International Journal of Mass Spectrometry 280 (2009) 226–234

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Reactions of Hf^+, Ta^+, and W^+ with O_2 and CO: Metal carbide and metal oxide cation bond energies

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ARTICLE INFO

Article history:
Received 5 August 2008
Received in revised form 27 August 2008
Accepted 27 August 2008
Available online 7 September 2008

This article is dedicated to Zdenek Herman on the occasion of his 75th birthday and in recognition of his outstanding contributions to ion chemistry and the mass spectrometry community over many years.

Keywords:
Bond energy
Ionization energy
Transition metal carbide
Transition metal oxide
Thermochemistry

ABSTRACT

The reactions of Hf^+, Ta^+, and W^+ with O_2 and CO are studied as a function of translational energy in a guided ion beam tandem mass spectrometer. All three reactions with O_2 form diatomic metal oxide cations in exothermic reactions that occur at the collision rate. In the CO systems, formation of both diatomic metal oxide and metal carbide cations is observed to be endothermic. The energy-dependent cross sections in the latter systems are interpreted to give 0 K bond energies (in eV) of $D_0(HfC^+) = 3.19 \pm 0.03$, $D_0(TaC^+) = 3.79 \pm 0.04$, $D_0(WC^+) = 4.76 \pm 0.09$, $D_0(HfO^+) = 6.91 \pm 0.11$, $D_0(TaO^+) = 7.10 \pm 0.12$, and $D_0(WO^+) = 6.77 \pm 0.07$. The present experimental values for TaO^+ and WC^+ agree well with literature thermochemistry, those for HfO^+ and WO^+ refine the available literature bond energies, and those for HfC^+ and TaC^+ are the first measurements available. The nature of the bonding in MO^+ and MC^+ is discussed and compared for these three metal ions and analyzed using theoretical calculations at a B3LYP/HW+/6-311+G(3df) level of theory. Bond energies for all MO^+ and MC^+ species are calculated using geometries calculated at this level and single point energies determined at B3LYP, CCSD, CCSD(T), QCISD, and QCISD(T) levels of theory with the same basis set. Reasonable agreement between the theoretical and experimental bond energies for the three metal oxide and three metal carbide cations is found. Potential energy surfaces for reaction of the metal cations with CO are also calculated at the B3LYP level of theory and reveal additional information about the reaction mechanisms.

1. Introduction

Transition metal carbides and oxides play an important role in many processes. Because of their high melting point, conductivity, and hardness, transition metal carbides play important roles in material science and electronics [1–3]. The oxides of transition metals play vital roles in industrial, organometallic, and atmospheric chemistry [4–6]. In understanding the origins of these important properties, it can be useful to understand the binding of the simplest examples of such species. In previous studies in our laboratory, guided ion beam mass spectrometry has been used to systematically study diatomic oxides, MO^+, and carbides, MC^+, of first-row [7,8], second-row [9–11], and third-row [12] transition metal cations. In the present work, these studies are extended to include the group 4–6 third-row transition metal cations, M = Hf, Ta, and W. The comparison of the metal carbides and oxides is interesting because both C and O have two unpaired valence electrons in their ^3P ground states, easily making two covalent bonds to metals. However, the empty p orbital on C versus the doubly occupied p orbital on oxygen can make an appreciable difference in the bonding of these species with metals.

The guided ion beam methods used in our laboratory can be used to investigate the bond dissociation energies (BDEs) for M^+–O and M^+–C species by analyses of the kinetic energy dependence of reactions (1)–(3).

$$M^+ + O_2 \rightarrow MO^+ + O \quad (1)$$

$$M^+ + CO \rightarrow MO^+ + C \quad (2)$$

$$M^+ + CO \rightarrow MC^+ + O \quad (3)$$

In previous work [7–11], it has been shown that the early transition metal cations (groups 3–5) react exothermically with O_2, whereas later transition metal cations (groups 6–11) react endothermically. To obtain metal oxide bond energies for these early metal cations, reactions with CO, which has a much stronger bond, $D_0(CO) = 11.108$ eV versus $D_0(O_2) = 5.115$ eV [13], can be used as now the processes are endothermic. Furthermore, the competing formation of MC^+ in reaction (3) is also observed, such that analyses of the energy-dependent cross section data for reactions (2) and (3) allow 0 K metal oxide and metal carbide BDEs to be obtained. Detailed theoretical calculations are also performed here in order

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doi:10.1016/j.ijms.2008.08.025

to provide information regarding the electronic states of the MC^+ and MO^+ species and to examine the potential energy surfaces for formation of the products in reactions (2) and (3).

2. Literature data

Literature information on thermodynamics of these transition metal oxide and carbide species is generally sparse, although all three metal oxides have been studied by Knudsen effusion techniques. Panish and Reif used Langmuir vaporization and Knudsen effusion to measure the 0 K dissociation energy of HfO as 7.92 ± 0.26 eV [14], and later Ackermann and Rauh measured a value of 8.19 ± 0.09 eV [15]. Pedley and Marshall critically evaluate these values and select $D_0(\mathrm{HfO}) = 8.26 \pm 0.13$ eV [16]. In contrast, an RKR analysis of spectroscopic information suggests that $D_0(\mathrm{HfO}) = 9.04 \pm 0.02$ eV [17], but this value is less reliable because of the long range extrapolation involved. Using Eq. (4),

$$D_0(\mathrm{M}-\mathrm{X}) + \mathrm{IE}(\mathrm{M}) = D_0(\mathrm{M}^+-\mathrm{X}) + \mathrm{IE}(\mathrm{MX}) \quad (4)$$

the ionization energy of this species, IE(HfO) = 7.55 ± 0.1 eV, measured by Rauh and Ackermann [18], and IE(Hf) = 6.825 eV [19] can be combined with the best neutral BDE to yield $D_0(\mathrm{Hf^+–O}) = 7.54 \pm 0.16$ eV. The review of transition metal oxide cations by Schroder et al. [20] lists $D(\mathrm{Hf^+–O}) = 7.50 \pm 0.22$ eV and cites the GIANT (Gas-phase Ion And Neutral Thermochemistry) compilation [21], which used the same reference data for HfO but an older value for IE(Hf) = 6.78 eV. ESR studies [22] identify HfO^+ as having a $^2\Sigma$ ground state and a variety of spectroscopic studies of HfO [23–25] have also been performed.

For tantalum oxide, the JANAF tables [26] discuss the large disparities obtained by several Knudsen cell mass spectrometry studies [27–29]: 2nd and 3rd law values for $\Delta_f H_{298}(\mathrm{TaO})$ values ranging from 2.14 to 4.35 eV. After correlating values with those for the 1st and 2nd row congeners, VO and NbO, Chase chooses a rounded value from a Birge–Sponer extrapolation corrected for iconicity, $\Delta_f H_{298}(\mathrm{TaO}) = 1.99_5 \pm 0.65$ eV and $D_0(\mathrm{TaO}) = 8.65 \pm 0.65$ eV. Pedley and Marshall [16] primarily utilize results from Smoes et al. [30] and select $D_0(\mathrm{TaO}) = 8.24 \pm 0.13$ eV. The situation for the ionization energy of TaO is equally unclear. The most precise and most recent value comes from a photoelectron measurement of Dyke et al., 8.61 ± 0.02 eV [31], which is well above previous electron impact measurements of $7.9_2 \pm 0.1$ eV from Ackermann et al. [32] and 7.5 ± 0.5 eV from Smoes et al. [30]. Combining the best values presently available with IE(Ta) = 7.5495 eV [33] yields $D_0(\mathrm{Ta^+–O}) = 7.18 \pm 0.14$ eV. The review by Schroder et al. [20] lists $D(\mathrm{Ta^+–O}) = 8.15 \pm 0.65$ eV, again citing the GIANT compilation [21], which uses older values for IE(Ta) = 7.4 eV and IE(TaO) = 7.92 eV, along with $D_0(\mathrm{TaO}) = 8.65$ eV. Additional work has examined the spectroscopy of TaO, identifying its ground state as $^2\Delta$ [34–38], and has characterized the photoelectron spectrum of TaO^- [39].

Finally, the JANAF tables [26] reanalyzed the Knudsen cell mass spectrometry data of DeMaria et al. [40] to determine $\Delta_f H_0(\mathrm{WO}) = 4.41 \pm 0.43$ eV, which can be combined with the heats of formation of W and O (also taken from JANAF) to give $D_0(\mathrm{WO}) = 6.95 \pm 0.44$ eV, somewhat higher than the value quoted directly by DeMaria et al. of 6.68 ± 0.44 eV. (Also, using $H_{298} - H_0$ data taken from the JANAF tables, one finds that $D_{298}(\mathrm{W–O}) - D_0(\mathrm{W–O}) = 0.043$ eV, yielding $D_{298}(\mathrm{WO}) = 7.00 \pm 0.44$ eV.) Pedley and Marshall use the same data to select $D_0(\mathrm{WO}) = 6.92 \pm 0.44$ eV. DeMaria et al. also quote a rough ionization energy for WO of 9.1 ± 1 eV, but recent gas-phase bracketing studies by Bohme and co-workers have refined this greatly to 8.1 ± 0.3 eV [41]. When combined with IE(W) = 7.864 eV [42] and $D_0(\mathrm{WO}) = 6.92 \pm 0.44$ eV, this IE value yields $D_0(\mathrm{W^+–O}) = 6.68 \pm 0.53$ eV. This value is well above that quoted in the review by Schroder et al. [20] who list $D(\mathrm{W^+–O}) = 5.46 \pm 0.43$ eV as taken from the GIANT compilation [21]. Bohme and co-workers verified the accuracy of their cation bond energy by determining that W^+ reacts at room temperature with COS to form WO^+, albeit with an efficiency of only 0.38. They took this to indicate that $D_{298}(\mathrm{W^+–O}) > D_{298}(\mathrm{O–CS}) = 6.85 \pm 0.04$ eV (although the inefficiency of this reaction could mean that these bond energies are nearly isoenergetic). They then combined this limit with $D_{298}(\mathrm{W^+–O}) = 6.81 \pm 0.82$ eV (which is slightly higher than the value derived above for reasons that are unknown and with an uncertainty determined by addition of the literature uncertainties rather than combining them in quadrature) to yield a refined range of values that is cited as $D_{298}(\mathrm{W^+–O}) = 7.20 \pm 0.43$ eV. This value is then combined with the ionization energies of W and WO to determine a value for $D_{298}(\mathrm{W–O})$ as 7.46 ± 0.74 eV, or equivalently $D_0(\mathrm{W–O}) = 7.42 \pm 0.74$ eV, consistent with the JANAF and Pedley and Marshall values within the broad uncertainties. Spectroscopic work [43,44] has identified the ground state of WO as $X^3\Sigma^-$.

For the carbide of Hf, we could find no literature reports of gas-phase studies. A number of neutral [45] and cationic [46,47] tantalum carbide clusters formed by laser vaporization have been studied. On the basis of the observation of several reactions involving TaC^+, McElvany and Cassady were able to bracket its bond energy as $3.38\ \mathrm{eV} < D(\mathrm{TaC^+}) < 6.11$ eV. Furthermore, Majumdar and Balasubramanian have studied this molecule and its neutral analogue theoretically [48,49]. For tungsten, spectroscopy has identified the ground state of WC as $^3\Delta$ [50]. The photoelectron spectrum of WC^- has been measured [51], and establishes the electron affinity of WC as well as the excitation energies for several excited states of this molecule. In addition, WC^+ has been observed as a product in the reaction of W^+ with CH_4 [52]. Measurement of the endothermic threshold for this double dehydrogenation reaction determined the 0 K bond energy of WC^+ as 4.96 ± 0.22 eV. WC^+ has also been observed in the fragmentation of $W(CO)_6$ ionized by electron impact [53] and by photoionization [54], and in the photoionization of W(CO) [55]. The appearance energies obtained in these studies suggest that $D_0(\mathrm{W^+–C}) = 5.26 \pm 0.78$, 3.93 ± 0.36, and 3.86 ± 0.35 eV, respectively. Finally, we note that Musaev et al. have examined the WCO^+ system theoretically, exploring the potential energy surface for activation of the CO molecule by W^+ [56].

3. Experimental

3.1. General procedures

The guided ion beam tandem mass spectrometer on which these experiments were performed has been described in detail previously [57]. Ions are generated in a direct current discharge flow tube (DC/FT) source described below [58]. The ions are extracted from the source, accelerated, and focused into a magnetic sector momentum analyzer for mass selection of primary ions, where either the ^{180}Hf isotope (35.2% natural abundance), the ^{181}Ta isotope (99.99% natural abundance), or ^{186}W isotope (30.67% natural abundance) are selected. The mass selected ions are then slowed to a desired kinetic energy and focused into an octopole ion guide that radially traps the ions [59]. The octopole passes through a static gas cell that contains the neutral reaction partner at a low pressure (ranging from 0.05 to 0.2 mTorr) so that multiple ion–molecule collisions are improbable. All results reported here result from single bimolecular encounters, as verified by the independence of the measured cross sections on the neutral reactant pressure. Product and remaining reactant ions are contained in the guide until