第二列金屬與含碳自由基之反應位能面計算

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I. Abstract

In this research work, we calculated the ground state and excited states PES of Be + CH, Li + CH. We focused on the pathways of chemical quenching: $Li(2^2P) + CH(X^2\Pi) \rightarrow LiC + H$, $Li(2^2P) + CH(X^2\Pi) \rightarrow LiH + C$, $Be(2^1P) + CH(X^2\Pi) \rightarrow BeC + H$ and $Be(2^1P) + CH(X^2\Pi) \rightarrow BeH + C$. The potential energy curves were calculated at the CASSCF level, while some important intermediates and saddle points were investigated with the MRCI method. Unlike the reactions of these metals with methane, where the ground state surface is repulsive, the reactions with CH can from stable intermediates on ground state.

我們計算 Be + CH 及 Li + CH 的位能曲線。我們的重點是化學反應：$Li(2^2P) + CH(X^2\Pi) \rightarrow LiC + H$, $Li(2^2P) + CH(X^2\Pi) \rightarrow LiH + C$, $Be(2^1P) + CH(X^2\Pi) \rightarrow BeC + H$ 和 $Be(2^1P) + CH(X^2\Pi) \rightarrow BeH + C$。位能曲線是以 CASSCF 方法計算，一些重要的中間產物和鞍點我們再以 MRCI 方法了解它們的電子組態。當這類金屬與與甲烷反應時，因為甲烷的軌域都有成對電子，所以基態位能面是排斥性，金屬和自由基反應因自由基有不成對電子，所以位能面的計算就複雜許多。

II. Key Words: potential energy surface, quenching, methylene and methylidyne.

III. Introduction and Purpose

In the reactions of metals with methane, MH and MCH_3 are formed via an stable intermediate $[CH_3M^*H]$, which then transitions to the saddle point on the ground state PES. In the reactions of metal with a C-H containing free radical, there are available coordination sites at carbon, then a stable intermediate would be formed on

the ground state PES. Methylene and methylidyne radicals exist in combustion process. They are also common adsorbates on metal surfaces. In contrast to the sp^3 hybridization in methane and methyl radical, the ground state methylene $\tilde{X}\,^3B_1$ is sp^2 hybridization at the carbon. It has a predominant configuration $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^1(3a_1)^1$, where $1a_1$ is the $1s$ of C, $2a_1$ and $1b_2$ represent the two C-H bonds, $3a_1$ and $1b_1$ are the in-plane and out-of-plane nonbonding orbitals, respectively. $\tilde{a}\,^1A_1$, $\tilde{b}\,^1B_1$ and $\tilde{c}\,^1A_1$ are 9.43, 33.33 and 516 kcal/mole above $\tilde{X}\,^3B_1$. $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ will be refered here as $^3CH_2$ and $^1CH_2$, respectively. Methylene can react with N_xO_y, H_2, CO_2. The reactions have various transition states, intermediates and final products. In the reaction with NO, NH and OH are two the products. So, we are interested in the possibility of MH production when a metal reacts with methylene.

The ground state of CH radical is $X^2\Pi$ with a configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^1$ and the first excited state $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$ ($^4\Sigma^-$) is 17 kcal/mol above. $A^2\Delta$ is 66 kcal/mol higher than $X^2\Pi$. The intermediate [XCH] in the reactions of an atom with CH can be thought as to form a derivative of methylene. The derivatives can be more stable than CH_2. Halvick et. al. have calculated the PES for the formation of C_2H radical from C + CH. The ground state of C_2H has triple bonds between the two carbons and is correlated to C + CH ($^4\Sigma^-$), not $X^2\Pi$. Attack of C to the H-site was also calculated, but was repulsive. We are looking for the possibility of π-bonding between metal and CH.

IV. Result and Discussion

We used the ROOS basis set for all atoms in this calculation. Comparing the calculated atomic transitions with different basis sets, such as cc-pVDZ, cc-pVTZ and cc-pVQZ, etc., we found that ROOS gave the atomic transitions that were most closed to experimental results. The potential energy curves were calculated at the CASSCF level with enough active spaces.

We first calculated the ^{3}A' and ^{3}A" potential energy curves for Li approaching the carbon of CH from a nearly linear attack, θ =179°. At far distance, R = 6.0 Å, the 2A' and 1A' energy difference is 0.0671 hartree, which is closed to the $2^2S - 2^2P$ atomic transition of Li. So, 1A' and 2A' are originally Li(2^2S) + CH($X^2\Pi$) and Li(2^2P) + CH($X^2\Pi$), respectively. At R = 2.6 Å, 2A' shows a 0.01 hartree barrier. This barrier may come from the non-adiabatic coupling between 3A' and 2A'. We predict that 3A' is Li(2^2Px) + CH($a^4\Sigma^-$) asymptotically and this configuration should be stable at short distance. On the other hand, the electron of Li(2^2Pz) and the z-pair of CH($X^2\Pi$) repel each other and causes 2A' rising and at R = 2.6 Å, 2A' and 3A' exchange electron configurations. This can be understood by the appearance of a potential well on 2A' at R < 2.6 Å, where a stable complex LiCH from Li(2^2Px) + CH($a^4\Sigma^-$) is formed. The

1A' curve looks repulsive because of the repulsion between Li(2^2S) and CH($X^2\Pi$).

From R = 1.8 Å, we extended the C-H distance to form LiC + H on 1A' and 2A'. 1A' and 2A' merge at long C-H distance, which are LiC($a^2\Pi$) + H.

At R = 6.0 Å, the energy difference between 2A" and 1A" is 0.0192 hartree, which is closed to the energy difference of CH($a^4\Sigma^-$) and CH($X^2\Pi$), 0.026 hartree. So, 1A" and 2A" are Li(2^2S) + CH($X^2\Pi$) and Li(2^2S) + CH($a^4\Sigma^-$) at long distance, respectively. 2A" and 1A" avoided cross at R = 3.6 Å and then exchange electronic configurations. There is then a potential well on 1A" at R = 1.8 Å, which is the ground state LiCH. At this place, d(Li-C) = 1.8 Å, d(C-H) = 1.09 Å, which are closed to the result of Ellis et. al. in 1996.

Next, we calculated the potential energy curves for Li approaching the carbon of C-H from an angle perpendicular to the C-H bond (θ = 90°). At R = 7.0 Å, the 2A' and 1A' energy difference is same as that at θ = 179°. At far distance the energy should be independent of θ, thus our computation here is correct. As Li approaches up to R = 3.0 Å, there is a barrier of 0.006 hartree (1894 K) on 2A'. Then a potential energy well on 2A' appears at R = 1.8 Å. At the same time, 1A' is repulsive and avoided crosses 2A' here. The energy difference between 2A' and 1A' at R = 1.8 Å is smaller than the avoided crossing at θ = 179°. Thus, surface jumping from 2A' reactants to 1A' will be easier at θ = 90°. If the C-H bond is defined along the y-axis and Li-C along the z-axis, then the electron on the 2px (or 2pz) of Li and the electron on the 2px (or 2pz) will repel each other at short distance due to the same spin (total spin is triplet). Then 2A' rises. On the other hand, 3A' should be Li(2^2P) + CH($a^4\Sigma^-$). At short distance the electrons of CH 2py and 2pz could enter the empty 2py and 2pz, respectively, to form two half σ-bonds at short distance. Thus 3A' lowers and at R = 3.0 Å, it meets 2A' and exchanges configurations. Thus, there is a 0.006 barrier on 2A' at R = 3.0 Å. Why is 1A' repulsive? It is because the Li 2s electron and the CH pz electron have the same spin.

We started the product potential energy curves at R = 1.8 Å by pulling the H atom out. The 2A' and 1A' asymptotical products are same as θ = 179°.

Next, we calculated the 2A" and 1A" potential curves for θ = 90°. Then energy difference of 2A" and 1A" at long distance is 0.0586 hartree, similar to that at θ = 179°. 2A" is repulsive and 1A" has a well at R = 1.8 Å. The energy gap between 2A" and 1A" is always large even at short distance. Thus, we predicted that it is difficult to have non-adiabatical transition at this angle, as compared to θ = 179°. The 2A" and 1A" products are LiC($a^2\Pi$) + H and LiC($X^4\Sigma^-$) + H, respectively. To form the 1A" products from the 2A" reactants is still endothermic.

Finally for Li + CH, we let Li

approach the H of CH via a linear attack, θ = 1°. At long distance, the 2A' and 1A' energy difference is similar to those at other anlges. Thus, they are Li(2^2P) + CH($X^2\Pi$) and Li(2^2S) + CH($X^2\Pi$), respectively. Both 2A' and 1A' are repulsive and has no chance to cross each other due to large energy gap. To form the LiH + C products, there is a barrier of 0.04 hartree (12630 K) on 1A'. So, it is difficult to allow this reaction to proceed in a heat pipe reactor.

For the 1A" and 2A" potential energy curves at θ = 1°, they are Li(2^2S) + CH($X^2\Pi$) and Li(2^2S) + CH($a^4\Sigma^-$), respectively, as at other angles. 2A" and 1A" have an avoided crossing at R = 2.4 Å, then 1A" has a potential well at R = 1.6 Å. From here, we started to pull C out. It costs energy. Forming the 1A" products LiH($X^2\Sigma^+$) + C(2^3P) is still endothermic.

Finally, we calculated the doublet potential energy curves for Be + CH at θ = 179°. At long distance, the energy difference of 2A' and 1A' is 0.08843 hartree. They are Be(2^1P) + CH($X^2\Pi$) and Be(2^1S) + CH($X^2\Pi$), respectively. 1A' and 2A' avoided cross at R = 2.4 Å, where 1A' shows a saddle point. It is because of the repulsion between the Be($2s^2$) pair and the CH pz pair. 2A' is attractive because the excited electron of Be can bond with CH($a^4\Sigma^-$). At R = 2.4 Å, the 2A' reactants will have chance to jump tp 1A' due to a very small energy gap. We started to calculate the BeC + H product potential energy curves at R = 1.8 Å. We find that forming the 1A' products from 2A' reactants is energy allowed.

At long distance, the 2A" and 1A" difference is similar to that of 2A' and 1A'. 2A" has a small barrier at R = 3.2 Å due to the repulsion between the excited electron of Be and the pz pair of CH. At long distance 3A" should be Be(2^3P) + CH($a^4\Sigma^-$), which is attractive and exchanges electron configurations with 2A" at R = 3.2 Å. Thus 2A" becomes attractive at R < 3.2 Å. 2A" and 1A" have chance to proceed non-adiabatic transition at R = 2.4 Å and then exothermically to form the 1A" products.

V. Self-Evaluation

It is a little slow for us to complete the project. We have not finished the pontential energy curves of Be + CH at θ = 90 and 1°. We are still working on the reaction of metal + CH_2 and wish they can be completed soon.