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Collision-induced dissociation of MO^+ and MO_2^+ (M = Ta and W): Metal oxide and dioxide cation bond energies[☆]

Christopher S. Hinton[a], Murat Citir[a], Manuel Manard[b], P.B. Armentrout[a,*]

[a] Chemistry Department, University of Utah, 315 S. 1400 E. Rm 2020, Salt Lake City, UT 84112, United States
[b] National Security Technologies, LLC, Special Technologies Laboratory, 5520 Ekwill St., Santa Barbara, CA 93111, United States

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ABSTRACT

The collision-induced dissociation (CID) of TaO^+, WO^+, TaO_2^+, and WO_2^+ with Xe along with reactions of TaO^+ and WO^+ with O_2 are studied as a function of kinetic energy using guided ion beam tandem mass spectrometry in order to elucidate the thermochemistry of the MO_2^+ species. The kinetic energy dependences for the CID reactions show endothermic behavior, whereas the $MO^+ + O_2 \rightarrow MO_2^+ + O$ reactions proceed near the collision limit indicating exothermic processes. Analyses of the endothermic CID reaction cross sections yield 0 K threshold energies in eV of $E_0(Ta^+–O) = 7.01 \pm 0.12$, $E_0(W^+–O) = 6.72 \pm 0.10$, $E_0(OTa^+–O) = 6.08 \pm 0.12$, and $E_0(OW^+–O) = 5.49 \pm 0.09$. The nature of the bonding in MO^+ and MO_2^+ is discussed and compared for Ta and W and analyzed using theoretical calculations at the B3LYP/HW+/6-311 + G(3df) level of theory. Bond energies for all MO^+ and MO_2^+ species are calculated using geometries calculated at this level as well as BHLYP and CCSD(T) levels and the Stuttgart–Dresden (SDD) and the Def2TZVPP basis sets. Reasonable agreement between the theoretical bond energies and experimental CID threshold energies for TaO^+, WO^+, TaO_2^+, and WO_2^+ is found. Potential energy surfaces for the reaction of the metal cations with O_2 are also calculated at the B3LYP level of theory and reveal additional information about the reaction mechanisms.

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1. Introduction

The oxides of transition metals have properties that enable them to play vital roles in industrial, organometallic, and atmospheric chemistry [1–3]. In understanding the origins of these important properties, it can be useful to study the binding of the simplest examples of each species. Insight into the interaction of the metals and their oxides with O_2 can be obtained by examining reactions in the gas phase using a guided ion beam tandem mass spectrometer. The gas phase is an ideal arena for detailed study of the energetics of bond-making and bond-breaking processes at a molecular level. Because metal supports and interactions are absent, quantitative thermodynamic and intrinsic mechanistic information for various bond activation processes can be obtained.

Our group has previously used guided ion beam tandem mass spectrometry to study diatomic metal monoxide cations, MO^+, of the first-row [4–12], second-row [6,10,13–18], transition metals and other metals [10,19–21], but as yet have examined only a few third-row transition metals [22–24]. Likewise, our work has encompassed fewer studies of metal dioxide cations, MO_2^+, which include first-row [10,11], second-row [10,15–18], third-row [25] transition metals, and other metal cations [10]. In the present study, we extend these studies to the third-row transition metal ions, tantalum and tungsten. Using guided ion beam tandem mass spectrometry, we obtain the kinetic energy dependences of both exothermic and endothermic processes involving these species. Analyses of such data provide experimental thermochemistry that can be used as benchmarks for comparison with theoretical models of the structure of the metal oxides and dioxides.

Previous thermodynamic information on the monoxide and dioxide cations of tantalum and tungsten originates from several sources and is summarized in Table 1. In our laboratory, we have examined the endothermic reaction of Ta^+ with CO, yielding the bond dissociation energy (BDE) of $Ta^+–O$ as 7.10 ± 0.12 eV [23]. This value agrees nicely with 7.18 ± 0.14 as derived using Eq. (1)

$$D(M–O) + IE(M) = D(M^+–O) + IE(MO) \tag{1}$$

and the values IE(Ta) = 7.5495 eV [26], $D_0(TaO) = 8.24 \pm 0.13$ eV from Pedley and Marshall [27], and $IE(TaO) = 8.61 \pm 0.02$ eV from a photoelectron experiment of Dyke et al. [28] (see [23] for further details). These values contrast with that listed in a review by Schröder et al. [29], $D(Ta^+–O) = 8.15 \pm 0.65$ eV, taken from information in the GIANT compilation [30], which uses older values for IE(Ta) = 7.40 eV [31] and $IE(TaO) = 7.92 \pm 0.1$ eV [32], along with $\Delta_f H_0(TaO) = 2.08 \pm 0.65$ eV [33], and also

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[☆] In honor of John R. Eyler's many contributions to ion chemistry and spectroscopy.
[*] Corresponding author. Tel.: +1 801 581 7885; fax: +1 801 581 8433.
E-mail address: armentrout@chem.utah.edu (P.B. Armentrout).

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Table 1
Experimental thermochemical data for tantalum and tungsten oxides and dioxides.

M^+–O	IE(M)	D_0(M–O)	IE(MO)	D_0(M^+–O)	
				Literature	This work
Ta^+–O	7.5495[a]	8.16 ± 0.12[b] 8.24 ± 0.13[c] 8.4 ± 0.5[d] 8.65 ± 0.65[e]	8.69 ± 0.18,[b] 8.61 ± 0.02[f] 7.92 ± 0.1,[g] 7.5 ± 0.5[h] 6 ± 0.5,[d] 8.70 ± 0.17[i]	7.10 ± 0.12[b] 7.18 ± 0.14[a,c,f] 8.15 ± 0.65[j]	7.01 ± 0.12
W^+–O	7.864[k]	7.01 ± 0.31[b] 6.92 ± 0.44[c] 6.95 ± 0.44[l]	8.04 ± 0.45,[b] 8.1 ± 0.3,[m] 9.1 ± 1,[n] 7.19 ± 0.32[i]	6.77 ± 0.07[b] 6.68 ± 0.53[c,k,m] 7.16 ± 0.43[m] 5.46 ± 0.43[j]	6.72 ± 0.10
OTa^+–O		6.87 ± 0.23[h] 6.61 ± 0.92[d,l]	8.5 ± 0.5,[h] 9 ± 0.5[d] 9.54 ± 0.32[i]	6.07 ± 1.05[j] 6.73 ± 0.80[d,f,h]	6.08 ± 0.12
OW^+–O		6.15 ± 0.53[l]	9.6 ± 0.3,[o] 9.5 ± 0.5,[p] 9.9 ± 1.0,[q] 9.8,[r] 9.9 ± 0.6[n] 8.76 ± 0.69[i]	5.72 ± 1.17[j] $4.6_5 \pm 0.7$[l,m,o]	5.49 ± 0.09

[a] Simard et al. [26].
[b] Armentrout et al. [23].
[c] Pedley and Marshall [27].
[d] Inghram et al. [37].
[e] Lias et al. (GIANT Tables) [30].
[f] Dyke et al. [28].
[g] Ackermann et al. [32].
[h] Smoes et al. [38].
[i] This work.
[j] Schröder et al. [29].
[k] Campbell-Miller and Simard [35].
[l] JANAF tables [33].
[m] Blagojevic et al. [34], corrected to 0 K.
[n] DeMaria et al. [36].
[o] Gusarov et al. [39].
[p] Balducci et al. [40].
[q] Yamdagni et al. [41].
[r] Drowart et al. [42].

leads to $D_0(TaO) = 8.65 \pm 0.65$ eV. Likewise, we have previously measured the W^+–O BDE as 6.77 ± 0.07 eV from the endothermic reaction of W^+ with CO [23]. Again this agrees well with $D_0(W^+–O) = 6.68 \pm 0.53$ eV calculated using Eq. (1) and $D_0(WO) = 6.92 \pm 0.44$ eV from Pedley and Marshall [27], $IE(WO) = 8.1 \pm 0.3$ eV measured by Bohme and co-workers [34], along with $IE(W) = 7.864$ eV [35]. As for TaO^+, this value disagrees with that quoted by Schröder et al. [29] of $D(W^+–O) = 5.46 \pm 0.43$ eV derived from information in the GIANT compilation [30], which uses $IE(W) = 7.60$ eV [31], $IE(WO) = 9.1 \pm 1$ eV [36], and $\Delta_f H_0(WO) = 4.41 \pm 0.43$ eV [33], and also leads to $D_0(WO) = 6.95 \pm 0.44$ eV. Bohme and co-workers [34] also determined that W^+ reacts with COS to form WO^+ at room temperature with an efficiency of 0.38. They took this to indicate that $D_{298}(W^+–O) > D_{298}(O–CS) = 6.85 \pm 0.04$ eV, which they combined with $D_{298}(W^+–O) = 6.81 \pm 0.82$ eV to yield a refined range of values that they cited as $D_{298}(W^+–O) = 7.20 \pm 0.43$ eV. This value can be adjusted to $D_0(W^+–O) = 7.16 \pm 0.43$ eV, Table 1.

Literature information on the dioxides of Ta^+ and W^+ is less plentiful. Bond energies and ionization energies of the metal monoxides and dioxides can be related according to the thermochemical cycle of Eq. (2) and can be used to provide some information from the literature.

$$D(OM - O) + IE(MO) = D(OM^+ - O) + IE(MO_2) \tag{2}$$

The review by Schröder et al. lists $D_0(OTa^+–O) = 6.07$ eV and $D_0(OW^+–O) = 5.72$ eV and cites the GIANT compilation. (Actually [30] contains no information about TaO_2^+, and the information in the GIANT compilation used to derive the WO_2^+ BDE indicates this value has an uncertainty of at least 1.17 eV, Table 1.) Heats of formation taken from the JANAF tables [33], which are based on Knudsen cell studies of Inghram et al. [37] provide D_0(OTa–O) as 6.61 ± 0.92 eV and this has also been measured as 6.87 ± 0.23 eV using the mass spectrometric Knudsen cell method [38]. The bond energy of 6.07 eV for $OTaO^+$ may have been obtained by combining the former neutral bond energy with $IE(TaO) = 7.92 \pm 0.1$ eV [32] and $IE(TaO_2) = 8.5 \pm 0.5$ [38], indicating it should have an uncertainty of 1.05 eV, Table 1. Alternatively, we can combine $IE(TaO) = 8.61 \pm 0.02$ eV [28] and $IE(TaO_2)$ values of 8.5 ± 0.5 [38] and 9 ± 0.5 eV [37] with the more precise $D_0(OTa–O) = 6.87 \pm 0.23$ eV to obtain $D(OTa^+–O)$ values of 6.98 ± 0.55 and 6.48 ± 0.55 eV, which we cite in Table 1 as 6.73 ± 0.80 eV given that neither $IE(TaO_2)$ value is precise. (Note that many of the literature IEs were determined solely to ascertain whether the species being probed were fragments or molecular species, hence their accuracy is questionable.) For WO_2, heats of formation given in the JANAF tables indicate the neutral OW–O bond energy is 6.15 ± 0.53 eV [33]. $IE(WO_2)$ has been reported as 9.6 ± 0.3 [39], 9.5 ± 0.5 [40], 9.9 ± 1.0 [41], 9.8 [42], and 9.9 ± 0.6 eV [36]. Along with $IE(WO) = 8.1 \pm 0.3$ eV [34] and D(OW–O), these IEs can be combined to indicate that $D(OW^+–O)$ is anywhere between 3.4 and 5.4 eV, with the most precise $IE(WO_2)$ value suggesting $D(OW^+–O) = 4.6_5 \pm 0.7$ eV. Finally, there have been a few spectroscopic studies in which the ground state of TaO_2^+ has been identified as $^1A_1$ [43–45].

2. Experimental and computational section

2.1. General procedures

The guided ion beam tandem mass spectrometer on which these experiments were performed has been described in detail previously [46]. Briefly, MO^+ and MO_2^+ ions are generated in a direct current discharge flow tube (DC/FT) source described below [47], extracted from the source, accelerated, and focused into a magnetic sector momentum analyzer for mass selection of primary

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