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Theoretical Study of the Reversible Storage of H_2 by BeS

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Abstract: The potential energy surface for the BeS + $H_2 \rightarrow SBeH_2 \rightarrow HBeSH \rightarrow Be + H_2S$ reaction has been investigated by ab initio calculations at the G2(MP2)//MP2/6-31G(d,p) level. The results demonstrate that BeS can readily trap molecular hydrogen. The reaction proceeds by barrierless addition of molecular hydrogen to the Be side of BeS to form the $SBeH_2$ molecular complex bound by 12.4 kcal/mol with respect to the reactants. The complex isomerizes to HBeSH with a low, 5.4 kcal/mol barrier (7.0 kcal/mol below the reactants). The HBeSH molecule is thermodynamically stable and can serve as a storage compound. The energy required for the release of H_2 is calculated to be 55.8 kcal/mol. The BeS + H_2 system has a relatively shallow energy well of 48.8 kcal/mol at HBeSH for reversible hydrogen storage and a very high barrier of 85.6 kcal/mol for the H_2S + Be decomposition. The difference in energy barriers for the release of molecular hydrogen and water is 36.8 kcal/mol, which should make the system of BeS + H_2 highly selective for the reversible hydrogen storage.

1. Introduction

H_2-complexes were synthesized and studied during the 1980s in transition metal compounds.[1,2] Ab initio studies by Valtazanos and Nicolaides showed that H_2 interacts with non-transition-metal atoms or dimers such as Be^{2+}, B^{2+}, Be^{+}, Li^{+}, or Be_2^{2+} to form dihydrogen complexes, e.g. $Be^{2+}(H_2)$, rather than ordinary dihydrides with the simultaneous scission of the H_2 bond.[3,4] The cases of BeH_2^{2+} and BeH_2^{+}, as well as of polyhydrogen complexes involving Be^{2+}, B^{2+}, and Be_2^{2+}, point to the fact that it is not necessary to have d orbitals to bind H_2 without breaking the molecule. The bonding mechanism consists of induced σ-bonding with H_2 σ-orbital and weak π back-bonding with the σ^* orbital of H_2. In similar studies of other compounds containing a non-transition metal or a metal−metal bond, the bonding with H_2 was interpreted in the same way.[3−5] Three neutral alkaline earth oxides and sulfides, $OBeH_2$, $SBeH_2$, and $SMgH_2$, were found to be local minima on the potential energy surfaces where H_2 is present in a molecular rather than in an atomic (dihydride) form.[5,6] The binding energies in $OBeH_2$, $SBeH_2$, and $SMgH_2$ with respect to the H_2 lost are calculated by electronic structure theory to be 17.3, 15.5, and 1.2 kcal/mol, respectively, at the MP2 (Møller−Plesset perturbation theory to the second order)[7] level with various basis sets, while MP2 calculations with reasonably large basis sets do not predict stable minima for $OMgH_2$, $OCaH_2$, and $SCaH_2$.[5] The reaction pathway from BeO + H_2 to a linear HOBeH has also been studied theoretically.[8]

Experimental studies[9−11] revealed that many atoms can react with water to produce hydroxyhydrides. Therefore, the compounds such as HOBeH or HSBeH could decompose releasing H_2 or H_2O (H_2S) depending on the corresponding energy barriers. Recently, we studied the potential energy surface from BeO + H_2 to Be + H_2O.[12] The calculations revealed that the energy barrier to eliminate H_2 from the most stable HOBeH intermediate is about 11 kcal/mol lower than that for the H_2O release. The difference of 11 kcal/mol in the barrier heights can be sufficient for the selective release of H_2. We concluded that it may be possible for solid BeO to chemically trap H_2 in a reversible manner.[12] However, the G2(MP2)//MP2/6-31G(d,p) calculations gave the energy barrier for the release of H_2 as 77.0 kcal/mol with respect to HBeOH. The reversible hydrogen storage in such a deep energy well might be used in some special cases but our goal was to find a compound that reacts with molecular hydrogen giving a “storage” intermediate in a shallower well on the potential energy surface. Therefore, in this work we studied the potential energy surface for the BeS + $H_2 \rightarrow HBeSH \rightarrow Be + H_2S$ reaction. The results of ab initio calculations reported in this paper include reliable structures of the reactants, products, intermediates, and transition states as well as their chemically accurate energies.

2. Computational Details

Since the reaction of BeS with H_2 is expected to follow the minimum energy pathway from the singlet ground state of BeS and H_2, we only 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 and the transition states at the MP2/6-31G(d,p) level of theory. Some of the structures were further

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Table 1. Relative Energies (kcal/mol) of Various Compounds in the Reaction of BeS + H_2 Calculated at the MP2/6-31G**, MP2/6-311G**, QCISD(T)/6-311G**, MP2/6-311+G(3df,2p), and G2(MP2) Levels of Theory with the MP2/6-31G** Optimized Geometries and ZPE Corrections Scaled by 0.967

		relative energies				
species	ZPE	MP2/6-31G**	MP2/6-311G**	QCISD(T)/6-311G**	MP2/6-311+G(3df,2p)	G2(MP2)
BeS + H_2[a]	8.05	0	0	0	0	0
$SBeH_2$	11.35	−11.9	−13.0	−12.8	−12.6	−12.4
TS1	10.24	−5.1	−6.2	−5.9	−7.3	−7.0
HBeSH	10.61	−55.7	−58.0	−57.4	−56.4	−55.8
TS2	8.75	41.6	34.9	28.3	36.3	29.8
Be + H_2S	9.97	13.3	10.2	3.2	12.8	5.8
BeS+$2H_2$	14.64	0	0	0	0	0
TS0	19.69	−7.8	−10.2	−9.7	−10.6	−10.2
$SBe(H_2)_2$	21.08	−7.7	−9.4	−9.2	−9.9	−9.7
TS1(H_2)	19.6	−2.2	−4.3	−3.2	−6.1	−5.0
HBeSH(H_2)	17.97	−55.3	−57.6	−57.0	−56.1	−55.6
TS2(H_2)	16.17	42.0	35.4	28.9	36.7	30.2
Be + H_2S + H_2	9.97	13.3	10.2	3.2	12.8	5.8

[a] Total energies of BeS and H_2 are given in the Supporting Information.

optimized at the MP2/6-311G(d,p), MP2/6-311+G(d,p), CCD/6-31G(d,p), and CCD/6-311G(d,p) levels of theory.[7] The harmonic vibrational frequencies were obtained at the MP2/6-31G(d,p) level to characterize the stationary points as local 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 MP2/6-31G(d,p) level to account for their average overestimation.[13] The intrinsic reaction coordinate IRC method[14] was used to track minimum energy paths from transition structures to the corresponding local minima. A step size of 0.1 amu$^{1/2}$ bohr was used in the IRC procedure. The relative energies were refined using the G2(MP2) theory[15] at the MP2/6-31G(d,p) optimized geometries. All the ab initio calculations described here were performed employing the Gaussian 94 programs.[16]

3. Results and Discussion

The relative energies and ZPE of various compounds in the reaction of BeS + H_2 calculated at the MP2/6-31G(d,p), MP2/6-311G(d,p), MP2/6-311+G(3df,2p), and QCISD(T)/6-311G(d,p) levels of theory and their G2(MP2) relative energies are listed in Table 1. Table 2 presents calculated vibrational frequencies. The energy diagram along the reaction path computed at G2(MP2)//MP2/6-31G(d,p) is shown in Figure 1. The optimized geometries of various compounds along the predicted pathway of the BeS + H_2 reaction are depicted in Figure 2.

Reaction Mechanism. As seen in Figures 1 and 2, at the first stage of the reaction the H_2 molecule attaches to the Be atom of BeS to form a molecular $SBeH_2$ complex of C_{2v} geometry without energy barrier. The structure of $SBeH_2$ shown in Figure 2 is planar and corresponds to a local minimum on the MP2/6-31G(d,p) potential energy surface. The $SBeH_2$ complex conserves the molecular structure of H_2 (R_{HH} = 0.765 Å) and both of its two hydrogen atoms have equal distances from the beryllium atom, 1.577 Å. The G2(MP2)//MP2/6-31G(d,p) calculated exothermicity of the BeS + H_2 → $SBeH_2$ reaction step is 12.4 kcal/mol.

Table 2. Vibrational Frequencies (cm^{-1}) of Various Compounds in the BeS + H_2 Reaction Calculated at the MP2/6-31G** Level

species	frequencies
BeS	1024
$SBeH_2$	167, 218, 813, 1230, 1426, 4083
TS1	903i, 973, 1009, 1024, 2027, 2128
HBeSH	419, 524, 644, 790, 2243, 2803
TS2	1564i, 387, 472, 996, 1470, 2795
TS0	311i, 37, 182, 241, 335, 439, 701, 800, 1131, 1363, 4115, 4430
$SBe(H_2)_2$	53, 293, 319, 318, 474, 606, 760, 1042, 1231, 1232, 4169, 4183
TS1(H_2)	889i, 135, 226, 317, 461, 953, 973, 1013, 1113, 2055, 2126, 4340
HBeSH(H_2)	55, 66, 93, 111, 223, 426, 523, 644, 790, 2243, 2804, 4591
TS2(H_2)	1554i, 41, 69, 110, 160, 194, 392, 482, 1004, 1474, 2796, 4589

From the $SBeH_2$ complex, the reaction proceeds by migration of one of the hydrogen atoms to a planar nonlinear intermediate HBeSH via transition state TS1. From $SBeH_2$ to TS1 the SBeH angle bends from 166.2° to 72.7°, the S−Be bond elongates by 0.038 Å, and two hydrogen atoms are still close to each other (0.977 Å). Thus, the transition state is quite early in accord with the high exothermicity of the process. The G2(MP2)//MP2/6-31G(d,p) calculated barrier is 5.4 kcal/mol and the $SBeH_2$ → HBeSH reaction step is found to be exothermic by 43.3 kcal/mol. This energy is much lower than the corresponding exothermicity of the $OBeH_2$ → HBeOH reaction step in the BeO + H_2 system, 73.3 kcal/mol.[12] The transition state optimization was followed by the frequency and IRC calculations at the MP2/6-31G(d,p) level of theory which confirmed that TS1 does connect $SBeH_2$ and the planar nonlinear HBeSH intermediate. From HBeSH, the reaction can continue to form the Be and H_2S products via a nonplanar transition state TS2. At MP2/6-31G(d,p), the Be−S bond in TS2 (2.193 Å) becomes weaker and the hydrogen atom from the Be side of the molecule is shifted to a position above the Be−S bond, with S−H of 1.583 Å. This finding is in line with the fact that the next reaction step leads to the cleavage of the Be−S bond. The calculated G2(MP2)//MP2/6-31G(d,p) energies place transition state TS2 85.6 kcal/mol higher in energy than HBeSH. The MP2/6-31G(d,p) IRC calculation confirmed that the first-order saddle point TS2 connects the HBeSH intermediate and the Be + H_2S. On the contrary to the BeO + H_2 system, no Be−SH_2

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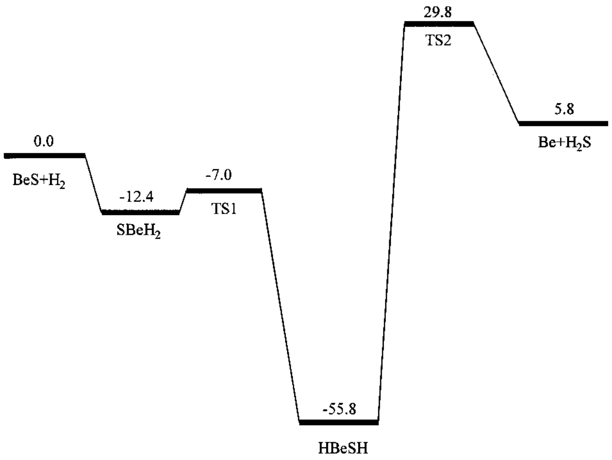

Figure 1. Potential energy diagram for the BeS + H_2 → Be + H_2S reaction calculated at the G2(MP2) level.

complex was found on the potential energy surface. This situation can change, in principle, if higher levels of theory are applied. However, existence or nonexistence of the Be−SH_2 complex is not relevant to the reversible storage of H_2 by BeS.

Generation of HBeSH and Reversible Storage of Molecular Hydrogen by BeS. As seen in Figure 1, the HBeSH molecule can be produced by two different pathways. BeS can easily react with molecular hydrogen to yield first the $SBeH_2$ complex without barrier and then HBeSH with a low barrier. According to the calculated potential energy surface, the BeS + H_2 → HBeSH reaction is expected to occur with negative activation energy and to be fast at low temperatures. On the other hand, HBeSH can be formed in the Be + H_2S reaction but in this case the system has to overcome a barrier of 24.0 kcal/mol. Hence, this reaction can take place at elevated temperatures. The HBeSH species can serve as a H_2 storage molecule. Upon heating, this compound can first rearrange to the $SBeH_2$ molecular complex overcoming a 48.8 kcal/mol barrier and then dissociate to BeS + H_2 losing an additional 12.4 kcal/mol. Since the barrier for the second channel of HBeSH decomposition producing Be atoms and H_2S is much higher, 85.6 kcal/mol, the storage molecule should selectively dissociate to BeS and molecular hydrogen.

From two points of view the BeS + H_2 system is expected to be more convenient for the reversible storage of H_2 than BeO + H_2. First, the well depth for the storage HBeSH molecule, 55.8 kcal/mol, is significantly smaller than that for HBeOH, 88.9 kcal/mol. Meanwhile, the HBeSH energy well is deep enough to avoid a leak of molecular hydrogen at low temperatures. Second, the difference in the barrier heights for the two dissociation channels, BeS + H_2 and Be + H_2S, is very high, 36.8 kcal/mol. The difference in corresponding energy barriers for HBeOH is only about 11 kcal/mol. This should make HBeSH a much more selective compound for the loss of molecular hydrogen than HBeOH. Interestingly, the barrier heights for the HBeSH → Be + H_2S and HBeOH → Be + H_2O reactions are comparable, 85.6 and 87.8 kcal/mol, respectively. The energies of complex formation with H_2, 15.6 kcal/mol for BeO and 12.4 kcal/mol for BeS, are also quite similar. The difference arises in the relative energies of HBeXH with respect to $XBeH_2$, 73.3 and 43.4 kcal/mol for the oxide and sulfide, respectively. This result can be attributed to the difference in the O−H and S−H bond strengths.[17]

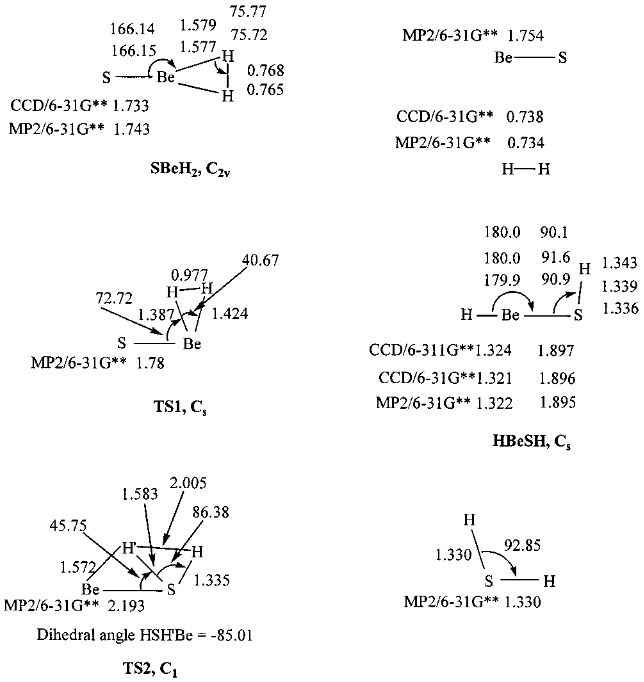

Figure 2. Geometries of the reactants, products, intermediates, and transition states of the BeS + H_2 → Be + H_2S reaction, optimized at various levels of theory. (Bond lengths are in angstroms and bond angles are in degrees.)

It should be mentioned that the reaction energetics discussed here is computed for the gas phase reaction. The possibility of solid or powder BeS to chemically trap H_2 would depend on whether H_2 could diffuse into the solid and the energy release from the exothermic BeS + H_2 → HBeSH reaction would be sufficient to separate BeS molecules from the lattice. Further experimental and theoretical investigations are required to clarify the feasibility of the reaction of solid BeS with H_2.

Other Possible Candidates for Reversible Storage of H_2. BeS is an unfortunate candidate for practical hydrogen storage because of the high toxicity of Be. Similar MX + H_2 → HMXH → M + H_2X reactions can, in principle, take place for other chalcogenides of alkaline earths. On the basis of the energetics of these reactions we can try to predict some other compounds as candidates for selective reversible storage of molecular hydrogen. In Table 3, we present experimental M−H, M−X, and X−H bond strengths, atomization energies for XH_2,[17,18] and estimated atomization energies for MX + H_2, HMXH, and M + H_2X (M = Be, Mg, Ca, Sr, Ba and X = O, S, Se). The atomization energy for M + H_2X coincides with that for H_2X, except for H_2Se where the experimental value is not available and we took for it the doubled Se−H bond strength.[18] For MX + H_2 the atomization energy is estimated as a sum of M−X and H−H bond strengths and for HMXH as a sum of M−H, M−X, and X−H bond strengths. For the latter, this gives a very crude estimation but allows us to follow some qualitative trends. The estimated atomization energies are used to compute the relative energies of HMXH and M + H_2X with respect to MX + H_2. This approach clearly underestimates the well depth for HMXH, which is 88.9 kcal/mol for HBeOH and 55.8 kcal/mol for HBeSH according to our ab initio calculations.

One can see that magnesium and calcium oxides can be immediately ruled out because their reactions with H_2 produce Mg and Ca + H_2O with high exothermicity. Therefore, when

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Table 3. Experimental[a] Bond Strengths for M−H, M−X, and X−H, Atomization Energies for XH_2, and Estimated Atomization Energies and Relative Energies for $MX + H_2$, HMXH, and $M + H_2X$ (M = Be, Mg, Ca, Sr, Ba; X = O, S, Se) in kcal/mol

M, X	Be, O	Be, S	Mg, O	Mg, S	Ca, O	Ca, S	Sr, O	Sr, S	Sr, Se	Ba, O	Ba, S
ΔE(M−H)	52.7	52.7	46.9	46.9	40.1	40.1	39.0	39.0	39.0	42.1	42.1
ΔE(M−X)	104.4	80.6	61.3[b]	66.7	91.6	79.2	102.0	79.8	68.1	132.0	100.0
ΔE(X−H)	102.4	85.0	102.4	85.0	102.4	85.0	102.4	85.0	75.2	102.4	85.0
$E_{atom}(H_2X)$	221.6	175.3	221.6	175.3	221.6	175.3	221.6	175.3		221.6	175.3
$E_{atom}(MX+H_2)$	208.6	184.8	165.5	170.9	195.8	183.4	206.2	184.0	172.3	236.2	204.2
E_{atom}(HMXH)	259.5	218.3	210.6	198.6	234.1	204.3	243.4	203.8	182.2	276.5	227.1
$E_{atom}(M+H_2X)$	221.6	175.3	221.6	175.3	221.6	175.3	221.6	175.3	150.3	221.6	175.3
$E_{rel}(MX+H_2)$	0	0	0	0	0	0	0	0	0	0	0
E_{rel}(HMXH)	−50.9	−33.5	−45.1	−27.7	−38.3	−20.9	−37.2	−19.8	−9.9	−40.3	−22.9
$E_{rel}(M+H_2X)$	−13.	9.5	−56.1	−4.4	−25.8	8.1	−15.4	8.7	22.0	14.6	28.9

[a] From refs 17 and 18. [b] From ref 19.

HMgOH and HCaOH are formed, the reverse reaction yielding oxides and molecular hydrogen is very unlikely. The energetics of the SrO reaction is qualitatively similar to that of BeO, so the possibility of reversible H_2 storage would depend on the barrier heights from HSrOH in the reverse (to an $OSrH_2$ complex if exists or to SrO + H_2) and forward (to Sr + H_2O) directions. BaO seems to be the best candidate among oxides. Most of the sulfides, except MgS, could show good selectivity for H_2 elimination from HMSH. The magnesium sulfide also cannot be completely excluded before barrier heights in the MgS + H_2 and Mg + H_2S directions are studied. SrSe could be a selective molecule for the H_2 storage but the well depth for HSrSeH seems to be too low for the existence of stable intermediate species. All these speculations have only a qualitative character and accurate calculations of the HMXH energies and reaction barriers are required for more reliable predictions.

Role of the Second H_2 Molecule in the Reaction with BeS. Recently, Gellene and co-workers[20] showed that while B^+ reacts with molecular hydrogen slowly with a very high barrier, in the presence of second and third H_2 molecules the barrier dramatically decreases and the reaction is greatly enhanced. This was attributed to the cooperative effect, which makes the activation of H_2 and formation of two new B−H bonds easier when the second and third H_2 molecules participate in the reaction. In this view, it is interesting to study how the second H_2 can affect the potential energy surface for the BeS + H_2 reaction. Therefore, we performed G2(MP2)//MP2/6-31G** calculations of the reaction intermediates and transition states in the presence of an additional hydrogen molecule. Optimized geometries of various species for the BeS + $2H_2$ reaction are shown in Figure 3 and their energies and vibrational frequencies are collected in Tables 1 and 2, respectively.

As one can see, the $SBe(H_2)_2$ molecular complex has a C_2-symmetric structure where two hydrogen molecules are equivalent. However, the energy of $SBe(H_2)_2$, −9.7 kcal/mol relative to BeS + $2H_2$ at the G2(MP2) level, is 2.7 kcal/mol higher than the energy of $SBeH_2$ + H_2. The complex with two hydrogen molecules can be separated from $SBeH_2$ + H_2 by a barrier. Indeed, the saddle point search between them gives transition state TS0. However, TS0 lies higher in energy than the complex only if zero-point energy corrections are not included. With ZPE taken into account, TS0 lies below $SBe(H_2)_2$, by 0.5 kcal/mol at the G2(MP2) level, indicating that the complex is unstable with respect to the loss of one H_2 molecule. The same is also true for the other intermediates and transition states, TS1(H_2), HBeSH(H_2), and TS2(H_2). All of them are slightly lower in energy than TS1 + H_2, HBeSH + H_2, and TS2 + H_2 without ZPE corrections but are not stable relative to H_2 elimination if ZPEs are included. Hence, the second H_2 molecule would not take part in the BeS + H_2 reaction and would not affect the potential energy surface. We can also conclude that the capacity of BeS for storage of molecular hydrogen would not exceed one H_2 molecule per one BeS molecule.

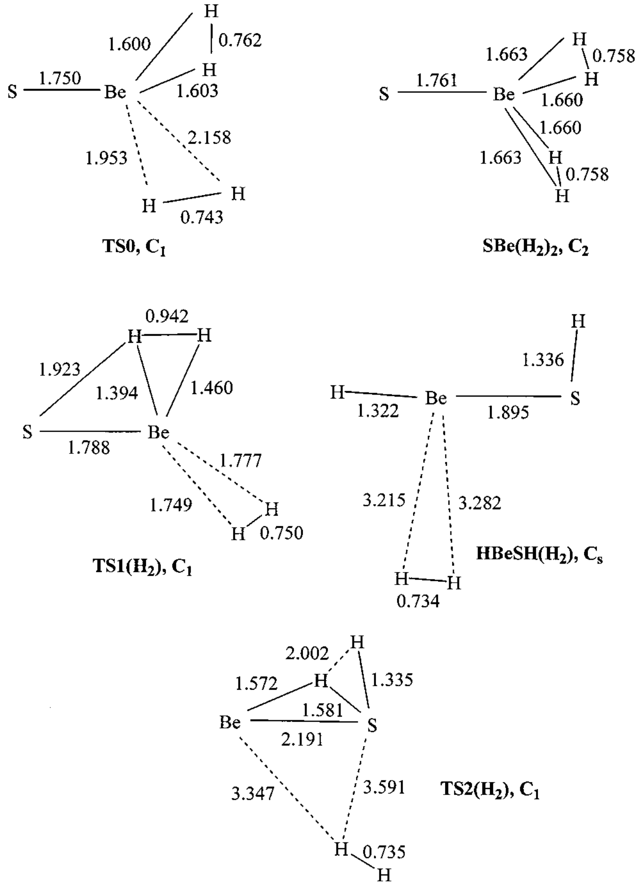

Figure 3. Geometries of the intermediates and transition states of the BeS + $2H_2$ reaction, optimized at the MP2/6-31G** level. (Bond lengths are shown in angstroms.)

4. Conclusions

G2(MP2)//MP2/6-31G(d,p) calculations of the potential energy surface for the BeS + H_2 → $SBeH_2$ → HBeSH → Be + H_2S reaction demonstrate that BeS can readily trap molecular hydrogen. The reaction proceeds by barrierless formation of the $SBeH_2$ molecular complex bound by 12.4 kcal/mol with respect to the reactants. The complex isomerizes to HBeSH with a low,

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5.4 kcal/mol barrier (7.0 kcal/mol below the reactants). The HBeSH molecule is thermodynamically stable and can serve as a storage compound. The energy required for the release of H_2 is calculated to be 55.8 kcal/mol. As compared to the BeO + H_2 system, BeS + H_2 has a shallower energy well of 48.8 kcal/mol at HBeSH for reversible hydrogen storage and much higher energy barrier of 85.6 kcal/mol for the H_2S + Be decomposition. In this system, the difference in energy barriers for the release of molecular hydrogen and water is 36.8 kcal/mol, i.e., much larger than in the BeO + H_2 system, 11 kcal/mol. Therefore, the system of BeS + H_2 is expected to be highly selective for the reversible hydrogen storage and requires lower energy for the hydrogen gas release. The calculations of the BeS + $2H_2$ potential energy surface showed that the second hydrogen molecule does not participate in the reaction and the capacity of BeS for storage of H_2 is not expected to exceed one H_2 molecule per one BeS molecule.

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Supporting Information Available: Total energies of BeS and H_2 calculated at various levels of theory and details of the reaction path (IRC) calculations for transition states TS1 and TS2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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