385	16.33	62.71	−203.83365	60.74	−203.87229	55.94	−203.95714	57.9	53.10
$OBeOCH_2$	−203.90644	22.25	−39.87	−204.00028	−38.10	−204.03264	−38.96	−204.12345	−40.74	−41.60
$BeO + H_2CO$	−203.83110	19.18	4.43	−203.92346	7.13	−203.95365	7.63	−204.04928	2.83	3.34
HBeOH	−90.94366	12.94		−90.99122		−91.00926		−91.04809		
HBeOH + CO	−203.96488	15.95	−82.63	−204.06565	−85.21	−204.10179	−88.44	−204.18432	−85.02	−88.25
TS3	−203.92667	17.99	−56.69	−204.02536	−57.96	−204.06078	−60.74	−204.14924	−61.04	−63.82
t-HCOBeOH	−203.95869	20.25	−74.59	−204.05439	−73.99	−204.08859	−76.01	−204.18011	−78.23	−80.24
c-HCOBeOH	−203.96628	21.18	−78.45	−204.06183	−77.76	−204.09604	−79.78	−204.18590	−80.96	−82.98
TS4	−203.82732	18.77	6.42	−203.91950	9.23	−203.94968	9.74	−204.04543	4.86	5.37

conversion of CO to H_2CO, i.e., catalyze the $CO + H_2 \rightarrow H_2CO$ reaction. This reaction itself is known to have a very high barrier both from experimental[14] and theoretical[15−21] investigations. The goal of the present study is to calculate PES for various reaction pathways and elucidate mechanisms of the $CO + H_2 + BeO \rightarrow H_2CO + BeO$ reaction and to compare them with that for the $H_2 + CO \rightarrow H_2CO$ reaction without a catalyst. We will discuss their differences in energy barriers and heats of reaction. The results of ab initio calculations reported in this paper also include reliable structures of the reactants, products, intermediates, and transition states as well as their accurate energies. The reasons for significant enhancement of the reduction of CO with H_2 to formaldehyde in the presence of BeO and HBeOH will be demonstrated.

Computational Details

Full geometry optimizations were run at the MP2/6-31G** level of theory[22] to locate various stationary points (reactants, intermediates, transition states, and products) on the ground singlet electronic state PES of the $CO/H_2/BeO$ system. Harmonic vibrational frequencies were obtained at the MP2/6-31G** level in order to characterize the stationary points as minima (number of imaginary frequencies NIMAG = 0) or first-order saddle points (NIMAG = 1), to obtain zero-point vibrational energy corrections (ZPE) and to generate force constants needed for intrinsic reaction coordinate (IRC)[23] calculations. To predict more reliable ZPE, the raw calculated ZPE values were scaled by 0.967 to account for their average overestimation.[24] The IRC method[23] was used to track minimum energy paths from transition structures to the corresponding minimum. A step size of 0.1 amu$^{1/2}$ bohr or larger was used in the IRC procedure. The relative energies were refined using single-point calculations with MP2/6-31G** optimized geometry employing the G2M(MP2) method,[25] a modification of G2(MP2)[26] where QCISD(T)/6-311G** calculations are replaced by the coupled cluster[27] CCSD(T)/6-311G**. All the ab initio calculations described here were performed employing the Gaussian 98 program.[28]

Results and Discussion

Total energies, ZPE, and ZPE-corrected relative energies of various species in the $CO/H_2/BeO$ system calculated at the MP2/6-31G**, MP2/6-311G**, CCSD(T)/6-311G**, MP2/6-311+G(3df,2p), and G2M(MP2) levels of theory are listed in Table 1. Table 2 presents unscaled MP2/6-31G** calculated vibrational frequencies. The energy diagram along various reaction pathways computed at the G2M(MP2) level is shown in Figure 1. The optimized geometries of various compounds along the predicted reaction pathways are depicted in Figure 2.

TABLE 2: Vibrational Frequencies (cm^{-1}) of Various Species in the $CO/H_2/BeO$ System Calculated at the MP2/6-31G Level**

species	frequencies
TS1	2042i, 840, 930, 1443, 1869, 3304
TS2	1978i, 111, 194, 315, 403, 444, 900, 939, 1548, 1629, 1826, 3113
$OBeOCH_2$	105, 227, 387, 471, 507, 1245, 1304, 1538, 1581, 1754, 3154, 3291
TS3	636i, 179, 238, 412, 474, 556, 607, 1074, 1392, 1653, 1991, 4006
t-HCOBeOH	80, 95, 264, 286, 430, 657, 835, 1414, 1460, 1618, 2932, 4094
c-HCOBeOH	267, 280, 344, 451, 626, 675, 822, 1312, 1424, 1501, 3113, 4002
TS4	672i, 123, 171, 386, 683, 953, 1165, 1385, 1426, 1644, 2146, 3049

$CO + H_2 \rightarrow H_2CO$ Reaction without a Catalyst. To assess the accuracy of our theoretical methods we first consider PES of the $CO + H_2 \rightarrow H_2CO$ reaction. The reaction of carbon monoxide with molecular hydrogen as well the reverse unimolecular decomposition of formaldehyde have been studied carefully both experimentally and theoretically.[14−21] The formation of H_2CO from CO and H_2 is slightly endothermic, by 2.3 kcal/mol.[29] The experimental barrier height for the unimolecular decomposition is 79.2 ± 0.8 kcal/mol,[14] so the barrier for the $CO + H_2$ reaction should be 81.5 ± 0.8 kcal/mol. The results of high level ab initio calculations quite well agree with these values. For instance, the QCISD(T)/6-311++G(3df,3pd)//QCISD/6-311++(2df,2pd) computation of Yu and Yu[18] gave 2.35 and 80.97 kcal/mol for the reaction heat and the barrier for unimolecular decomposition of formaldehyde, respectively. MRMP calculations of Nakano et al.[19] and MCSCF calculations by de A. Martins et al.[20] also resulted in similar values for the reaction barrier, 79.1 and 83.2 kcal/mol, respectively. The most

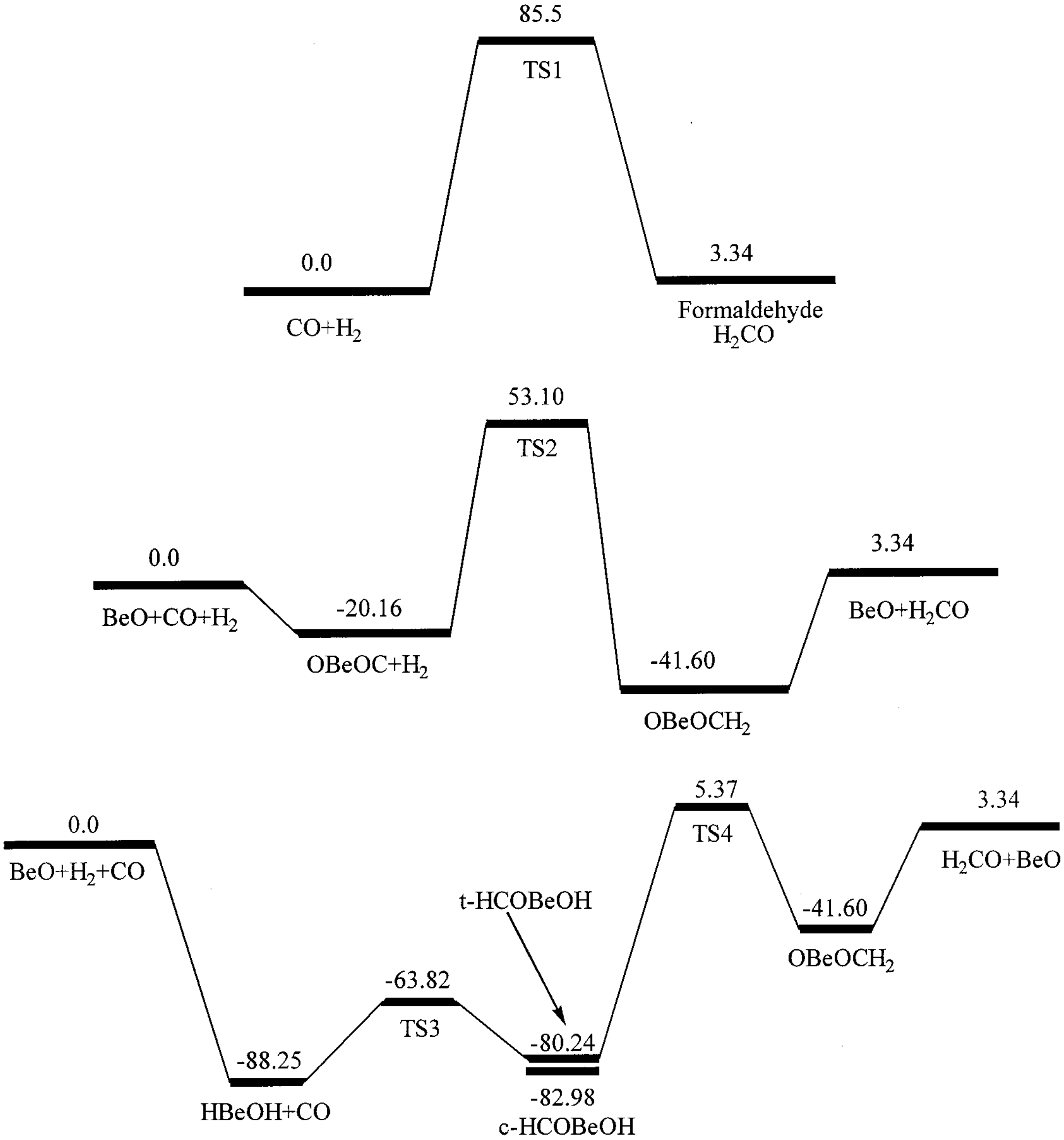

Figure 1. Potential energy diagram of various reactions in the CO/H_2/BeO system calculated at the G2M(MP2)//MP2/6-31G** level of theory. (All relative energies are given in kcal/mol.)

accurate up-to-date CCSDT and MRCI calculations with extrapolation to the complete basis set limit[21] predicted the H_2CO decomposition barrier as 81.9 ± 0.3 kcal/mol.

The present G2M(MP2)//MP2/6-31G** calculations give 3.3 kcal/mol for the heat of the $CO + H_2 \rightarrow H_2CO$ reaction and 85.5 and 82.2 kcal/mol, respectively, for the barriers in the forward and reverse directions, in satisfactory agreement with previous theoretical studies, and overestimate the experimental values by 1−3 kcal/mol. The MP2/6-31G** optimized geometry of TS1 (see Figure 1) also quite similar to those obtained by QCISD,[18] CCSD,[17] and MCSCF[20] calculations. Because of the very high barrier, carbon monoxide and molecular hydrogen do not react to produce formaldehyde at ambient temperatures.

Carbon Monoxide Addition to BeO Followed by the OBeOC + H_2 Reaction. As was demonstrated earlier,[8] beryllium oxides reacts with CO without a barrier to form linear OBeOC and OBeCO complexes with exothermicities of 21.6 and 36.9 kcal/mol, respectively, at the G2(MP2)//MP2/6-31G* level of theory. OBeCO is not expected to react with H_2 because the carbon atom is shielded by its donor−acceptor bond with Be. Hence, here we consider only the OBeOC + H_2 reaction. As seen in Figure 1 and Table 1, the G2M(MP2)//MP2/6-31G* energy of the OBeOC complex formation from BeO and CO is 20.2 kcal/mol, slightly lower than the G2(MP2) value. The subsequent step is H_2 addition to the terminal carbon of OBeOC (or insertion of the complex into the H−H bond), which proceeds via transition state TS2 to a planar OBe−OCH_2 intermediate. The BeOC angle in TS2 is bent to 119.64° and the H−H bond length is stretched to 1.109 Å. The G2M(MP2)//MP2/6-31G** calculated barrier is 73.3 kcal/mol and the exothermicity of the OBeOC + $H_2 \rightarrow$ OBe−OCH_2 reaction step is 21.4 kcal/mol. The transition state optimization was followed by frequency and IRC calculations at the MP2/6-31G** level of theory which confirmed that TS2 actually connects OBeOC + H_2 and the planar OBe−OCH_2 complex. The calculated barrier for the H_2 addition to OBeOC is 12.2 kcal/mol lower than the barrier for the H_2 addition to isolated carbon monoxide. Thus, the barrier is somewhat reduced due to complexation of CO to the strong Lewis acid BeO. This result can be attributed to the fact that beryllium oxide forms a donor−acceptor bond with CO and withdraws some amount of electron density from the latter thus decreasing the repulsion between closed electronic shells of CO and H_2 while they approach each other. Noteworthy, the transition state TS2 shows a significantly earlier

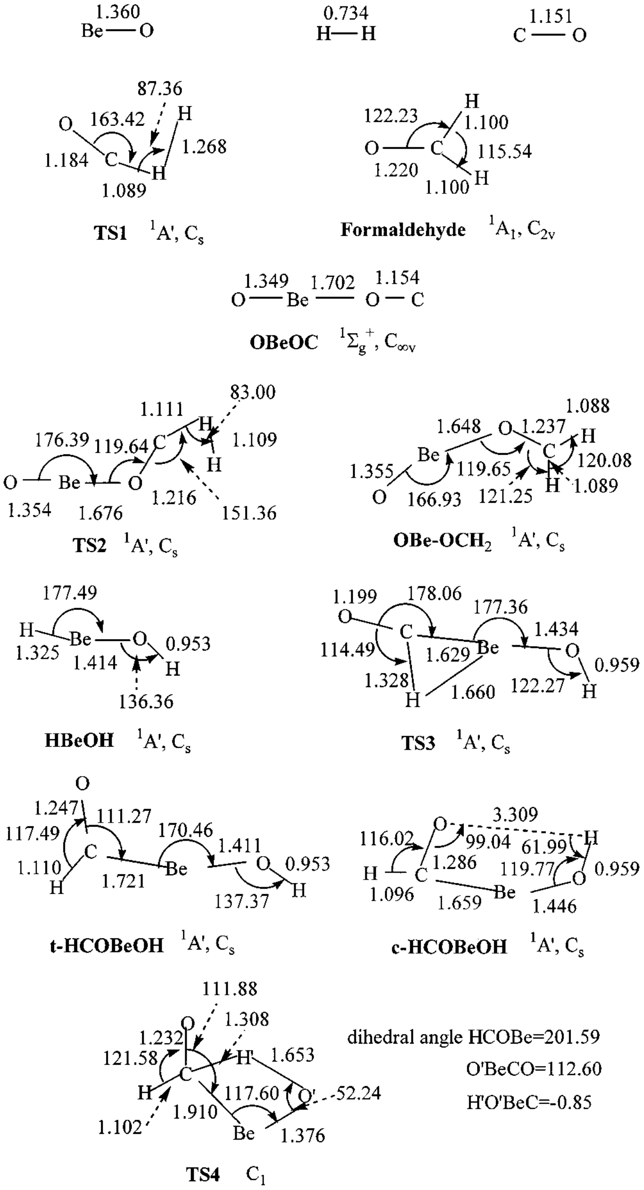

Figure 2. Geometries of the reactants, products, intermediates, and transition states of various reactions in the CO/H_2/BeO system optimized at the MP2/6-31G** level of theory. (Bond lengths are in Å and bond angles are in degrees).

character than TS1 as indicated by the length of the H−H bond (1.109 vs 1.268 Å), which is being broken during the reaction. This is in line with the fact that the OBeOC + H_2 → OBe−OCH_2 reaction is exothermic, while CO + H_2 → H_2CO is slightly endothermic.

At the G2M(MP2)//MP2/6-31G** level, the OBe−OCH_2 intermediate lies 41.6 kcal/mol lower in energy than the initial reactants, BeO + CO + H_2, and 44.9 kcal/mol below the products, H_2CO + BeO. Thus, formaldehyde and beryllium oxide can form a strong complex. A similar prediction was also made earlier by Frenking and co-workers[12] who calculated the complex formation energy as 44.2 kcal/mol at the MP4/6-311G-(2df,2pd)/ MP2/6-31G** level. The highest barrier on the Be + CO + H_2 → OBeOC + H_2 → OBe−OCH_2 → BeO + H_2CO reaction pathway occurs at TS2 and is 53.1 kcal/mol relative to the reactants. As compared to the CO + H_2 → H_2CO reaction barrier of 85.5 kcal/mol, the activation energy decreases due to two factors, the reduction of the barrier for H_2 addition to CO in the OBeOC complex (12.2 kcal/mol) and the complex formation energy (20.2 kcal/mol). Therefore, if molecular hydrogen reacts in the gas phase with chemically activated (energized) OBeOC intermediate produced from BeO and CO, the reaction barrier to form formaldehyde decreases by 32.4 kcal/mol. In this sense, beryllium oxide can catalyze the CO + H_2 → H_2CO reaction in the gas phase. Still, the effect of the BeO presence in this reaction mechanism should not be significant at ambient temperatures since the calculated barrier is as high as 53 kcal/mol.

Molecular Hydrogen Addition to BeO Followed by the HBeOH + CO Reaction. Now let us consider the second reaction pathway where beryllium oxide first reacts with H_2. As shown earlier,[13] the reaction proceeds by the formation of the $OBeH_2$ complex bound by 15.6 kcal/mol with respect to the reactants. The complex rearranges to the HBeOH intermediate via a 3.7 kcal/mol barrier with a transition state 11.9 kcal/mol lower in energy than BeO + H_2. In Figure 1, we do not show the details of the first reaction step and connect the reactants directly with the HBeOH intermediate, 88.3 kcal/mol below BeO + H_2 at the G2M(MP2)//MP2/6-31G** level. At the next step, CO reacts with HBeOH to insert into the Be−H bond. During this process the Be−H bond is broken and two new bonds, C−H and Be−C, are formed to produce a HCOBeOH intermediate via transition state TS3. In the transition state the Be−H bond is stretched by 25%, from 1.325 to 1.660 Å, as compared to HBeOH, while the forming C−H and Be−C bonds are, respectively, 20% longer and 5% shorter than the corresponding distances in HCOBeOH. In this view, TS3 is a rather late transition state, in accord with the fact that the HBeOH + CO → HCOBeOH reaction is 8 kcal/mol endothermic. The HCOBeOH molecule can have several conformers. According to our IRC calculations at the MP2/6-31G** level TS3 connects the reactants with the conformer where the C−O and O−H bonds of HCOBeOH are located in trans position with respect to each other and we designate this intermediate as *t*-HCOBeOH. The G2M(MP2)//MP2/6-31G** calculated barrier is 24.4 kcal/mol relative to HBeOH + CO and transition state TS3 lies 63.8 kcal/mol below the initial reactants, BeO + H_2 + CO. As compared to the CO + H_2 reaction, the barrier reduces by ~60 kcal/mol because the CO insertion into the strong H−H bond in molecular hydrogen (the bond strength is 103.3 kcal/mol[29]) is replaced by the insertion into a much weaker Be−H bond (the bond strength is 52.7 kcal/mol in BeH[29]). The *t*-HCOBeOH intermediate resides 80.2 kcal/mol lower in energy than BeO + H_2 + CO and is kinetically stabilized by a barrier of 16.4 kcal/mol with respect to the decomposition to HBeOH + CO. To our knowledge, no such molecule (much more thermodynamically stable isomer of the complex of BeO with formaldehyde, $OBeOCH_2$) was reported so far. Another conformer of this intermediate, *c*-HCOBeOH, has a cis arrangement of the C−O and O−H bonds and is calculated to be 2.7 kcal/mol more stable than *t*-HCOBeOH, apparently, due to a weak intramolecular hydrogen bond between terminal O and H atoms. The two conformers should be able to isomerize to each other by a rotation about the single Be−O with a low barrier. Since this rotation is expected to be facile and is not related to the reaction pathway we do not calculate its transition state here.

The next reaction step is a 1,3-hydrogen shift from the oxygen to carbon atom to produce the $OBeOCH_2$ complex between formaldehyde and BeO via transition state TS4. A new C−H bond (1.308 Å) is partially formed in TS4 and the C−Be (1.910 Å) and O−H (1.653 Å) bonds are nearly broken, while the Be−O distance (1.376 Å) approaches its value in $OBeOCH_2$. All this points to a late character of the transition state, in line with high endothermicity of the *t*-HCOBeOH → $OBeOCH_2$ reaction step, 38.6 kcal/mol. Meanwhile, a new Be−O bond between beryllium oxide and H_2CO barely starts to form in the transition state where the Be−O distance is 2.630 Å. According to IRC calculations at the MP2/6-31G** level, the minimal energy reaction path is rather asynchronous; at the initial stage the hydrogen shift takes place to give the BeO and H_2CO fragments, then, these fragments start to turn with respect to each other to eventually form the additional Be−O bond. At the 60th step the IRC calculations when they were terminated, the Be−O distance and BeCO angle are 2.070 Å and 66.6°, respectively. In the reverse direction, the IRC calculations confirmed that TS4 is connected to *t*-HCOBeOH. The G2M-(MP2)//MP2/6-31G** calculated barrier for the hydrogen shift via TS4 is 85.6 kcal/mol but the transition state lies only 5.4 kcal/mol above BeO + H_2 + CO. At the final step, the $OBeOCH_2$ complex dissociates to beryllium oxide and formaldehyde with the energy loss of 44.9 kcal/mol but without an exit barrier.

The largest barrier on the BeO + H_2 + CO → HBeOH + CO → *t*-HCOBeOH → $OBeOCH_2$ → BeO + H_2CO reaction pathway is calculated for the 1,3-H shift at TS4. This barrier, 85.6 kcal/mol relative *t*-HCOBeOH, is similar to the barrier of the CO + H_2 → H_2CO reaction. However, because the intermediate lies 80.2 kcal/mol below the initial reactants the barrier relative to BeO + H_2 + CO decreases to only 5.4 kcal/mol. In this view, BeO catalyzes the conversion of carbon monoxide to formaldehyde in the gas phase; if CO reacts, instead of H_2, with the energized HBeOH molecule produced in the BeO + H_2 reaction, the barrier to form H_2CO drops from 85.5 to merely 5.4 kcal/mol and the reaction should be fast even at low temperatures. Interestingly, the CO insertion in this reaction mechanism is not the rate-determining step because this insertion takes place into a weak Be−H bond and has a barrier of 24.4 kcal/mol. The reaction mechanism with initial addition of H_2 to BeO followed by the reaction with CO is clearly favorable as compared to the pathway where CO reacts with BeO first, since the highest barrier relative to BeO + CO + H_2 is 5.4 kcal/mol for the former vs 53.1 kcal/mol for the latter.

The reverse reaction, BeO + H_2CO, can be considered as decomposition of formaldehyde to CO + H_2 catalyzed with beryllium oxide. The unimolecular decomposition of H_2CO exhibits a high ∼79 kcal/mol barrier[14] and cannot occur at ambient temperatures. On the contrary, the reaction of H_2CO with BeO should be fast even at low temperatures, since the calculated barrier is as low as 2.0 kcal/mol. The reaction is expected to produce first the $OBeOCH_2$ complex which would then isomerize to HCOBeOH and dissociate to HBeOH + CO. The energized HBeOH primary product would preferably decompose to BeO + H_2 rather than to Be + H_2O since the barrier for the former channel was calculated[13] to be ∼11 kcal/mol lower than that for the latter. Thus, the overall reaction yields molecular hydrogen in addition to CO and the catalyst, BeO, is restored.

Catalytic Conversion of CO to Formaldehyde with Beryllium Oxide. Summarizing the reaction mechanisms described above, we can conclude that BeO can serve as a catalyst in the gas-phase both for the H_2 + CO reaction and the reverse decomposition of formaldehyde. The catalytic role of BeO is due to its ability to easily insert into the H−H bond of molecular hydrogen with highly exothermic formation of the HBeOH intermediate. The latter can react with carbon monoxide by CO insertion into a weak Be−H bond. Because of weakness of this bond, the insertion exhibits a relatively low barrier. The rate-determining reaction step is the H atom migration from O to C in HCOBeOH. The barrier for this step is high but due to exothermicity of the BeO + H_2 → HBeOH reaction, the transition state lies only a few kcal/mol above the reactants. Thus, the role of beryllium oxide in the catalytic conversion of CO to formaldehyde is 2-fold: supplying the system with internal energy through exothermic formation of HBeOH and substitution of the strong H−H bond by a weaker Be−H, which facilitates the insertion of carbon monoxide.

The reaction mechanism described here may be typical for the catalysis of the CO + H_2 → H_2CO reaction by other metal oxides. Many metal oxides and chalcogenides[30,31] including those of transition metals[32] can react with molecular hydrogen yielding HMXH. The insertion of CO into relatively weak M−H bonds may be feasible and the possibility to form formaldehyde with restoration of MX would depend on the energy balance between the exothermicity of the MX + H_2 → HMXH reactions and the barrier for the 1,3-H shift in the HCOMXH intermediates.

Meanwhile, the reaction scheme for the catalytic conversion of CO to formaldehyde with BeO has certain disadvantages. First, in the gas phase, the reaction mechanism requires collisions between three different molecules to occur in a certain order. For instance, BeO should first react with H_2 producing energized HBeOH molecules, which need to collide with CO before they are deactivated by collisions with other molecules or decompose. Second, the reaction is not feasible in solution because the barriers of some reaction steps calculated relative to the corresponding intermediates are still high and collisional deactivation of intermediates in solution is fast. Third, it might be possible for solid or powder BeO to catalyze the CO + H_2 → H_2CO reaction only if the energy release from the highly exothermic BeO + H_2 → HBeOH reaction would be sufficient not just to compensate the high barrier for thce *t*-HCOBeOH → $OBeOCH_2$ hydrogen shift step but also to separate BeO molecules from the lattice.

Conclusions

Ab initio calculations at the G2M(MP2)//MP2/6-31G** level of PES for the BeO/CO/H_2 system show that the conversion of carbon monoxide to formaldehyde can be catalyzed by beryllium oxide in the gas phase. The reaction can proceed by two different mechanisms. In the first one, BeO + CO + H_2 → OBeOC + H_2 → $OBeOCH_2$ → BeO + H_2CO, beryllium oxide first reacts with CO to form the OBeOC complex, which interacts with molecular hydrogen to give the complex between BeO and formaldehyde via a barrier of 53.1 kcal/mol relative to the initial reactants, and $OBeOCH_2$ decomposes to BeO + formaldehyde without an exit barrier. In the second mechanism, BeO + H_2 + CO → HBeOH + CO → *t*-HCOBeOH → $OBeOCH_2$ → BeO + H_2CO, the initial step is the reaction of BeO with molecular hydrogen. Then, CO inserts into the Be−H bond of HBeOH to form the HCOBeOH intermediate, which, in turn, undergoes a 1,3-hydrogen shift from carbon to oxygen yielding the $OBeOCH_2$ complex and the latter decomposes to the final products. On this pathway, the highest barrier is calculated for the *t*-HCOBeOH → $OBeOCH_2$ hydrogen shift step with the transition state TS4 lying only 5.4 kcal/mol above BeO + H_2 + CO thus making the gas-phase reaction possible even at low temperatures. On the other hand, the reverse reaction of the H_2CO decomposition to H_2 + CO can be also catalyzed by BeO in the gas phase, since the barrier decreases from ∼80 kcal/mol for the unimolecular dissociation to only 2.0 kcal/mol for the reaction involving BeO.

Acknowledgment. Funding from Tamkang University was used to buy the computer equipment used in part of this investigation. Partial support from Academia Sinica and from the National Science Council of Taiwan, R.O.C., is also appreciated.

Supporting Information Available: Supporting Information Available: Summary of reaction paths. This material is available free of charge via the Internet at http://pubs.acs,org.

References and Notes

(1) Wang, H. Y.; Ruckenstein, E. *J. Catal.* **1999**, *186*, 181.

(2) Fox, J. M. *Catal. Rev. Sci. Eng.* **1993**, *35*, 169.

(3) Tanabe, K. In *Catalysis, Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: New York, 1981.

(4) (a) Klabunde, K. J.; Kaba, R. A.; Morris, R. M. *Inorganic Compounds with Unusual Properties-II*; King, R. B., Ed.; American Chemical Society: Washington, DC, 1979; Adv. Chem. Ser. No. 173. (b) Studies in Surface Science and Catalysis 21. Adsorption and Catalysis on Oxide Surfaces; Che, M., Bond, G. C., Eds.; Elsevier: Amsterdam, 1985.

(5) (a) Hei, M. J.; Chen, H. B.; Yi, J.; Lin, Y. J.; Lin, Y. Z.; Wei, G.; Liao, D. W. *Surf. Sci.* **1998**, *417*, 82. (b) Tomishige, K.; Chen, Y. G.; Fujimoto, K. *J. Catal.* **1999**, *181*, 91. (c) Bradford, M. C. J.; Vannice, M. A. *Catal. Rev. Sci. Eng.* **1999**, *41*, 1. (d) Wurzel, T.; Malcus, S.; Mleczko, L. *Chem. Eng. Sci.* **2000**, *55*, 3955.

(6) Morris, R. M.; Klabunde, K. J. *J. Am. Chem. Soc.* **1983**, *105*, 2633.

(7) Andrews, L.; Tague, T. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 6856.

(8) Hwang, D.-Y.; Mebel, A. M. *Chem. Phys. Lett.* **2000**, *325*, 639.

(9) Frenking, G.; Koch, W.; Collins, J. R. *J. Chem. Soc., Chem. Commun.* **1988**, 1147.

(10) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917.

(11) Koch, W.; Collins, J. R.; Frenking, G. *Chem. Phys. Lett.* **1986**, *132*, 330.

(12) Frenking, G.; Dapprich, S.; Köhler, K. F.; Koch, W.; Collins, J. R. *Mol. Phys.* **1996**, *89*, 1245.

(13) Hwang, D.-Y.; Mebel, A. M. *Chem. Phys. Lett.* **2000**, *321*, 95.

(14) Guyer, D. R.; Polik, W. F.; Moore, C. B. *J. Chem. Phys.* **1983**, *79*, 12.

(15) (a) Jaffe, R. L.; Hayes, D. M.; Morokuma, K. *J. Chem. Phys.* **1974**, *60*, 12. (b) Jaffe, R. L.; Morokuma, K. *J. Chem. Phys.* **1976**, *64*, 12.

(16) Dupuis, M.; Lester, W. A., Jr.; Lengsfield, B. H., III.; Lui, B. *J. Chem. Phys.* **1983**, *79*, 6167.

(17) Scuseria, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 3629.

(18) Yu, J.-S.; Yu, C.-H. *Chem. Phys. Lett.* **1997**, *271*, 259.

(19) Nakano, H.; Nakayama, H.; Hirao, K.; Dupuis, M. *J. Chem. Phys.* **1997**, *106*, 4912.

(20) de A. Martins, L. M. M.; Arbilla, G.; da Silva, E. C. *J. Phys. Chem. A* **1998**, *102*, 10805.

(21) Feller, D.; Dupuis, M.; Garrett, B. C. *J. Chem. Phys.* **2000**, *113*, 218.

(22) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(23) Gonzales, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(24) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(25) Mebel, A. M.; Morokuma, K.; Lin, M. C. *J. Chem. Phys.* **1995**, *103*, 7414.

(26) (a) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. (b) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622. (c) Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1990**, *93*, 2537. (d) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5523.

(27) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7, Gaussian, Inc.: Pittsburgh, PA, 1998.

(29) *NIST Chemistry Webbook*, NIST Standard Reference Data Base Number 69, February 2000 Release (http://webbook.nist.gov/chemistry/).

(30) Hwang, D.-Y.; Mebel, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 11406.

(31) (a) Simandiras, E. D.; Nicolaides, C. A. *Chem. Phys. Lett.* **1991**, *185*, 529. (b) Nicolaides, C. A.; Valtazanos, P. *Chem. Phys. Lett.* **1991**, *176*, 239. (c) Valtazanos, P.; Nicolaides, C. A. *J. Chem. Phys.* **1993**, *98*, 459. (d) Nicolaides, C. A.; Simandiras, E. D. *Commun. Inorg. Chem.* **1996**, *18*, 65.

(32) (a) Zhang, L.; Dong, J.; Zhou, M. *J. Phys. Chem. A* **2000**, *104*, 8882. (b) Hwang, D.-Y.; Mebel, A. M. *Chem. Phys. Lett.* **2001**, *341*, 393.