The Mechanisms of the Reactions of W and W^+ with CO_x ($x = 1, 2$): A Computational Study†

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Received: December 19, 2006; In Final Form: February 12, 2007

The mechanisms of the reactions of W and W^+ with CO_x ($x = 1, 2$) were studied at the CCSD(T)/[SDD + 6-311G(d)]//B3LYP/[SDD + 6-31G(d)] level of theory. It was shown that the gas-phase reaction of W with CO_2 proceeds with a negligible barrier via an insertion pathway, $W(^7S) + CO_2(^1A_1) \rightarrow W(\eta^2\text{-OCO})(^6A') \rightarrow OW(\eta^1\text{-CO})(^1A) \rightarrow WO(^3\Sigma^+) + CO(^1\Sigma)$. This oxidation process is calculated to be exothermic by 32.4 kcal/mol. Possible intermediates of this reaction are the $W(\eta^2\text{-OCO})$ and OWCO complexes, among which the latter is 37.4 kcal/mol more stable and lies 39.7 and 7.3 kcal/mol lower than the reactants, $W(^7S) + CO_2(^1A_1)$, and the products, $WO(^3\Sigma^+) + CO(^1\Sigma)$, respectively. The barrier separating $W(\eta^2\text{-OCO})$ from OWCO is 8.0 kcal/mol (relative to the $W(\eta^2\text{-OCO})$ complex), which may be characterized as a $W^{+\delta}-(CO_2)^{-\delta}$ charge-transfer complex. Ionization of W does not change the character of the reaction of W with CO_2: the reaction of W^+ with CO_2, like its neutral analog, proceeds via an insertion pathway and leads to oxidation of the W-center. The overall reaction $W^+(^6D) + CO_2(^1A_1) \rightarrow W(\eta^1\text{-OCO})^+(^6A) \rightarrow OW(\eta^1\text{-CO})^+(^4A) \rightarrow WO^+(^4\Sigma^+) + CO(^1\Sigma)$ is calculated to be exothermic by 25.4 kcal/mol. The cationic reaction proceeds with a somewhat large (9.9 kcal/mol) barrier and produces two intermediates, $W(\eta^1\text{-OCO})^+(^6A)$ and $OW(\eta^1\text{-CO})^+(^4A)$. Intermediate $W(\eta^1\text{-OCO})^+(^6A)$ is 20.0 kcal/mol less stable than $OW(\eta^1\text{-CO})^+(^4A)$, and separated from the latter by a 35.2 kcal/mol barrier. Complex $W(\eta^1\text{-OCO})^+(^6A)$ is characterized as an ion−molecular complex type of $W^+\text{-}(CO_2)$. Gas-phase reactions of M=W/W^+ with CO lead to the formation of a W−carbonyl complex $M(\eta^1\text{-CO})$ for both M=W and W^+. The C−O insertion product, OMC, lies by 5.2 and 69.3 kcal/mol higher than the corresponding $M(\eta^1\text{-CO})$ isomer, for M=W and W^+, respectively, and is separated from the latter by a large energy barrier.

I. Introduction

Carbon oxides are naturally abundant carbon sources and products of various combustion processes, which have been implicated as major contributors to global warming. Therefore, activation and utilization of their strong C=O bond(s) have been the focus of chemists for many years. Numerous studies have shown that transition metal systems are efficient catalysts for utilization of C=O bond(s), among many other systems.[1] Therefore, understanding the mechanisms and factors governing the reactions of transition metal systems with CO_x ($x = 1$ and 2) are essential. Knowledge on these atomistic level properties can facilitate the design of novel and more efficient catalysts for utilization of carbon mono- and di-oxides. It is well-established that these catalytic reactions are usually influenced by numerous factors, including redox activity and spin states of transition metal centers, the nature of their ligand environment, the identity of reactive intermediates, and the nature of solvent and support materials. The first step toward elucidating the role of these various factors is to study the gas-phase reactions of transition-metal (TM) atoms and ions with CO_x ($x = 1$ and 2) molecules, because these gas-phase processes are free from ligand, solvent, and support effects. In obtaining atomistic level understanding of these reactions, computational approaches along with gas-phase experiments have proved to be very useful.[2,3] In the literature, numerous experimental studies have been reported on gas-phase reactions of transition metal atoms/ions with CO_x ($x = 1$ and 2) molecules.[4−17] However, for better understanding of these experiments and elucidation of the mechanisms and controlling factors of the reaction of transition metal atoms/ions with CO_x ($x = 1$ and 2) molecules with state-of-the-art quantum chemical studies are absolutely necessary. In the literature, there are several theoretical papers on the reaction of transition metals with CO_2.[18−23]

In this paper we report comprehensive computational studies on the mechanisms of gas-phase reactions of the W atom and W^+ cation with CO_x ($x = 1$ and 2) molecules. Previously, reaction of laser-ablated W atoms with CO_2/Ar mixtures has been a subject of experimental studies.[12] In these experiments the reaction products, OWCO and $O_2M(CO)_2$, have been trapped in Ar matrices, and their infrared spectra have been identified. Geometries, frequencies and isotope ratios of WCO, OWCO, and WCO^+ molecules have also been a subject of several theoretical studies.[12,23,24] However, to our best knowledge, detailed computational studies on the mechanisms and controlling factors of the reactions of W and W^+ with CO_x ($x = 1$ and 2) molecules were not reported. Such studies are important and will provide vital information on the role of lower-lying electronic states of W atom and W^+ cation in the utilization of the C=O bond(s) of CO_x ($x = 1$ and 2) molecules.

II. Computational Procedures

The potential energy surfaces (PES) of the reactions W/W^+ + CO_x in several low-lying electronic states of W and W^+ were

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† Part of the special issue "M. C. Lin Festschrift".

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10.1021/jp0687293 CCC: $37.00

calculated using the Gaussian03 quantum chemical software package.[25] The geometries of the reactants, intermediates, transition states, and products of these reactions were optimized without imposing symmetry constraints at the B3LYP density functional level.[26] In these calculations we used the Stuttgart/Dresden relativistic effective core potential (ECP)[27] and associated triple-ζ SDD basis set for W, and the 6-31G(d) basis set for main group elements. Below, we call this approach B3LYP/[SDD+6-31G(d)]. The nature of all stationary points was confirmed by performing normal-mode analysis. In addition, the nature of the calculated transition states was clarified using the intrinsic reaction coordinate (IRC) approach.[28] Previously, it was demonstrated that the B3LYP method with double-ζ plus polarization basis sets provides generally excellent agreement with experiments for geometries of transition metal systems.[29] However, B3LYP-calculated energies could be off from the most accurate values by several kcal/mol. Therefore, we improved the energies of the calculated structures by performing single-point UCCSD(T) (for simplicity called below as CCSD(T)) calculations at their B3LYP-optimized geometries. In the CCSD(T) calculations, we used the 6-311G(d) basis set for C and O atoms. Unscaled zero-point energy corrections (ZPC) estimated at the B3LYP level were added to the final CCSD(T) energetics. The single determinant nature of wavefunction of all calculated structures was examined by performing T1 diagnostics (the T1 parameter for most structures is calculated to be within 0.02 − 0.06, see Table S2 of Supporting Materials). We also checked the $<S^2>$ values to evaluate the spin contamination in these calculations. As seen from the Table S2 of the Supporting Materials, in general, spin contamination for most of these calculations is not significant. Throughout the paper we discuss the CCSD(T) + ZPE energetics, while the B3LYP-calculated relative energies are included in the Supporting Material (Table S2).

As will be discussed below, PESs of several lower-lying electronic states of the studied reactions cross many times upon completion. Search for the exact locations of minima on the seam of crossing of these PESs would require the use of computationally much more demanding methods and inclusion of the spin−orbit coupling (SOC) effect in the calculations. Because of technical limitations, in this paper, we did not perform SOC calculations and did not search for the minima on the seam of crossing of lower-lying electronic state PESs of the studied reactions, following our previous computational methodology.[30,31]

III. Results and Discussions

As we discussed previously,[30,31] at the B3LYP and CCSD(T) levels of the theory used in this paper, the ground electronic state of the W atom is calculated to be a septet ^{7}S state associated with the s^1d^5 electronic configuration, while its quintet ^{5}D state associated with the s^2d^4 electronic configuration is slightly, 4.6 kcal/mol, higher in energy (at the CCSD(T) level of theory). This datum is not consistent with that of Campbell-Miller and Simard,[32] who have reported the ^{5}D ground electronic state for the W atom. This discrepancy is probably result of lack the comprehensive spin−orbit interaction in the calculations. The triplet ^{3}P (s^2d^4) and singlet ^{1}S (s^2d^4) states of W are calculated to be 45.0 and 71.5 kcal/mol higher in energy, respectively, at the CCSD(T)/[SDD+6-311G(d)] level of theory. Meanwhile, the ground electronic state of W^+ is the sextet ^{6}D state associated with the s^1d^4 electronic configuration: its quartet ^{4}F (s^1d^4) and doublet ^{2}P (s^1d^4) states are 27.6 and 47.0 kcal/mol higher in energies, which are in good agreement with 24.9 and 55.5 kcal/mol experimental values,[33] respectively. The CCSD(T)-calculated ionization energy of W(^{7}S) is 171.0 kcal/mol, which also is in reasonable agreement with the experimental value of 181.344 ± 0.002 kcal/mol.[32] Previously we have demonstrated that the computational approach used in this paper describes the heat of formation of diatomic molecules of W/W^+ with various ligands reasonably accurate.[30,31]

Below, we present potential energy surfaces (PESs) of the reaction of CO_x with the ^{7}S, ^{5}D, ^{3}P and ^{1}S spin states of the W atom, while the reaction of $W^+ + CO_x$ is investigated for the ^{6}D, ^{4}F, and ^{2}P states of W^+. The calculated structures of intermediates, transition states and products of the reaction W + CO_2 are shown in Figure 1, while their energetics calculated at the CCSD(T)[SDD+6-311G(d)]//B3LYP[SDD+6-31G(d)] + ZPC (from the B3LYP calculations) level of theory are presented in Figure 2. Those for the reaction $W^+ + CO_2$ are given in Figures 3 and 4, respectively. The B3LYP/[SDD + 6-31G(d)] calculated energies (in au) of the intermediates, transition states and products of the reactions of W and W^+ with CO_2 at their several lower-lying electronic states are presented in Table S1 of Supporting Materials. The CCSD(T)/[SDD+6-311G(d)]//B3LYP/[SDD+6-311G(d)] calculated relative energies (in kcal/mol) and CCSD(T) T1 values of intermediates, transition states and products of the reactions W/W^+ + CO_2 at their several lower-lying electronic states are given in Table S2 of Supporting Materials.

1. Mechanism of the Reaction of W with CO_2. As it should be expected, the first possible intermediate of this reaction is the W(CO_2) complex, which, in general, may have four different structures, W(η^1-OCO), W(η^1-CO_2), W(η^2-OCO), and W(η^2-O_2C), presented in Chart 1, and two different types of electronic structures: $W^+-(CO_2)^-$ and $W-CO_2$. In the $W^+-(CO_2)^-$ type of structures, the CO_2 molecule is expected to have a bent, but in $W-CO_2$ structures to have a linear, geometry.

After extensive search we were able to localize only two isomers, W(η^2-OCO) and W(η^2-O_2C), for the W(CO_2) complex. Isomer W(η^2-O_2C), which has septet electronic ground state, is only 0.2−0.1 kcal/mol stable relative to the W(^{7}S) + CO_2 dissociation limit. The calculated insignificant $W-CO_2$ bonding energy is consistent with the long $W-CO_2$ distance. Analysis of the Mulliken charges (W and CO_2 fragments have almost zero charges) and spin distributions (all unpaired electrons are located on W center) of this isomer indicates that it is, in fact, a $W-CO_2$ system. Since this isomer is only slightly stable it is not expected to have any significant contribution to the mechanism and kinetics of the W + CO_2 reaction. Therefore, below we excluded it from the discussion.

The located second isomer of W(CO_2) is W(η^2-OCO) (see Figure 1). At all of its calculated electronic spin states (singlet, triplet, quintet and septet), this isomer is found to have a bent CO_2-fragment with a ∠OCO angle of 134−135°. (in the “free” CO_2^- anion the −OCO angle is calculated to be 133.67°.), which indicates that this is, in fact, a $W^+-(CO_2)^-$complex. The calculated Mulliken charges and spin densities are consistent with this assessment: In singlet, triplet, quintet, and septet electronic states of W(η^2-OCO), about 0.77, 0.78, 0.78, and 0.56 e is transferred from the W center to the CO_2 fragment, respectively.

The septet state of W(η^2-OCO) is calculated to be about 20 kcal/mol higher than that of the W(η^2-O_2C) isomer, and therefore, will not be discussed below. At its quintet ground state the isomer W(η^2-OCO) is calculated to be 2.8 and 6.9 kcal/mol lower than W(^{7}S) + CO_2 and W(^{5}D) + CO_2 dissociation limits (see Figure 2a). In the other words, the septet and

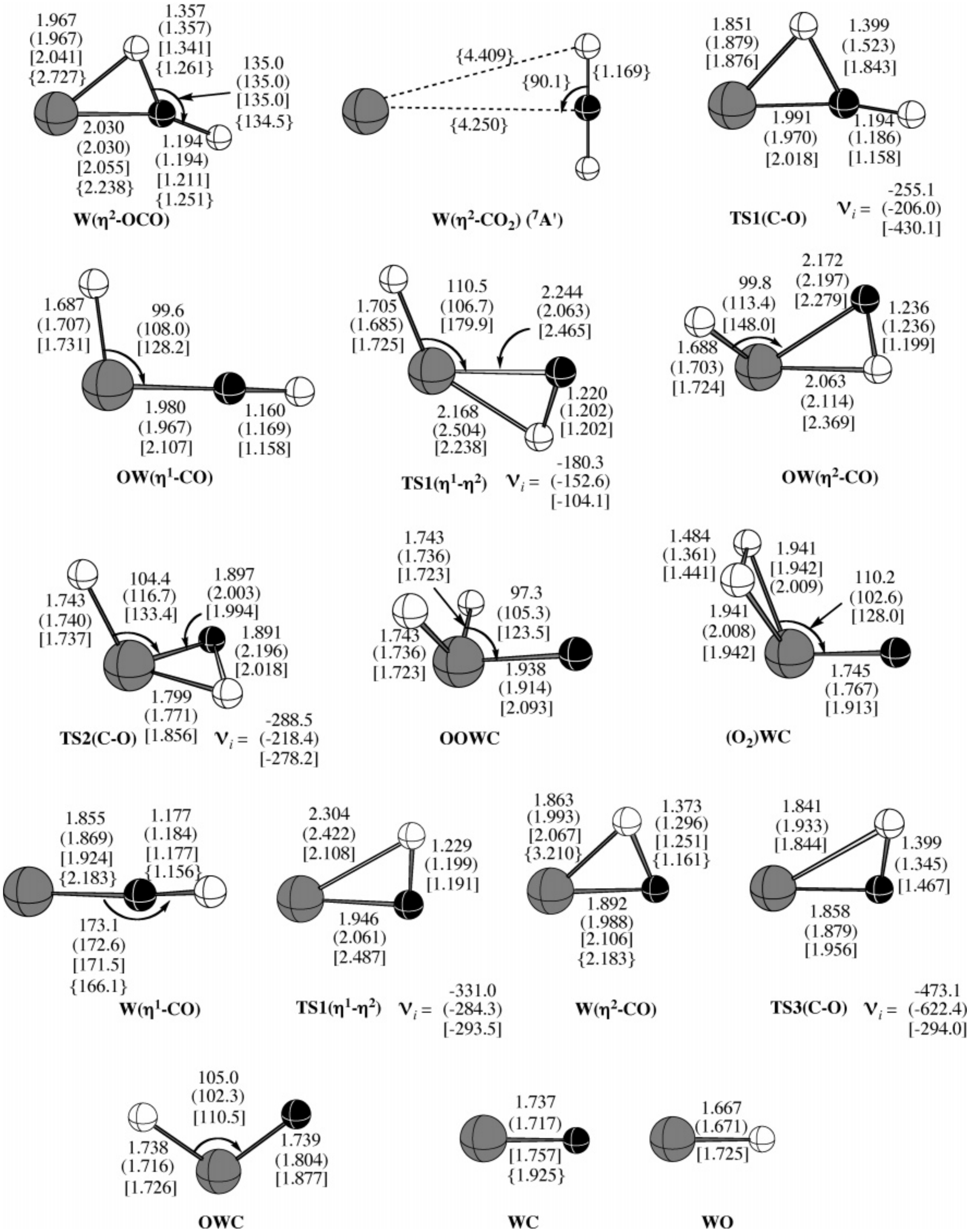


Figure 1. Optimized geometry (distances are in Å, angles are in deg) of intermediates, transition states, and products of the reaction of W with CO_2 molecule. For transition states, values of imaginary frequencies (in cm^{-1}), ν_i, corresponding to the reaction coordinates are also presented. Numbers given without parenthesis are for singlet state structures, with parentheses, square brackets ([...]), and curly brackets ({...}) are for triplet, quintet, and septet state structures, respectively.

quintet potential energy surfaces of the reaction W + CO_2 are expected to cross at the beginning of the reaction. In this paper, we did not locate the minima on the seam of crossing for the septet and quintet PESs. Furthermore, ^5D state of W is experimentally reported to be lower in energy than ^7S-state, therefore, there is no need to locate the exact position of the seam of crossing for the septet and quintet PESs.

Triplet and singlet states of W(η^2-OCO) are found to be 11.8 and 30.0 kcal/mol higher than its quintet ground state.

The W(η^2-OCO)(^5A) complex can rearrange to the energetically most stable intermediate OWCO with only 8.0 kcal/mol barrier at the transition state TS1(C−O). As can be seen in Figure 2a, the ground state of the TS1(C−O) is also a quintet state, and its triplet and singlet states are 17.4 and 63.1 kcal/mol higher in energy. TS1(C−O) at its quintet ground state lies only 5.7 kcal/mol higher than W(^7S) + CO_2 dissociation limit. In other words, reaction W(^7S) + CO_2 → OWCO may proceed with a negligible barrier. This conclusion is consistent with the experimental findings of Souter and Andrews[12] showing that the only product of the reaction of laser-ablated W atoms with CO_2/Ar mixtures is OWCO (and $O_2W(CO)_2$ if more than one CO_2 molecule is used). However, the energy of the reaction

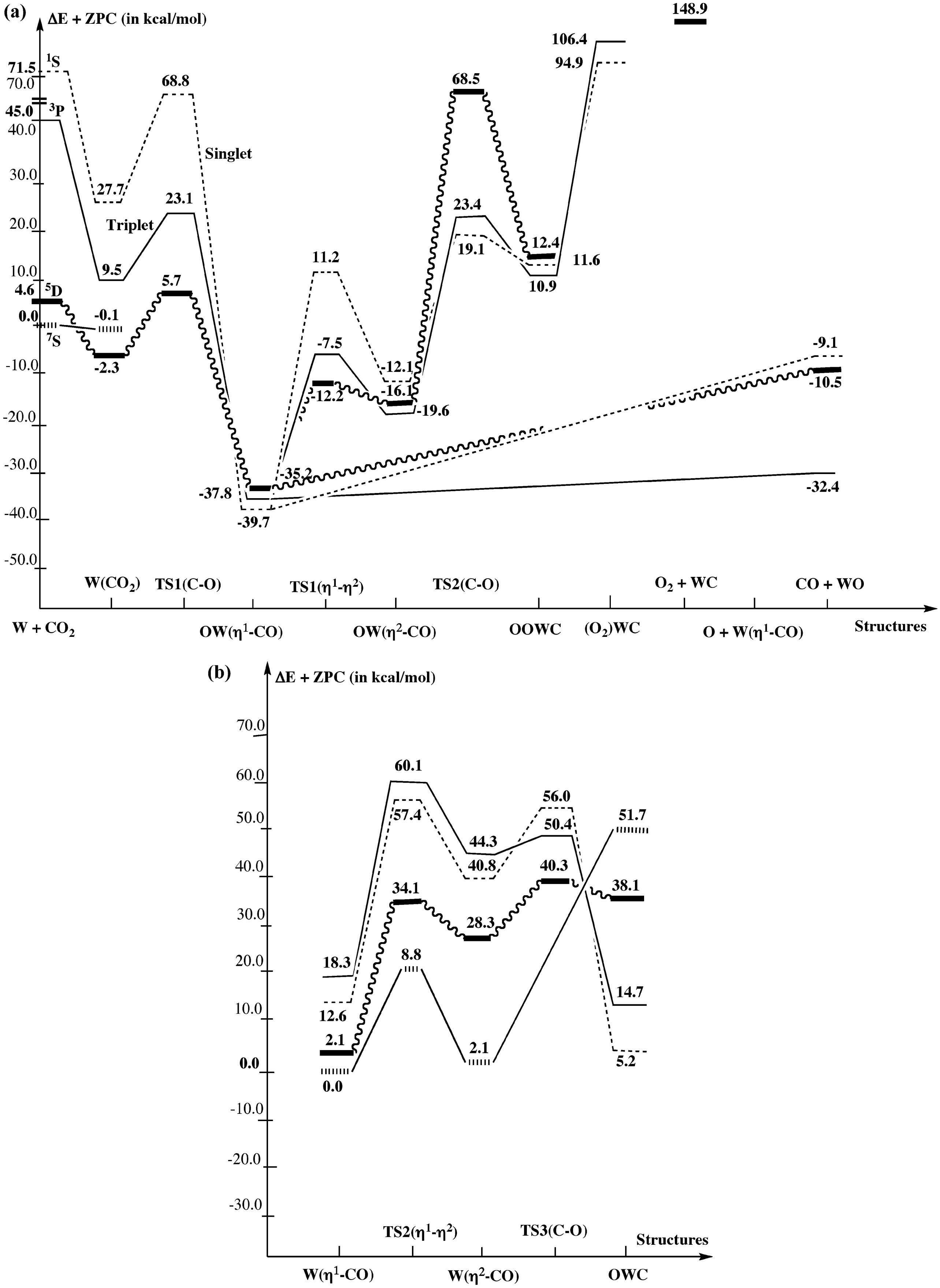


Figure 2. The calculated relative energies (in kcal/mol) of important intermediates, transition states and products of the reaction of W with the CO_2 molecule: (a) potential energy surface of the oxidation pathway and (b) potential energy surface for isomerization of WCO molecule.

W(^{7}S) + CO_2 → OWCO reported in this work, 39.7 kcal/mol, is significantly smaller than 54.4 and 82.8 kcal/mol reported by Souter and Andrews[12] at the LDA+BP and BP86 levels of density functional theory.

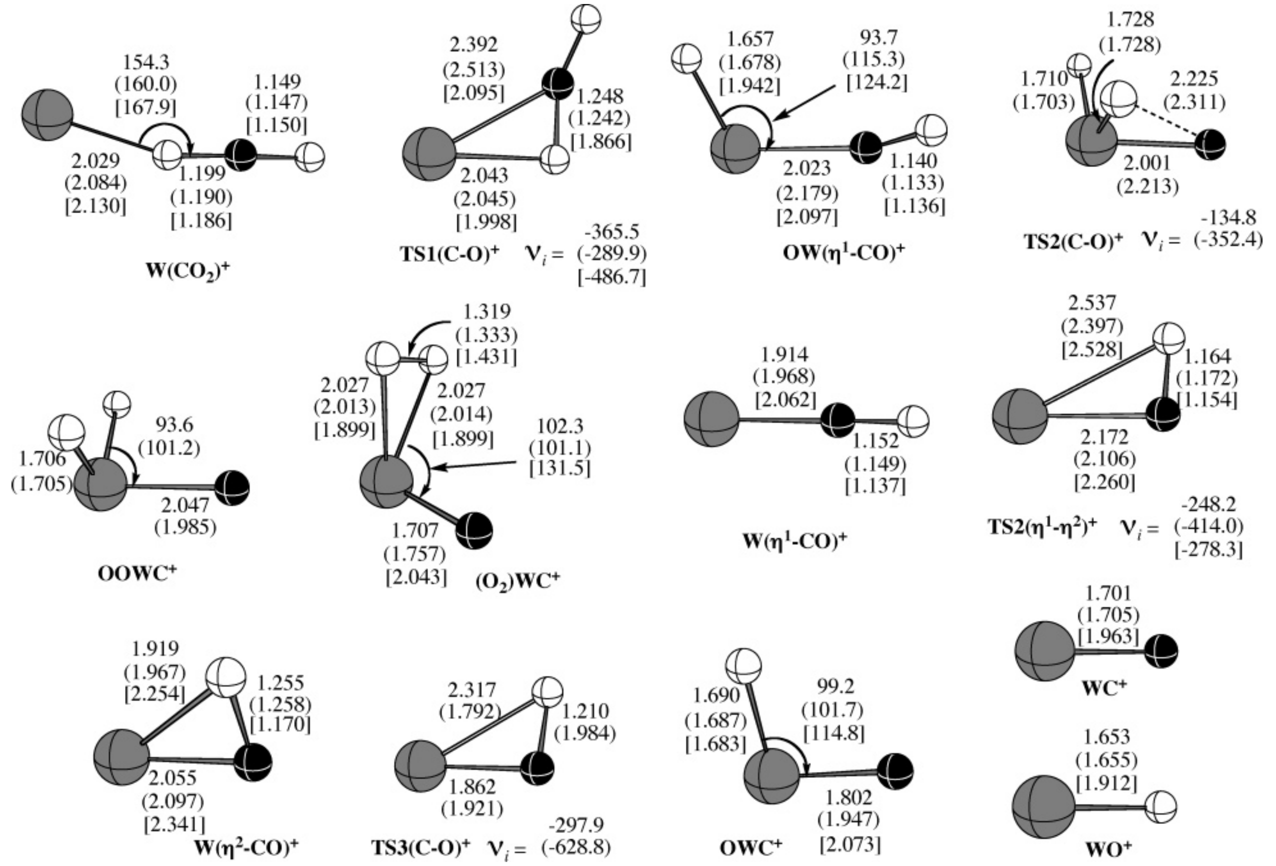


Figure 3. Optimized geometry (distances are in Å, angles are in deg) of intermediates, transition states and products of the reaction of W^+ with CO_2 molecule. For transition states, values of imaginary frequencies (in cm^{-1}), ν_i, corresponding to the reaction coordinates are also presented. Numbers given without parenthesis are for doublet state structures, with parentheses and square brackets ([...]) are for quartet and sextet state structures, respectively.

The resulting complex OWCO can have three different isomers, OW(η^1-CO), OW(η^2-CO), and OW(η^1-OC). The isocarbonyl isomer OW(η^1-OC) is expected to be energetically less favorable compared to isomer OW(η^1-CO), and, therefore, was not studied in this work. Among the other two isomers the OW(η^1-CO), which is the direct product of the C=O bond insertion in W(η^2-OCO), is energetically almost 18−20 kcal/mol more favorable, and is separated from the OW(η^2-CO) by about 27.5 kcal/mol barrier.

The ground state of OW(η^1-CO) is found to be singlet state, while its triplet and quintet states lie only 2 and 4 kcal/mol higher in energy. Souter and Andrews have reported[12] triplet $^3A'$ state to be a ground state of OWCO molecule at the DFT (LDA + BP and BP86) level.

From the energetically most stable OW(η^1-CO) intermediate, the reaction may proceed via three different channels: (1) oxidation of the W-center via formation of WO + CO products, (2) isomerization followed by O_2 + WC formation, and (3) dissociation of the oxo ligand and formation of O + WCO products.

As shown in Figure 2a, the oxidation pathway leading to WO + CO products is energetically the most favorable channel, and is only 7.9 kcal/mol endothermic (relative to the singlet ground state of the OW(η^1-CO) intermediate). The overall oxidation reaction of W by CO_2, $W(^7S) + CO_2 \rightarrow OW(\eta^1\text{-CO})(^1A') \rightarrow WO\ (^5\Sigma^+) + CO$, is calculated to be exothermic by 32.4 kcal/mol. Souter and Andrews have reported[12] this value to be 29.1 kcal/mol at the LDA+BP level.

The second pathway, leading to the O_2 + WC formation, starts with a OW(η^1-CO) → TS1(η^1-η^2) → OW(η^2-CO) isomerization process, followed by the second C=O bond activation (at the transition state TS2(C−O)) to for OOWC intermediate, which later rearranges to the molecular complex (O_2)−WC. The latter complex can eliminate an O_2 molecule to form O_2 + WC products. The entire process $W(^7S) + CO_2 \rightarrow OW(\eta^1\text{-CO})(^1A') \rightarrow TS1(\eta^1\text{-}\eta^2)(^5A') \rightarrow OW(\eta^2\text{-CO})(^3A') \rightarrow TS2(C{-}O)(^1A') \rightarrow OOWC(^3A') \rightarrow (O_2)WC(^1A') \rightarrow O_2(^3\Sigma_g) + WC(^5\Sigma^+)$ is calculated to be highly endothermic (148.9 kcal/mol). Therefore, this pathway is unlikely to be a major channel of the reaction of W with the CO_2 molecule.

The third pathway originating from the OW(η^1-CO) intermediate is an O-ligand dissociation leading to the O + WCO products. As it could be expected, the ground state reaction $W(^7S) + CO_2 \rightarrow O\ (^3P) + W(\eta^1\text{-CO})(^7A')$ is also highly endothermic (108.6 kcal/mol).

Our calculations show that the ground electronic state of the W(η^1-CO) species is a septet $^7A'$ state, and its singlet, triplet, and quintet states lie 12.6, 18.3, and 2.1 kcal/mol higher in energy, respectively (see Figure 2b). These findings are consistent with data of Tan et al.,[24] who have predicted a septet electronic ground state for this species using the MCSCF method and including spin-orbital coupling into the calculation. However, these findings contradict with the data of Andrews and co-workers, who have reported, at the DFT level of theory, triplet[12] and quintet[23] ground states for the W(η^1-CO) molecule.

In general, the [WCO] system may have four different structures like W(η^1-CO), W(η^1-OC), W(η^2-CO) and OWC. As usual the iso-carbonyl isomer W(η^1-OC) is expected to be higher in energy than the carbonyl isomer W(η^1-CO). Therefore, below

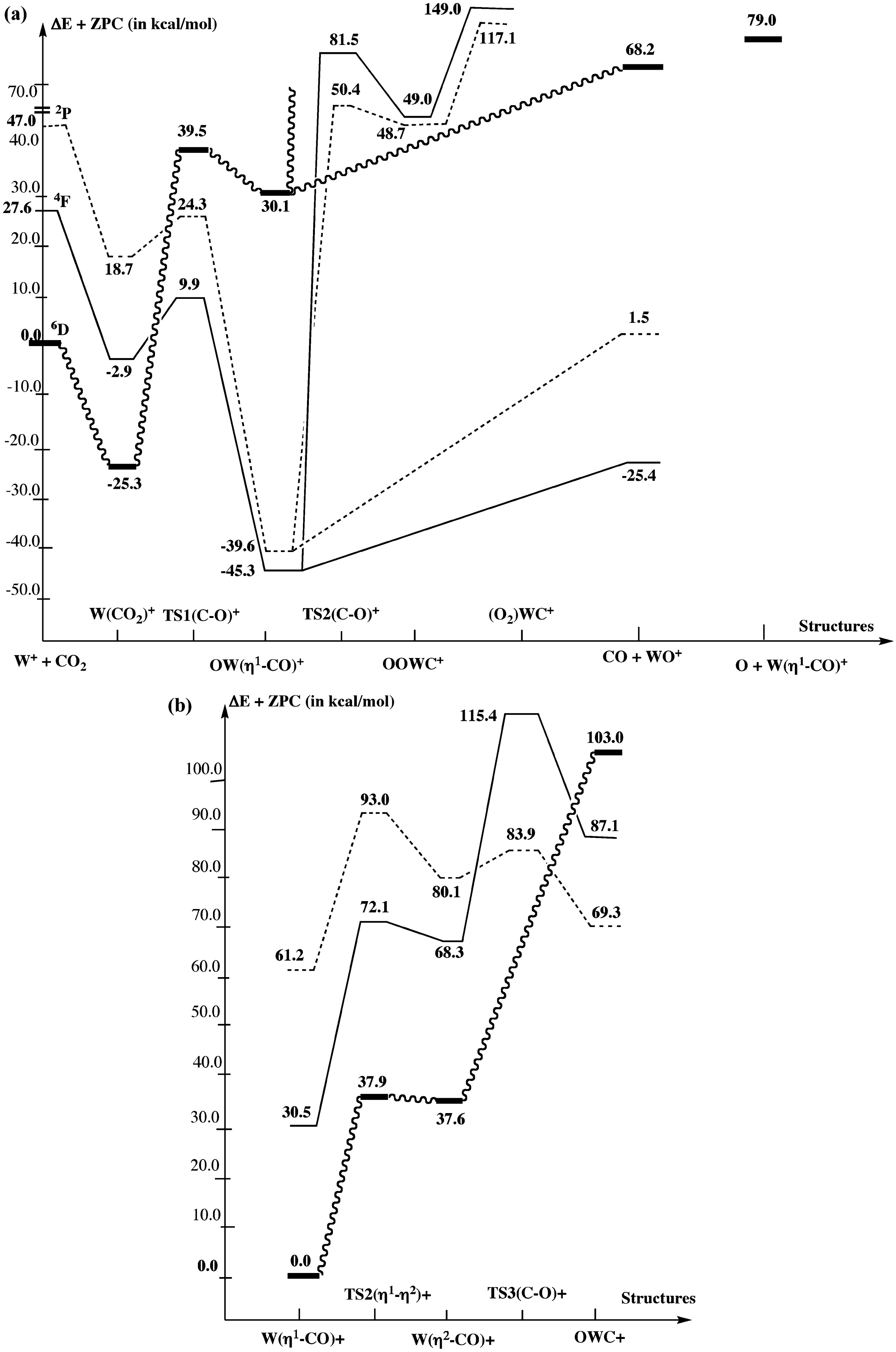
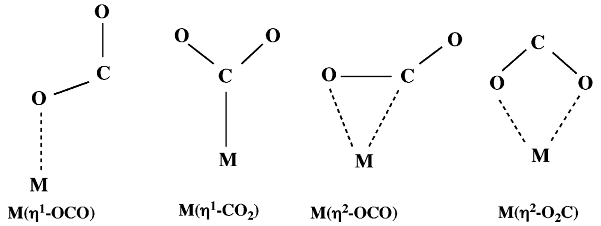


Figure 4. The calculated relative energies (in kcal/mol) of important intermediates, transition states and products of the reaction of W$^+$ with the CO$_2$ molecule: (a) potential energy surface of the oxidation pathway and (b) potential energy surface for isomerization of WCO$^+$ molecule.

CHART 1: Possible Isomers of the M(CO$_2$) Intermediate



we will not discuss the iso-carbonyl isomer W(η^1-OC), as well as the W(η^1-CO) → W(η^1-OC) isomerization process, in detail.

Among all the other three structures, the carbonyl isomer W(η^1-CO) is found to be the energetically most stable one. It is separated from the cyclic W(η^2-CO) isomer by 8.8 kcal/mol barrier (at the septet potential energy surface), and lies almost 2.1 kcal/mol lower than the septet W(η^2-CO) isomer. One should note that the W(η^1-CO) → W(η^2-CO) isomerization on the septet PES occurs via dissociation-and-addition mechanism while it occurs on the quintet, triplet and singlet surfaces via a migration mechanism. Another isomer, OWC, which is the product of the W(η^2-CO) → TS3(C−O) → OWC isomerization, has a singlet ground state and is separated from the reactant by a huge barrier. OWC isomer is calculated to be only 3.1 and 5.2 kcal/mol higher in energy than W(η^1-CO) and W(η^2-CO) isomers, respectively.

The above presented discussion (see also Figures 1, 2a and 2b) clearly show that at mild experimental conditions the gas-phase reaction of W with CO$_2$ proceeds with no (or small) barrier required for the first C═O bond activation and leads to the OWCO intermediate. At moderate temperature, intermediate OWCO can dissociate to give the WO + CO products. Thus, in the gas phase the reaction of W with CO$_2$ is an oxidation process, W(^{7}S) + CO$_2$ → OW(η^1-CO)(^{1}A′) → WO ($^5\Sigma^+$) + CO, and involves several low-lying electronic states of the reactants and intermediates.

Gas-phase reactions of W with CO lead to the formation of M(η^1-CO) complex, which is a 5.2 kcal/mol more stable than the C−O insertion product, OMC, and is separated from the latter by a large energy barrier.

2. Mechanism of the Reaction of W$^+$ with CO$_2$. Correspondingly, the first intermediate of the reaction of W$^+$ with CO$_2$ is found to be a W(CO$_2$)$^+$ complex. However, in contrary to the neutral W(CO$_2$) complex, where the most stable isomer has a W(η^2-OCO) structure, for the cationic complex W(CO$_2$)$^+$ the energetically most stable isomer is found to have a quasi-linear W(η^1-OCO)$^+$ structure.

This difference in structures of the W(CO$_2$) and W(CO$_2$)$^+$ complexes can be explained by the difference in the electron-transfer capability of the W atom and the W$^+$ cation: As could be expected, the W atom can easily (more so than the W$^+$ cation) transfer electron to CO$_2$ ligand to form the W$^{+\delta}$-(CO$_2$)$^{-\delta}$ structure with a bent CO$_2$ fragment. The ground electronic state of the cationic W(CO$_2$)$^+$ complex is found to be the high-spin sextet state. Its quartet and doublet states are 28.2 and 44.0 kcal/mol higher in energy.

As seen in Figure 4a, the reaction of W$^+$ with CO$_2$ proceeds via an insertion mechanism from the W(η^1-OCO)$^+$ intermediate. The transition state associated with this C═O bond insertion, TS1(C−O)$^+$, has a quartet ground state. Its sextet and doublet states are 29.6 and 14.4 kcal/mol higher in energy. Analysis of the geometry of the doublet, quartet and sextet TS1(C−O)$^+$ indicates that it is an earlier TS for quartet and doublet states (with activated C−O bond distances of 1.248 and 1.242 Å, respectively), but is a later TS for the sextet state (with the activated C−O bond distance of 1.866 Å). These geometrical features of TS1(C−O)$^+$ are consistent with the calculated energy of the W(η^1-OCO)$^+$ → TS1(C−O)$^+$ → OW(η^1-CO)$^+$ process: it is highly exothermic for the quartet and doublet states, but is endothermic for the sextet state process.

The product of the C−O bond insertion, OW(CO)$^+$, may have three different isomers, OW(η^1-CO)$^+$, OW(η^2-CO)$^+$, and OW-(η^1-OC)$^+$. However, we were able to localize only the OW(η^1-CO)$^+$ isomer, which has a quartet electronic ground state. Its doublet and sextet states are 5.7 and 75.4 kcal/mol higher in energy. The overall “ground state-to-ground state” insertion process, W(η^1-OCO)$^+$ (^{6}A) → TS1(C−O)$^+$ (^{4}A) → OW(η^1-CO)$^+$ (^{4}A) is calculated to be exothermic by 20.0 kcal/mol.

From the resulting OW(η^1-CO)$^+$ intermediate, the reaction may proceed via three distinct pathways, similar to the neutral W + CO$_2$ reaction discussed above. The first of them is an oxidation pathway, which occurs via the dissociation of the CO molecule. The ground state oxidation process OW(η^1-CO)$^+$ (^{4}A) → WO$^+$($^4\Sigma^+$) + CO ($^1\Sigma$) is calculated to be endothermic by 19.9 kcal/mol, while the overall W$^+$(^{6}D) + CO$_2$(^{1}A$_1$) → WO$^+$-($^4\Sigma^+$) + CO ($^1\Sigma$) oxidation reaction is 25.4 kcal/mol exothermic.

The second process starting from the OW(η^1-CO)$^+$ intermediate proceeds via the second C═O bond activation transition state TS2(C−O)$^+$, leading to the formation of the OOWC$^+$ intermediate, which later rearranges to the ion−molecular complex (O$_2$)−WC$^+$. The resulting (O$_2$)−WC$^+$ complex eliminates an O$_2$ molecule to form O$_2$ + WC$^+$ products.

The calculated barrier at the TS2(C−O)$^+$ is very high, 95.7 kcal/mol (calculated from the ground quartet state of OW(η^1-CO)$^+$ to the ground doublet state of TS2(C−O)$^+$). Ground-state reactions OW(η^1-CO)$^+$ (^{4}A) → WC$^+$($^4\Sigma^+$) + O$_2$ ($^3\Sigma_g$) and W$^+$-(^{6}D) + CO$_2$(^{1}A$_1$) → WC$^+$($^4\Sigma^+$) + O$_2$ ($^3\Sigma_g$) are found to be highly endothermic, 213.2 and 167.9 kcal/mol, respectively. Therefore, this pathway of the reaction of W$^+$ with CO$_2$ is unlikely to compete with the oxidation process.

Similarly, the third possible pathway, leading to the formation of atomic O and a W(CO)$^+$ complex via eliminatiion of the O-ligand from OW(η^1-CO)$^+$, is unlikely to be feasible under mild experimental conditions because the reactions OW(η^1-CO)$^+$ → W((η^1-CO)$^+$($^6\Sigma$) + O ($^3\Sigma$) and W$^+$(^{6}D) + CO$_2$(^{1}A$_1$) → W((η^1-CO)$^+$($^6\Sigma$) + O ($^3\Sigma$) are highly, 124.3 and 79.0 kcal/mol, endothermic, respectively.

Comparison of the above presented energetics for the three different pathways of the reaction of W$^+$ with CO$_2$ shows that the oxidation has generally lower barriers and is energetically the most accessible and feasible pathway. Therefore, we conclude that in the gas phase the reaction of W$^+$ with CO$_2$ proceeds via an oxidation pathway W$^+$(^{6}D) + CO$_2$(^{1}A$_1$) → WO$^+$($^4\Sigma^+$) + CO ($^1\Sigma$), which is 25.4 kcal/mol exothermic process. It proceeds with a moderate energy barrier and may produces two different intermediates W(η^1-OCO)$^+$ and OW-(η^1-CO)$^+$, among which the latter is energetically the most stable one, as it was the case for the neutral W + CO$_2$ reaction discussed above.

One should note that the W(CO)$^+$ complex which is the high-energy-product of the reaction of the W-cation with CO$_2$ could have several isomers, such as W(η^1-CO)$^+$, W(η^1-OC)$^+$, W(η^2-CO)$^+$, and OWC$^+$. We have excluded isomer W(η^1-OC)$^+$ from our discussion because it is clearly less stable than carbonyl complex W(η^1-CO)$^+$. As seen in Figure 4b, W(η^1-CO)$^+$ is the most stable isomer among all possible isomers of W(CO)$^+$. It has a sextet ground state. Its lowest quartet and doublet states are 30.5 and 61.2 kcal/mol higher in energy. The cyclic W(η^2-CO)$^+$ isomer is most likely to exist in its excited quartet or/and doublet electronic states. At its ground sextet state, cyclic W(η^2-CO)$^+$ isomer converges to the most stable linear W(η^1-CO)$^+$ isomer with almost no barrier. Another isomer of M(CO)$^+$, isomer OWC$^+$, also lies very high in energy compared to the linear W(η^1-CO)$^+$ isomer. The calculated energy difference between the ground state structures of W(η^1-CO)$^+$($^6\Sigma$) and OWC$^+$(^{2}A′) is 69.3 kcal/mol. The barrier separating OWC$^+$-(^{2}A′) from the W(η^1-CO)$^+$($^6\Sigma$) corresponds to the minimum on the seam of crossing of double and sextet PESs, and most likely is within 80 kcal/mol.

IV. Conclusions

From the above presented discussion, one can draw the following conclusions:

(i) At mild experimental conditions, the gas-phase reaction of W with CO$_2$ proceeds with a negligible barrier via an insertion pathway, which is a multi-state process and leads to the oxidation of the W center. The overall process W(^{7}S) + CO$_2$-(^{1}A$_1$) → W(η^2-OCO)(^{6}A′) → OW(η^1-CO)(^{1}A) → WO ($^3\Sigma^+$) + CO($^1\Sigma$) is calculated to be exothermic by 32.4 kcal/mol at the CCSD(T)[SDD+6-311G(d)]//B3LYP[SDD+6-31G(d)] level of theory. Possible intermediates of this reaction are the W(η^2-OCO) and OWCO complexes, among which the latter is 37.4 kcal/mol more stable, and lies 39.7 and 7.3 kcal/mol lower than reactants, W(^{7}S) + CO$_2$(^{1}A$_1$), and products, WO ($^3\Sigma^+$) + CO-($^1\Sigma$), respectively. The barrier separating W(η^2-OCO) from OWCO is small (8.0 kcal/mol, relative to the W(η^2-OCO) complex). The W(η^2-OCO) complex is characterized by W$^{+\delta}$−(CO$_2$)$^{-\delta}$ charge transfer.

(ii) Ionization of W does not change the character of the reaction of W with CO$_2$: Reaction of W$^+$ with CO$_2$, like its neutral analog, proceeds via an insertion pathway and leads to oxidation of W-center. The overall reaction W$^+$(^{6}D) + CO$_2$(^{1}A$_1$) → W(η^1-OCO)$^+$(^{6}A) → OW(η^1-CO)$^+$(^{4}A) → WO$^+$($^4\Sigma^+$) + CO($^1\Sigma$) is calculated to be exothermic by 25.4 kcal/mol. It proceeds with slightly large (9.9 kcal/mol) barrier and produces W(η^1-OCO)$^+$-(^{6}A) and OW(η^1-CO)$^+$(^{4}A) intermediates. Intermediate W(η^1-OCO)$^+$(^{6}A) is 20.0 kcal/mol less stable than OW(η^1-CO)$^+$(^{4}A), and separated from the latter by 35.2 kcal/mol barrier. Furthermore, complex W(η^1-OCO)$^+$(^{6}A) is characterized to be an ion-molecular complex of the type W$^+$−(CO$_2$).

(iii) Gas-phase reactions of M═W/W$^+$ with CO lead to the formation of W-carbonyl complex M(η^1-CO) for both M═W and M═W$^+$. The C−O insertion product, OMC, lies 5.2 and 69.3 kcal/mol higher than M(η^1-CO) isomer for M═W and W$^+$, respectively, and is separated from the latter by a large energy barrier.

Acknowledgment. We gratefully acknowledge financial support from the Office of Naval Research under a MURI Grant (Prime Award # N00014-04-1-0683 and Subaward # 2794-EU-ONR-0683) and the Emerson Center for the use of its resources.

Supporting Information Available: Complete ref 25; Table S1, B3LYP/[SDD + 6−31G(d)] calculated energies (in au) of the intermediates, transition states and products of the reactions of W and W$^+$ with CO$_2$ at their several lower-lying electronic states; Table S2, CCSD(T)/[SDD+6−311G(d)]//B3LYP/[SDD+6-311G(d)] calculated relative energies (in kcal/mol) and CCSD(T) T1 values of intermediates, transition states and products of the reactions W/W$^+$ + CO$_2$ at their several lower-lying electronic states. This material is available free of charge via the Internet at http://pubs.acs.org.

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