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Theoretical study on the reaction of W^+ with CO_2 in the gas phase

Xiao-Yan Yang [a], Yong-Cheng Wang [a,*], Zhi-Yuan Geng [a], Ze-Yu Liu [a], Han-Qin Wang [b]

[a] *Gansu Key Laboratory of Polymer Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, LanZhou, Gansu 730070, People's Republic of China*

[b] *Institute of Chemistry and Physics, Chinese Academy of Sciences, LanZhou, Gansu 730070, People's Republic of China*

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Abstract

The reaction pathway and energies for the gas-phase CO_2–CO conversion by W^+ are discussed from density functional theory (DFT) UB3LYP calculation at the relativistic effective core potential (ECP) of Stuttgart basis sets with W^+ and 6-311+G(2d) with CO_2. The reaction mechanism between W^+ and CO_2 is an insertion–elimination mechanism. The W^+ inserts with no energy barrier into a CO bond resulting in an $OWCO^+$ insertion product. The intrinsic reaction coordinate for the insertion process has been defined and the reaction mechanism has been investigated by analyzing various structures along this path. Crossing points (CPs) are localized, and possible spin inversion processes are discussed by means of the intrinsic reaction coordinate (IRC) approach.

Keywords: Two-state reactivity; Potential energy surfaces crossing points (CPs); Insertion–elimination mechanism; Endothermic process

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1. Introduction

Carbon dioxide is a very important natural source of carbon on our planet, and therefore the possibility of using it as a starting material for the synthesis of chemically useful compounds has received considerable attention [1–4]. Moreover, anthropogenic emissions of CO_2 are known to contribute to the greenhouse effect. Thus, recycling CO_2 through conversion to useful chemical compounds is also important from an environmental point of view. However, carbon dioxide is a thermodynamically very stable compound that needs to be activated for its utilization, for example through its interaction with transition metal complexes. For these reasons a good knowledge of the metal–CO_2 interaction is important to understand the role of the metal in these processes.

Recently, an experimental investigation was reported for transition metal cations with carbon dioxide in the gas phase by Bohme [5]. Carbon dioxide was found to react in a bimolecular fashion by O atom transfer only with 9 early transition-metal cations: the group 3 cations Sc^+, Y^+, and La^+, the group 4 cations Ti^+, Zr^+, and Hf^+, the group 5 cations Nb^+ and Ta^+, and the group 6 cation W^+. These systems exhibit complicated behavior because the ground states of the reactants and products have different spin states. The DFT calculation used in this paper is to study the reaction pathways of carbon dioxide with W^+ including reliable structures of the reactants, products, intermediates, and transition states as well as their accurate energies. Meanwhile, the crossing between the two potential energy surfaces (PESs) of different spin states is discussed as well as the crossing points (CPs) is located and characterized.

2. Computational details

In the present work, all molecular geometries (reactants, intermediates, transition states (TSs) and products) were fully optimized on three PESs. A spin-unrestricted hybrid functional of exact (Hartree–Fock) exchange with local and gradient-corrected exchange and correlation terms, as

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* Corresponding author. Tel.: +86 931 7970237; fax: +86 931 7971989.
E-mail address: wangyc@nwnu.edu.cn (Y.-C. Wang).

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first suggested by Becke [6,7], was used in our calculations, which is commonly known as UB3LYP. We have chosen this method since recent calibration calculations on transition metal compounds have shown that this hybrid functional provides accurate results for the geometries and vibrational frequencies of systems containing transitional metal atoms [8–12]. Our previous investigations [13,14] also have underlined the reliability of the B3LYP functional for describing PESs, predicting electronic structures and calculating thermochemical properties for the systems containing a relatively large number of electrons. The basis set used consists of the relativistic effective core potential (ECP) of Stuttgart on W, the 5d and 6s in W are treated explicitly by a (8s7p6d) Gaussian basis set contracted to [6s5p3d]. For O and C, we use 6-311+G(2d) basis set. All stationary points are characterized by vibrational analysis and the zero-point energy (ZPE) corrections are included. The transition state structures all represent saddlepoints, characterized by one negative eigenvalue of the Hessian matrix. To ensure reliability of the reaction path, the pathways between the transition structures and their corresponding minima have been characterized by the internal reaction coordinate (IRC) calculations. All computations are carried out using the GAUSSIAN98 program package [15].

3. Results and discussion

3.1. Overview of the stationary points

The optimized geometries of various compounds in three different spin surfaces are collected in Fig. 1. Fig. 2 demonstrates computed potential energy diagrams in three spin states, the diagrams connecting the reaction intermediates (local minima) and the transition states (saddle points) on the PESs. Table 1 shows the total and relative energies for the optimized species which are calculated at UB3LYP level.

Carbon dioxide can behave both as a bidentate ligand (η^2-O,O or η^2-C,O) or as a monodentate ligand (η^1-O or η^1-C) when interacting with neutral metal atom [16–18]. However, cationic metals are bound to CO_2 electrostatically, and since the leading term is charge-quadrupole and CO_2 has a negative quadrupole moment, the linearη^1-O (end-on) coordination is the most favorable. Test calculations on reaction of the first-row transition metal cations with CO_2 have confirmed this expectation [9]. In this paper, the η^2-C,O mode is found on the doublet and quartet PESs. Moreover, their energies are all higher than the η^1-O one. Any attempt to optimize other structures for the W-metal ion in different electronic states collapse to the linear isomer. The reason is that the repulsion between the occupied d orbitals of the metal and CO_2 is larger in those coordination modes than in theη^1-O one, while the electrostatic stabilization is smaller. So the linear η^1-O (end-on) coordination is the most favorable, which is similar to the reaction of the first transition metal cations with CO_2 [9].

First considering the linear W^+–OCO (IM1) systems, the first step of the reaction is spontaneous formation of IM1 along three state spin PESs. All IM1 structures are planar. Since the bonding is mainly electrostatic, the interaction between carbon dioxide and metal cation produces only a small asymmetry in the two CO bond lengths; the CO bond length adjacent to the metal ion increases about 0.02 Å, while the other CO bond length decreases about 0.02 Å. This variation is very similar to the reaction of first transition-metal cations with CO_2 [9], which indicates that no significant π back-donation from the metal ion to CO_2 is present.

In this reaction, the insertion of W^+ into a CO bond can easily occur to form $OWCO^+$ (IM3) complex that is viewed as carbonyl complexes of diatomic WO^+ species [19]. The bond lengths of WO^+ and CO in IM3 are shorter than those of IM1 and close to that in the free WO^+ and CO. The relative energies of $OWCO^+$ computed with respect to the ground state W^++CO_2 asymptote show that the insertion reaction is exothermic (except in sextet spin state). This is due to the fact that W^+ form a strong metal oxide bond. In doublet state the W—O bond becomes shorter and W—C bond becomes longer than those of in quartet and sextet states. Comparison of the energy of IM3 in three spin states also reveals that the dissociation of CO from the insertion product is more feasible on the doublet surface (Table 1).

In order to explain the reason of forming the bent structure, we analyze the frontier molecular orbital of $OWCO^+$. The analysis of a″ occupied orbitals in Fig. 3b, d and f show the mixture of W^+ $5d_{xz}$ and O $2p_z$ orbitals. The other interaction of a″ occupied orbitals in Fig. 3a, c and e is the bonding character between the W^+ $5d_{yz}$ and O $2p_z$ orbitals. Because the $5d_{xz}$ orbital is virtually orthogonal to the $5d_{yz}$ orbital, $OWCO^+$ has a bent structure, which will reduce the repulsion between the WO^+ and CO orbitals.

3.2. Crossing point

CPs and crossing seams are the subjects here. The potential energy surface (PES) of the system that consists of four atoms is a function of internal degree of freedom of dimension 6. The crossing seam between the two PESs is therefore a hyperline of dimension 5, and it is difficult to perform a detailed inspection of the crossing seam as a practical example. Thus to locate the crossing between the two PESs of different spin states, the procedure used by Yoshizawa et al. [20] has been selected. We have carried out single-point energy calculations (in the excited state) as a function of the structural change along the IRC of the ground state, and vice versa [21,22].

In this reaction, two electronic states are involved: the reactant, W^+, which has a sextet spin multiplicity as ground state, while the product, WO^+, which has a doublet spin multiplicity. Therefore, at least a crossing and spin inversion process must take place in the reaction