



Theoretical Study on the Reactions of Pd⁺ and Pd with CO₂ in Gas Phase

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Density functional theory (DFT) calculations have been performed to explore the potential energy surfaces of C-O bond activation in CO₂ molecule by gas-phase Pd⁺ cation and Pd atom, for better understanding the mechanism of second-row metal reacting with CO₂. The minimum energy reaction path is found to involve the spin inversion in the different reaction steps. This potential energy curve-crossing dramatically affects reaction energetic. The present results show that the reaction mechanism is insertion-elimination mechanism along the C-O bond activation. All the theoretical results can lead us to understand deeply the mechanism of the reactions of Pd²⁺ and Pd with CO₂ in gas phase and may be helpful for the further experimental investigation of the reaction.

Key Words: Density functional theory, Potential energy surface, Transition-metal, Reaction mechanism.

INTRODUCTION

As a long-lived greenhouse gas, carbon dioxide is the main contributor to global warming. Nowadays, it has become one of the most challenging subjects to remove this gas from industrial emission and to recycle it¹. As it is very difficult to reduce significantly CO₂ emissions from anthropic sources, in the past many years, considerable attention has been paid to convert this species into more useful chemical materials, such as fine chemicals and clean fuels due to its abundance and renewability. But new ways must be found to activate this molecule if its potential has to be realized. Activation is one of the effective routes to induce inert molecules to react. In previous years, many types of metal and metal oxide were used as catalysts to activate CO₂ and much interest has been focused on the experimental and theoretical studies of transition metal-CO₂ complexes²⁻³⁹, as such complexes have potential for practical application in activating CO₂. To the best of our knowledge, there are no correlative experimental researches on the reactions about Pd and Pd⁺ with CO₂. Armentrout and Kretzschmar⁴⁰ have examined the reaction between Pd⁺ and CS₂, where metal-oxygen bond energies were determined. In this reaction, PdS⁺ is found to be the dominant product at the low energy condition. Based on the experiment, Armentrout and Kretzschmar⁴⁰ investigated the gas-phase CS₂ activation by Pd⁺ cation at the density functional level of theory also. They brought out that the CS₂ activation mediated by Pd⁺ cation is an exothermic spin-forbidden process resulting from a crossing between quartet and doublet energetic profiles. But as an

analogue of CS₂, detailed information for the potential energy surface of reaction CO₂ activation by Pd⁺ is still scarce. Can a similar reaction mechanism be applicable to the reactions of Pd⁺ cation and Pd atom with CO₂? What are the different behaviours between them? Promoted by these questions, we investigated the reactions of Pd⁺ cation and Pd atom with CO₂ by using DFT methods in detail in order to shed some light on these reactions. A comparative theoretical study on the reactions of Pd⁺ cation and Pd atom with CO₂ is interesting and important since Pd is a representative of the second-row late transition metal.

COMPUTATIONAL METHOD

The doublet and quartet potential energy surfaces (PESs) for the reaction Pd⁺ + CO₂ and the singlet, triplet PESs for the reaction Pd + CO₂ have been considered in detail. We optimized all molecular geometries by employing the B3LYP density functional theory method^{41,42}. The spin-unrestricted version of this methodology was used for the calculations of different PESs. These methods are chosen in this study since the previous calibration calculations on transition-metal compounds have shown that this hybrid functional provides accurate results for the geometries and vibrational frequencies of systems containing transition-metal cations^{43,44}. In all of our calculations, the 6-311+G(2d) basis set was used for the carbon and oxygen atoms and the effective core potentials (ECP) of Dolg *et al.*⁴⁵ basis set was used for the Pd, the 5s and 4d in Pd were treated explicitly by a (8s7p6d) Gaussian basis set contracted to [6s5p3d]. The harmonic vibration analyses were performed

at the same level of theory for all optimized stationary points to determine their characters (minimum or first-order saddle point) and to evaluate the zero-point vibrational energies (ZPEs). To verify whether the located transition states connect the expected minima, intrinsic reaction coordinate (IRC) calculations were carried out for each transition state at the same level⁴⁶. All calculations in the present study were performed using the Gaussian 03 program⁴⁷.

RESULTS AND DISCUSSION

The optimized geometries of the stationary points for the reactions of Pd⁺ and Pd with CO₂ are depicted in Fig. 1(a) and Fig. 1(b), respectively. The profiles of the PESs are shown in Fig. 2. The relevant energies of various compounds in the reactions are listed in Tables 1 and 2 and the potential energies curve-crossing diagrams between the different potential energy surfaces are drawn in Fig. 3.

TABLE-1
ENERGY OF VARIOUS COMPLEXES IN THE REACTION OF Pd⁺ CATION WITH CO₂ (TOTAL ENERGY E_T, ZPE CORRECTIONS HAVE BEEN TAKEN INTO ACCOUNT, RELATIVE ENERGY E_R)

Species	E _T (Hartree)	E _R (kJ mol ⁻¹)
² Pd + CO ₂	-314.3611541	0.0
² IM1	-314.422854	-162.0
—	—	—
—	—	—
² TS ₁₃	-314.304029	150.0
² IM3	-314.314155	123.4
² PdO + CO	-314.215835	381.5
Species	E _T (Hartree)	E _R (kJ mol ⁻¹)
⁴ Pd + CO ₂	-314.1697624	502.5
⁴ IM1	-314.2231760	362.3
⁴ TS ₁₂	-314.2187420	373.9
⁴ IM2	-314.2612970	262.2
⁴ TS ₂₃	-314.2552410	278.1
⁴ IM3	-314.3084020	138.5
⁴ PdO + CO	-314.2401370	317.7

TABLE-2
ENERGY OF VARIOUS COMPLEXES IN THE REACTION OF Pd ATOM WITH CO₂ (TOTAL ENERGY E_T, ZPE CORRECTIONS HAVE BEEN TAKEN INTO ACCOUNT, RELATIVE ENERGY E_R)

Species	E _T (Hartree)	E _R (kJ mol ⁻¹)
¹ Pd + CO ₂	-314.708528	0.0
¹ IM1	-314.731857	-61.3
¹ TS ₁₂	-314.730578	-57.9
¹ IM2	-314.759771	-134.5
¹ TS ₂₃	-314.636724	188.5
¹ IM3	-314.646205	163.6
¹ PdO + CO	-314.55173	411.7
Species	E _T (Hartree)	E _R (kJ mol ⁻¹)
³ Pd + CO ₂	-314.624781	219.9
³ IM1	-314.646097	163.9
³ TS ₁₂	-314.643636	170.4
³ IM2	-314.657220	134.7
³ TS ₂₃	-314.623288	223.8
³ IM3	-314.653210	145.2
³ PdO + CO	-314.584379	326.0

Reaction between Pd⁺ cation and CO₂: First, we will discuss the doublet PES. The reaction starts with the formation of a η¹-O encounter complex ²IM1 (²A', C_s), which is 162.0

kJ/mol below the entrance channel ²Pd⁺ + CO₂. It should be pointed out that although numerous trials are taken to search for possible transition states that connect reactants and original complex, no such structures are obtained. For example, in the case of the formation of this encounter complex ²IM1, for a given Pd-O bond length, all other geometrical degrees of freedom are optimized, as Pd approaches the oxygen atom, the energy of the complex decreases monotonically until the encounter complex ²IM1 formed. Clearly, the formation of ²IM1 is spontaneous and it is a barrier free process. Subsequently, this encounter species proceeds to form an insertion complex ²IM3 through the transition state ²TS₁₃. This insertion process is endothermic by 285.4 kJ/mol and has a barrier of 312.0 kJ/mol. As shown in Fig. 1(a), the Pd-O distance in ²TS₁₃ is shortened from 2.062 to 1.926 Å and the Pd-C bond is shortened to 1.848 Å. These facts indicate that the weak electrostatic interaction between Pd⁺ and CO₂ has strengthened when it is converted into ²TS₁₃. Synchronously, the C-O bond breaks gradually, the bond length is increased by 0.683 Å. ²TS₁₃ has a three-membering structure with C_s symmetry. The imaginary frequency is -400.81 cm⁻¹ and the normal mode corresponds to the rupture of C-O bond and the formation of Pd-O and Pd-C bonds.

As shown in Fig. 1(a), ²IM3 (²A'', C_s) is an insertion species of Pd⁺ cation into the C-O bond. Compared with the transition state ²TS₁₃, the structures of these two species are very similar and the energy of ²IM3 is only 26.6 kJ/mol more stable. Obviously, ²TS₁₃ is a typical late transition state. To analyze the bond characteristics of the molecules, the natural bond orbital (NBO) calculations were carried out⁴⁸. The NBO analysis will allow us to quantitatively evaluate the charge transfer (CT) involving the formation of a bond. Natural bond orbital calculation shows that in ²IM3 one single bond and one single bond have formed between Pd and O, Pd and C atoms respectively. The NBO charge on the Pd atom increases to about +0.377e, whereas the atomic charge on carbon atom decreases to 0.254e (it is 0.997e in free CO₂). The OPd-CO binding energy is 258.1 kJ/mol which can be basically attributed to the Pd-C bond arising from a strong CO→Pd σ-donation.

The next step is the nonreactive-dissociation of ²IM3 to generate products. After calculation, we found the insertion species ²IM3 can dissociate directly without exit barrier to products ²PdO⁺ + CO, endothermic by 258.1 kJ/mol. It is clear that the reaction mechanism of ²Pd⁺ with CO₂ over doublet PES is the typical insertion-elimination mechanism.

With respect to the quartet state pathway, the first step of the reaction on this PES starts with the formation of the η¹-O encounter complex ⁴IM1 (⁴A'', C_s). The relative energy of ⁴IM1 is calculated to be 524.3 kJ/mol higher than that of the doublet analogue, ²IM1. After passing ⁴TS₁₂, it can convert into a η²-CO encounter complex ⁴IM2 (⁴A'', C_s), which is 241.2 kJ/mol below the entrance channel ⁴Pd⁺ + CO₂. Starting from ⁴IM2, it can rearrange to form ⁴IM3, which undergoes a rupture of C-O bond *via* a transition state ⁴TS₂₃ that is 15.9 kJ/mol above ⁴IM2. As is shown in Fig. 1(a), the distance between Pd and O in ⁴TS₂₃ is shortened from 2.020 Å to 1.961 Å. This fact indicates that the weak electrostatic interaction between Pd⁺ and CO₂ strengthens when it is converted into ⁴TS₂₃ and the Pd-O bond is nearly formed. The distance between Pd and

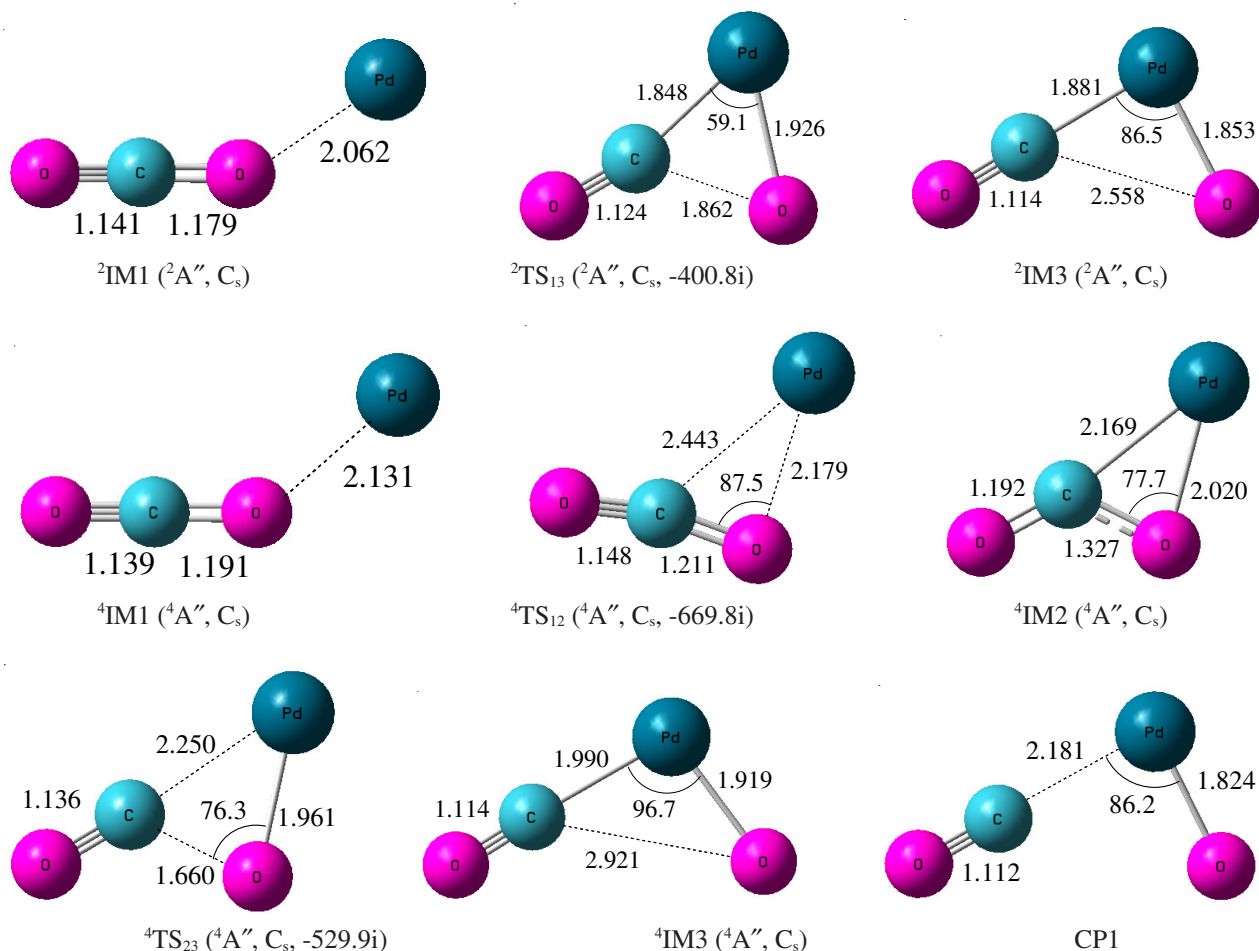


Fig. 1(a). Optimized geometries for the various stationary points located on the Pd⁺ + CO₂ potential energy surfaces (distances in angstroms, angles in degrees)

C is shortened by 0.081 Å, which suggests that the Pd-C bond is forming. At the same time, the activated C-O bond is almost broken and the bond length is elongated by 0.333 Å. Geometrically, one can see that ⁴TS₂₃ is similar to the η²-CO encounter complex ⁴IM₂, so ⁴TS₂₃ is a typical "early" transition state on the quartet PES, this is different from the analogue (²TS₁₃) on the doublet PES. The imaginary frequency of ⁴TS₂₃ is 529.9i cm⁻¹ and the normal mode corresponds to the rupture of C-O bond with the result of Pd⁺ insertion into C-O bond. For the insertion intermediate ⁴IM₃, the most possible dissociation channels is the Pd-C bond rupture to form ²PdO⁺ + CO, which is calculated to be endothermic by 179.2 kJ/mol.

From the above discussion, the product PdO⁺ is predicted to have ground state ⁴Σ. So the energetically favourable channel of the titled reaction is ²Pd⁺ + CO₂(¹Σ_g) → PdO⁺(⁴Σ) + CO(¹Σ), but this channel is spin-forbidden and has to go through inter-system quartet-doublet crossing. Our following calculation is aimed at determining the region where the spin inversion occurs and acquiring the structure and energy information of crossing point between the two different potential energy surfaces. We choose a simple approach suggested by Yoshizawa *et al.*⁴⁹ for approximately locating the crossing points of two PESs of different multiplicities. The main idea of this approach is to perform a series of single-point computations of one spin state along the IRC of the other spin state.

Thus, this discussion suggests that the energy of insertion species ²IM₃ is lower 15.1 kJ/mol than that of the quartet analogue. But, the ground state of dissociation product PdO⁺ is in quartet. Clearly, the dissociation process from IM₃ may involve spin inversion. Then we define the distance between Pd and C as a function, which is depicted in Fig. 3(a). For a given Pd-C bond length, all other geometrical degrees of freedom are optimized for each spin. Along the energy curve, we find a crossing point CP1, which is at the length of Pd-C bond = 2.181 Å with relative energy of -314.3085 Hartree. The structure of CP1 is collected in Fig. 1(a). Therefore, the reaction may jump from the doublet PES to the quartet PES near the crossing point CP1. As can be seen from Fig. 3(a), after passing point CP1, the quartet PES can provide a low-energy reaction pathway toward the dissociation products PdO⁺ + CO.

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)⁵⁰⁻⁵³, which has been confirmed by experimental studies. In previous theoretical researches about CO₂ activation by Nb⁺ and Zr⁺ cations, Toscano *et al.*^{2,3} have ascertained the presence of some spin inversion during the reaction process, CO₂ activation mediated by metal cations was found to be an exothermic spin-forbidden

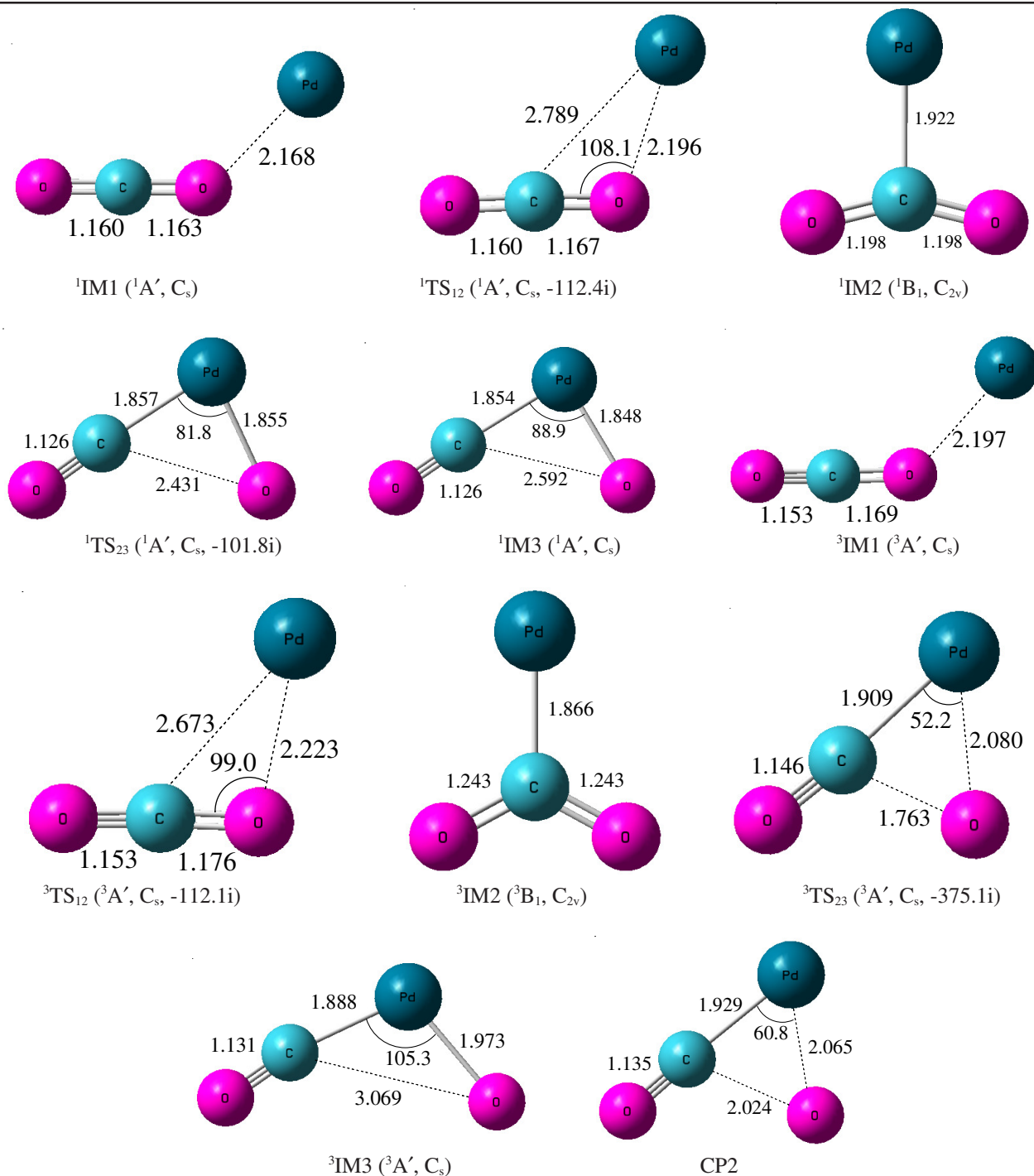


Fig. 1(b). Optimized geometries for the various stationary points located on the Pd + CO₂ potential energy surfaces (distances in angstroms, angles in degrees)

process resulting from a crossing between different energetic profiles.

Reaction between Pd atom and CO₂: Now let's turn to the reaction between Pd atom and CO₂. If CO₂ approaches the ground state ¹Pd atom *via* its oxygen side, a η¹-O encounter complex denoted as ¹IM1 is formed, -61.3 kJ/mol more stable than the reactants. The next step corresponds to the coordinate between Pd and O, Pd and C atoms respectively to form a η²-(OCO) encounter complex ¹IM2 (¹B₁, C_{2v}), which is -134.5 kJ/mol below the entrance channel ¹Pd + CO₂. This step only requires a low activation energy of 3.4 kJ/mol. Starts from

this complex ¹IM2, the next step in the reaction mechanism is the insertion of the Pd atom into the C-O bond generating ¹IM3. This step is endothermic by 298.1 kJ/mol and requires a high energy barrier of 323.0 kJ/mol. ¹IM3 can be considered as a bound complex between ¹PdO and CO, the dissociation of this species into ¹PdO + CO requires 248.1 kJ/mol energy at the UB3LYP levels.

With respect to the triplet state pathway, the first step of the reaction over this PES starts with the formation of a η¹-O initial complex ³IM1 (³A', C_{∞v}), 56.0 kJ/mol more stable than the reactants ³Pd + CO₂. Obviously, the ground state of IM1 is

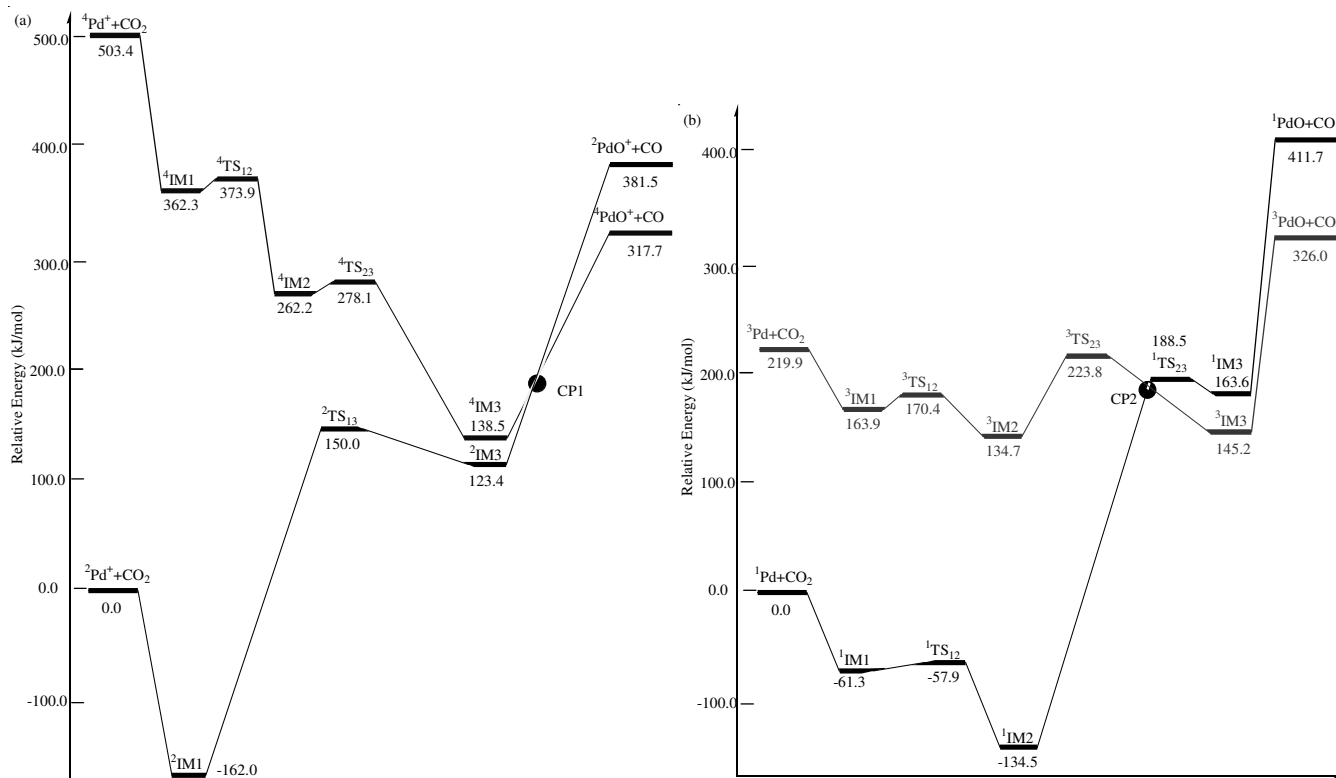


Fig. 2. Potential energy surface profiles for the reaction of (a) Pd⁺ cation with CO₂, (b) Pd atom with CO₂

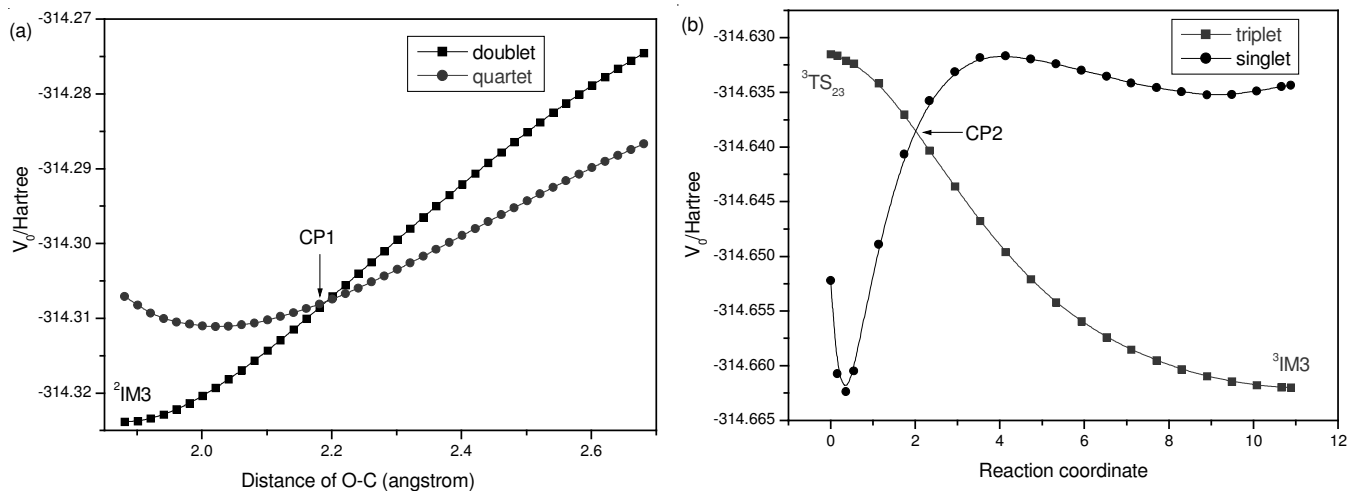


Fig. 3. (a) Potential energies from ²IM3 to ⁴PdO⁺ + CO along the distance between oxygen and carbon atom., (b) Potential energies from ¹IM2 to ³IM2 along the triplet IRC

in its singlet. With reaction proceeding, this species may isomerize into a η^2 -(OCO) encounter complex ³IM2 (³B₁, C_{2v}). The C-O in ³IM2 may activation through inserting the Pd atom into the C-O bond via a transition state ³TS₂₃ that is 89.1 kJ/mol above ³IM2. As shown in Fig. 1(b), the distance between Pd and O in ³TS₂₃ is shortened to 2.080 Å. At the same time, the activated C-O bond is elongated by 0.52 Å. The imaginary frequency of ³TS₂₃ is -375.11 cm⁻¹ and the normal mode corresponds to the rupture of C-O bond with the result of Pd atom insertion into C-O bond. With respect to the insertion intermediate ³IM3, the most possible dissociation channel is the Pd-C bond rupture to form ³PdO + CO, which is calculated to

be endothermic by 180.8 kJ/mol. The whole reaction ³Pd + CO₂ → ³PdO + CO is calculated to be exothermic by 106.1 kJ/mol. Obviously, from above discussion, one can see the CO₂ activation mediated by ³Pd atom is a spin-forbidden process resulting from a crossing between different energetic profiles.

On the basis of the analysis of Fig. 2(b), one spin crossings can be found to be possible along the optimal reaction pathway of the C-O bond activation in CO₂ by Pd atom. First, the reaction may start with the formation of an encounter complex ¹IM2 on the singlet PES. Then, the singlet surface could likely cross the triplet surface somewhere between the region from ¹IM2 to ³IM3. After passing the crossing point, the reaction may

jump to the triplet PES since $^3\text{IM3}$ is 18.4 kJ/mol below the analogous insertion complex $^1\text{IM3}$ over singlet PES, *i.e.*, the insertion complex IM2 on the triplet PES is thermodynamically more favourable than the corresponding singlet species.

Fig. 3(b) gives the potential energy profiles of the triplet state from the complex IM2 to IM3 along the triplet IRC. Along the triplet IRC we find a singlet-triplet crossing point CP2, which is before $^1\text{TS}_{23}$ with the energy of -314.6372 Hartree. Thus, the reaction may jump from the singlet PES to the triplet one near the crossing point CP2 before passing the transition state $^1\text{TS}_{23}$, until leading to the $^3\text{IM3}$ formation.

From the above theoretical studies on the reactions of Pd and Pd⁺ with CO₂, we can see the reactions between Pd and Pd⁺ with CO₂, the lowest energy path corresponds to the $\eta^1\text{-O}$ coordination of CO₂ followed by the insertion of Pd or Pd⁺ into the C-O bond, the minimum energy reaction path requires the crossing of two adiabatic surfaces with different spin states. Both the reactions between atom or cation with CO₂ are energy no-spontaneously and greatly endothermic. From these facts, we conjecture that the insertion reaction and TSR could be general mechanisms for the reactions of Pd atom and Pd⁺ cation with CO₂.

Conclusion

Density functional calculations have been performed to investigate the reactions of Pd⁺ cation and Pd atom with CO₂ in gas phase. The ground and excited potential energy surfaces (PESs) of the titled reactions have been explored. The following conclusions can be drawn from the present calculations.

(i) The reactions of Pd⁺ cation and Pd atom toward CO₂ proceed according to the insertion-elimination mechanism. Both reactions are energy spontaneous.

(ii) For the reaction between Pd⁺ cation and CO₂, the minimum energy channel requires the crossing of different adiabatic surfaces with different spin states, *i.e.*, the reaction starts with the formation of a doublet encounter complex, then the C-O bond is activated to form an inserted complex $^2\text{IM2}$. After passing the crossing point CP1, the reaction systems may move on the quartet PES toward the products.

(iii) Similar with the C-O bond activation by Pd⁺ cation, the PES crossing behaviour occurs along the reaction between Pd atom and CO₂ also. Specifically, it can be described as $^1\text{Pd} + \text{CO}_2 \rightarrow ^1\text{IM1} \rightarrow ^1\text{TS}_{12} \rightarrow ^1\text{IM2} \rightarrow \text{CP2} \rightarrow ^3\text{IM3} \rightarrow ^3\text{PdO} + \text{CO}$.

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