

ARTICLES

Reactions of ScO^+ , TiO^+ , and VO^+ with D_2 : M^+ -OH Bond Energies and Effects of Spin ConservationD. E. Clemmer, N. Aristov,[†] and P. B. Armentrout^{*‡}

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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Cross sections for the reactions of ScO^+ , TiO^+ , and VO^+ with D_2 have been measured as a function of translational energy in a guided ion beam tandem mass spectrometer. All three MO^+ ions react with D_2 to form three products, M^+ , MD^+ , and MOD^+ , in endothermic processes. Production of M^+ in all systems is accompanied by formation of water. The energetics measured for these reactions correspond to production of M^+ primarily in an excited low-spin electronic state. Formation of ground-state M^+ is also observed, even though this reaction channel does not conserve spin. Reaction mechanisms and qualitative potential energy surfaces are proposed to explain this behavior. Thresholds for the formation of MOD^+ in these systems are interpreted to give the 0 K bond energies, $D^\circ(\text{Sc}^+-\text{OD}) = 5.17 \pm 0.09$, $D^\circ(\text{Ti}^+-\text{OD}) = 4.82 \pm 0.12$, and $D^\circ(\text{V}^+-\text{OD}) = 4.50 \pm 0.15$, all in electronvolts. The large bond strengths for the M^+-OD species indicate that the lone pairs of electrons on the oxygen atom are involved in the bonding.

Introduction

Much work in our laboratories has focused on the reactivity of atomic transition-metal ions with molecular hydrogen.^{1,2} The simplicity of these atom-diatom systems allows a detailed elucidation of the ability of a metal to activate dihydrogen and the thermochemistry and bonding character of metal hydrides. In this paper, we focus on the activation of D_2 by the diatomic metal oxides ScO^+ , TiO^+ , and VO^+ and address how the oxo ligand influences the metal chemistry, mechanisms, and thermodynamics.

Previous work involving reactions of diatomic transition metal oxide ions, such as CrO^+ ,^{3,4} MnO^+ ,⁵ FeO^+ ,^{6,7} and OsO^+ ,⁸ has shown that the oxo ligand increases the reactivity of the bare metal. However, for systems involving the early metals, Sc^9 and V^10 , oxidation of the metal suppresses the reactivity relative to the bare metal ions. These results can be rationalized by noting that the M^+-O bond energy is relatively weak (ranging from 3.0 to 4.3 eV)^{8,11} for $\text{M} = \text{Cr}, \text{Mn}, \text{Fe},$ and Os but much stronger for scandium and vanadium, 6.0–7.2 eV.^{11,12} Thus, the overall reactivity of the MO^+ species seems to inversely correlate with its stability. In the present study, all the MO^+ ions considered are strongly bound (Table I). Thus, the reactions with D_2 cannot occur under thermal conditions but can be studied by using guided ion beam mass spectrometry in order to kinetically activate reactions.

Our motivations for work involving metal oxides are similar to those for the bare metal studies in that we would like to determine the ability of these species to activate simple bonds in the gas phase. In the condensed phase, metal oxides are used in literally hundreds of oxygen-transfer reactions.¹³ In the present work, we are particularly interested in understanding the constraints associated with transfer of the oxygen atom to D_2 in order to form water. One possible restriction for this reaction is that formation of ground-state products [$\text{Sc}^+(\text{}^3\text{D})$, $\text{Ti}^+(\text{}^4\text{F})$, and $\text{V}^+(\text{}^5\text{D}) + \text{D}_2\text{O}(\text{}^1\text{A}_1)$] is spin-forbidden from ground-state reac-

tants [$\text{ScO}^+(\text{}^1\Sigma^+)$, $\text{TiO}^+(\text{}^2\Delta)$, and $\text{VO}^+(\text{}^3\Sigma^-) + \text{D}_2(\text{}^1\Sigma_g^+)$]. Since this system is the simplest possible oxygen-transfer reaction that is catalyzed by a transition metal, we hope to gain a more direct understanding of the role that spin conservation plays in such oxidation reactions.

The present system is also related to studies of the reactions of Sc^+ , Ti^+ , and V^+ with water.¹⁴ For Ti^+ and V^+ , our work finds that the low-spin (doublet states in the case of Ti^+ and triplet states in the case of V^+) are substantially more efficient at dehydrogenating water than the high-spin quartet and quintet states of these ions. The present study allows this process to be studied in reverse.

The final motivation for this study is to determine accurate thermochemistry for the products that are formed in these reactions. Of particular interest in these studies is the ionic metal hydroxide thermochemistry. The only experimental measurements of the bond energies for Sc^+-OH , Ti^+-OH , and V^+-OH are those of Magnera, David, and Michl (MDM), who used a collision-induced dissociation method.¹⁵ Their values are listed in Table I. Their value for ScOH^+ is much smaller than that calculated by Tilson and Harrison¹⁶ (TH), who typically obtain bond energies that are within 10% of experimental values. This discrepancy demonstrates that the metal hydroxide ion bond energies obtained by MDM are not yet well established.

Experimental Section

General. Complete descriptions of the apparatus and experimental procedures are given elsewhere.¹⁷ MO^+ production is described below. These ions are extracted from the source, accelerated, and focused into a magnetic sector momentum analyzer for mass analysis. Mass-selected ions are slowed to a desired kinetic energy and focused into an octopole ion guide that radially traps the ions. The octopole passes through a static gas cell containing the neutral reactant. The pressure of D_2 in the cell is kept low (typically ≤ 0.5 mTorr) so that multiple ion-molecule collisions are improbable. Product and unreacted beam ions are contained in the guide until they drift out of the gas cell where they are focused into a quadrupole mass filter for mass analysis and then detected. Ion intensities are converted to

[†] Present address: Institute for Chemical Education, Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706.

[‡] Camille and Henry Dreyfus Teacher-Scholar, 1987-1992.

TABLE I: Bond Energies (in eV) at 0 K

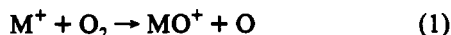
M	$D^{\circ}(M^+-O)$	$D^{\circ}(M^+-D)^a$	$D^{\circ}(M^+-OH)$	$D^{\circ}(M^+-OH_2)$
Sc	7.11 (0.08) ^b	2.48 (0.09) ^c	3.81 (0.13) ^d	1.36 (0.13) ^d
	7.16 (0.09) ^e		4.68 ^f	
	7.14 (0.06) ^g		5.17 (0.09) ^e	
Ti	6.93 (0.10) ⁱ	2.35 (0.11) ^j	4.90 (0.13) ^d	1.65 (0.13) ^d
			4.82 (0.12) ^e	1.74 (0.07) ^k
V	5.99 (0.10) ^b	2.09 (0.06) ^l	4.64 (0.13) ^d	1.57 (0.13) ^d
			4.50 (0.15) ^e	1.41 (0.05) ^k
				1.52 (0.10) ^m

^a These values are obtained by adjusting $D^{\circ}(M^+-H)$ values for zero-point energy (~ 0.03 eV). ^b Reference 12. ^c Reference 36. ^d Reference 15. ^e This work. ^f Reference 16. ^g Best value. Weighted average of the values obtained from this study and the reactions of Sc⁺ with CO and D₂O, ref 12 and 14, respectively. ^h Reference 48. ⁱ Reference 11. ^j Reference 37. ^k Homna, K.; Dalleska, N. F.; Sunderlin, L. S.; Armentrout, P. B. Unpublished results. ^l Reference 38. ^m Marinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101.

absolute cross sections as described previously. Uncertainties in cross sections are estimated to be $\pm 20\%$.¹⁷

Laboratory ion energies relate to center-of-mass (CM) frame energies by $E_{CM} = E_{lab}m/(M+m)$, where M and m are the ion and neutral reactant masses, respectively. The zero of the absolute energy scale and the ion energy distribution are measured by a retarding potential technique described elsewhere.¹⁷ Absolute energy scale uncertainties are ± 0.05 eV lab. Two effects broaden the data: the ion energy spread, which is independent of energy and has a fwhm of 0.3–0.5 eV lab, and thermal motion of the neutral gas, which has a width of $\sim 0.5E_{CM}^{1/2}$ for these reactions.¹⁸

Ion Source. ScO⁺, TiO⁺, and VO⁺ are produced in a 1.0-m-long dc-discharge/flow tube (FT) source that has been described in more detail previously.¹⁹ The flow gases used in this experiment are He, Ar, and O₂, maintained at pressures of ~ 0.50 , ~ 0.05 , and ~ 0.01 Torr, respectively. Ti⁺ and V⁺ ions are generated by 1.5–3.0-keV Ar ion impact on a cylindrical rod (1.25 cm in diameter and ~ 2.5 cm in length) made of titanium (Aesar) or vanadium (ESPI) metal. Sc⁺ was produced by bombardment of ScCl₃ salt (obtained from Aesar as ScCl₃·6H₂O and dehydrated before use) contained in a small (~ 2 cm³ capacity) tantalum bowl. The He and Ar flow carries the M⁺ ions downstream 25 cm where the oxygen is introduced. Interaction of the bare metal ions with oxygen forms MO⁺ via the reaction



This process is exothermic and highly efficient for Sc⁺, Ti⁺, and V⁺.¹¹ The MO⁺ ions are carried the remaining 75 cm of the flow tube where they undergo $\sim 10^5$ collisions with He and $\sim 10^4$ collisions with Ar. Thus, we assume that the internal energy of the ions in the beam is characterized by the flow gas temperature (~ 300 K) according to a Maxwell–Boltzmann distribution. This means that the ground vibrational states of these ions comprise more than 99% of the beams (assuming that the vibrational frequencies of ScO⁺, TiO⁺, and VO⁺ are all similar to the neutral MO frequencies of ~ 1000 cm⁻¹).²⁰ For the TiO⁺ and VO⁺ systems, collision-induced dissociation (CID) with Xe as a target gas was used to test the internal excitation of the ions. In both systems, the CID thresholds were equal to the bond energies for these molecules listed in Table I. Results for VO⁺ agreed with our previous study of cold VO⁺.²¹ Further, no indications of internal excitation are present in the chemistry with D₂ for any of the metal oxide ions.

Thermochemical Analysis. Previous work^{22,23} has shown that cross sections for endothermic reactions can be analyzed by using the equation

$$\sigma(E) = \sigma_0(E - E_0 + E_{vib} + E_{rot})^n/E \quad (2)$$

where σ_0 is a scaling factor, E is the relative kinetic energy, n is an adjustable parameter, and E_0 is the 0 K threshold for reaction

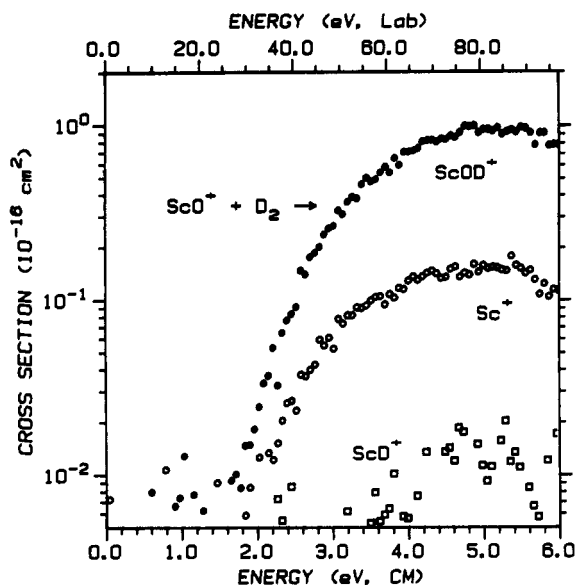


Figure 1. Variation of product cross sections for reaction of ScO⁺ + D₂ to form Sc⁺ + D₂O (open circles), ScOD⁺ + D (solid circles), and ScD⁺ + OD (open squares) as a function of kinetic energy in the center-of-mass frame (lower scale) and the laboratory frame (upper scale).

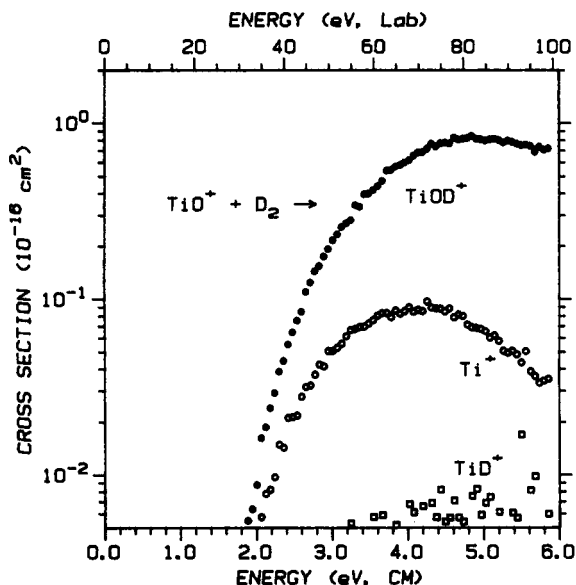


Figure 2. Variation of product cross sections for reaction of TiO⁺ + D₂ to form Ti⁺ + D₂O (open circles), TiOD⁺ + D (solid circles), and TiD⁺ + OD (open squares) as a function of kinetic energy in the center-of-mass frame (lower scale) and the laboratory frame (upper scale).

of ground electronic, vibrational, and rotational state reactants. In this study, E_{vib} represents the average reactant vibrational energy (0.001 eV) and E_{rot} is the total reactant rotational energy ($2kT = 0.053$ eV) at 305 K (the nominal temperature of the octopole). After convoluting the model over the neutral and ion kinetic energy distributions as described previously,¹⁷ the σ_0 , n , and E_0 parameters are optimized by using a nonlinear least-squares analysis to give the best fit to the data. Error limits for E_0 are calculated from the range of threshold values for different data sets with different values of n and the error in the absolute energy scale.

Results

Figures 1, 2, and 3 show cross sections for reactions of D₂ with ScO⁺, TiO⁺, and VO⁺, respectively. Three products corresponding to reactions 3–5 are observed and have similar cross sections in all three systems.

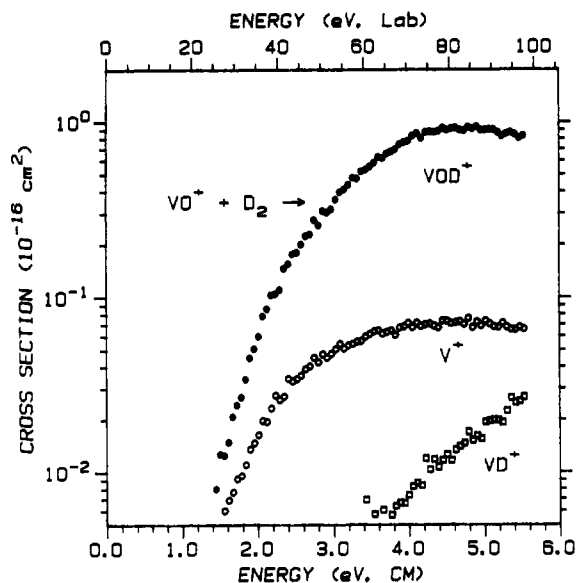
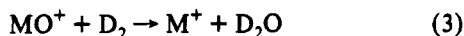


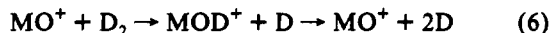
Figure 3. Variation of product cross sections for reaction of $\text{VO}^+ + \text{D}_2$ to form $\text{V}^+ + \text{D}_2\text{O}$ (open circles), $\text{VOD}^+ + \text{D}$ (solid circles), and $\text{VD}^+ + \text{OD}$ (open squares) as a function of kinetic energy in the center-of-mass frame (lower scale) and the laboratory frame (upper scale).



$\sigma(\text{M}^+)$. The apparent thresholds of reaction 3 in Figures 1–3 (between 1 and 2 eV) indicate that M^+ is accompanied by formation of water since collision-induced dissociation of MO^+ to form $\text{M}^+ + \text{O}$ cannot begin until the collision energy exceeds the MO^+ bond energy, 6–7 eV for these molecules (Table I). The absolute magnitudes of the M^+ cross sections decrease from Sc to Ti to V, suggesting that some property of the metal controls the process by which water is eliminated. This is discussed in more detail below.

$\sigma(\text{MD}^+)$. Reaction 4 is a metathesis reaction that cleaves both reactant bonds and forms two new product bonds. This is a minor process in all systems, and the magnitudes of MD^+ formation increase from Sc and Ti to V. Using the known ionic and neutral thermochemistry given in Tables I and II, we calculate that process 4 can begin at 4.75 ± 0.11 , 4.67 ± 0.15 , and 3.99 ± 0.12 eV in the Sc, Ti, and V systems, respectively. These thresholds are consistent with the onsets of the ScD^+ , TiD^+ , and VD^+ cross sections shown in Figures 1–3. (The apparent threshold appears somewhat lower on the logarithmic scale of these figures due to contributions of the kinetic energy distributions of the reactants and small amounts of mass overlap from the neighboring M^+ channel.)

$\sigma(\text{MOD}^+)$. Figures 1–3 show that the cross sections for reaction 5 rise from apparent onsets similar to those for reaction 3, but the magnitudes of the cross sections for process 5 are larger in all three systems. At ~ 4.0 eV, the branching ratios between reactions 5 and 3 favor the former process by factors of ~ 6 , ~ 9 , and ~ 15 for the Sc, Ti, and V systems, respectively. The cross sections for reaction 5 peak near $D^\circ_0(\text{D}_2) = 4.56$ eV in all systems, a consequence of product decomposition, the net reaction 6.



Threshold Analysis. Cross sections for reactions 3 and 5 were analyzed for all systems by using eq 2. The cross sections for MD^+ formation, reaction 4, were not analyzed since in general the data are too scattered to obtain meaningful results, but the

TABLE II: Heats of Formation and Bond Strengths for Neutral Species (0 K)^a

neutral	$\Delta_f H^\circ$, eV	bond	D° , eV
D	2.278	D–D	4.556
H	2.239	H–H	4.478
O	2.558 (0.001)		
OD	0.373 (0.013)	O–D	4.463 (0.013)
OH	0.398 (0.013)	O–H	4.399 (0.013)
OD_2	-2.552 (0.001)	DO–D	5.203 (0.013)
OH_2	-2.476	HO–H	5.113 (0.013)

^a Reference 32.

TABLE III: Summary of Parameters of Eq 2 Used To Fit Cross Sections^a

product ion	E_0 , eV	σ_0	n
Sc^+	2.08 (0.13)	0.23 (0.01)	1.3 (0.1)
Ti^+	2.06 (0.08)	0.12 (0.02)	1.6 (0.4)
V^+	1.25 (0.09)	0.04 (0.01)	2.2 (0.3)
ScOD^+	2.06 (0.07)	0.70 (0.08)	1.9 (0.1)
TiOD^+	2.20 (0.07)	0.67 (0.10)	1.9 (0.1)
VOD^+	1.58 (0.11)	0.40 (0.08)	2.2 (0.2)

^a Uncertainties in parentheses.

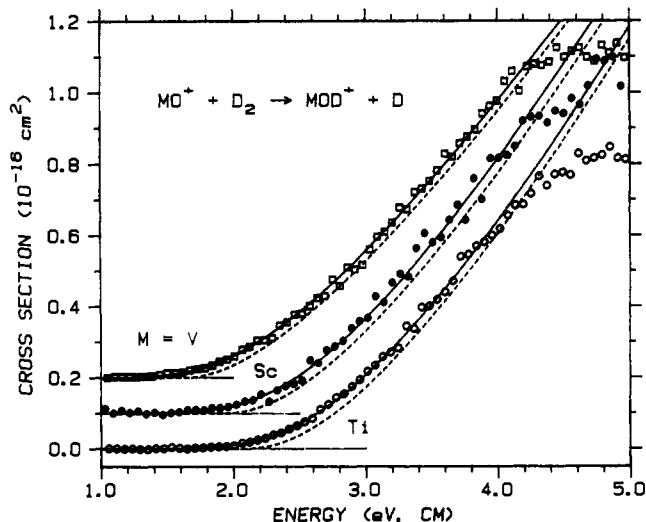


Figure 4. Cross sections for formation of TiOD^+ (open circles), ScOD^+ (solid circles, offset by 0.1 \AA^2), and VOD^+ (open squares, offset by 0.2 \AA^2) from the reactions of $\text{MO}^+ + \text{D}_2$ ($M = \text{Ti, Sc, and V}$, respectively) as a function of translational energy in the center-of-mass scale. Dashed lines are the models of eq 2 with the parameters in Table III, while solid lines are the model convoluted over the experimental kinetic energy distributions.

cross sections could be reproduced by using eq 2 with the calculated thresholds mentioned above. For reactions 3 and 5, the optimum values of the parameters E_0 , σ_0 , and n are given in Table III. Figure 4 shows that, for the MOD^+ reaction channel, all fits accurately reproduce the data from the thresholds to near the peaks of the cross sections. The MOD^+ cross sections have nearly identical shapes as seen by the similar values of n given in Table III.

Unlike the MOD^+ cross sections, the M^+ cross sections have shapes that vary between the metal systems. The thermochemistry listed in Tables I and II allows calculation of the thermodynamic thresholds for reaction 3 when the atomic metal ion is formed in its ground electronic state: 2.03 ± 0.06 , 1.82 ± 0.10 , and 0.88 ± 0.10 eV for the scandium, titanium, and vanadium systems, respectively. Analysis of $\sigma(\text{Sc}^+)$ using eq 2 with the parameters given in Table III gives $E_0 = 2.08 \pm 0.13$ eV, in good agreement with the predicted value. Figure 5 shows that this model also accurately represents the cross section from the threshold to near the peak of the cross section. For the titanium and vanadium systems, a similar procedure yields thresholds that are higher than the thermodynamic values calculated above (Table III).

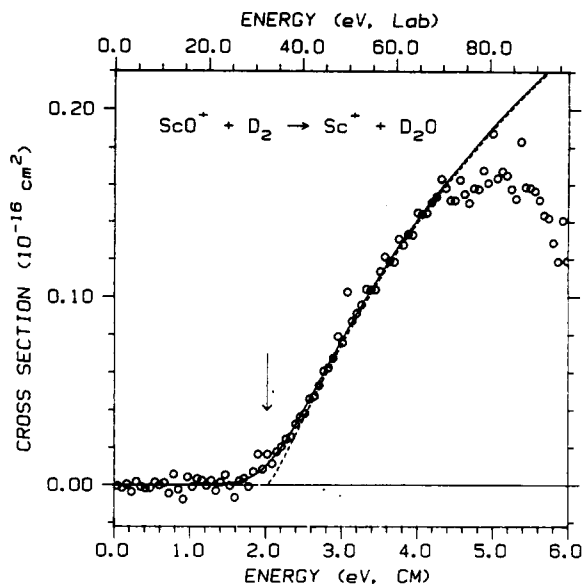


Figure 5. Cross section for reaction 3 for $M = \text{Sc}$ as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis) in the threshold region. The dashed line is the model of eq 2 with the parameters in Table III, while the solid line is the model convoluted over the experimental kinetic energy distributions. The arrow at 2.03 eV shows the calculated thermodynamic threshold for this reaction.

These models accurately reproduce the data from threshold to the peak of the cross section. (Alternatively, if the E_0 values in eq 2 are restricted to the thermodynamic values, modeling of the cross sections for reaction 3 requires unusually large values of the parameter n (>3). Although these models can reproduce the threshold region of the cross sections for approximately 1.5 eV above the calculated thresholds, they are poor representations of the data at higher energies.)

One potential explanation for the elevated thresholds listed in Table III is that there is a barrier associated with formation of $M^+ + \text{D}_2\text{O}$ from $\text{MO}^+ + \text{D}_2$. If this were the case, then this barrier would also be observed for the reverse reaction. Our results¹⁴ for the formation of $\text{MO}^+ + \text{D}_2$ from $M^+ + \text{D}_2\text{O}$ are complicated by severe dependence on the electronic state of the atomic metal ion, but the results demonstrate that there are no barriers in excess of the endothermicity for reaction 3.

The most probable explanation is that the elevated thresholds measured by using this simple analysis are an average for producing both ground- and excited-state metal ions. Indeed, the measured thresholds lie between the calculated thresholds for the ground and low-spin excited states. This idea can be explored more quantitatively by making some simple assumptions about the form of eq 2 used to analyze the cross sections. As shown for reactions of atomic metal ions with H_2 and D_2 ,¹ one of the simplest and most useful forms of eq 2 is the line-of-centers model (eq 2 with $n = 1$). Therefore, we model the cross sections for reaction 3 by summing line-of-centers models for forming several electronic states of M^+ , the a^4F ($E_{el} = 0.03$ eV), b^4F ($E_{el} = 0.14$ eV), and a^2F ($E_{el} = 0.59$ eV) states of Ti^+ , and a^5D ($E_{el} = 0.03$ eV), a^5F ($E_{el} = 0.36$ eV), and a^3F ($E_{el} = 1.10$ eV) states of V^+ ,²⁴ where the thresholds for producing these states are held to the calculated thermodynamic values. The only variable parameters in these analyses are the overall scaling parameter, σ_0 , and the relative efficiencies for formation of each electronic state of the atomic metal ion. For titanium, we find that an optimum representation of the data (shown in Figure 6) is obtained when the $\text{Ti}^+(a^2F)$ is formed 13 ± 7 times more efficiently than the lower-lying $\text{Ti}^+(a^4F)$ and $\text{Ti}^+(b^4F)$ states (which are assumed to have equal formation probabilities). For the vanadium system, the optimum representation of the data (shown in Figure 7) is obtained when the relative probability of forming the a^3F state is 8 ± 2 times greater than that for the a^5F state. If formation

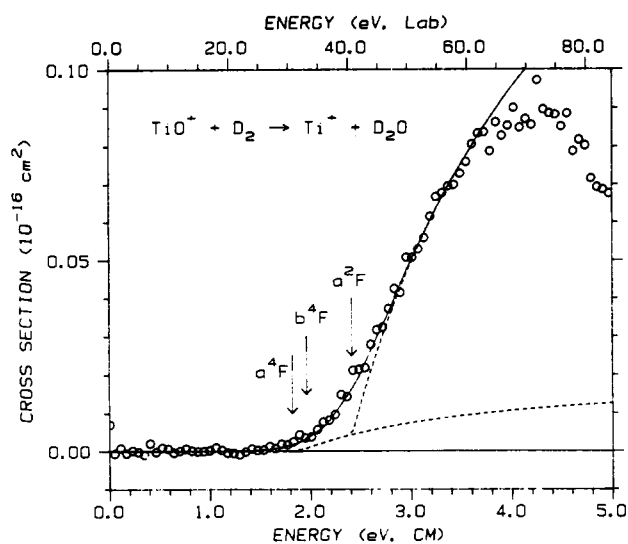


Figure 6. Cross section for reaction 3 with $M = \text{Ti}$ as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis) in the threshold region. The lower dashed line shows the line-of-centers model cross section (eq 2 with $n = 1$) for formation of $\text{Ti}^+(a^4F)$ and $\text{Ti}^+(b^4F)$, while the upper dashed line is the sum of this model and that for formation of $\text{Ti}^+(a^2F)$. The solid line is this model sum convoluted over the experimental kinetic energy distributions. Arrows show the calculated thermodynamic thresholds for formation of Ti^+ in the a^4F , b^4F , and a^2F states.

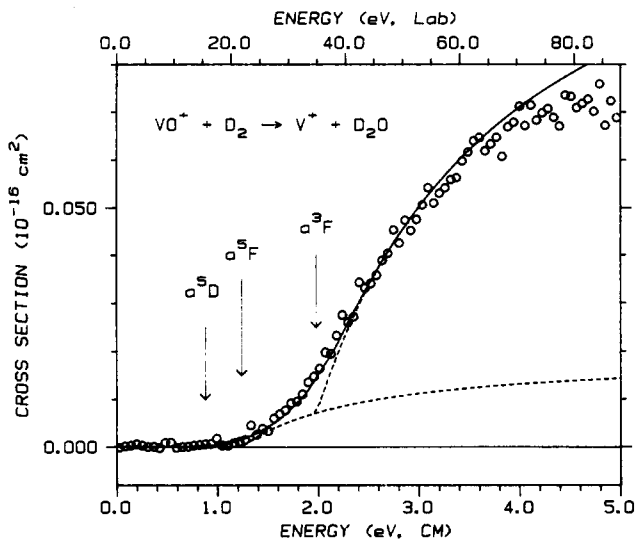


Figure 7. Cross section for reaction 3 with $M = \text{V}$ as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis) in the threshold region. The lower dashed line shows the line-of-centers model cross section (eq 2 with $n = 1$) for formation of $\text{V}^+(a^5F)$, while the upper dashed line is the sum of this model and that for formation of $\text{V}^+(a^3F)$. The solid line is this model sum convoluted over the experimental kinetic energy distributions. Arrows show the calculated thermodynamic thresholds for formation of V^+ in the a^5D , a^5F , and a^3F states.

of the a^5D state is included to any appreciable degree, the data can no longer be reproduced. The accuracy of this analysis is substantiated by our observation that the reverse reaction, $\text{V}^+(a^5D) + \text{D}_2\text{O} \rightarrow \text{VO}^+ + \text{D}_2$, does not occur within our experimental sensitivity.¹⁴ Alternatively, we can assume that the value of n in eq 2 is 1.3 for these systems, as found in the standard analysis of the scandium system. Again, the data are reproduced nicely if the relative probability of forming the a^2F state is a factor of 10 ± 5 times greater than the a^4F and b^4F states in the titanium system, and the relative probability of forming the a^3F state is a factor of 5 ± 2 times greater than the a^5F state in the vanadium system. In both analyses ($n = 1$ and 1.3), it is clear that the data for the titanium and vanadium systems are dominated by production of excited low-spin $\text{Ti}^+(a^2F)$ and $\text{V}^+(a^3F)$ states.

Given the complexity of the titanium and vanadium systems, it is useful to reconsider the analysis for scandium where it was implicitly assumed that Sc^+ was formed in its ground a^3D state. As for the other systems, we use a line-of-centers model to analyze $\sigma(\text{Sc}^+)$ and vary the reaction efficiencies for forming the first excited low-spin state, $\text{Sc}^+(a^1D)$ ($E_{el} = 0.315$ eV), relative to the high-spin states, $\text{Sc}^+(a^3D)$ ($E_{el} = 0.013$ eV) and $\text{Sc}^+(a^3F)$ ($E_{el} = 0.608$ eV). In this case, since the thermochemistry for ScO^+ is not as well established as for TiO^+ and VO^+ , we allow E_0 to optimize as well. If the reaction efficiencies for producing all states are assumed to be equal, a threshold of 2.06 ± 0.10 eV for $E_0(\text{Sc}^+)$ is obtained. If the a^1D state is assumed to be formed 10 times more readily (a factor similar to those found in the Ti and V systems), then the threshold obtained is 2.02 ± 0.09 eV. These values are nearly identical to the standard analysis discussed above where $E_0 = 2.08 \pm 0.13$ eV. This indicates that this system is not very sensitive to production of excited-state ions, presumably because the low-spin and high-spin states in Sc^+ lie much closer in energy to one another than in Ti^+ and V^+ .

Discussion

Thermochemistry. By assuming that E_0 is the enthalpy difference between reactants and products, we can calculate 0 K metal–ligand bond energies. This assumes that there are no activation barriers in excess of the endothermicity, as is often true for ion–molecule reactions.^{23,25}

MO^+ . While the thermochemistry of TiO^+ and VO^+ is well established,¹¹ the most precise value for $D^0(\text{ScO}^+)$ comes from our study of the reaction of Sc^+ with CO .¹² We provide a check of this thermochemistry from the reaction 3 cross section studied here. As discussed above, this cross section was analyzed in three ways, yielding thresholds of 2.08 ± 0.13 , 2.06 ± 0.10 , and 2.02 ± 0.09 eV. The average value, $E_0 = 2.05 \pm 0.09$ eV, leads to a 0 K bond energy of $D^0(\text{ScO}^+) = 7.16 \pm 0.09$ eV (slightly revised from a preliminary value previously reported for this reaction, 7.15 ± 0.10 eV).¹² This bond energy is in excellent agreement with $D^0_0(\text{ScO}^+) = 7.11 \pm 0.08$ eV obtained from the $\text{Sc}^+ + \text{CO}$ reaction¹² and $D^0_0(\text{Sc}^+-\text{O}) = 7.16 \pm 0.15$ eV determined from the reaction of $\text{Sc}^+ + \text{D}_2\text{O}$.¹⁴ We take the weighted average of these three bond energies as the best value, $D^0_0(\text{Sc}^+-\text{O}) = 7.14 \pm 0.06$ eV (Table I), consistent with the previously recommended value of 7.14 ± 0.11 eV.¹²

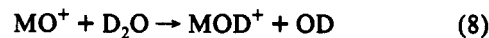
MOH^+ . There are two possible isomers, M^+-OD and $\text{O}-\text{M}^+-\text{D}$, for the ionic products formed in reaction 5. The theoretical calculations by Tilton and Harrison show that the scandium hydroxide structure, Sc^+-OH , is more stable than the hydrido oxide species by 4.0 eV.¹⁶ This makes intuitive sense since O–H bonds are much stronger than M^+-H bonds (Tables I and II). The instability of the OScH^+ isomer can also be rationalized by the inability of Sc^+ (which has only two valence electrons) to support the three covalent bonds necessary to form $\text{O}=\text{Sc}^+-\text{H}$ and thus forms $\text{O}-\text{Sc}^+-\text{H}$ with the radical electron on the oxygen atom. In the titanium and vanadium systems, where there have been no theoretical calculations, the metal ions can form the three covalent bonds needed for the $\text{O}=\text{M}^+-\text{D}$ isomer, thereby stabilizing this structure. The M^+-OD structure is probably still the ground state, however, because Ti^+-D and V^+-D bonds are still much weaker than O–D bonds (Table I). Further, the TiOD^+ and VOD^+ cross sections are nearly identical in shape and magnitude to the ScOD^+ cross section, implying that reaction 5 is similar for all three systems. Given the theoretical assignment of the Sc^+-OD isomer as the most stable structure, we conclude that reaction 5 forms the M^+-OD isomer in the Ti and V systems also.

The thresholds for formation of ScOD^+ , TiOD^+ , and VOD^+ in reaction 5, $E_0(5)$ as listed in Table III, can be converted to

MO^+-D bond energies at 0 K by using the equation

$$D^0_0(\text{MO}^+-\text{D}) = D^0_0(\text{D}_2) - E_0(5) \quad (7)$$

This yields the bond energies $D^0(\text{ScO}^+-\text{D}) = 2.50 \pm 0.07$ eV, $D^0(\text{TiO}^+-\text{D}) = 2.36 \pm 0.07$ eV, and $D^0(\text{VO}^+-\text{D}) = 2.98 \pm 0.11$ eV. We have further tested the accuracy of these MO^+-D bond energies by preliminary studies of reaction 8.²⁶



Combining our measured thresholds for these reactions with the appropriate thermochemistry gives $D^0(\text{MO}^+-\text{D}) = 2.6 \pm 0.2$, 2.2 ± 0.3 , and 3.1 ± 0.2 eV for $\text{M} = \text{Sc}$, Ti , and V , respectively, in agreement with the more precise values from the present study.

To compare our thermochemistry with that in the literature, we need to convert $D^0_0(\text{MO}^+-\text{D})$ to $D^0_0(\text{M}^+-\text{OD})$ and then to $D^0_0(\text{M}^+-\text{OH})$. The first step is accomplished by using eq 9 where

$$D^0_0(\text{M}^+-\text{OD}) = D^0_0(\text{MO}^+-\text{D}) + D^0_0(\text{M}^+-\text{O}) - D^0_0(\text{OD}) \quad (9)$$

the auxiliary thermochemistry is taken from Tables I and II. This yields the values $D^0_0(\text{M}^+-\text{OD}) = 5.17 \pm 0.09$, 4.82 ± 0.12 , and 4.50 ± 0.15 eV for $\text{M} = \text{Sc}$, Ti , and V , respectively. To convert to $D^0_0(\text{M}^+-\text{OH})$, we require the vibrational frequencies for these species, which are unknown. Previously, we have shown for metal amide ions that deuteration does not affect the bond energies within the precision of our measurements, i.e., $D^0(\text{M}^+-\text{ND}_2) \approx D^0(\text{M}^+-\text{NH}_2)$.²⁷ This should also be true for the metal hydroxides, and we therefore list the present results as M^+-OH bond energies in Table I.

It can be seen that our M^+-OH bond energies agree well with those measured by MDM for TiOH^+ and VOH^+ . For ScOH^+ , our value is ~ 1.4 eV larger than that of MDM but only $10 \pm 2\%$ higher than the value calculated by TH. This is typical agreement between calculated and experimental ionic metal–ligand bond energies, corroborating the accuracy of our value and that the species formed does correspond to Sc^+-OD .

We have recently discussed various systematic effects that can influence the determination of thresholds in collision-induced dissociation (CID) experiments.²⁸ Of these, there are two that are the most likely to explain why the value of $D^0(\text{Sc}^+-\text{OH})$ obtained by MDM may be too low. First are effects associated with internally excited ions. MDM made $\text{ScOH}(\text{H}_2\text{O})^+$ ions by argon ion impact at kilovolt impact energies. The ions could cool evaporatively, but no other means were used to remove internal excitation before examining CID to form ScOH^+ and Sc^+ . The parent ions can be formed in both vibrationally and electronically excited states and thus may decompose to different states of ScOH^+ and Sc^+ than the ground states, which could explain a shift of 1.4 eV. MDM's accurate thermochemistry for TiOH^+ and VOH^+ could be used to argue against this idea; however, the scandium system may be more sensitive to such excitation. A second possibility involves multiple collisions with the target gas (Ar or Xe in the experiments of MDM). We have found that even when such collisions are improbable ($<0.3\%$), they lower the apparent thresholds for CID processes.²⁸ We find that the magnitude of the downward energy shift increases as the extent of dissociation increases, which could explain the low ScOH^+ bond energy observed by MDM. Again, such an effect should also be observed in the titanium and vanadium systems, but only if the same neutral target gas pressure was used by MDM in all cases.

Finally, it is straightforward to calculate the proton affinities (PAs) of the neutral metal oxides from the present thermochemistry by using eq 10. The ionization energies for the metal oxides, $\text{IE}(\text{MO})$, are 6.43 ± 0.13 ,²⁹ 6.819 ± 0.006 ,³⁰ and 7.230 ± 0.005 eV,³¹ and $\text{IE}(\text{H}) = 13.598$ eV.³² The values for $D^0(\text{MO}^+-$

$$\text{PA}(\text{MO}) = D^{\circ}_0(\text{MO}-\text{H}^+) = D^{\circ}_0(\text{MO}^+-\text{H}) + \text{IE}(\text{H}) - \text{IE}(\text{MO}) \quad (10)$$

H) are calculated from $D^{\circ}_0(\text{MO}^+-\text{D})$ after correcting by 0.06 eV, equivalent to the zero-point energy difference of $D^{\circ}(\text{OD}) - D^{\circ}(\text{OH})$. The results are 9.61 ± 0.15 , 9.08 ± 0.07 , and 9.29 ± 0.11 eV for the proton affinities of ScO , TiO , and VO , respectively.

Character of M^+-OH Bonding. The bonding in the MOH^+ species can be understood by comparing the metal hydroxide bond energies with those for metal methyls and metal amides, since OH is isoelectronic to CH_3 and NH_2 (in the sense that each group has only a single unpaired electron and thus can form only a single covalent bond).³³ Previously, we have found that the M^+-NH_2 bond strengths for $\text{M} = \text{Sc}$, Ti , and V are stronger by ~ 1.1 , ~ 1.2 , and ~ 1.0 eV, respectively, than values for $D^{\circ}(\text{M}^+-\text{CH}_3)$.^{27,34} This enhanced bond energy was attributed to the ability of the NH_2 group to donate its lone pair of electrons into empty metal d orbitals to form a dative bond, effectively increasing the metal–nitrogen bond order from 1 to 2.

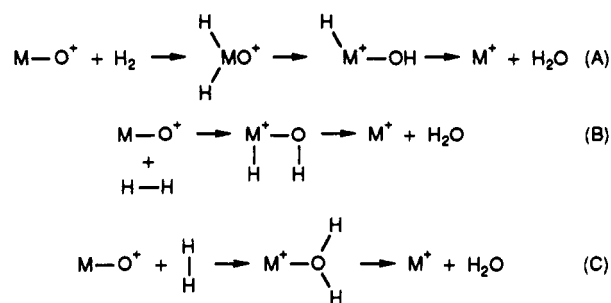
The present results show that M^+-OH bond energies are larger than the M^+-CH_3 bond energies by ~ 2.7 , ~ 2.5 , and ~ 2.4 eV for $\text{M} = \text{Sc}$, Ti , and V , respectively, roughly twice the enhancement observed for the M^+-NH_2 species. This enhancement can be explained if the M^+-OH bonding consists of one covalent and two dative interactions resulting from the two lone pairs of electrons on the oxygen, effectively giving a metal–oxygen bond order of 3. Assuming that the metal electrons not involved in the covalent $\text{M}-\text{O}$ bond remain unpaired, ScOH^+ , TiOH^+ , and VOH^+ should have doublet, triplet, and quartet spin ground states, respectively. This agrees with the spin states and bonding schemes calculated for ScOH^+ and suggested for TiOH^+ and VOH^+ by Tilson and Harrison.¹⁶ They approached the bonding in ScOH^+ by binding $\text{H}(^2\text{S})$ to the $\text{ScO}^+(^3\Delta)$ excited state to form ground-state $\text{ScOH}^+(^2\Delta)$ having a linear geometry and a triple bond between Sc^+ and OH.

One interesting aspect of the thermochemistry that can now be explored is whether bond additivity holds for the metal hydroxide ions. That is, is it true that $D^{\circ}(\text{M}^+-\text{OH}) = D^{\circ}(\text{M}^+-\text{O}) + D^{\circ}(\text{O}-\text{H})$ and $D^{\circ}(\text{MO}^+-\text{H}) = D^{\circ}(\text{O}-\text{H}) + D^{\circ}(\text{M}^+-\text{O})$? Table I clearly shows that the metal hydroxide ion bond energies are much weaker than the metal oxide ion bond energies, and since $D^{\circ}(\text{M}^+-\text{OH}) + D^{\circ}(\text{OH}) = D^{\circ}(\text{MO}^+-\text{H}) + D^{\circ}(\text{M}^+-\text{O})$, the O–H bond energy in MOH^+ must be much weaker than that for free hydroxide. In essence, the differences are because the two covalent and one dative interaction that comprise the M^+-O bond are intrinsically stronger than the one covalent and two dative bonds of M^+-OH .

With these ideas about bond additivity in mind, it is interesting to consider the usefulness of the bond additivity arguments presented by MDM in their attempt to ascertain the structures of MOH^+ . By comparing $D^{\circ}(\text{MO}^+-\text{H})$ with $D^{\circ}(\text{M}^+-\text{H})$ and $D^{\circ}(\text{OH})$, they concluded that ScOH^+ and VOH^+ probably have the hydroxide structures but that TiOH^+ might have the $\text{H}-\text{Ti}^+=\text{O}$ structure. The present thermochemistry finds that $D^{\circ}(\text{MO}^+-\text{D}) \approx D^{\circ}(\text{M}^+-\text{D})$ for both Sc and Ti and that all three MO^+-D bonds are weaker than $D^{\circ}(\text{OD})$. The analysis of the metal hydroxide ion bonding we have given above shows that such comparisons are misleading and cannot always be used to unambiguously determine the structures of even very simple metal–ligand complexes. If bond additivity arguments are to be utilized in this fashion, the rehybridization of the bonds must be taken into account.

Reaction Mechanism. Scheme I shows three possible mechanisms for the elimination of water in the reaction of metal oxide ions with hydrogen. Irikura and Beauchamp have discussed these mechanisms for the reaction of OsO_x^+ ($x = 1-4$) ions with dihydrogen.⁸ They ruled out mechanism A since it leads to an unreasonable +9 Os oxidation state for the OsO_3^+ reaction (although a reviewer correctly notes that this conclusion is

SCHEME I



disputable because the formal oxidation state of osmium in this species does not accurately predict the stability of such an intermediate). Similarly, mechanism C was dismissed since it predicts that OsO_4^+ will eliminate water while no reaction was observed experimentally. Thus, mechanism B was found to best account for their experimental observations. Similarly, Kang and Beauchamp concluded that activation of alkanes by CrO^+ occurs by addition of a C–H bond across the metal–oxide bond.⁴

Proceeding in the spirit of Irikura and Beauchamp, we assume that the reactions of ScO^+ , TiO^+ , and VO^+ with D_2 occur by the same mechanism based on the similarity of the results in the three systems (Figures 1–3). We note that mechanism A is improbable for two reasons. First, if the metal ion forms two covalent $\text{M}-\text{H}$ σ bonds, the $\text{M}-\text{O}$ bond can only be a dative interaction in the case of Sc^+ , which has only two valence electrons, or a single and double covalent bond in the Ti^+ and V^+ cases, respectively. Certainly in the case of Sc^+ , and probably Ti^+ , such an intermediate should be relatively unstable. Second, in the vanadium system where such an intermediate is at least feasible, the resulting species would have a singlet spin ground state and therefore would not account for the enhancement observed for production of M^+ in its excited triplet vs its quintet states.

Mechanism B forms the $\text{H}-\text{M}^+-\text{OH}$ intermediate which has a singlet, doublet, and triplet spin state for $\text{M} = \text{Sc}$, Ti , and V , respectively, assuming that covalent $\text{M}-\text{H}$ and $\text{M}-\text{OH}$ bonds are formed. These intermediates conserve spin with the $\text{MO}^+ + \text{D}_2$ reactants and the low-spin $\text{M}^+ + \text{D}_2\text{O}$ products, but not the ground-state $\text{M}^+ + \text{D}_2\text{O}$ products of reaction 3. Therefore, this mechanism can be used to explain the relative reaction efficiencies that we have measured. This is discussed more extensively below. For mechanism C, Rosi and Bauschlicher have calculated that the M^+-OH_2 intermediates have high-spin ground states for all three metals.⁴⁸ This mechanism can account for our observed state-specific behavior, but only if the M^+-OH_2 intermediates are formed preferentially in excited low-spin states (that correlate to low-spin products) and the coupling between this surface and the ground-state surface is weak.

Although both mechanisms B and C can account for the state-specific reactivity observed, it is useful to consider their ability to explain formation of MOH^+ and MH^+ . Clearly, the $\text{H}-\text{M}^+-\text{OH}$ intermediate of mechanism B is consistent with formation of these products since cleaving the $\text{M}-\text{H}$ bond results in M^+-OH formation and breaking the $\text{M}-\text{O}$ bond forms MH^+ . The former process is preferred due to thermodynamic considerations because $D^{\circ}(\text{M}^+-\text{OH}) \gg D^{\circ}(\text{M}^+-\text{H})$ (Table I). In mechanism C, M^+-OH could be formed from direct H atom loss; however, $\text{MH}^+ + \text{OH}$ formation cannot occur directly from this intermediate without rearrangement. Thus, while either mechanism B or C can be used to explain the dehydration reaction, observation of the MH^+ product suggests that a $\text{H}-\text{M}^+-\text{OH}$ species is formed although it could be a minor reaction pathway.

Potential Energy Surfaces. Figure 8 shows qualitative triplet and singlet potential energy surfaces for mechanism B evolving from the $^1\Sigma^+$ ground state of ScO^+ and its $^3\Delta$ excited state, 3.45 eV higher in energy.¹⁶ Surfaces for mechanism C vary from

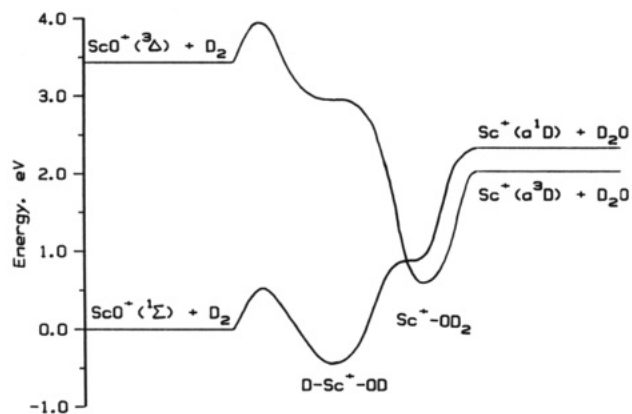


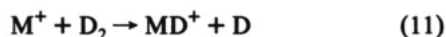
Figure 8. Semi-quantitative potential energy diagram for the interaction of ScO^+ with D_2 to form $\text{Sc}^+ + \text{D}_2\text{O}$.

these only in that there need be no potential well associated with the $\text{D-Sc}^+-\text{OD}$ intermediate. High- and low-spin surfaces for the vanadium and titanium systems are similar to those shown in Figure 8. For VO^+ , the $^5\Pi$ excited state is calculated to lie 3.98 eV above the $^3\Sigma^-$ ground state,³⁵ similar to the splitting between the states of ScO^+ .¹⁶ TiO^+ must also have a high-spin excited state although there have been no calculations or experimental measurements of the energetics of this state. The main difference between the scandium system shown and the titanium and vanadium systems is that the splitting between the high- and low-spin states of the M^+ product is 0.56 eV for Ti^+ and 1.07 eV for V^+ , instead of only 0.30 eV shown for Sc^+ .²⁴

In Figure 8, the long-range interactions of the $\text{Sc}^+ + \text{OD}_2$ products are attractive due to ion-induced-dipole and ion-dipole interactions. The depth of the Sc^+-OD_2 well for both Sc^+ states is taken to be $D^0(\text{Sc}^+-\text{OH}_2) = 1.46$ eV, the average of MDM's measured value and TH's calculated value.^{15,16} TH calculate that the energy of the $\text{D-Sc}^+-\text{OD}$ intermediate is ~ 0.2 eV lower than the $\text{ScO}^+ + \text{D}_2$ reactants. We attempted to produce this intermediate in our flow tube by adding D_2 to the flow downstream from where the ScO^+ was produced. No evidence of a species 4 mass units higher than ScO^+ was observed even when the D_2 pressure in the flow tube was increased by ~ 20 mTorr (roughly a factor of 200 times greater than the O_2 pressure). These results suggest that there is either a barrier associated with $\text{D-Sc}^+-\text{OD}$ or Sc^+-OD_2 formation from $\text{ScO}^+ + \text{D}_2$ (as shown in Figure 8) or that the intermediates of mechanisms B or C lie at higher energies than $\text{ScO}^+ + \text{D}_2$.

No matter whether mechanism B or C is operative, Figure 8 shows that there must a crossing of the triplet and singlet surfaces, which probably occurs near the region where Sc^+-OD_2 is formed. Such a crossing explains how reaction 3 can yield the high-spin ground-state $\text{Sc}^+(a^3D) + \text{D}_2\text{O}(^1A_1)$ from $\text{ScO}^+(^1\Sigma^+) + \text{D}_2(^1\Sigma_g^+)$. Similar crossings must also exist in the titanium and vanadium systems, and thus the inefficiency of forming the ground-state metal ions in these systems can be explained by the need to undergo a spin-forbidden surface crossing. Further, this model can rationalize why the amount of M^+ formed decreases from the Sc to the Ti to the V system. Because the energy splittings between the high- and low-spin M^+ states increase from Sc (0.3 eV) to Ti (0.6 eV) to V (1.1 eV), the coupling efficiency between the reaction surfaces evolving from these states decreases and the total amount of M^+ formed decreases.

Comparison of MO^+ and M^+ Reactivity with D_2 . Insight into the details of MO^+ reactivity can be obtained by comparing the present results with those for the reactions of Sc^+ , Ti^+ , and V^+ with D_2 (process 11).³⁶⁻³⁸ The cross sections for reaction 11 where



$\text{M} = \text{Sc, Ti, and V}$ all peak near $D^0_0(\text{D}_2) = 4.56$ eV and have

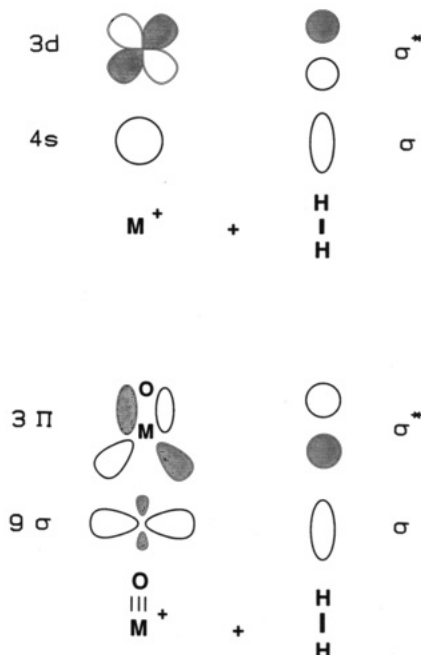


Figure 9. Molecular orbital diagrams for the interactions of M^+ and MO^+ with D_2 . The 9σ acceptor orbital for MO^+ is displayed as a $4s-3d\sigma$ hybrid in cross section, where the large lobe has the toroidal shape.

magnitudes of ~ 0.75 , ~ 0.45 , and $\sim 0.30 \text{ \AA}^2$, respectively. This decrease in cross section magnitude as one changes from Sc^+ to Ti^+ to V^+ is a typical trend of the reactivity of these metal ions and is also observed in reactions with methane,^{39,40,41} ammonia,^{27,34} water,¹⁴ and carbon monoxide.¹² While the $\text{MO}^+ + \text{D}_2$ system is more complex than the $\text{M}^+ + \text{D}_2$ reaction, formation of $\text{MOD}^+ + \text{D}$ is the channel analogous to reaction 11. As for process 11, the MOD^+ cross sections peak near the D_2 bond energy, but in contrast to results for process 11, the magnitudes of the MOD^+ cross sections are about 1.0 \AA^2 (somewhat larger than for the bare metal systems) and independent of M .

The activation of bonds by M^+ and MO^+ can be understood qualitatively by considering simple molecular orbital ideas. As discussed in detail elsewhere,^{1,42,43} activation of D_2 at metal centers is achieved by donation of electrons from the $\sigma(\text{D}_2)$ bonding orbital into an acceptor orbital on the metal and back-donation of electrons from the metal into the $\sigma^*(\text{D}_2)$ antibonding orbital. This increases the electron density between the metal and deuterium atoms while weakening the D-D bond. For atomic metal ions, the acceptor orbital is largely $4s$ with some $3d\sigma$ character and the donor orbital is a $3d\pi$ (Figure 9). For MO^+ , the appropriate orbitals can be identified by examining the electron configurations for the ground states of ScO^+ , TiO^+ , and VO^+ , Table IV (taken from ref 11). This shows that, in all three molecules, the acceptor orbital is the empty 9σ orbital (largely $4s$ character with some $3d\sigma$ for the early metal oxides)⁴⁴ and the donor orbital is the occupied metal oxide 3π bonding orbital. These interactions are shown in Figure 9, where it can be seen that this type of molecular orbital interaction corresponds to oxidative addition of D_2 across the M-O bond via a four-center transition state, i.e., mechanism B. (Note that this four-center interaction is symmetry allowed because of the d character involved in the 3π donor orbital.) Further consideration of the molecular orbital interactions suggests that mechanism C is an unlikely pathway for reaction because there is no acceptor orbital on the oxygen end of the MO^+ molecule. Therefore, mechanism B appears to be the only mechanism consistent with all experimental and molecular orbital considerations.

In the atomic metal systems, it has been suggested that the observed variation in the magnitudes for reactions 11 is related to the probability that the acceptor orbital is empty.¹ The most reactive surfaces are those where the $4s$ and $3d\sigma$ orbitals are both

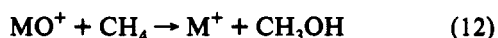
TABLE IV: Metal Oxide Electron Configurations

M	ion state	atom confign	molecular confign	LUMO
Ca	² Π	4s	8σ ² 3π ³	3π
Sc	¹ Σ ⁺	3d ²	8σ ² 3π ⁴	9σ
Ti	² Δ	3d ³	8σ ² 3π ⁴ 1δ ¹	9σ
V	³ Σ ⁻	3d ⁴	8σ ² 3π ⁴ 1δ ²	9σ
Cr	⁴ Π	3d ⁵	8σ ² 3π ⁴ 1δ ² 4π ¹	9σ
	⁴ Σ ⁻	4s3d ⁴	8σ ² 3π ⁴ 1δ ² 9σ ¹	4π
Mn	⁵ Σ ⁺	3d ⁶	8σ ² 3π ⁴ 1δ ² 4π ²	9σ
	⁵ Π	4s3d ⁵	8σ ² 3π ⁴ 1δ ² 4π ¹ 9σ ¹	4π
Fe	⁴ Δ	3d ⁷	8σ ² 3π ⁴ 1δ ³ 4π ²	9σ
Co	³ Σ ⁻	3d ⁸	8σ ² 3π ⁴ 1δ ³ 4π ²	9σ
	³ Φ, Π	3d ⁸	8σ ² 3π ⁴ 1δ ³ 4π ³	9σ
	⁵ Δ	4s3d ⁷	8σ ² 3π ⁴ 1δ ³ 4π ² 9σ ¹	9σ
Ni	² Π	3d ⁹	8σ ² 3π ⁴ 1δ ⁴ 4π ³	9σ
	² Π	4s3d ⁸	8σ ² 3π ⁴ 1δ ⁴ 4π ¹ 9σ ²	4π
	⁴ Σ ⁻	3d ⁹	8σ ² 3π ⁴ 1δ ⁴ 4π ² 9σ ¹	9σ
Cu	³ Σ ⁻	3d ¹⁰	8σ ² 3π ⁴ 1δ ⁴ 4π ² 9σ ²	4π
Zn	² Π	4s3d ¹⁰	8σ ² 3π ⁴ 1δ ⁴ 4π ³ 9σ ²	4π

empty. Since the 3d orbitals are degenerate, the 3dσ remains empty on 60% of the surfaces evolving from Sc⁺(3d²), on 40% from Ti⁺(3d³), and on 20% from V⁺(3d⁴). These percentages are roughly proportional to the observed magnitudes for reactions 11 with Sc⁺, Ti⁺ and V⁺, approximately 0.75, 0.45, and 0.30 Å², respectively.¹ For the metal oxide systems, Table IV shows that the ground states of ScO⁺, TiO⁺, and VO⁺ always have an empty 9σ orbital and vary only in their occupation of the nonbonding 1δ orbitals localized on the metal. Since these orbitals are orthogonal to the 9σ orbital that is used to accept electrons from the σ(D₂) bond, the degree that they are occupied makes little or no difference to the ability of the metal oxide to activate the bond. Thus, the probability that the acceptor orbital is empty is 100% for the metal oxide ions, consistent with the slightly higher cross sections for these species relative to the atomic metal ions. In essence, the oxo ligand has removed the degeneracy of the 3d orbitals on the metal, thus keeping the acceptor orbital unoccupied for ground-state MO⁺ reactants.

Reactions of Other Metal Oxide Ions. In the past, the ability of a metal oxide to transfer its oxygen atom to another molecule has been viewed primarily from a thermodynamic standpoint (i.e., species where this bond is weak are more likely to be good oxygen donors than species where the M–O bonds are strong). Our results show that, in addition to this consideration, species where the splitting between the high- and low-spin states of the M⁺ product are small should transfer oxygen more efficiently than species where this splitting is large. Further, the molecular orbital ideas discussed above suggest that the most reactive metal oxides will have empty acceptor orbitals and occupied donor orbitals. These considerations should be applicable not only to the activation of hydrogen but also to any single covalent bond, as previously demonstrated for the reactions of atomic metal ions.⁴²

Relevant data exist for the oxidation of methane, reaction 12.



Kang and Beauchamp have found that at thermal energies CrO⁺ does not undergo reaction 12,⁴ while Schröder and Schwarz find that FeO⁺ does.⁷ This is interesting because the metal oxide bond energies of CrO⁺ and FeO⁺ are similar, 3.72 ± 0.12 and 3.53 ± 0.06 eV,¹¹ respectively, such that the oxidation of methane to methanol is exothermic for both species, by 0.11 ± 0.12 and 0.30 ± 0.06 eV,⁴⁵ respectively. Further, both CrO⁺ and FeO⁺ have empty 9σ and occupied 3π orbitals (Table IV). The difference in reactivity can be explained in terms of the spin conservation criteria discussed above. Both CrO⁺ and FeO⁺ have quartet ground states,¹¹ such that quartet states of Cr⁺ and Fe⁺ must be formed for reaction 12 to conserve spin. These lie 2.46 and 0.30 eV,²⁴ respectively, above the sextet ground states, such

that the spin-conserving processes 12 are endothermic by 2.35 ± 0.12 eV for CrO⁺ and thermoneutral for FeO⁺.

Thus, reaction 12 for FeO⁺ occurs efficiently because it can conserve spin and still occur exothermically. For CrO⁺, reaction 12 can only occur by crossing from the quartet spin surface of the reactants to the sextet spin surface of the products, and the results of Kang and Beauchamp indicate that this crossing point is higher in energy than the CrO⁺ + CH₄ reactants. Kang and Beauchamp also found that CrO⁺ will oxidize ethane and larger alkanes at thermal energies. This indicates that the quartet–sextet surface crossing in these systems must lie below the energy of the reactants, as also concluded by Kang and Beauchamp, presumably due to the increased long-range attractions associated with more polarizable alkanes and alcohols.

Given this background, we can make qualitative predictions for the reactivity of other metal oxide ions with methane. For M = Sc, Ti, and V, reaction 12 is endothermic by 3.31 ± 0.06, 3.10 ± 0.10, and 2.16 ± 0.10 eV, respectively, for formation of the ground-state atomic metal ions. Thus, the early metal ions are poor oxygenators due to their strong metal–oxygen bonds. In the manganese system, the ⁵Σ⁺ state of MnO⁺ has an empty 9σ orbital and reaction 12 is exothermic by 0.88 ± 0.13 eV if the ground state Mn⁺(⁷S) is formed but endothermic by 0.29 ± 0.13 eV if Mn⁺(⁵S) is produced in the spin-allowed process. Thus, the reactivity of MnO⁺ with methane is not easily predicted and is a useful case to test the influence of spin conservation on reactivity.

For the late transition metals, CoO⁺ and NiO⁺ have states with empty 9σ orbitals and triplet and doublet ground electronic states, respectively. Since the ground-state atomic ions are Co⁺(³F) and Ni⁺(²D), reaction 12 can conserve spin and is exothermic by 0.54 ± 0.06 and 1.05 ± 0.07 eV, respectively. Thus, methane oxidation should proceed efficiently for these systems.

The ability of CuO⁺ to oxygenate alkanes is interesting since this bond is quite weak, 1.62 ± 0.15 eV, but the electron configuration of CuO⁺ (Table IV) is not suitable for covalent bond activation since the 9σ orbital is occupied. Spin conservation is also an issue since the CuO⁺(³D) ground state is high-spin, while the Cu⁺(¹S) ground state is low-spin. (Note that this is the opposite of most of the metals where the metal oxide ion is low-spin and the atomic metal ion is high-spin.) Thus, while reaction 12 is exothermic by 2.21 ± 0.15 eV, the spin-allowed reaction to form Cu⁺(³D) is endothermic by 0.60 ± 0.15 eV. Overall, it seems unlikely that CuO⁺ will be a good oxygen donor, despite its weak bond.

ZnO⁺ might be a useful test case concerning the importance of the occupation of the acceptor orbital for controlling the reactivity. ZnO⁺ has a doubly occupied 9σ orbital, but reaction of ZnO⁺(²Π) conserves spin to form ground-state Zn⁺(²S) and reaction 12 is exothermic by 2.18 ± 0.12 eV.

Summary

All three MO⁺ ions (M = Sc, Ti, and V) react with D₂ to form M⁺ + D₂O, MD⁺ + OD, and MOD⁺ + D. Formation of MOD⁺ is the dominant reaction pathway at all energies for all three systems. The thresholds for formation of MOD⁺ are used to derive 0 K values for the ionic metal hydroxide bond energies (Table I). Our results for TiOH⁺ and VOH⁺ are in agreement with the experimental results reported by MDM;¹⁵ however, our Sc⁺–OH bond energy is much larger than the value given by MDM and is in much better agreement with a theoretical calculation by TH.¹⁶ Comparison of these bond energies with those for the isoelectronic M⁺–NH₂ and M⁺–CH₃ molecules indicates that there is a significant bonding interaction between the lone pairs of electrons on the O atom and empty metal orbitals.

Based on spin conservation and molecular orbital concepts, the reaction mechanism for the interaction of MO⁺ with D₂ that is most consistent with our results is the oxidative addition of D₂

across the M–O bond to form the D–M⁺–OD intermediate. Simple M–D and M–O bond cleavage then leads to the MOD⁺ and MD⁺ products, respectively. Reductive elimination of D₂O forms the M⁺ product preferentially in a low-spin electronic state.

The MO⁺ + D₂ → M⁺ + D₂O reaction channel is the first bimolecular, transition-metal reaction to our knowledge that shows convincing evidence that excited-state products can be formed preferentially over ground-state products. The overriding constraint in these systems is conservation of spin rather than overall reaction energetics. Similar results have also been postulated in bond dissociation processes of transition-metal complexes.^{28,33,46,47} Although similar spin-conservation constraints have previously proven useful for understanding the state-specific behavior of atomic metal ion reactions,² such as the reverse of reaction 3, the spin-allowed processes in these systems are also thermodynamically favored, unlike the present results.

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