DFT study on the reaction of La (2D) with CH₃CHO

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The reaction mechanism of the ground state (2D) La atom with CH₃CHO has been studied in detail by density functional theory. All the stationary points have been determined at the UB3LYP/ECP/6-311+G** level of theory. Single point UCCSD(T)/ECP/6-311+G** calculations have been used to get accurate values of energies. The titled reaction starts with the formation of a La(CH₃CHO)metal complex followed by C−C, C−O, aldehyde C−H and methyl C−H activation. These reactions can lead to four products, i.e., LaCO+CH₄, HLaCH₃+CO, LaO+C₂H₆ and LaCH₂CO+H₂. As the energies of the intermediates, transition states and products involved in the reaction lie below those of the reactants, La(CH₃CHO), (except TS₂, only 0.18 kcal/mol relative to the reactants), the reaction between La(2D) and CH₃CHO is expected to occur spontaneously over the doublet potential energy surface. The present results may be helpful in understanding the mechanism of the titled reaction and further experimental investigation of the reaction.

Keywords: Theoretical chemistry, Density functional calculations, Potential energy surfaces, Reaction mechanisms, Lanthanum, Acetaldehyde

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 research due to its great importance in catalytic and material science. To better understand the fundamental aspects of this reaction, several studies have been reported on the investigation of the relevant mechanism. As one of the simple carbonyl-containing organic molecule, acetaldehyde is used in many practical application fields such as organic synthesis, catalysis, etc. Since catalytic hydrogenation of carbon monoxide as well as C−H activation of aldehyde is usually promoted by metal-bearing catalysts, it is interesting and instructive to explore the reactions of gas-phase transition metal ions and atoms with aldehyde, which may lead to a better understanding of fundamental aspects of elementary transition metal reactions initiated by C−H insertion. Earlier studies have focused mainly on the reactions between acetaldehyde and first row transition metal cations such as Co⁺, Fe⁺, Cr⁺, Ni⁺, etc. Some experimental techniques such as ion beam mass spectrometry and crossed-beam methods, have revealed that decarbonylation of acetaldehyde to yield CH₄+MCO⁺ is a dominant process at low energy condition. Based on these experiments, Guo et al. have theoretically investigated the gas-phase reaction of Co⁺, Fe⁺, Cr⁺ and Ni⁺ with CH₃CHO to study the corresponding mechanism. Their results show that for Co⁺, Fe⁺ and Cr⁺, 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 ion, larger sized metal ions have received relatively less attention, and only a few theoretical and experimental studies have been reported. Bayse et al. have investigated the reaction between yttrium atom and acetaldehyde in detail. Their DFT calculations based on crossed molecular beams experiments predict 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 in the reaction of the first row transition metal with CH₃CHO.

From the previous experimental and theoretical studies on the decarbonylation of acetaldehyde by first row ions and the larger transition metal Y, it is clear that the change in transition metal from first row to metal Y leads to change in reaction mechanism, both in early and late reaction stages. As is known, the metal Y can usually be categorized as a lanthanum analogous metal because of its similar chemical properties with those of the lanthanum metals. To the best of our knowledge, no studies has been carried out with typical lanthanum metal such as La in this reaction system. To know if the reaction mechanism of Y atom with CH₃CHO can be applicable to lanthanum atom such as the representative La, or if different behaviour can be observed in the reaction of La atom with CH₃CHO, it was thought worthwhile to investigate in detail the reaction of La atom with
CH$_3$CHO using DFT methods. We expected to observe difference in catalytic behaviour due to the larger size of the lanthanum atoms.

**Methodology**

The potential energy surface for the titled reaction has been considered in detail. All molecular geometries (reactants, intermediates, transition states and products) were optimized by employing the UB3LYP density functional theory method$^{22}$. In all calculations, the basis set used consisted of the quasirelativistic effective core potential (ECP) of Stuttgart group on La, the 5s, 5p, 5d and 6d in La were treated explicitly by a (7s6p5d) Gaussian basis set contracted to (5s4p3d)$^{23,24}$. For nonmetal atoms, a standardized 6–311+G** basis set was used. 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 level$^{25}$. To obtain an accurate evaluation of the energy, single point coupled-cluster calculations were performed using the UB3LYP structures. All calculations in the present study were performed using the Gaussian 03 program$^{26}$.

**Results and discussion**

The optimized geometries of the stationary points over the PES for the titled reaction are depicted in Fig. 1. The profiles of the PES are shown in Fig. 2. We also inspected the values of $<S^2>$ for all species involved in the reaction, and found that the deviation of $<S^2>$ is less than 5%. This suggests that spin contamination is small in all the calculations.

The first product generated from the reaction between La (3D) and CH$_3$CHO was LaCO+CH$_4$ (P1). Three different channels are confirmed by calculations, which can lead to formation of P1. As shown in Fig. 2, the first reaction channel starts with the formation of an intermediate complex IM1 (1A'), which is ~48.10 kcal/mol below the energy of the reactants, La(2D) + CH$_3$CHO (0.0 kcal/mol). From Fig. 1, one can see that in IM1, the La atom bonds with the carbon and oxygen simultaneously. As a result of oxygen polarizing charge toward La, the C–O bond is weakened, and is lengthened by 0.321 Å. It should be pointed out that although several trials were undertaken to search for possible transition states that connect reactants and IM1, no such transition states were obtained. Obviously, the formation of IM1 is a barrier-free exothermic reaction. IM1 can rearrange to form IM2, which undergoes a rupture of C–C bond via a transition state TS$_{12}$ that is 29.83 kcal/mol above the energy of IM1. From Fig. 1, one can see the distance between two carbon atoms in TS$_{12}$ is lengthened from 1.51Å to 2.108 Å. This suggests that the C–C bond is activated. The unique imaginary frequency is 352.3i cm$^{-1}$, and the corresponding normal mode corresponds to the rupture of the C–C bond with the La atom inserted into it. For the inserted intermediate IM2, the ground state is 1A' with $C_1$ symmetry, and it is 10.84 kcal/mol above the energy of intermediate complex IM1 and 37.26 kcal/mol more stable in energy than the reactants. As shown in Fig. 1, the C–C bond length in IM2 is lengthened to 3.74 Å, which means that this bond has ruptured thoroughly. The two calculated La–C bonds and one La–O bond are 2.497 Å, 2.460 Å, and 2.428 Å respectively, suggesting that the La atom interacts with all these three atoms. Along the reaction coordinate, the C–C bond activation is followed by a H-shift to form IM3, with an energy loss of 15.03 kcal/mol. From Fig. 2, one can see that via the transition state TS$_{23}$, there is an aldehyde H migration on to the La centre. In IM3, the La atom tricoordinates with CO, H and CH$_3$ group simultaneously, and this species is 40.19 kcal/mol more stable than the reactants. The results shows that IM3 can decompose in a barrierless process to P1(HLaCH$_3$+CO) directly, requiring an energy of 5.35 kcal/mol.

Alternatively, originating from IM3, the next metal-H migration may lead to the formation of product P2. In P2, the methane moiety is coordinated to the La atom. The binding energy between CH$_4$ and LaCO is calculated to be 5.25 kcal/mol. IM3 and P2 are connected by the transition state TS$_{3P2}$. The relative energy of TS$_{3P2}$ to the reactants is 0.18 kcal/mol, which is a little higher than that of the reactants (0.0kcal/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 this analogous metal-H migration transition state typically occurs early, and the decarbonylation process leading to M$(^+$(CO)+CH$_4$ is highly exothermic. Bayse et al.$^{14}$ have examined the reaction between yttrium atom and CH$_3$CHO, both
Fig. 1 – Optimized geometries for various stationary points located on La+CH₃CHO potential energy surfaces. (distances in Å, angles in °).
experimentally and theoretically. No Y(CO)+CH$_4$ species were observed, and no feasible Y(CO)+CH$_4$ formation channel was determined in their studies. Though no relevant experimental researches on lanthanum with aldehyde are available, from the discussion above, we propose that compared to the P1 formation channel, P2 formation is not competitive, and thus there may be no formation of La(CO)+CH$_4$.

As compared to the first row metals, the larger metal atoms of the second and third rows can not effectively capture methane from aldehyde. Figure 2 suggests that there are two other pathways for the P2 formation, i.e., R→IM1→TS$_{14}$→IM4→TS$_{43}$→IM3→TS$_{3P2}$→P2 and R→IM1→TS$_{15}$→IM5→TS$_{56}$→IM6→TS$_{64}$→IM4→TS$_{43}$→IM3→TS$_{3P2}$→P2. These two mechanisms originate from aldehyde C−H and methyl C−H activations, respectively. As the H-shift energy barrier (TS$_{3P2}$) is too high (40.37 kJ/mol), the possibility for P2 formation originating from IM3 may be neglectable. Obviously, the C−C bond activation followed by an aldehyde H-shift is the dominant channel of P1 (HLaCH$_3$+CO) formation, which is similar to the reaction of ground state Y($^2$D) and CH$_3$CHO.$^{14}$

With respect to the P3(LaCH$_2$CO+H$_2$) formation channel, two main channels have been confirmed, which originate from different C−H bond activations, i.e., the aldehyde C−H and methyl C−H activations respectively. In the former, the IM1 can interconvert to IM4 via TS$_{14}$, over a barrier height of 19.67 kcal/mol. In IM4, the La atom is inserted into the aldehyde C−H bond with the relative energy of -39.06 kcal/mol. The next step corresponds to the isomerization between IM4 and P3 via TS$_{4P3}$; the relative energy of this transition state is -17.27 kcal/mol, which is 11.16 kcal/mol higher than that of the first step. Through this step, one methyl hydrogen atom is transferred towards the La atom,
and binds with the H atom that connects the metal centre, to form a H2 molecule subsequently. From Fig. 2, one can see that the second step, i.e., the process of P3 formation is the rate determining step along this path.

Considering the alternative P3 formation, which also originates from IM1, one can see that the second pathway of P3 formation is completed by two steps (Fig. 2). In contrary to the case of the first pathway of P3 formation, the first step in this mechanism is a methyl C–H activation reaction. The La centre captures one methyl H atom via TS15, with an energy barrier of 15.58 kcal/mol, which is lower by 4.09 kcal/mol than that of the aldehyde C–H activation step (TS14) in the previous mechanism. According to the exponential law of reaction rate \( \dot{c} = \text{exp}(-E/RT) \), the reaction rate from TS15 is approximately 1.0x10^3 times as fast as that from TS14 at room temperature. In addition, from Fig. 2, one can see the rate determining step along this branch, i.e., the aldehyde H atom transfer to form H2 via TS25, is also calculated to be lower than the analogous rate determining step (TS35) by 4.54 kcal/mol. Clearly, starting from the intermediate complex IM1, the second reaction channel which leads to P3LaCH2CO+H2 formation through methyl C–H activation and the aldehyde C–H activation is the dominant channel.

In a previous study on the reaction of Y(D)+CH3CHO, Bayse et al.14 have found two product channels for YCO+H2 formation, which originated from aldehyde C–H and methyl C–H activation respectively. From their calculation, one can see that the first channel is of no importance, as the relative energy of the rate determining transition state is 6.61 kcal/mol. However, in the present study, the energies of both reaction PESs were below 0.0 kcal/mol. Therefore, both the H2 elimination pathways were spontaneous. From the above discussion, we can see that as representative of early transition metals, the typical lanthanum (such as La) is more effective in dehydrogenation from acetaldehyde than the analogous lanthanum (such as Y).

Previous studies of M (or M+) +CH3CHO focused only on the C–C or C–H activation reaction, which may lead to formation of HMCH2+CO or MCH2CO+H2. In the present study, we also explored the possibility of aldehyde C–O bond activation mechanism. Our results predict that C2H4 elimination through aldehyde C–O bond activation is also a possible reaction channel.

Originating from IM1, the C–O bond activation species, IM7, can be formed by the insertion of La atom into the aldehyde C–O bond. Energetically, the transition state (TS17) is calculated to be -17.78 kcal/mol below the energies of the reactants. However, 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 not very favorable. Subsequently, the direct, one-step H shift occurring via saddle point TS7p4 may yield a product P4. This step can release a large amount of energy (20.41 kcal/mol). Obviously, the product P4 is the lowest point along the PES of the titled reaction step. However, when compared with the first step, we can see that the second step of this mechanism, i.e., IM7→P4 isomerization process, requires a high activation energy of 32.75 kcal/mol. Therefore, this channel is of no importance and cannot compete with the reaction of P1 or P3 formation. From Fig. 1, one can see that there exist weak interactions between ethene and LaO. The calculated binding energy of C2H4-LaO is 9.1 kcal/mol. The entire reaction, La+CH3CHO→C2H4+LaO, is exothermic by 65.61 kcal/mol. In the previous study on the reaction between yttrium atom and aldehyde14, no C2H4 and YO species were detected, and no C2H4+YO formation channel was observed theoretically. Obviously, in both reactions, the aldehyde C–O activation is not competitive as compared with C–C and C–H insertion.

In the present study, four main reactive pathways have been proposed for the title reaction, based on DFT studies. Originating from the intermediate complex IM1, initial C–C insertion may lead to two decarbonylation products, LaCO+CH4 and HLACH2+CO. Comparison between the two different channels yields products P1 and P2. The rate determining step of the first pathway has a higher energy barrier (40.37 kcal/mol relative to IM3), and hence during the C–C activation, the second pathway which leads to HLACH2+CO formation is expected to be the major pathway. This is different from reactions of the first row metal ions, as reported before. Our calculations confirm two channels to LaCH2CO+H2 formation. The reaction occurs through La insertion into aldehyde C–H (or methyl C–H), followed by a methyl H-shift (or aldehyde H-shift) that yields LaCH2CO+H2. On comparing the rate determining step of these two different dehydrogenation mechanisms, the first one is found to be more
favorable energetically. Also, the aldehyde C−O activation pathway can lead to formation of C$_2$H$_4$+LaO, serving as a minor channel because of the large energy barrier as compared with the C−C and C−H insertion reactions.

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References