DFT Study on the Reaction of Molybdenum with Acetaldehyde in Gas Phase

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The gas-phase reaction of molybdenum atom with acetaldehyde is investigated using density functional theory. Geometries and energies of the reactants, intermediates and products involved are calculated. Both ground and excited state potential energy surfaces are investigated. The present results show that the reaction of molybdenum and acetaldehyde start with the formation of a η^2 -CH₃CHO-metal complex followed by C-C, aldehyde C-H, methyl C-H and C-O bonds activation. These reactions can lead to six different products (HMoCH₃ + CO, MoCO + CH₄, MoCH₂CO + H₂, MoCOCH₃ + H, MoCH₂CHO + H and MoO + C₂H₄). The spin inversion is involved in the reaction step and this potential energy curve-crossing may affect reaction exothermic. The present results may be helpful in understanding of the mechanism of the reaction of molybdenum and acetaldehyde and further experimental investigation of the reaction.

Key Words: DFT, Potential energy surfaces, Molybdenum, Acetaldehyde.

INTRODUCTION

The chemistry of interaction of gas-phase transition metal atoms and cations with hydrocarbon molecules has been an active area of both theoretical and experimental researches due to its great importance in catalytic and material science¹⁻⁶. To better understand the fundamental aspects of this reaction, several studies have been reported on the investigation of the relevant mechanism⁷⁻²⁰. These gas-phase reactions can offer an unique possibility to probe the intrinsic properties of reactive organometallic species and the details of activate C-H, C-C and C-O bonds in the initial steps are of fundamental interest in catalysis. As one of the simple carbonyl-containing organic molecules, acetaldehyde is particular interest in understanding C-H, C-C and C-O bonds activation in small hydrocarbons by transition metal atoms and ions as well as in unveiling oxidative processes of metal. The reactions of metal cations with acetaldehyde have been extensively studied⁶⁻⁹. Some experimental techniques such as ion beam mass spectrometry and crossed-beam, have revealed that decarbonylation of acetaldehyde to yield CH₄ + MCO⁺ is a dominant process at low energy condition⁶. Based on these experiments, Guo *et al.*⁷⁻⁹ have theoretically investigated the gas-phase reaction of Co⁺, Fe⁺, Ti⁺, Cr⁺ and Ni⁺ cations with CH₃CHO to unveil the corresponding mechanism. Their results show that for Co⁺, Fe⁺ and Cr⁺ cations, decarbonylation proceeds through C-C activation rather than aldehyde C-H activation, whereas both

C-C and aldehyde C-H activation may result in the decarbonylation of CH₃CHO by Ni⁺ cation. Compared with the first-row cation, heavier metal atoms and cations have received relatively less attention and only a few theoretical and experimental studies have been reported¹²⁻¹⁴. Bayse *et al.*¹⁴ have investigated the reaction between yttrium atom and acetaldehyde in detail. Their DFT calculations based on crossed molecular beams experiments predict the CO elimination to be the most exoergic channel, with the H₂ elimination products being slightly higher in energy. It should be noted that in their study, no CH₄ + YCO products channel was observed, which is quite different from the observations of reaction of the first row transition metal with CH₃CHO.

From the previous experimental and theoretical studies on the decarbonylation of acetaldehyde by first row cations and the larger transition-metal Y, it is clear that the transition metal change from first row to metal Y leads to the reaction change in mechanism both in early and late reaction stages. In addition, previous studies mainly focused on the reaction between first row cations and aldehyde, studies of the reaction between aldehyde and neutral are still scarce. Actually, the charge may often affect the mechanistic details. Therefore, it is necessary to extend the research to the reaction between neutral metal and aldehyde. To the best of our knowledge, the previous investigation mainly focused on the first row elements, few studies with second row metals but yttrium have been performed in this reaction system. As is known, the metal Y

can usually be categorized as a lanthanum analogous metal because of its similar chemical properties. Therefore, the research on typical second row metal and aldehyde reactions has important theoretical and experimental significances. As is known to all, molybdenum is typical second row early transition metal. Can a similar reaction mechanism be applicable to the reactions of Mo and Y atoms with CH₃CHO? What are the different behaviours between them? Prompted by these questions, we investigated the reactions of Mo atom with CH₃CHO by using DFT methods in order to shed some light on these reactions. Although there is no experimental study reported on the reaction of Mo atom with CH₃CHO, a detail theoretical study on the reactions of Mo atom with CH₃CHO is interesting and important since molybdenum is a typical representative of the second row transition metal, the calculated results are expected to forecast further experimental findings and to give new suggestions that could not be reached experimentally under the considered conditions.

COMPUTATIONAL METHOD

The potential energy surface for the reaction of molybdenum and acetaldehyde has been considered in detail. All molecular geometries (reactants, intermediates, transition states and products) were optimized by employing the UB3LYP density functional theory method²¹. In all of our calculations,

the effective core potentials (ECP) of Stuttgart^{22,23} basis set was used for the molybdenum, the 5s and 4d in molybdenum were treated explicitly by a (8s 7p 6d) Gaussian basis set contracted to [6s 5p 3d]. For nonmetal atoms, a standardized 6-311++G** basis set was used. For all the species involved in the reaction, the enthalpies at 0 K is discussed in our study and this energy is used to construct Fig. 2. The harmonic vibration analyses were performed at the same level of theory for all optimized stationary points to determine their properties (minimum or first-order saddle point) and to evaluate the zero-point vibrational energies (ZPEs). To verify whether the located transition states connected the expected minima, intrinsic reaction coordinate (IRC) calculations were carried out for each transition state at the same level²⁴. All calculations in the present study were performed using the Gaussian 03 program²⁵.

RESULTS AND DISCUSSION

The relevant energies of various compounds in the reaction are listed in Table-1. The optimized geometries of the stationary points over the PESs for the title reaction are depicted in Fig. 1. The profiles of the PES are shown in Fig. 2. We also inspected the values of $\langle S^2 \rangle$ for all species involved in the reaction and found that the deviation of $\langle S^2 \rangle$ is less than 5 %. This shows that spin contamination is small in all the calculations.

TABLE-1
ENERGY OF VARIOUS COMPLEXES IN THE REACTION OF Mo ATOM WITH CH₃CHO (TOTAL ENERGY E_T, ZPE CORRECTIONS HAVE BEEN TAKEN INTO ACCOUNT, RELATIVE ENERGY E_R)

Species	E _T /Hartree	E _R (kcal mol ⁻¹)	Species	E _T /Hartree	E _R (kcal mol ⁻¹)	Species	E _T /Hartree	E _R (kcal mol ⁻¹)
⁵ Mo+CH ₃ CHO	-220.882702	0	³ Mo+CH ₃ CHO	-220.819396	39.7	¹ Mo+CH ₃ CHO	-220.765541	73.5
⁵ IM0	-220.925126	-26.6	³ IM0	-220.877897	3.0	¹ IM0	-220.873364	5.9
⁵ IM1	-220.964743	-51.5	³ IM1	-220.928465	-28.7	³ IM1	-220.891738	-5.7
⁵ IM2	-220.958483	-47.6	³ IM2	-220.952865	-44.0	¹ IM2	-220.916281	-21.1
⁵ IM3	-220.963173	-50.5	³ IM3	-220.955763	-45.8	¹ IM3	-220.910875	-17.7
⁵ IM4	-220.925590	-26.9	³ IM4	-220.963428	-50.7	¹ IM4	-220.944462	-38.8
⁵ IM5	-220.965494	-52.0	³ IM5	-220.993642	-69.6	¹ IM5	-220.989514	-67.0
⁵ IM6	-220.978006	-59.8	³ IM6	-220.975292	-58.1	¹ IM6	-220.990304	-67.5
⁵ IM7	-220.939103	-35.4	³ IM7	-220.945352	-39.3	¹ IM7	-220.919185	-22.9
⁵ IM8	-220.960682	-48.9	³ IM8	-220.997194	-71.8	¹ IM8	-220.987455	-65.7
⁵ IM9	-220.952067	-43.5	³ IM9	-220.957768	-47.1	¹ IM9	-220.926583	-27.5
⁵ TS ₀₁	-220.922363	-24.9	³ TS ₀₁	-220.872702	6.3	—	—	—
⁵ TS ₁₂	-220.920470	-23.7	³ TS ₁₂	-220.897292	-9.2	¹ TS ₁₂	-220.866325	10.3
⁵ TS ₁₃	-220.934814	-32.7	³ TS ₁₃	-220.915519	-20.6	¹ TS ₁₃	-220.888604	-3.7
⁵ TS ₁₄	-220.902341	-12.3	³ TS ₁₄	-220.878301	2.8	¹ TS ₁₄	-220.855953	16.8
⁵ TS ₁₉	-220.931186	-30.4	³ TS ₁₉	-220.919124	-22.9	¹ TS ₁₉	-220.890572	-4.9
⁵ TS ₂₅	-220.953253	-44.3	³ TS ₂₅	-220.933781	-32.1	¹ TS ₂₅	-220.904868	-13.9
⁵ TS ₃₇	-220.890042	-4.6	³ TS ₃₇	-220.876700	3.8	¹ TS ₃₇	-220.837591	28.3
⁵ TS ₄₈	-220.885844	-2.0	³ TS ₄₈	-220.893177	-6.6	¹ TS ₄₈	-220.878606	2.6
⁵ TS ₅₆	-220.947515	-40.7	³ TS ₅₆	-220.968574	-53.9	¹ TS ₅₆	-220.984608	-63.9
P1(⁵ HMoCH ₃ +CO)	-220.937141	-34.2	P1(³ HMoCH ₃ +CO)	-220.8868	-2.6	P1(¹ HMoCH ₃ +CO)	-220.861676	13.2
P2(⁵ MoCO+CH ₄)	-220.965152	-51.7	P2(³ MoCO+CH ₄)	-220.937105	-34.1	P2(¹ MoCO+CH ₄)	-220.92377	-25.8
P3(⁴ MoCOCH ₃ +H)	-220.855798	16.9	P3(² MoCOCH ₃ +H)	-220.861624	13.2	P3(² MoCOCH ₃ +H)	-220.861624	13.2
P4(⁵ MoCH ₂ CO+H ₂)	-220.927364	-28.0	—	—	—	—	—	—
P5(⁴ MoCH ₂ CHO+H)	-220.867166	9.7	P5(² MoCH ₂ CHO+H)	-220.844323	24.1	P5(² MoCH ₂ CHO+H)	-220.844323	24.1
P6(³ MoO+C ₂ H ₄)	-220.907245	-15.4	P6(³ MoO+C ₂ H ₄)	-220.89501	-7.7	P6(¹ MoO+C ₂ H ₄)	-220.867095	9.8

Fig. 1. (a) Optimized geometries for the various stationary points located on the $^5\text{Mo} + \text{CH}_3\text{CHO}$ potential energy surfaces [distances in angstroms]

Fig. 1. (b) Optimized geometries for the various stationary points located on the $^3\text{Mo} + \text{CH}_3\text{CHO}$ potential energy surfaces [distances in angstroms]

Fig. 1. (c) Optimized geometries for the various stationary points located on the $^1\text{Mo} + \text{CH}_3\text{CHO}$ potential energy surfaces [distances in angstroms]

Fig. 2. Potential energy surface profiles for the reaction of (a) $^5\text{Mo} + \text{CH}_3\text{CHO}$ (b) $^3\text{Mo} + \text{CH}_3\text{CHO}$ (c) $^1\text{Mo} + \text{CH}_3\text{CHO}$

From Fig. 2, we can see the reaction of molybdenum and acetaldehyde start with the formation of a CH_3CHO -metal encounter complex IM0. In IM0, the molybdenum atom bonds with the oxygen. As a result of oxygen polarizing charge toward

molybdenum, the C-O bond is weakened and is lengthened by 0.086, 0.084 and 0.06 Å in $^5\text{IM0}$, $^3\text{IM0}$ and $^1\text{IM0}$, respectively. Energetically, $^5\text{IM0}$ lies -26.6 kcal/mol lower than the separate reactants of $^5\text{Mo} + \text{CH}_3\text{CHO}$. For $^3\text{IM0}$ and $^1\text{IM0}$, they are computed to be 29.6 and 32.5 kcal/mol higher than the corresponding triplet initial complex $^5\text{IM0}$, respectively. It should be pointed out that although several trials were undertaken to search for possible transition states that connect reactants and IM0, no such transition states were obtained. Obviously, the formation of IM0 is a barrier-free exothermic reaction. IM0 stores relative high energy and it will isomerize into more stable structure IM1 by bonding between molybdenum and carbon atoms synchronously. IM1 is a $\eta^2\text{-CH}_3\text{CHO}$ -metal complex.

Once the IM1 is formed, four possible reaction pathways can be followed by C-C, aldehyde C-H, methyl C-H and C-O activation, which will be discussed over different PESs, respectively in the following text.

First, we will discuss the quintet PES. The first product generated from the reaction between Mo and CH_3CHO was P1. As shown in Fig. 2(a), starts with the encounter complex $^5\text{IM1}$, the Mo atom can insert into the C-C bond *via* a transition state $^5\text{TS}_{12}$. From Fig. 1(a), one can see the distance between two carbon atoms in $^5\text{TS}_{12}$ is lengthened from 1.504-1.807 Å. This indicates that the C-C bond is activated. The unique imaginary frequency is 434.0i cm^{-1} and the corresponding normal mode corresponds to the rupture of the C-C bond with the Mo atom inserted into it. For the inserted intermediate $^5\text{IM2}$, the ground state is $5A'$ with C1 symmetry and it is 47.6 kcal/mol more stable in energy than the ground state reactants $^5\text{Mo} + \text{CH}_3\text{CHO}$. As shown in Fig. 1(a), the C-C distance in $^5\text{IM2}$ is lengthened to 3.592 Å, which means that this bond has ruptured thoroughly. Along this reaction coordinate, the C-C bond activation is followed by a H-shift to form $^5\text{IM5}$, with an energy barrier of only 3.3 kcal/mol. From Fig. 2(a), one can see that *via* the transition state $^5\text{TS}_{25}$, there is an aldehyde H migration on to the Mo centre. In $^5\text{IM5}$, the Mo atom tricoordinates with CO, H and CH_3 group simultaneously, NBO analysis of this complex shows that the Mo atom interacts with all these three atoms and this species is 52 kcal/mol more stable than the ground reactants. The calculation shows that $^5\text{IM5}$ can decompose in a barrierless process to P1 ($^5\text{HMoCH}_3 + \text{CO}$) directly, requiring energy of 17.8 kcal/mol.

Alternatively, originating from $^5\text{IM5}$, the next metal-H migration may lead to the formation of complex $^5\text{IM6}$. In $^5\text{IM6}$, the methane moiety is coordinated to the Mo atom. The binding energy between CH_4 and $^5\text{MoCO}$ is calculated to be 8.1 kcal/mol. $^5\text{IM5}$ and $^5\text{IM6}$ are connected by the transition state $^5\text{TS}_{56}$. The relative energy of $^5\text{TS}_{56}$ to the ground reactants is -40.7 kcal/mol. In earlier theoretical studies on the gas-phase reactions of acetaldehyde with first-row transition metal cations (such as Cr^+ , Fe^+ , Co^+ , Ni^+), Guo *et al.*⁷⁻⁹ reported that the decarbonylation process leading to $\text{M}^+(\text{CO}) + \text{CH}_4$ is highly exothermic. Bayse *et al.*¹⁴ have examined the reaction between yttrium atom and CH_3CHO , both experimentally and theoretically. No $\text{Y}(\text{CO}) + \text{CH}_4$ species were observed and no feasible $\text{Y}(\text{CO}) + \text{CH}_4$ formation channel was determined in their studies. Though no relevant experimental researches on molybdenum with aldehyde are available, from the discussion above. It is found that all the species along this decarbonylation channel

are computed to be below the separated ground reactants ($^5\text{Mo} + \text{CH}_3\text{CHO}$), we propose even at low energies, these decarbonylation products can be observed in the reaction of Mo atom with acetaldehyde. So, compared with the metal yttrium, the molybdenum atom may capture methane from aldehyde more effectively.

With respect to the P4 ($^5\text{MoCOCH}_2 + \text{H}_2$) formation channel, one channel has been confirmed, which originate from aldehyde C-H bond activation. In this mechanism, the $^5\text{IM1}$ can interconvert to $^5\text{IM3}$ via $^5\text{TS13}$, over a barrier height of 18.8 kcal/mol. In $^5\text{IM3}$, the Mo atom inserted into the aldehyde C-H bond with the relative energy of -50.5 kcal/mol. The next step corresponds to the isomerization between $^5\text{IM3}$ and $^5\text{IM7}$ via $^5\text{TS37}$ directly, the relative energy of this transition state is -4.6 kcal/mol, which is 28.1 kcal/mol higher than that of the first step. Through this step, one methyl hydrogen atom is transferred toward the Mo atom and binds with the H atom that connects the metal centre, to form a H_2 molecule subsequently. From Fig. 2(a), one can see that the second step, *i.e.*, the process of $^5\text{IM7}$ formation is the rate determining step along this path.

In a previous study on the reaction of $\text{Y}(^2\text{D}) + \text{CH}_3\text{CHO}$, Bayse *et al.*¹⁴ have found the product channel for $\text{YCO} + \text{H}_2$ formation. From their calculation, one can see that this channel is of no importance, as the relative energy of the rate determining transition state is 6.6 kcal/mol, which is above the separated reactants. However, in the present study, the energies of this reaction channels are below 0.0 kcal/mol. Therefore, the H_2 elimination pathway is spontaneous in energy. From the above discussion, we can see that as representative of early second-row transition metals, the Mo is more effective in dehydrogenation of acetaldehyde than Y.

Another exit of $^5\text{IM3}$ is direct rupture of the H-MoCOCH₃ bond to give rise to the product P3 ($^2\text{H} + ^4\text{MoCOCH}_3$) and this dissociation process is computed to be endothermic by 67.4 kcal/mol. Compared with the P4 formation channels mentioned above, as the dissociation energy is too high than the methyl H-shift energy barriers (67.4 *versus* 46.9 kcal/mol), the possibility for $^2\text{H} + ^4\text{MoCOCH}_3$ formation originating from $^5\text{IM3}$ may be neglectable.

Now we will discuss the alternative C-H activation channel, which may lead to product P5 formation. It is very clear from Fig. 2(a) that this route pass through metal-mediated methyl H migration followed by the non-reactive-dissociation. Initial complexes $^5\text{IM1}$ and $^5\text{IM9}$ are connected through a direct, one-step methyl H shift occurring via saddle point $^5\text{TS19}$. Geometrically, the activation C-H bond is elongated to 1.535 Å, synchronously, the distance between molybdenum and hydrogen atoms is shortened to 1.792 Å. The imaginary frequency of $^3\text{TS19}$ is 946.8i cm^{-1} and the normal mode corresponds to the rupture of methyl C-H bond with the result of molybdenum binding with the H atom. One exit of $^5\text{IM9}$ is direct rupture of the H-MoCH₂CHO bond to account for the products $^2\text{H} + ^4\text{MoCH}_2\text{CHO}$, but this is a greatly endothermic process with the dissociation energy of 53.2 kcal/mol.

Previous studies of M (or M^+) + CH_3CHO mainly focused on the C-C or C-H activation reaction, which may lead to formation of $\text{HMCH}_3 + \text{CO}$ or $\text{MCH}_2\text{CO} + \text{H}_2$. In the present study, we also explored the possibility of aldehyde C-O bond

activation mechanism. Present results predict that C_2H_4 elimination through aldehyde C-O bond activation is also a possible reaction channel. Originating from $^5\text{IM1}$, the C-O bond activation species, $^5\text{IM4}$, can be formed by the insertion of Mo atom into the aldehyde C-O bond. Energetically, the transition state ($^5\text{TS14}$) is calculated to be -12.3 kcal/mol below the energies of the ground reactants. Compared with the PESs of the C-C and C-H activation routes as discussed above, we found that the aldehyde C-O activation is most unfavorable. Subsequently, the direct, one-step H shift occurring via saddle point $^5\text{TS48}$ may yield a complex $^5\text{IM8}$. This step can release a large amount of energy (22.0 kcal/mol). As the energy of rate determine step is still under reactants, this channel is also spontaneous. From Fig. 1(a), one can see that in $^5\text{IM8}$, there exist interactions between ethene and ^5MoO and this complex can dissociate without energy-barrier to product P6 ($\text{C}_2\text{H}_4 + ^5\text{MoO}$), endothermic by 33.5 kcal/mol. In the previous study on the reaction between yttrium atom and aldehyde¹⁴, no C_2H_4 and YO species were detected and no feasible $\text{C}_2\text{H}_4 + \text{YO}$ formation channel was determined theoretically. Obviously, in the reaction between Mo and CH_3CHO , the aldehyde C-O activation is also feasible.

Similar with that on the quintet PES, we also explored possible activation mechanism on the triplet and singlet ones. As shown in Figs. 1 and 2, the reaction mechanism over these two PESs are in general similar with that of the quintet one. The reaction starts with a CH_3CHO -metal complex followed by four possible pathways: C-C, aldehyde C-H, methyl C-H and C-O activation. Comparing all the channels shown in Fig. 2, it is clear that only P1 and P2 formation mechanisms are spontaneous in energy over triplet PES. For the reaction over singlet one, no products can form spontaneously. In addition, over both these two PESs, no feasible H_2 formation channel is determined, this is quite different from that of the quintet surface.

From Fig. 2, one can see $^3\text{IM8}$ is the lowest point over the PES of present reaction, with the relative energy of only -71.8 kcal/mol. But as can be seen from the C-O bond activation pathway, only after past TS14 , all the complexes except dissociation product P6 involved in the reaction over the triplet PES, lie below the analogues on the quintet one. Obviously, after TS14 formation, the triplet pathways may energetically preferred with respect to the corresponding quintet routes. In addition, as the transition state $^5\text{TS14}$ is calculated to be 15.1 kcal/mol more stable than triplet analogues (Fig. 2), while the C-O activation species $^3\text{IM4}$ is 23.8 kcal/mol more stable than the quintet one, we can speculate that the intersystem triplet-quintet crossing occurs during the process of $^5\text{TS14} \rightarrow ^3\text{IM4}$. The aim of our following calculation is to determine the region where the spin inversion occurs and to acquire the structure and energy of crossing point between the two different potential energy surfaces.

We choose an approach suggested by Yoshizawa *et al.*²⁶, for approximately locating the crossing points of two PESs of different multiplicities. Along the energy curve, we find a crossing point CP1 with energy of -220.9623 Hartree. Therefore, the reaction may jump from the quintet PES to the triplet one near the crossing point CP1. As can be seen from Fig. 3(a), after passing point CP1, the triplet PES can provide a low-energy

Fig. 3. (a) Potential energies from ${}^5\text{TS}_{14}$ to ${}^3\text{IM4}$ along the quintet IRC Fig. 3. (b) Potential energies from ${}^3\text{IM8}$ to P6 along the triplet IRC

reaction pathway toward the species ${}^3\text{IM8}$. As the products ${}^5\text{MoO} + \text{C}_2\text{H}_4$ dissociation from ${}^5\text{IM8}$ is lower about 7.7 kcal/mol than that of ${}^3\text{MoO} + \text{C}_2\text{H}_4$ which dissociation from ${}^3\text{IM8}$, obviously, another crossing point CP2 exists in the process of IM8 dissociation. Then we define the distance between Mo and the center (X) of C-C bond as a function, which is depicted in Fig. 3(b). For a given Mo-X bond length, all other geometrical degrees of freedom are optimized for each spin. Along the energy curve, we find a crossing point CP2, which is at the length of Mo-X bond 2.960 Å with energy of -220.9655 Hartree. Therefore, the reaction may jump from the triplet PES to the quintet one near the crossing point CP2. To conclude, the minimum energy pathway of C-O bond activation may proceed as ${}^5\text{Mo} + \text{CH}_3\text{CHO} \rightarrow {}^5\text{IM0} \rightarrow {}^5\text{TS}_{01} \rightarrow {}^5\text{IM1} \rightarrow {}^5\text{TS}_{14} \rightarrow \text{CP1} \rightarrow {}^3\text{IM4} \rightarrow {}^3\text{TS}_{48} \rightarrow {}^3\text{IM8} \rightarrow \text{CP2} \rightarrow {}^5\text{MoO} + \text{C}_2\text{H}_4$, which is calculated to be exothermic by -15.4 kcal/mol. Obviously, due to the existence of the crossing points, both the formations of lowest point (${}^3\text{IM8}$) over the PESs of title reaction and the C-C activation products (${}^5\text{MoO} + \text{C}_2\text{H}_4$) are spontaneous in energy. Actually, the reactions catalyzed by metallic systems may often involve a change in the spin states and proceed *via* a non-adiabatic way on two or more potential energy surfaces, denoted as "two state reactivity" (TSR)²⁷⁻³⁰, which has been confirmed by experimental studies.

Conclusion

In the present study, the reaction mechanisms between Mo atom and CH_3CHO have been investigated over three different PESs. Originating from the intermediate complex ${}^5\text{IM1}$, initial C-C bond insertion may lead to two decarbonylation products ${}^5\text{HMoCH}_3 + \text{CO}$ and ${}^5\text{MoCO} + \text{CH}_4$. Our calculations confirm two channels for C-H bond activation, initial aldehyde C-H insertion or direct methyl H shift to the molybdenum centre. But the reaction occurs through molybdenum insertion into aldehyde C-H, followed by a methyl H-shift that yields $\text{MoCH}_2\text{CO} + \text{H}_2$ is more feasible. Also, the initial aldehyde C-O activation pathway can lead to formation of $\text{C}_2\text{H}_4 + \text{MoO}$, serving as a minor channel because of the relatively high energy barrier compared with the C-C and C-H insertion reactions.

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