Gas phase reactions of La$^+$ with acetone: A density functional theory investigation

Gui-hua Chen$^*$ & Danxia Liang
School of Pharmaceutical and Chemical Engineering, Taizhou University, Linhai, 317000, PR China
Email: chenguihua518@hotmail.com

Received 20 September 2011; revised and accepted 10 April 2012

The gas phase reaction of La$^+$ cation with acetone is investigated using density functional theory. Both ground and excited state potential energy surfaces are investigated in detail. The present results show that the title reaction starts with the formation of an O-attached complex (IM0). All possible pathways starting with C−O, C−H, and C−C activation have been searched. These reactions can lead to four different products, (1)LaO$^+$+C$_2$H$_6$, (2)LaCH$_3$COCH$_3$+H, (3)LaCOCH$_3$+CH$_4$ and (4)LaCH$_3$+CH$_3$CHO. The minimum energy reaction path is found to involve spin inversion after IM0 formation, and this potential energy curve-crossing dramatically affects the reaction exothermic. As all the triplet intermediates, transition states and products involved in the reaction lie below the ground reactants ($^2$La$^+$ + CH$_3$COCH$_3$) after IM0 formation, the reaction is expected to occur spontaneously over the singlet potential energy surface. The present results may be helpful in understanding the mechanism of the title reaction and further experimental investigation of the reaction.

Keywords: Theoretical chemistry, Density functional calculations, Gas phase reactions, Potential energy surfaces, Acetone, Lanthanum

Due to their great importance in catalytic and material science$^{1-6}$, transition metal ions and their oxides have been widely used in many industrial processes. The gas phase reactions of transition metal atoms and ions with small organic molecules have aroused considerable attention; many studies have been reported on the investigation of the relevant mechanism$^{7,29-32}$. Gas phase reactions offer a unique possibility to probe the intrinsic properties of reactive organometallic species. The details of the activation of C−H, C−C and C−O bonds in the initial steps are of fundamental interest in catalysis. As one of the most important industrial synthetic raw materials, acetone is of particular interest in understanding C−H, C−C and C−O bonds activation in small hydrocarbons by transition metal atoms and ions, hence in the past several years, the reactions of metal cations with acetone have been extensively studied$^{15,28-32}$. Experimentally, it has been shown that the early transition metal cations such as Sc$^+$ and Ti$^+$ can react readily with acetone to give MO$^+$ and C$_2$H$_6$ as products, while for the later transition metal cations, such as Fe$^+$, Co$^+$ and Ni$^+$, the reaction gives completely different products, i.e., MCO$^+$ and C$_2$H$_6$. Chen et al.$^{28}$ have reported the potential energy surfaces of the gas phase reaction of Ni$^+$ with acetone. Their theoretical study rationalizes experimental findings and gives a deeper insight to the reaction mechanism, leading to the loss of C$_2$H$_6$ and CO. For the reaction between early transition metal ion with acetone, Kim et al.$^{29}$ investigated the detailed reaction mechanism of Ti$^+$ towards acetone, and the most favorable reaction pathway leads to the formation of MO$^+$ and C$_2$H$_6$, which is quite different from that of Ni$^+$ with acetone. From the discussion above, one can see that the earlier studies focused mainly on the reactions between acetone and first row transition metal cations such as Co$^+$, Fe$^+$, Cr$^+$, Ti$^+$, Ni$^+$, etc.$^{28-32}$. The heavier metal atoms and cations have received relatively less attention, and only a few theoretical and experimental studies have been reported$^{15}$. Bayse et al.$^{15}$ have investigated the reaction between yttrium atom and acetone in detail. Their studies based on crossed molecular beams experiments predict CO elimination to be the most feasible channel. It may be noted that in their study no YO+C$_2$H$_6$ products channel was observed, which is quite different from the observations of reaction of the first row transition metal with acetone.

From the previous experimental and theoretical studies$^{15,28-32}$ on the reactions between acetone and first row cations or the larger transition metal Y, it is clear that the change from first row transition metal to metal Y leads to change in reaction mechanism, both in the early and late stages of the reaction. Studies on typical lanthanoids and acetone reactions has
important theoretical and experimental experiments. To the best of our knowledge, few studies with typical lanthanoid elements have been performed in this reaction system. It is thus of interest to know if the mechanism of the reaction of lanthanum, a typical lanthanide, with acetone is similar to that of first or second row early transition metal with acetone. We have investigated the reactions of La$^+$ cation with acetone by using DFT methods. This is important since there is no experimental study reported on the reaction of La$^+$ cation with acetone. The present work is expected to predict further experimental findings that could not be reached experimentally under the considered conditions.

Methodology
The potential energy surface for the title 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$^{33}$. In all the calculations, the basis set used consisted of the quasi relativistic effective core potential (ECP) of Stuttgart on La. The 5$d$ and 6$s$ in La were treated explicitly by a (7$s$6$p$5$d$) Gaussian basis set contracted to (5$s$4$p$3$d$)$^{34}$. For nonmetal atoms, a standardized 6–311++G** basis set was used. For all the species involved in the reaction, the enthalpy at 0 K is discussed in the present study, and this energy is used to construct the profiles of the PES. Harmonic vibration analyses were performed at the same level of theory for all the optimized stationary points to determine their properties (minimum or first order saddle point) and to evaluate the zero point vibrational energies (ZPEs). To verify whether the located transition states connected the expected minima, intrinsic reaction coordinate (IRC) calculations were carried out for each transition state at the same level$^{35}$. All calculations in the present study were performed using the Gaussian 03 program$^{36}$.

Results and Discussion
The optimized geometries of the stationary points over the PESs for the title reaction are depicted in Fig. 1 and 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 shows that spin contamination is small in all the calculations.

As shown in Fig. 2, the title reaction starts with the formation of an O-attached complex (IM0). From Fig. 1, one can see that in $^1$IM0 or $^1$IM0, the lanthanum cation bonds with the oxygen, with the La–O distance being 2.223 (triplet) and 2.247 (singlet) Å. Owing to electron donation from the oxygen lone pair orbitals to the La center, the C–O bond is weakened, and is lengthened by 0.087 and 0.058 Å in $^1$IM0 and $^1$IM0 respectively. The weakened C–O bonds are expected to be easily activated by the metal atom to produce different products. Energetically, $^1$IM0 is -48.93 kcal/mol lower than $^3$La$^+$ + CH$_3$COCH$_3$. For $^1$IM0, it is computed to be 8.04 kcal/mol higher in energy than the corresponding triplet initial complex $^3$IM0. It should be pointed out that although several trials were undertaken to search for possible transition states that connect the reactants and IM0, no such transition states were obtained. Obviously, the formation of IM0 is a barrier-free exothermic reaction. Starting from IM0, the oxidative addition of acetone toward the La$^+$ cation accounts for IM1 formation which stabilizes the system by 13.62 kcal/mol over singlet PES, while the analogue in triplet is 4.54 kcal/mol higher than $^1$IM0. Obviously, the intersystem crossing occurs between IM0 and IM1. From Fig. 1, one can see that IM1 is a $^1$-CH$_3$COCH$_3$-metal encounter complex with the lanthanum cation binding with the carbon and oxygen simultaneously. The electron donation from the oxygen lone pair orbitals to the lanthanum center stretches the C–O bond of carbonyl in acetone and thus weakens this bond. Once the encounter complex IM1 is formed, three reaction pathways are possible, i. e., C–O, C–H, and C–C bonds activation, each of which will be discussed in detail over singlet and triplet PESs.

First, we will discuss the singlet PES. The first product generated from the reaction between lanthanum cation and acetone is P1($^1$LaO$^+$+C$_3$H$_6$). As shown in Fig. 2, this reaction channel starts with the formation of the $^1$-CH$_3$COCH$_3$-metal complex $^1$IM1. Along this reaction pathway, the lanthanum cation can insert into the C–O bond via a transition state $^3$TS$_{12}$ with the energy barrier of 18.88 kcal/mol. From Fig. 1, one can see that the distance between the carbon and oxygen atoms in carbonyl in $^3$TS$_{12}$ is lengthened from 1.451 to 2.724 Å, which indicates that the C–O bond is activated. The corresponding normal mode of imaginary frequency corresponds to the rupture of the C–O bond with the La cation being inserted into it. The C–O bond activation intermediate $^1$IM2 is 36.58 kcal/mol more stable in energy than $^3$La$^+$ + CH$_3$COCH$_3$. As shown in Fig. 1,
Fig. 1—Optimized geometries for the various stationary points located on the La⁺+CH₃COCH₃ potential energy surfaces (distances in angstroms).
the C−O distance in \(^1\text{IM2}\) is lengthened to 2.875 Å, which means that this bond has ruptured thoroughly. The calculated La−C and La−O bonds are 2.658 and 2.875 Å respectively. Along this reaction coordinate, the C−O bond activation is followed by a H-shift to form \(^1\text{IM3}\), with an energy barrier of 10.35 kcal/mol. From Fig. 1, one can see that via the transition state \(^1\text{TS}_{23}\), there is a methyl H migration to the middle carbon centre. In the structure of \(^1\text{IM3}\), the La cation is weakly coordinated to two carbon atoms of CH\(_3\)CHCH\(_2\) simultaneously. This intermediate is determined to be the deepest energy well along the reaction coordinate, lying 76.04 kcal/mol below the ground reactants. In \(^1\text{IM3}\), the geometry parameters of the CH\(_3\)CHCH\(_2\) unit are similar to those of propene except for the C=C bond, which is a little longer than the one in propene (1.345 vs 1.331 Å). NBO analysis indicates that there exists a strong interaction between the 5d orbital of lanthanum and the π* orbital of C=C bond, which can account for the high dissociation energy of 18.66 kcal/mol between \(^1\text{LaO}^+\) and C\(_3\)H\(_6\) in \(^1\text{IM3}\). From Fig. 2, the reaction energy of the \(^3\text{La}^+\text{CH}_3\text{COCH}_3 \rightarrow ^1\text{LaO}^+\text{C}_3\text{H}_6\) reaction is calculated to be -57.38 kcal/mol at the chosen level. In addition, as all the critical points along this C−O bond activation pathway are below the reactants, obviously the reaction leading to \(^1\text{LaO}^+\text{C}_3\text{H}_6\) formation is spontaneous and a highly exothermic process. Davis et al.\(^{15}\) have examined the reaction between yttrium atom and CH\(_3\)COCH\(_3\), both experimentally and theoretically. They did not observe any YO+C\(_3\)H\(_6\) species, or YO+C\(_3\)H\(_6\) formation channel. Though no relevant experimental studies on reaction of lanthanum with acetone are available, from the discussion above we propose that even at low energies the MO\(^+\)C\(_3\)H\(_6\) products can be observed in the reaction of lanthanum cation with acetone. As is known, the metal Y can usually be categorized as a lanthanide analogous metal because of chemical properties similar to these of the lanthanides. From the above discussion, we can see that as representative of early transition metals, the typical lanthanide (such as La) is more effective in capturing propene from acetone than the analogous lanthanide (such as Y). Obviously, the reaction mechanism of Y atom with CH\(_3\)COCH\(_3\) can not be applicable to lanthanides such as the representative La.

Now we will discuss the C−H bond activation channel, which may lead to product P2 (\(^1\text{LaCH}_3\text{COCH}_3\)H) formation. It is very clear from Fig. 2 that this route also starts with the formation of η\(^3\)-CH\(_3\)COCH\(_3\)-metal encounter complex, \(^1\text{IM1}\). Along the reaction channel, the next step corresponds to the metal-mediated methyl H migration followed by the non-reactive-dissociation. \(^1\text{IM1}\) and \(^1\text{IM6}\) are connected through a direct, one-step methyl C−H activation occurring via saddle point \(^1\text{TS}_{16}\). Geometrically, the activation C−H bond is elongated to 1.613 Å and synchronously the distance between lanthanum and hydrogen atoms is shortened to 2.132 Å. The imaginary frequency of \(^1\text{TS}_{16}\) is 973.8i cm\(^{-1}\), and the normal mode corresponds to the rupture of methyl C−H bond with the lanthanum cation binding with the H atom. One dissociation channel of \(^1\text{IM6}\) is direct rupture of the H−La bond to account for the product P2 (\(^1\text{LaCH}_3\text{COCH}_3\)H). However, this is a highly endothermic process with dissociation energy of 61.72 kcal/mol. In addition, as the rate determining step (\(^1\text{TS}_{16}\)) along this channel is very low in energy, we propose that the species, \(^1\text{IM6}\), is rather abundant in title reaction.

With respect to the C−C bond activation mechanism, one possible channel has been confirmed, which may lead to formation of P3 (\(^1\text{LaCOCH}_3\)H). Originating from \(^1\text{IM1}\), the C−C bond activation species, \(^1\text{IM4}\), can be formed by the...
insertion of La cation into the C–C bond. Energetically, the transition state \( ^1\text{TS}_{1\text{d}} \) is calculated to be -34.80 kcal/mol below the energies of the ground reactants. Compared with the PESs of the C–O and C–H activation routes as discussed above, we found that the C–C activation is most unfavorable due to the relatively high energy barrier. As shown in Fig. 1, the C–C bond in \( ^1\text{IM4} \) is ruptured thoroughly; the two calculated La–C bonds and one La–O bond are 2.458, 2.418, and 2.367 Å respectively. Subsequently, originated from this C–C bond activation species, \( ^1\text{IM4} \), the methyl-H shift could convert it into \( ^1\text{IM7} \), over a barrier height of 32.41 kcal/mol. Through this step, the methyl hydrogen atom is transferred toward the other terminal methyl group, to form a CH\(_4\) molecule subsequently. From Fig. 2, one can see that the second step, i.e., the process of \( ^1\text{IM7} \) formation is the rate-determining one along this path. In \( ^1\text{IM7} \), the methane moiety is \( ^1\text{η}^2 \) coordinated to the La cation. The binding energy between CH\(_4\) and \( ^1\text{LaCOCH}_2^+ \) is calculated to be 7.98 kcal/mol. Obviously, from Fig. 2, one can see that this CH\(_4\) loss channel, \( ^1\text{La}^+ + \text{CH}_3\text{COCH}_3 \rightarrow ^1\text{LaCOCH}_2^+ + \text{CH}_4 \), is also spontaneous in energy, and highly exothermic by 38.17 kcal/mol. In earlier theoretical studies on the gas phase reactions of acetone with first-row transition metal cations and some second-row transition metal atom (such as Ti\(^+\), Ni\(^+\) and Y\(^+\))\(^{15,28,29}\), no feasible channel for formation of M(COCH\(_3\))CH\(_4\) was determined. Though no experimental researches on lanthanum with acetone are available, from the discussion above, we found all the species along this decarbonylation channel are computed to be below \( ^3\text{La}^+ + \text{CH}_3\text{COCH}_3 \). We propose that even at low energies, these decarbonylation products can be observed in the reaction of lanthanum cation with acetone. So, compared with the metals, Ti\(^+\), Ni\(^+\) and yttrium, the lanthanum cation may capture methane from acetone more effectively.

Alternatively, the direct one-step H shift occurring via saddle point \( ^1\text{TS}_{1\text{d}} \) may yield the complex \( ^1\text{IM5} \). A striking feature of this new intermediate is the dicoordination of La cation with the aldehyde and methylene group. It should be pointed out such a minimum was not observed in the previous studies of M (or M\(^+\), M = Ti, Ni, and Y) + CH\(_3\)COCH\(_3\)\(^{15,28,29}\). When compared with the \( ^1\text{IM1} \) formation step, one can see that this step, i.e., \( ^1\text{IM1} \rightarrow ^1\text{IM5} \) isomerization process, requires a high activation energy of 43.16 kcal/mol, but with the excess energy gained in the formation of \( ^1\text{IM1} \), this isomerization process can compete favorably. One dissociation channel of \( ^1\text{IM5} \) is direct rupture of the O—La bond to give rise to the product P4 \( ^1\text{LaCH}_2^+ + \text{CH}_2\text{CHO} \); this dissociation process is computed to be endothermic by 31.82 kcal/mol. In the previous studies on the reaction between M (or M\(^+\), M = Ti, Ni, and Y) and acetone\(^{15,28,29}\), no acetaldehyde and MCH\(_2\) species were detected, and no feasible MCH\(_2\)+CH\(_2\)CHO formation channel was observed theoretically. From the present theoretical work, it is obvious that in the reaction between lanthanum cation and acetone, the C–C activation which leads to CH\(_2\)CHO formation is also feasible and spontaneous in energy.

Similar to that on the singlet PES, we have also located possible activation channels on the triplet PES. From the calculated result, we find that the reaction mechanism on the triplet PES is in general similar to that on the singlet one. The reaction starts with a \( ^1\text{η}^2\text{-CH}_3\text{COCH}_3\)-metal complex followed by three possible pathways: C–O, C–H and C–C activation. Comparing all the relative energy in Table S1 (Supplementary data) and channels shown in Fig. 2, it is clear that the C–C insertion branch which leads to product P3 \( ^1\text{LaCOCH}_2^+ + \text{CH}_2\text{CHO} \) is most feasible due to the relative low energy barrier. As all the rate determining steps along these channels are above \( ^1\text{La}^+ + \text{CH}_3\text{COCH}_3 \), these reaction pathways are not spontaneous, which is quite different from that of the singlet PES. As after IM1 formation, almost all the intermediates, transition states and products involved in the reaction on the singlet PES, lie below the analogues on the triplet PES, obviously after IM1 formation, the singlet pathways are always energetically preferred with respect to the corresponding triplet routes. In addition, as the initial O-attached complex \( ^1\text{IM0} \) is calculated to be 8.04 kcal/mol more stable than the singlet analogue (see Fig. 2), we can speculate that the inter-system singlet-triplet crossing occurs during the process of \( ^3\text{IM0} \rightarrow ^1\text{IM1} \). 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 chose an approach suggested by Yoshizawa et al.\(^{37}\) for locating the crossing points of two PESs of different multiplicities approximately. The potential energy profile of the singlet state from \( ^1\text{TS}_{0\text{d}} \) to \( ^1\text{IM1} \) is shown in Fig. 3. Along the IRC we find a
the singlet PES after initial complex CP. The reaction is expected to occur spontaneously over the following steps:

\[ {\text{La}}^+ + \text{CH}_3\text{COCH}_3 \rightarrow {\text{IM}}_0 \rightarrow CP \rightarrow {\text{IM}}_1 \rightarrow {\text{TS}}_{12} \rightarrow {\text{IM}}_2 \rightarrow {\text{TS}}_{23} \rightarrow {\text{IM}}_3 \rightarrow P_1. \]

The present theoretical work adds new insight into the reaction between transition metal M with acetone.

**Supplementary data**

Supplementary data, Table S1, associated with this article, is available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA 51A(05) 669-675_Suppl Data.pdf.

**Acknowledgement**

This work was supported by the Zhejiang Provincial Natural Science Foundation of China under grant No. Y4090387.

**References**


**Conclusions**

In the present study, the reaction mechanisms between lanthanum cation and CH₃COCH₃ have been investigated in detail, both on singlet and triplet PESs. The reaction is expected to occur spontaneously over the singlet PES after initial complex IM₀ formation. All possible pathways starting with C−O, C−H, and C−C activation have been searched. The C₄H₆ loss of acetone by La⁺ proceeds through the initial C−O activation. The initial C−H activation accounts for the H elimination products (LaCH₃COCH₃⁺+H). Originating from the intermediate complex IM₁, initial C−C bond activation may lead to two decarbonylation products, LaCOCH₃⁺+CH₄ and LaCH₃⁺+CH₂CHO. Our calculations confirm the initial carbonyl C−O activation pathway, which leads to formation of LaO⁺+C₃H₆. This serve as a major channel because of the low energy barrier and dissociation energy of exit-channel complex compared with the C−C and C−H insertion reactions. The most feasible channel may thus be described as:

\[ {\text{La}}^+ + \text{CH}_3\text{COCH}_3 \rightarrow {\text{IM}}_0 \rightarrow CP \rightarrow {\text{IM}}_1 \rightarrow {\text{TS}}_{12} \rightarrow {\text{IM}}_2 \rightarrow {\text{TS}}_{23} \rightarrow {\text{IM}}_3 \rightarrow P_1. \]
36 Gaussian 03, rev. B04, (Gaussian Inc, Pittsburgh PA, USA) 2003.