Competition Mechanism Study of Mg+H_2O and MgO+H_2O Reaction

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Abstract. Magnesium/water reaction and Magnesia/water reaction mechanism are investigated theoretically. The optimized geometries and frequencies of the stationary points of two reaction are calculated at B3LYP/6-311++G(d,p) level. The transition state and intermediate are confirmed. The potential energy surfaces of two reactions are calculated. It is shown that Magnesia will react with water firstly.

1. Introduction

Magnesium has been widely used in light emitting, heating and smoke pyrotechnic because its combustion can produce a lot of heat, emit dazzling white light and generate white smoke, etc. In the process of the production of magnesium containing pyrotechnics, due to the limited production process and other reasons, pyrotechnics will inevitably mix a certain amount of moisture. However, magnesium can also react with water at low temperature [1]. At the same time in storage water may also lead to the damp failure of the pyrotechnic. In order to solve this problem, Magnesium Oxide was added to the pyrotechnics with magnesium as stabilizer. However, the mechanism of Magnesium Oxide as a stabilizer is not clear, and the order of reaction between magnesium and Magnesium Oxide is still controversial. In this paper, the mechanism of Mg/H_2O reaction and MgO/H_2O reaction is calculated by quantum chemical method, and the mechanism of Magnesium Oxide as stabilizer is explained theoretically.

2. Reaction Mechanism

Magnesium is a very active element that can react with water at low temperature to produce magnesium hydroxide and hydrogen. Magnesium Oxide also reacts with water to produce the corresponding hydroxide, magnesium hydroxide. The reaction mechanisms are as follows:

$$Mg + 2H_2O = Mg(OH)_2 + H_2$$
$$MgO + H_2O = Mg(OH)_2$$

In this paper, the Mg/H_2O reaction and MgO/H_2O reaction competition mechanism was calculated, the geometries of the reactants and products of two kinds of reaction and vibration frequencies were calculated. The transition states and intermediates were determined. The potential energy curves were calculated, and ultimately the competition mechanism between the two reactions was determined.

3. Theoretical Calculation

3.1. Calculation Method

All electronic structures and energy calculations are performed by the Guassain 09 package. Use the density functional method [2] (Density Functional Theory, DFT) hybrid B3LYP method [3, 4]. At B3LYP/6-311++G (d, p) levels, the geometries of reactants, products and transition states in each reaction were optimized, and vibrational frequencies were calculated. The transition state was calculated by the intrinsic reaction coordinate [5, 6] (IRC), and the transition state was confirmed. The system was closed shell calculation. At the B3LYP/6-311++G (d, p) level, the potential energy curves of the two reactions under gaseous conditions are calculated.

3.2. Structure and Frequency

At the B3LYP/6-311++G (d, p) level, the geometry of each stationary point in each reaction is optimized, the electronic structure of the stagnation point is analyzed and the vibration frequency is calculated. The structural information is obtained, including bond lengths and bond angles, as shown in Table 1.

Table 1. Geometric parameters of all stationary points

Species	Bonds	Length/ Å	Bonds	Angles/degree
MgO	Mg (1)-O (2)	1.7627		
H_2O	H (2)-O(1)	0.9612	H(2)-O(1)-H(3)	105.1016
	H (3)-O(1)	0.9612		
Mg(OH)	Mg(1)-O(2)	1.7992	H(3)-Mg(1)-O(2)	179.8855
	H(3)-O(2)	0.9511		
$Mg(OH)_2$	Mg(1)-O(2)	1.7982	H(3)-Mg(1)-O(2)	149.0791
	H(3)-O(2)	0.9520	O(4)-Mg(1)-O(2)	178.3841
	Mg(1)-O(4)	1.7804	Mg(1)-O(2)- H(3)	177.5221
	H(5)-O(4)	0.9493		
$HOMg(H_2O)$	Mg(1)-O(2)	1.8942	Mg(1)-O(2)- H(3)	139.8033
	Mg(1)-O(4)	2.1487	O(4)-Mg(1)-O(2)	75.4250
	H(3)-O(2)	0.9555	H(5)-O(4)-Mg(1)	83.8524
	H(5)-O(4)	0.9929	H(6)-O(4)-Mg(1)	134.7893
	H(6)-O(4)	0.9616		
$OMg(H_2O)$	Mg(1)-O(2)	1.7649	O(3)-Mg(1)-O(2)	176.8002
	Mg(1)-O(3)	2.0992	O(3)-Mg(1)-H(4)	126.4681
	H(5)-O(3)	0.9671	O(3)-Mg(1)-H(5)	125.9687
	H(4)-O(3)	0.9671		
OMg(OH)	Mg(1)-O(2)	1.8894	O(3)-Mg(1)-O(2)	179.9623
	Mg(1)-O(3)	1.7777	O(3)-Mg(1)-H(4)	179.9246
	H(4)-O(2)	0.9496		
H_2	H(2)-H(1)	0.7441		
TS1	H(3)-O(1)	0.9661	H(3)-O(1)-H(2)	124.1449
	H(2)-O(1)	1.5842	H(3)-O(1)-Mg(4)	173.8203
	Mg(4)-O(1)	1.8850		
TS2	Mg(1)-O(2)	1.7714	H(3)-O(2)-Mg(1)	135.3136
	Mg(1)-O(4)	1.9160	O(4)-Mg(1)-O(2)	160.1583
	H(3)-O(2)	1.4832	H(5)-O(4)-Mg(1)	132.6904
	H(5)-O(4)	0.9640	H(6)-O(4)-Mg(1)	67.6960
	H(6)-O(4)	1.4857		

The frequencies of the various stationary points in the two reactions are shown in Table 2.

Table 2. Vibrational frequencies of all reactants, transition states and products

Species	frequencies/cm^{-1}	
MgO	788	820[5]
H_2O	3924 3818 1602	3756 3657 1595[6]
Mg(OH)	4031 729 216	4045 752 123[5]
$Mg(OH)_2$	4066 4020 895 599 253 203 195 162 160	
$HOMg(H_2O)$	3963 3878 3327 1569 841 616 526 512 320 301 276 256	
$OMg(H_2O)$	3842 3747 1640 836 477 320 273 69 46	
OMg(OH)	4060 854 551 222 203 151	
H_2	4418	4401[5]
TS1	3797 1387 660 569 291 1121*i*	
TS2	4025 3836 1074 808 682 488 366 198 156 149 140 721*i*	

The transition states TS1 and TS2 have only one imaginary frequency. The virtual frequency of TS1 in the reaction of magnesium water is 1121*i*, and the virtual frequency of TS2 is 721*i*. At the same time, relevant experimental values and literature values are listed in the table. The calculated results are in good agreement with the experimental values and the literature values.

3.3. Competition Mechanism

Under the B3LYP/6-311++G (d, p) level, the structural energies, Zero-point energy correction and enthalpy of each stagnation point in the two reactions are calculated. The results are shown in Table 3.

Table 3. Energy values of all stationary points

Species	*E*/hartree	*ZPE*/(Kcal·mol^{-1})	*H*/hartree
H_2	-1.1795715	6.32	-1.167146
MgO	-275.2601812	1.13	-275.254999
H_2O	-76.4585307	13.35	-76.433464
Mg(OH)	-275.9640065	7.11	275.948255
$Mg(OH)_2$	-351.8916661	15.09	-351.860776
MgO(OH)	-351.192469	8.64	-351.172950
$MgO(H_2O)$	-351.7544367	16.08	-351.722225
$MgOH(H_2O)$	-352.4514416	23.43	-352.407943
TS1	-276.4912737	9.58	-276.471478
TS2	-352.4037727	16.8	-352.369353

At the B3LYP/6-311++G (d, p) level, the reaction potential energy curves of the two reactions are calculated, as shown in Figure 1.

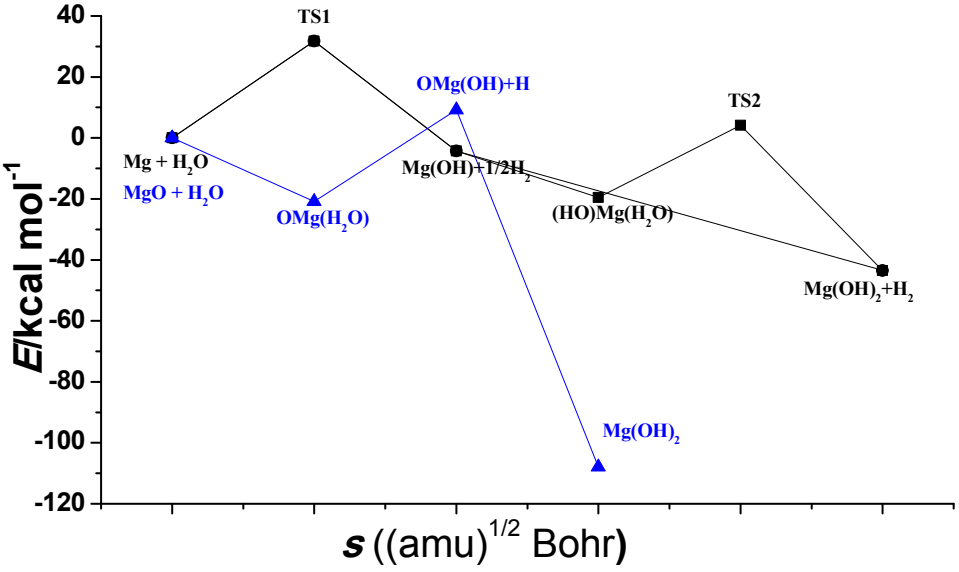

Figure 1. The reaction potential energy curves of two reactions

The reaction between magnesium and water is relatively complex. Mg and H_2O form intermediate Mg (OH) via transition state TS1, in which the energy barrier of transition state TS1 is 37.98kcal/mol (158.76kJ/mol). Bond length of Mg(4)-O(1) in TS1 is 1.8850 Å, and after the formation of intermediate Mg(OH), the bond length becomes 1.7992 Å. Intermediate Mg(OH) reacts with H_2O to form the reaction products H_2 and $Mg(OH)_2$. There are two kinds of reaction channels. One is to directly form the final product. The other is Mg (OH) and H_2O to form an intermediate (HO) Mg (H2O). Then through the transition state TS2, form the final product Mg $(OH)_2$ + H_2. The reaction energy barrier is 11.88kcal/mol (49.7kJ/mol).

The MgO/H_2O reaction mechanism is relatively simple. MgO and H_2O firstly forms MgO (H_2O). This process has no energy barrier. Then MgO (H_2O) overcomes the barrier to form intermediate MgO (OH) + H. Mg (1)-O (2) bond length is 1.8894 Å, Mg (1)-O (3) bond length is 1.7777 Å. The reaction energy barrier of intermediate MgO (OH) is 15.05kcal/mol (62.90kJ/mol). In comparison to the two reactions, the barrier of MgO/H_2O reaction is lower, and it is concluded that Magnesium Oxide reacts with water first.

4. Conclusion

In this paper, the competition mechanism between magnesium and Magnesium Oxide has been theoretically calculated. The calculation results show that Magnesium Oxide which acts as a stabilizer in pyrotechnic reacts with water in the first and generates magnesium hydroxide.

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