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Theoretical study on the mechanism of the reaction of Li_2O with CH_4

Song Qin, Changwei Hu*, Zhishan Su

Key Laboratory of Green Chemistry and Technology (Sichuan University), Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

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Abstract

B3LYP/6-311++G(3df,3pd) and CCSD(T)/6-311++G(2d,2p) calculations show that the reaction of Li_2O with CH_4 can proceed by two distinct reaction channels, that is, channel A: $Li_2O+CH_4 \rightarrow CH_3Li+LiOH$, and channel B: $Li_2O+CH_4 \rightarrow CH_3OH+Li_2(^1\Sigma^+)$. The former is predicted to be endothermic by about 111.1 kJ/mol with an energy barrier of 157.4 kJ/mol, and the latter endothermic by about 219.1 kJ/mol with an energy barrier of 322.3 kJ/mol. With the relatively lower energy required, the formation of CH_3Li would be more feasible comparing to the formation of methanol with a rather higher energy barrier.

Keywords: B3LYP; Li_2O; CH_4

1. Introduction

The activation of methane is currently an important subject and attracts increasingly considerable attention in pure and applied chemistry, because the catalytic conversion of methane to produce more useful compounds is one of the desirable goals of current chemical industry [1]. Theoretical investigations on the gas-phase reaction of small molecules as model catalyst with hydrocarbons have been considered capable of providing a wealth of insight concerning the intrinsic interactions between the active site of catalysts and organic substances [2–6].

The adsorption and the dissociation of methane on MgO or lithium-doped MgO catalysts have been extensively investigated [7,8], and the abstraction of hydrogen from methane with the formation of methyl radical has been generally accepted as the initial step in methane activation [9]. To obtain further information about this process, many theoretical studies on the interaction of methane with metal oxide have been performed using ab initio calculation. Zicovich-Wilson et al. [10] investigated the direct abstraction of hydrogen atom from methane by gas-phase LiO, MgO, and AlO. Rodı́guez et al. [11], as well as Børve and Petterson [12] investigated the gas-phase reactions of the diatomic metal oxides MgO, LiO and AlO towards CH_4, and predicted an exothermicity of 6–14 kcal/mol with an energy barrier of 6–16 kcal/mol for those reactions. Later, Stiakaki et al. [13] examined the methane dissociation on the gas-phase diatomic metal oxides (e.g. LiO, BeO, AlO, MgO and CdO). Recently, Hwang et al. [14] studied in detail the reaction of BeO with CH_4 and predicted a rather high energy barrier of 113.5 kcal/mol for the production of methanol. Our previous investigation on the reaction of MgO with CH_4 using MP2 method gives the reasonable product of methanol with also a high energy barrier of 348.2 kJ/mol [15].

Li_2O has been proved to be an effective catalyst to activate methane [16] and its properties have been examined by some theoretical investigations [17,18]. In these researches, Burk et al. [19] suggested that B3LYP method could give desirable results in those systems involving the alkali metal oxide such as Li_2O. To our aware, however, the detailed mechanism for the reaction of lithium oxide (Li_2O) with CH_4 has not been investigated so far. In order to find the mode of CH_4 activation on Li_2O, the reaction of CH_4 with Li_2O is studied at the CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(3df,3pd) levels in the present work,

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* Corresponding author. Tel./fax: +86 2885411105.

E-mail addresses: chwehu@mail.sc.cninfo.net (C. Hu), gchem@scu.edu.cn (C. Hu).

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which may give an essential piece of information for a better understanding of such reaction mechanism and for the design of new catalysts.

2. Computational details

All calculations are carried out using GAUSSIAN 03 programs. The geometries of all reactants, products, various intermediates and transition states for the reaction of Li_2O with CH_4 are optimized using B3LYP method with the 6-311++G(3df,3pd) basis set for all atoms. Vibrational frequencies are calculated at the B3LYP/ 6-311++G(3df,3pd) level to check whether the obtained stationary point is an intermediate or first-order transition state and scaled by 0.963 to correct the overestimation [20]. For each transition states, intrinsic reaction coordinate (IRC) calculations were performed in both directions to connect these corresponding intermediates at the above level. Furthermore, the single-point energies are also calculated at the CCSD(T)/ 6-311++G(2d,2p) level at the B3LYP/ 6-311++G(3df,3pd) optimized geometries. Unless otherwise specified, the CCSD(T)/6-311++G(2d,2p) single-point energies are used in the following discussions.

3. Results and discussions

The total and relative energies of all species in the reaction calculated at the B3LYP/6-311++G(3df,3pd) and the CCSD(T)/6-311++G(2d,2p) levels are listed in Table 1. For the reactants, intermediates, transition states and products, the calculated frequencies are listed in Table 2. The energy diagram along the singlet reaction pathway of various species obtained from the CCSD(T)/ 6-311++G(2d,2p) single point calculation is shown in Fig. 1. The optimized structures of various intermediates and transition states on the singlet potential energy curve of the Li_2O+CH_4 reaction are depicted in Fig. 2.

The Li–O bond lengths and the Li–O–Li angle in the free Li_2O molecule optimized at the B3LYP/6-311++G(3df,3pd) are predicted to be 1.611 Å and 180.0°, respectively. Both are in excellent agreement with the experimental values and the theoretical results obtained by Burk et al. [19]. *NIST Standard Reference Data Base* gives the C–H bond lengths of 1.087 Å for isolated CH_4 molecule [21], which are accurately reproduced to be 1.088 Å at the B3LYP/6-311++G(3df,3pd) level. Furthermore, according to the vibrational analysis, the isolated CH_4 molecule is characterized by a triply degenerate C–H asymmetric stretching mode at 3014–3016 cm^{-1} (ν_3) and by a nondegenerate C–H symmetric stretching mode at 2915 cm^{-1} (ν_1); the two degenerate H–C–H deformation modes are at 1499 cm^{-1} (ν_2) and 1290–1291 cm^{-1} (ν_4). The symmetric stretching mode at 2915 cm^{-1} and the deformation mode at 1499 cm^{-1} are IR forbidden by symmetry but Raman active. These results are in good accord with literature [22,23]. The above results show that the present theoretical method is appropriate for Li_2O+CH_4 system.

As shown in Table 1, as well as in Figs. 1 and 2, there exist two different reaction channels when Li_2O react with

Table 1
Total energies (hartree) E_{ZPE} corrected by ZPE and relative energies (kJ/mol) E_R with respect to the reactants calculated at the B3LYP/6-311++G(3df,3pd) and the CCSD(T)/6-311++G(2d,2p) levels of all various species along the predicted Li_2O+CH_4 reaction

Species	B3LYP/6-311++G(3df,3pd)		CCSD(T)/6-311++G(2d,2p)	
	E_{ZPE} (hartree)	E_R (kJ/mol)	E_{SP} (hartree)	E_R (kJ/mol)
CH_4	−40.492834		−40.420064	
Li_2O	−90.343257		−90.072512	
CH_4+Li_2O	−130.836091	0.0	−130.492576	0.0
HCH_3–LiOLi	−130.838896	−7.4	−130.498129	−14.6
a-TS1	−130.819403	43.8	−130.471907	54.2
CH_3–Li_2OH	−130.880042	−115.3	−130.541007	−127.1
a-TS2	−130.821536	38.2	−130.481033	30.3
$LiCH_3$–LiOH	−130.825053	29.0	−130.484446	21.3
CH_4–OLi_2	−130.836513	−1.1	−130.495460	−7.6
b-TS1	−130.717130	312.2	−130.372679	314.7
CH_3O–Li_2H	−130.854846	−49.2	−130.513288	−54.4
b-TS2	−130.741918	247.1	−130.399620	244.0
CH_3OH–Li_2	−130.746469	235.2	−130.415749	201.6
b-TS3	−130.745636	237.4	−130.415415	202.5
CH_3OH–Li–Li	−130.761272	196.4	−130.434281	153.0
CH_3Li	−47.390351		−47.249218	
LiOH	−83.405066		−83.201015	
$CH_3Li+LiOH$	−130.795417	106.7	−130.450233	111.1
CH_3OH	−115.723204		−115.507936	
$Li_2(^1\Sigma^+)$	−15.015307		−14.901155	
CH_3OH+Li_2	−130.738511	256.1	−130.409091	219.1