

Reactions of fourth-period metal ions ($\text{Ca}^+ - \text{Zn}^+$) with O_2 : Metal-oxide ion bond energies

Ellen R. Fisher,^{a)} J. L. Elkind,^{b),c)} D. E. Clemmer,^{a)} R. Georgiadis,^{b),d)}
S. Klamb,^{b),e)} N. Aristov,^{b),f)} L. S. Sunderlin,^{b)} and P. B. Armentrout^{a),g)}

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112
Department of Chemistry, University of California, Berkeley, California 94720

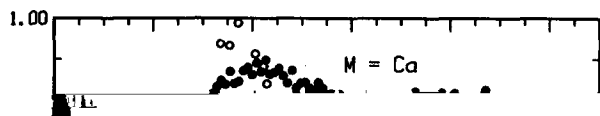
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Reactions of Ca^+ , Zn^+ and all first row atomic transition metal ions with O_2 are studied using

guided ion beam techniques. While reactions of the ground states of Sc^+ , Ti^+ , and V^+ are

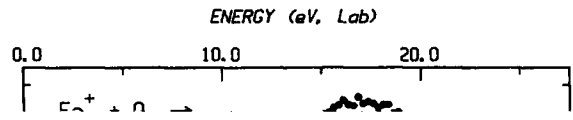
TABLE I. Electronic states of first row transition metal ions

Element	Ground state	Excited states
Scandium (Sc)	3d ¹ 4s ²	3d ⁰ 4s ² , 3d ² 4s ¹
Titanium (Ti)	3d ² 4s ²	3d ¹ 4s ² , 3d ³ 4s ¹
Vanadium (V)	3d ³ 4s ²	3d ² 4s ² , 3d ⁴ 4s ¹
Chromium (Cr)	3d ⁵ 4s ¹	3d ⁴ 4s ² , 3d ⁶ 4s ⁰
Manganese (Mn)	3d ⁵ 4s ²	3d ⁴ 4s ² , 3d ⁶ 4s ¹
Iron (Fe)	3d ⁶ 4s ²	3d ⁵ 4s ² , 3d ⁷ 4s ¹
Cobalt (Co)	3d ⁷ 4s ²	3d ⁶ 4s ² , 3d ⁸ 4s ¹
Nickel (Ni)	3d ⁸ 4s ²	3d ⁷ 4s ² , 3d ⁹ 4s ¹
Copper (Cu)	3d ¹⁰ 4s ¹	3d ⁹ 4s ²
Zinc (Zn)	3d ¹⁰ 4s ²	3d ⁹ 4s ²



cates that the excess energy is distributed statistically. If the peak of the cross section occurs at higher energies than $D_0(O_2)$, this indicates that the reaction dynamics tend to

as $\sigma(\text{VO}^+)$ changes earlier, ~ 0.25 eV. These deviations are due to constraints in the reaction probability imposed by angular momentum conservation. We have previously out-

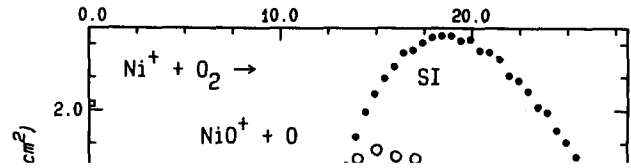


however, previous studies with H₂¹⁷ and ethane²⁴ have ob-

ENERGY (eV, Lab)

served the reactivity of the 0.2% excited states of Mn⁺ present in an SI generated beam. This is because the excited quintet states of Mn⁺ are much more reactive with these two molecules than the nearly inert septet ground state.

To see if this is true with O₂, reaction (1) was also stud-



ENERGY (eV, Lab)

0.0

10.0

20.0

in Murad's results. These differences can be attributed to inefficient product ion collection, a problem which is avoid-

a wide range of systems.^{31,33,34} For the Fe⁺ + O₂ system, a

TABLE III. Metal oxide ion bond dissociation energies at 0 K (eV).

scattering data for both the ⁶D and ⁴F electronic states of Fe⁺ 9

M

This study

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For the Al⁺ + O₂ system several choices of *m* (including

TABLE IV. Thermochemical data for gaseous metal monoxides at 0 K^a

M	IE(M) ^b	D ⁰ (M ⁺ -O) ^c	D ⁰ (MO) ^d	IE(MO) ^e	Δ _f H(MO) ^f	Δ _f H(MO ⁺) ^g
Ca	6.113	3.57(0.05)	4.12(0.17)	6.66 (0.18) 6.5 (1) ^h	6(4)	160(1)
Sc	6.561	6.9 (0.3) ⁱ	7.01(0.12)	6.6 (0.3) ^j	-13(3)	141(7)
Ti	6.820	6.93(0.10) ⁱ	6.92(0.10)	6.819(0.006) ^k	11(2) ^l	168(2)
V	6.740	6.00(0.10) ⁱ 6.00(0.35) ^o	6.49(0.09) ^m	7.230(0.005) ⁿ 7.25 (0.01) ^p	31(3) ^l	199(3)
Cr	6.767	3.72(0.12)	4.41(0.30) 4.80(0.14) ⁱ 4.51(0.15) ^r	7.46 (0.32) 7.85 (0.02) ^q 7.56 (0.19)	49(4)	223(3)
Mn	7.434	2.95(0.13)	3.82(0.08) ^s	8.30 (0.15) 7.7 (0.3) ^s	40(2)	229(3)
Fe	7.902	3.53(0.06) 3.40(0.13) ⁱ	4.21(0.09) ^t 4.21(0.09)	8.58 (0.11) 8.71 (0.10) ^u	61(2)	258(1)
Ni	7.638	2.78(0.07) ^v	3.91(0.17)	9.0 (0.5) ^x 8.77 (0.18) 9.5 (0.3) ^y	71(4)	273(2)
Cu	7.726	1.62(0.15)	2.75(0.22)	8.86 (0.27)	76(5)	280(4)
Zn	9.394	1.65(0.12)	<2.77(0.43)	<10.51 (0.45)	>26(10)	269(3)

^a Δ_fH values given in kcal/mol. IEs and bond energies given in eV. Uncertainties in parentheses.^b Values from Ref. 20. Uncertainties are <0.01 eV.^c Recommended value from Table III, except where noted.

0.0(0.0) low low energy and high temperature and lead to a threshold for reaction of ground state

three times more reactive than the ground state, the E_0 value shifts up by 0.05 eV. We consider this to be our most accurate determination of the true threshold value, but include

A more detailed consideration of the contributions of Co⁺ excited states is more difficult than in the Mn system since the excited state cross-section features in the RI data

the uncertainty associated with the different excited state interpretations

are not very distinct (Fig. 6). In the Fe and Mn systems, we observed that excited states having electron configurations

We can also analyze the EI data for Ni⁺ in a manner similar to the Mn system. A crude analysis of the low-energy

Zinc

Since the EI spectrum for Zn⁺ is shown in Figure 7, it is

centers (LOC) model ($n = m = 1$) to analyze their data.

One indication of the uniqueness of the Ca⁺ and Cu⁺

This model rises rapidly from threshold, resulting in an E_0 value that is high compared to models which rise more slowly.

reactions is the value of n required to reproduce the data. As mentioned above, $m = 1$ was selected to reproduce the experimental results; this is indicated as model 1 for

efficiencies of these reactions depend strongly (factors of 10–100) on the electronic state of the metal ion.^{17,71,73,74} These differences have been explained in terms of molecular

MO^+ thermochemistry with that previously discussed for $\text{M}^+ - \text{CH}_n$ species and with the better understood neutral metal oxides.

Ti,⁸³ V,⁸⁰ and Cr.⁸⁰ To make this comparison properly, we note that formation of a triple bond with CH requires pro-

therefore cannot be described in the same terms as the more covalently bonded MO⁺ species on the left-hand side of the

state 0.74 eV higher in energy. When this correction is in-

Comparison to the neutral metal oxides. Unlike the ionic

NiO, the successive electrons are now placed in the non-bonding 1δ and 0σ orbitals (Table V) and the bond energies

$4s^1 3d^{n-1}$.⁸⁸ Another way of thinking of this change is that the bonds of the ions are weaker than those of the neutral $3d^n$

change only slightly. In this region of the Periodic Table, the metals to the right in the Periodic Table because the d orbitals

values change increases to the point where the character of the orbitals is more s -like than d -like.

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