On the electronic structure of mono-rhenium oxide clusters: ReO$_n^-$ and ReO$_n$ ($n = 3, 4$)

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Abstract

We report a photoelectron spectroscopy and density-functional study on mono-rhenium oxide clusters: ReO$_n^-$ and ReO$_n$ ($n = 3, 4$). Electron affinities of ReO$_3$ and ReO$_4$ are measured to be 3.53 ± 0.05 and 5.58 ± 0.03 eV. ReO$_3$ is shown to possess a planar $D_{3h}$ ($^1A_1$) ground state and ReO$_4$ adopts a nonplanar $C_{3v}$ ($^2A_1$) structure. ReO$_3$ has $T_d$ ($^2A_1$) structure, whereas ReO$_4$ has $C_1$ ($^2A_1$) symmetry due to Jahn–Teller effects and contains a Re–O$^-$ radical unit. Localized Re 5d electrons in ReO$_3^-$ and ReO$_4^-$ give rise to Re$^{5+}$ and Re$^{6+}$ centers, making them simple models for O$_2$ activation.

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1. Introduction

Rhenium oxides are used as industrial catalysts for olefin metatheses [1–3], and have been examined as well for other catalytic reactions such as hydrogenation, selective reduction of NO, and oxidation reactions. The prominent rhenium oxo-compound, methyltrioxorhenium (MTO, CH$_3$ReO$_3$), represents one of the most versatile oxidation catalysts known to date [4–6]. However, the underlying mechanisms and kinetics of many rhenium oxide catalytic processes are still not well understood. Gas-phase clusters can be used as effective models toward mechanistic understanding of catalysis at the molecular level [7]. Mono-rhenium oxide clusters have been studied in a number of previous works, both experimentally [8–12] and theoretically [9,12,13]. Collision induced dissociation (CID) and ligand exchange reactions were conducted for a series of rhenium–oxygen complex cations, Re(O$_2$)$_n^+$ ($n = 0–3$), Re(O$_2$)$_4^+$, Re(O$_2$)$_4^+$, Re$_2$(O$_2$)$_4^+$, ReO$_4$$_2^-$, and ReO$_4$(O$_2$)$_2^-$, revealing ReO$_3^-$ as a stable core for the ReO$_3^-$ complex [8]. The ReO$_2^-$ and ReO$_3^-$ cluster anions were studied using photoelectron spectroscopy (PES), yielding electron affinities of 2.5 ± 0.1 and 3.6 ± 0.1 eV for ReO$_2^-$ and ReO$_3^-$, respectively [11]. Matrix infrared spectra were reported for Re, Ru, and Os oxide molecules, including ReO$_2^-$ and ReO$_3^-$ [12].

We are interested in probing the structural and electronic properties of early transition metal oxide clusters [14–22], aiming at providing controllable molecular models for mechanistic insight into oxide catalysis [23]. In the current study, we combine anion PES with density-functional theory (DFT) calculations to elucidate the structures and bonding in the simplest rhenium oxide clusters: ReO$_3$ and ReO$_4$ ($n = 3, 4$). The electron affinity of ReO$_4$ is measured to be very high (5.58 ± 0.03 eV), suggesting that this neutral cluster is an extremely strong oxidizer and belongs to the class of high electron affinity species called superhalogen [24,25]. DFT calculations show that ReO$_3$ and ReO$_4$ possess $D_{3h}$ and $T_d$ symmetries, respectively, with classical oxo Re=O bonds. The ReO$_4$ cluster features an elongated Re–O$^-$ oxyl bond with oxygen radical character. The ReO$_3^-$ and ReO$_4^-$ clusters possess two and one localized Re 5d electrons, respectively, and provide well-defined Re$^{5+}$ and Re$^{6+}$ centers. The localized 5d electrons can be transferred to an approaching O$_2$ molecule, making ReO$_2^-$ and ReO$_3^-$ simple cluster models for O$_2$ activation.

2. Experimental and computational methods

2.1. Photoelectron spectroscopy

The experiment was carried out using a magnetic-bottle-type PES apparatus equipped with a laser vaporization cluster source, details of which were described elsewhere [26]. Briefly, ReO$_n^-$ type anion clusters were produced by laser vaporization of a rhenium disk target in the presence of a helium carrier gas seeded with 0.5% O$_2$. The cluster anions were analyzed using a time-of-flight mass spectrometer. The ReO$_3^-$ and ReO$_4^-$ clusters of current interest were each mass-selected and decelerated before being photodetached. The photodetachment experiment was conducted at 193 nm (6.424 eV) from an ArF excimer laser. Effort was made to choose colder clusters (that is, those with long resident times in the nozzle) for photodetachment, which was shown previously to be critical for obtaining high quality PES data. Photoelectrons were collected at nearly 100% efficiency by the magnetic-bottle...
and analyzed in a 3.5 m long electron flight tube. The PES spectra were calibrated using the known spectrum of Au, and the energy resolution of the apparatus was $\Delta E/E_k \sim 2.5\%$, that is, ~25 meV for 1 eV electrons.

2.2. Theoretical density functional theory calculations

Theoretical calculations were performed at the DFT level using the hybrid B3LYP functional [27–29]. A number of structural candidates including different spin states and initial structures were evaluated, and the search for the global minima was performed using analytical gradients with the Stuttgart relativistic small core potential and the valence basis sets [30,31] augmented with two f-type and one g-type polarization functions \([\zeta(f) = 0.327, 0.955; \zeta(g) = 0.636]\) for Re as recommended by Martin and Sundermann [32] and the aug-cc-pVTZ basis set for oxygen [33,34]. Scalar relativistic effects, that is, the mass velocity and Darwin effects, were taken into account via the quasi-relativistic pseudo-potentials. Vibrational frequency calculations were performed at the same level of theory to verify the nature of the stationary points. Vertical detachment energies (VDEs) were calculated using the generalized Koopmans’ theorem by adding a correction term to the eigenvalues.

The electron binding energy for ReO$_3$ is predicted to be a planar $D_{2h}$ (1$A'_1$) closed-shell structure (Figure 2a), consistent with that from previous DFT calculations by Zhou et al. [12]. The Re–O bond length is 1.733 Å. The lowest triplet state of ReO$_3$ ($C_{6v}$, $3A'$) is 1.67 eV higher

![Figure 1. Photoelectron spectra of (a) ReO$_3$ and (b) ReO$_4$ at the 193 nm (6.424 eV).](image)

### Table 1

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$^a$ All energies are in eV.

$^b$ Numbers in the parentheses represent experimental uncertainties in the last digit.

The ground-state electron configurations for the anions are \([(5e)^0(1a'_2)^2(5a'_1)^2]/2\) for ReO$_3$ and \([(5e)^0(1a'_2)^2(5a'_1)^2]/2\) for ReO$_4$.

$^c$ Electron affinity of the neutral cluster.

$^d$ The X–A energy gap of ReO$_3$ is defined by the ADE difference to be 2.48 ± 0.05 eV.

3. Experimental results

The PES spectra of the ReO$_3$ and ReO$_4$ clusters at 193 nm are shown in Figure 1. The observed spectral bands are labeled with letters, X and A. The measured adiabatic detachment energies (ADEs) and VDEs are summarized in Table 1, where they are compared with theoretical data at the B3LYP level.

The PES spectrum of ReO$_3$ (Figure 1a) exhibits two well-separated bands: X and A. Both bands are reasonably sharp, and band X shows substantially higher intensity relative to band A. The VDEs for bands X and A are measured from their well-defined band maxima to be 3.62 and 6.08 eV, respectively (Table 1). Since no vibrational structures are resolved for band X, the ground-state ADE is evaluated to be 3.63 eV, and the smallest Re/Lanl2dz/O/6-31G basis sets, and the eigenvalues appear to be relatively insensitive to the choice of basis sets. This is in contrast to the cases of atomic anions, for which the applicability of DFT has been controversial [36,37]. Only the B3LYP/Re/Stuttgart + 2f/1g/O/aug-cc-pVTZ results will be presented in this Letter. All calculations were performed with the Gaussian 03 software package [38]. Three-dimensional contours of the molecular orbitals (MOs) were visualized using the VMD software [39].
in energy (not shown). The neutral ReO$_3$ cluster is found to have a doublet ground state, (C$_3$v, 2A$_1$) (Figure 2b), also in agreement with the previous calculations[12]. The planar D$_{3h}$ neutral structure is a transition state for inversion with a low out-of-plane imaginary vibrational frequency ($\sim$143.1 cm$^{-1}$) and a small energy barrier ($\sim$0.1 eV). The Re–O bond length for neutral ReO$_3$ (1.706 Å) is decreased by about 0.03 Å as compared to the anion. Significant anion-to-neutral geometric change occurs in the out-of-plane angle for ReO$_3$, with a dihedral angle of 24.6° between the OReO and OOO planes, showing a pyramidalization at the central Re site in the neutral cluster.

4.2. ReO$_n$ and ReO$_4$

Using the isomeric structures of ReO$_3$ as the starting points, we searched the potential energy surfaces for ReO$_n$ and located a number of isomers. Selected structures are shown in Figure 2. The ground state of ReO$_4$ is predicted to be T$_d$ (1A$_1$) symmetry (Figure 2c) with a Re–O bond length of 1.738 Å, consistent with the previous calculations[12]. Alternative structures for ReO$_4$ are well separated in energy from the ground state (>3 eV). The lowest triplet state, C$_{2v}$ (3B$_2$) (Figure 2d), with the four oxygen atoms bonded to Re in a distorted tetrahedron, is 3.21 eV above the ground state. A singlet structure with a di-oxygen (O–O) bond [C$_{2v}$ (1A$_1$), Figure 2e] is found to be 4.02 eV higher in energy, in which the peroxy O–O bond length is calculated to be 1.453 Å, close to that of the peroxide anion (1.49 Å).

For neutral ReO$_4$, the ground state is predicted to be a doublet state, C$_i$ (2A') (Figure 2f), which is distorted from the T$_d$ symmetry due to the Jahn–Teller effect, in agreement with a recent theoretical study [13]. The distortion leads to two kinds of Re–O bonds: one with the longer bond (1.830 Å), which we label as oxyl (–O$^-$) oxygen, and three as oxo (=O) oxygen atoms with shorter bonds (1.703, 1.703, and 1.743 Å). A D$_{2d}$ (2A$_2$) structure with the Re–O bond lengths of 1.739 Å is predicted to lie 0.23 eV above the neutral ground state (Figure 2g). In addition, a doublet dioxide peroxy (O$_2$)ReO$_2$ structure (Figure 2h) is found to be 1.55 eV above the ground state.

5. Comparison between experiment and theory

While anion clusters are challenging for the standard DFT methods, for transition metal systems the DFT methods remain the default choice. Recent benchmarking studies have shown that different DFT methods (such as pure DFT versus hybrid DFT) are highly complimentary with each other, and the key is to choose an appropriate method for a particular system [40,41]. B3LYP appears to perform well for Re oxide clusters. The ground state of ReO$_3$ is D$_{3h}$ (1A$_1$) with a valent electron configuration...
Figure 4. (a) The pictures of the degenerate HOMO orbitals of the ReO$_3$ (1A$_1$) anion. (b) Spin densities of the ReO$_3$ (C$_2$v-A') neutral cluster. The numerical spin densities over O atoms are shown (in parentheses) in |e|. Blue represents the location of maximum density. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

. . . .(2a$^1$)$_1^2$(5e)$_1^2$(1a$^2$)$_1^3$(5a$^1$)$_1^2$, where the 5a$^1$ HOMO (Figure 3a) is nonbonding mainly composed out of the d$_{z^2}$ atomic orbital of Re. All deeper MOs are of O 2p character. The ReO$_3$ neutral is predicted to be a doublet (C$_{2v}$, 2A$_1$) with an electron configuration . . . (6a$_1$)$_1^2$(6e)$_1^2$(1a$_2$)$_1^3$(7a$_1$)$_1^1$. The half-occupation of the 7a$_1$ MO induces a distortion in which Re is substantially out of the plane (24.6°) defined by the three oxygen atoms (Figure 2b). There are only minor changes in the Re–O bond length between ReO$_3$ and ReO$_4$, and thus the Franck–Condon envelope for the ground–state transition should be dominated by the inversion mode. The ADE and VDE for electron detachment from the 5a$^1$ MO are predicted as 3.50 and 3.63 eV (Table 1), respectively, in excellent agreement with the experimental data (ADE: 3.53 ± 0.05 eV; VDE: 3.62 eV). Pramanik et al. [11] previously reported an electron affinity of 3.6 ± 0.1 eV for ReO$_3$. The first excited state of ReO$_4$ (band A; Figure 1a) is observed at a VDE of 6.08 eV, which should be assigned to electron detachment from the (1a$_2$) orbital (calculated VDE: 5.83 eV). It seems that the calculation underestimates the higher VDEs by more than 0.25 eV. Assuming similar theoretical errors, we predicted that detachments from the 5e and 2a$^2$ orbitals are probably not accessible in the current experiment.

The ReO$_3$ anion is a stoichiometric molecule. The ground state of ReO$_3$ is predicted to be a closed-shell $T_d$ (1A$_1$) with a valent electron configuration . . . (5t$_2$)$_1^3$(1t$_1$)$_1^3$, which primarily consist of O 2p characters. The triply degenerate HOMO (1t$_1$) orbitals are depicted in Figure 4a. The calculated ground-state ADE and VDE upon detachment from the 1t$_1$ HOMO are 5.65 and 5.83 eV, respectively, in excellent agreement with the experimental measurements (ADE: 5.58 ± 0.03 eV; VDE: 5.83 eV). Removal of an electron from the tetrahedral $T_d$ ReO$_3$ results in a jahn–Teller effect, distorting the neutral to a lower C$_2v$ symmetry, consistent with the relatively broad ground-state PES band (Figure 1b). The next detachment channel is from 5t$_2$ with a calculated VDE of 6.48 eV, which is experimentally not accessible at the 193 nm (6.424 eV) photon energy.

6. Discussion

6.1. The PES spectrum of ReO$_3^-$ and comparison with the electronic structure of ReO$_3$ bulk oxide

The PES spectrum of ReO$_3^-$ exhibits two bands with distinct electron binding energies: X (VDE: 3.62 eV) versus A (VDE: 6.08 eV). The X band is from the metal-based d$_z^2$ lone pair (Figure 3a) and the A band is from O 2p type orbitals. Our prior PES studies on metal oxide clusters have shown that metal-based PES bands are normally well separated from the O 2p-based ones, and the latter appear at much higher binding energies (typically >5 eV) [14–19]. The ADE difference between bands X and A defines the electronic excitation energy (2.48 eV; Table 1) for the ReO$_3$ neutral cluster, which is the molecular analog of the energy gap between the Re 5d conduction band and the O 2p valence band of bulk ReO$_3$ oxide.

Rhenium trioxide crystallizes in a simple cubic lattice [42], comprising of a network of corner-sharing ReO$_6$ octahedra. The ReO$_3$ oxide is unique in that it is the only stable trioxide of the group VIIb elements (Mn, Tc, and Re) and it behaves as a metal because of the availability of one 5d electron on each Re center. Optical reflectivity measurements of the ReO$_3$ single crystal by Feinleib et al. [43] revealed an interband threshold of about 2 eV. Interestingly, the energy separation we observed for the gas-phase ReO$_3$ cluster (2.48 eV) is comparable to that of the bulk ReO$_3$ oxide.

6.2. On the high electron affinity of ReO$_4^-$

The perrenate anion, ReO$_4^-$, dominates the chemistry of rhenium [44]. However, the exact value of the electron affinity of ReO$_4^-$ has been elusive. An early ion–molecule reactivity study in 1972 suggested a lower limit of the electron affinity of ReO$_4$ to be 2.5 eV [45]. This was refined later in 1975 on the basis of thermochemical data to be 4.46 ± 0.50 eV (430 ± 50 kJ/mol) [46]. The current PES measurement yields an electron affinity of 4.58 ± 0.03 eV for ReO$_4$ as is also borne out from our theoretical calculation, which is far greater than the previously known values (by ~1.1 eV). The electron affinity of ReO$_4$ is among the highest ever reported in the gas phase [47], suggesting that this neutral cluster is an extremely strong oxidizer and belongs to the class of novel chemical species called superhalogens [24,25]. It should be noted that the electron affinity of ReO$_4^-$ is substantially higher than that of its valent isoelectronic 3d counterpart MnO$_4^-$ (electron affinity: 4.80 ± 0.10 eV) [48]. The current measurement suggests that ReO$_4^-$ is a more stable anion than MnO$_4^-$, which appears to be consistent with their known chemistries, that is, the ReO$_4^-$ anion is more stable in solution than MnO$_4^-$.

6.3. Chemical bonding in ReO$_3^n-$ and ReO$_n$ (n = 3, 4)

The Re–O bonding in bulk Re oxides involves both ionic and covalent characters. For the simple mono-rhenium oxide clusters, ReO$_3$ and ReO$_n$ (n = 3, 4), the chemical bonding can be understood using the valence-bond description as schematically shown in Figure 5. In ReO$_3$, the valence electrons of Re form three Re=O double bonds and an electron lone pair on the Re center (Figure 5a), resulting in a closed-shell, planar $D_{3h}$ (1A$^1$) structure. Removal of an electron from the d$_z^2$ orbital of Re gives rise to a significantly nonplanar configuration in the ReO$_3$ neutral cluster (Figure 5c), but no significant changes occur in the Re–O bond length between ReO$_3$ and
ReO$_3$ and thus the three Re=O terminal bonds retain intact in ReO$_3$.

In the stoichiometric ReO$_3$ anion, all the valence electrons on Re are used to form Re=O double bonds, resulting in a highly stable tetrahedral molecule (Figure 5b). Removal of an electron from ReO$_3$ destabilizes the tetrahedral symmetry in the ReO$_4$ neutral, due to the Jahn–Teller effect. Interestingly, the ReO$_4$ neutral cluster features three Re=O double bonds and an elongated Re–O bond (720 ± 71 kJ/mol)[49].

Indeed, the Re–O bond strength may be caused by the different M–O bond strengths. In- deed, the ReO$_4$ structure may be caused by the different M–O bond strengths. Indeed, the ReO$_4$ structure may be caused by the different M–O bond strengths. Indeed, the ReO$_4$ structure may be caused by the different M–O bond strengths.

As shown in Figure 3, MO analysis shows that Re 5d electrons in ReO$_3$ and ReO$_4$ are essentially localized on the Re center, giving rise to well-defined Re$^{4+}$ and Re$^{5+}$ sites, respectively. These sites should be chemically active and may act as simple molecular models for catalytic centers in bulk catalysts such as the Re$^{4+}$–oxo complexes. The localized 5d electrons on the Re$^{4+}$ and Re$^{5+}$ sites may be readily transferred to the π* orbital of an approaching O$_2$ molecule, which would activate O$_2$ and yield peroxide (ReO$_3$)$_2$(O$_2$)$^{2-}$ and superoxide (ReO$_3$)$_2$(O$_2$) complexes, respectively.

7. Conclusions

Anion photoelectron spectroscopy has been combined with density-functional theory calculations to study the electronic structure and chemical bonding of the simplest rhodium oxide clusters: ReO$_3$ and ReO$_5$ (n = 3, 4). The experimentally measured adiabatic and vertical detachment energies for both anions are important physical properties of rhodium oxide species. DFT calculations predict that the ReO$_3$ and ReO$_5$ clusters possess $D_3h$ ($A_1'$) and $C_3v$ ($A_1'$) ground states with three o xo Re=O bonds, respectively. A tetrahedral coordination environment is found for ReO$_3$ and ReO$_5$, where the Re$^{5+}$ and Re$^{6+}$ sites may be chemically active and may act as simple molecular models for catalytic centers in bulk catalysts such as the Re$^{4+}$–oxo complexes. The localized 5d electrons on the Re$^{4+}$ and Re$^{5+}$ sites may be readily transferred to the π* orbital of an approaching O$_2$ molecule, which would activate O$_2$ and yield peroxide (ReO$_3$)$_2$(O$_2$)$^{2-}$ and superoxide (ReO$_3$)$_2$(O$_2$) complexes, respectively.

Acknowledgments

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