

# Gas-phase thermochemistry of the group 3 dioxides: $\text{ScO}_2$ , $\text{YO}_2$ and $\text{LaO}_2$

D.E. Clemmer, N.F. Dalleska and P.B. Armentrout<sup>1</sup>

*Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA*

Received 10 December 1991

Gas-phase  $\text{ScO}_2$ ,  $\text{YO}_2$ ,  $\text{LaO}_2$  and the singly charged cations of these species are formed in endothermic reactions between  $\text{MO}^+$  ( $\text{M}=\text{Sc}$ ,  $\text{Y}$ , and  $\text{La}$ ) and  $\text{NO}_2$  in a guided ion beam mass spectrometer. The cross sections of these reactions are measured as a function of kinetic energy and are interpreted to give the following 0 K bond energies (in eV):  $D^0(\text{OSc-O})=3.95\pm 0.33$ ,  $D^0(\text{OY-O})=4.14\pm 0.22$ ,  $D^0(\text{OLa-O})=4.20\pm 0.33$ ,  $D^0(\text{OSc}^+-\text{O})=1.72\pm 0.19$ ,  $D^0(\text{OY}^+-\text{O})=1.76\pm 0.16$ , and  $D^0(\text{OLa}^+-\text{O})=0.99\pm 0.31$ . Values for the  $\text{MO}_2$  ionization energies (in eV) are determined to be  $\text{IE}(\text{ScO}_2)=8.66\pm 0.20$ ,  $\text{IE}(\text{YO}_2)=8.23\pm 0.16$  and  $\text{IE}(\text{LaO}_2)=8.11\pm 0.35$ . The differences between these values and estimates in the literature are discussed by considering the nature of the bonding in  $\text{MO}_2$  and  $\text{MO}_2^+$ .

## 1. Introduction

In contrast to the extensive thermochemical database available for transition metal monoxides [1,2], reliable thermochemistry for the metal dioxides is relatively scarce. Some  $\text{MO}_2$  thermochemistry is available for metals that commonly exhibit a +4 oxidation state, such as the group 4–6 and 8–10 transition metals [3–6], however, there is no experimental thermochemistry for the group 3 dioxides,  $\text{ScO}_2$ ,  $\text{YO}_2$ , and  $\text{LaO}_2$ . This is primarily because the group 3 metal oxides exist in the solid phase as sesquioxides ( $\text{M}_2\text{O}_3$ ) that form mainly  $\text{MO}$  and small amounts of the atomic metal when vaporized [7,8]. Thus, traditional mass spectrometric and effusion experiments involving these metal oxides [7–9] and chemiluminescence studies of the bimolecular oxidation of the bare metal atoms [10,11] have measured thermochemistry for  $\text{MO}$  but have not mentioned  $\text{MO}_2$ . To fill this void, Kordis and Gingerich [5] have empirically estimated the atomization energies for the group 3 metal dioxides as a factor of 1.9 greater than the dissociation energies for the metal monoxides. This factor was based on their measured thermochemistry for four other rare earth oxides (Ce,

Nd, Gd and Ho), and predicts  $\text{OM-O}$  bond energies of 6.3, 6.6, and 7.5 eV (all  $\pm 1.0$  eV) for  $\text{M}=\text{Sc}$ ,  $\text{Y}$ , and  $\text{La}$ , respectively. Also, Cockett et al. have estimated the ionization energy of  $\text{LaO}_2$  as  $9.5\pm 1.5$  [12] and  $9.5\pm 0.5$  eV [13] based on a comparison to  $\text{CeO}_2$ .

In this paper, we report the first direct experimental measurements of the  $\text{OM-O}$  bond energies and ionization energies for the gas-phase group 3 metal dioxides:  $\text{ScO}_2$ ,  $\text{YO}_2$ , and  $\text{LaO}_2$ . This is achieved by using guided ion beam mass spectrometry to monitor the kinetic energy dependence of the reaction of  $\text{MO}^+$  with  $\text{NO}_2$ . This continues our ongoing pursuit of accurate thermochemistry for small molecules containing transition metals and oxygen [2,14–19].

## 2. Experimental

Complete descriptions of the apparatus and experimental procedures are given elsewhere [20].  $\text{MO}^+$  ions are produced in a dc-discharge/flow-tube (FT) source (described previously [21]) by allowing  $\text{M}^+$  (produced via argon ion bombardment of

<sup>1</sup> Camille and Henry Dreyfus Teacher-Scholar, 1987–1992.

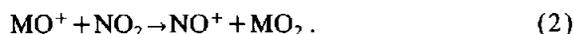
the metal chloride salt<sup>#1</sup>) to react with O<sub>2</sub> downstream<sup>#2</sup>. The MO<sup>+</sup> ions undergo  $\approx 10^5$  collisions with the Ar/He buffer gas mixture before exiting the flow tube and are expected to equilibrate at a temperature of 300 K with respect to all internal states. The 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 trap. This device guides the ions through a static gas cell containing a low pressure ( $\approx 0.02$ – $0.3$  mTorr) of NO<sub>2</sub> that has been purified as described before [18]. After exiting the gas cell, product and unreacted beam ions drift to the end of the octopole where they are directed into a quadrupole mass filter for mass analysis and then detected by using a Daly-type detector and pulse counting electronics. Conversion of raw ion intensities into reaction cross sections and the calibration of the absolute energy scale are treated as described previously [20]. The beams are found to have a Gaussian kinetic energy distribution with a fwhm of  $\approx 0.4$  eV in the laboratory frame. All product cross sections reported are results of single ion–molecule collisions as verified by examining the pressure dependence of the product intensities.

### 3. Results and analyses

Only two ionic products, MO<sub>2</sub><sup>+</sup> and NO<sup>+</sup>, are formed for all three metal systems in the reaction of MO<sup>+</sup> with NO<sub>2</sub>. The cross sections for these processes are shown in fig. 1 and correspond to the reactions



and

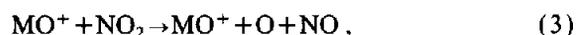


Reactions (1) and (2) are clearly endothermic for all three systems, and MO<sub>2</sub><sup>+</sup> formation is favored at

<sup>#1</sup> Scandium chloride hexahydrate (Strem, 99.9%), yttrium chloride hexahydrate (Aesar, 99.9%), and lanthanum chloride heptahydrate (Aesar) were dehydrated by pumping a vial containing the sample to  $\approx 100$  mTorr for several hours.

<sup>#2</sup> A more complete description of MO<sup>+</sup> formation from this source will be published soon [22].

low energies. Since the products of these processes differ only in the location of the charge, we expect these reactions to compete with one another, consistent with the relatively smooth variation of the total cross sections with energy. There is no ambiguity that the neutral product of reaction (2) is MO<sub>2</sub> since the thresholds for producing MO+O or M+O<sub>2</sub> (as calculated from known literature thermochemistry in table 1) are much higher than the observed thresholds in fig. 1. In all three systems, the cross sections for reaction (1) peak near  $D_0^0(\text{ON-O}) = 3.116$  eV [4]. This behavior suggests that the MO<sub>2</sub><sup>+</sup> products can dissociate in the overall process



at these higher energies. While there is no unambiguous evidence of competition between reactions (2) and (3), we presume that such competition exists since reaction (1) and (2) are tightly coupled, as noted above.

Previous work [2,17,25,26] has shown that cross sections for endothermic reactions can be analyzed by using

$$\sigma(E) = \sigma_0 \sum_i g_i (E - E_0 + E_i + E_{\text{rot}})^n / E, \quad (4)$$

which involves an explicit sum of the contributions of individual states of the reactants, denoted by *i*, weighted by their populations, *g<sub>i</sub>*. Here,  $\sigma_0$  is a scaling factor, *E* is the relative kinetic energy, *n* is an adjustable parameter, *E<sub>0</sub>* is the 0 K threshold for reaction of ground electronic and vibrational state reactants. In this study, *E<sub>i</sub>* represents the vibrational levels of NO<sub>2</sub> populated at 305 K<sup>#3</sup> (the nominal temperature of the octopole) and *E<sub>rot</sub>* (=0.065 eV) is the total rotational energy of the reagents (*kT* for MO<sup>+</sup> and  $\frac{3}{2}kT$  for NO<sub>2</sub>). In order to model the high energy portion of  $\sigma(\text{MO}_2^+)$  and  $\sigma(\text{NO}^+)$ , we use a modified form of eq. (4) (discussed previously [27]) that accounts for a decline in the product ion cross section above an energy, *E<sub>D</sub>*, where a dissociation channel or competing reaction can begin.

Before comparison with the experimental data, eq. (4) is convoluted with the neutral and ion kinetic energy distributions as described previously [20].

<sup>#3</sup> Vibrational frequencies for NO<sub>2</sub> are 1357.8, 756.8, and 1665.5 cm<sup>-1</sup> as given in ref. [4].

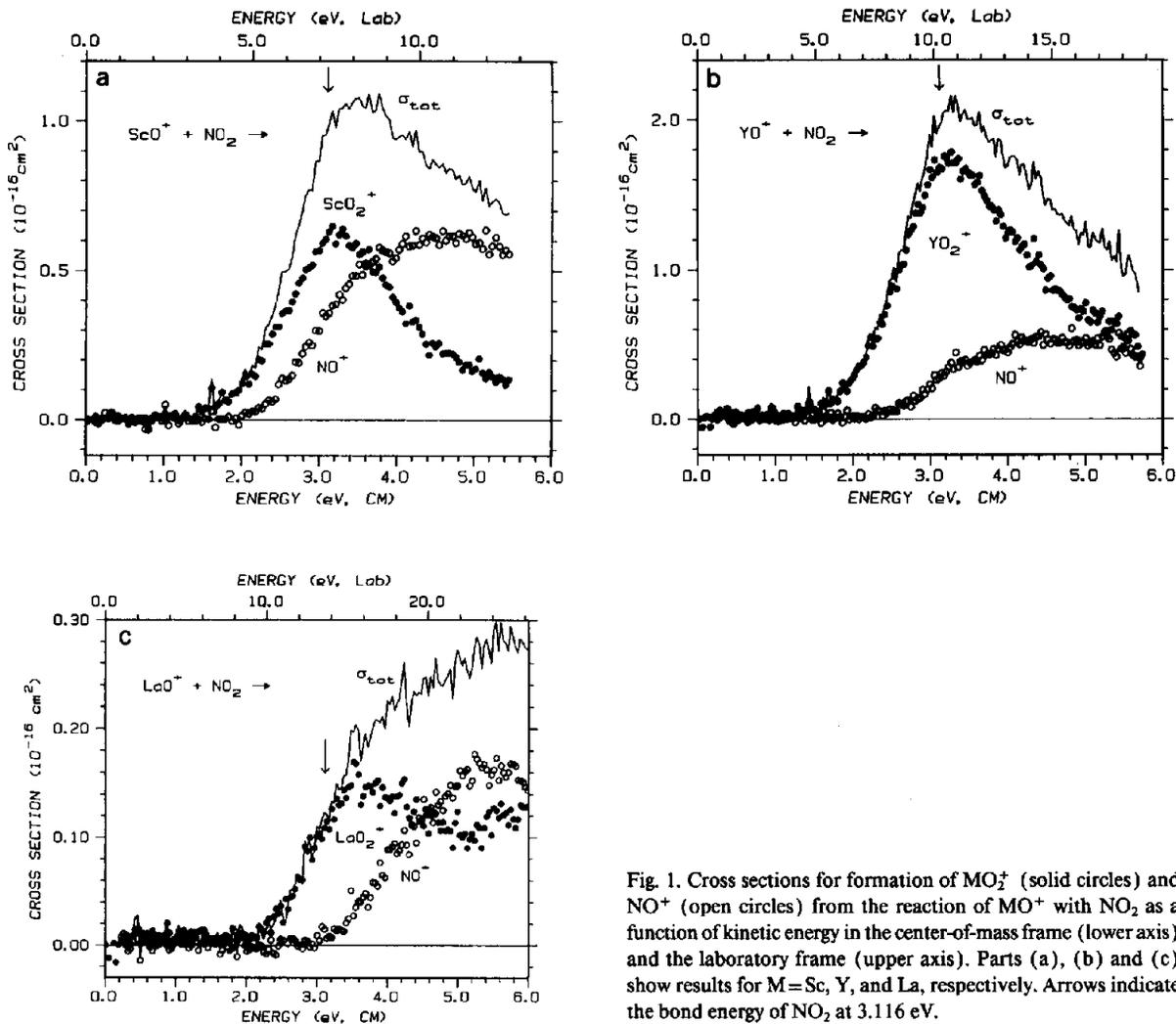


Fig. 1. Cross sections for formation of  $MO_2^+$  (solid circles) and  $NO^+$  (open circles) from the reaction of  $MO^+$  with  $NO_2$  as a function of kinetic energy in the center-of-mass frame (lower axis) and the laboratory frame (upper axis). Parts (a), (b) and (c) show results for  $M=Sc, Y,$  and  $La,$  respectively. Arrows indicate the bond energy of  $NO_2$  at 3.116 eV.

The  $\sigma_0$ ,  $n$ ,  $E_0$ , and  $E_D$  parameters are then optimized by using a non-linear least squares analysis to give the best reproduction of the data. Error limits for  $E_0$  are calculated from the range of threshold values obtained for different data sets (four independent data sets for Sc and Y, and three for La) with different values of  $n$  and the uncertainty in the absolute energy scale. The resulting parameters found upon this treatment of the cross sections for reactions (1) and (2) are given in table 2. Overall, eq. (4) and its modified form accurately reproduce all cross sections shown in fig. 1.

## 4. Discussion

### 4.1. Thermochemistry

If there are no energy barriers in excess of the reaction endothermicity, as is often true for endothermic ion-molecule reactions [26,28], then the threshold energy  $E_0$  can be equated with the reaction enthalpy. Thus, we can calculate  $D_0^0(OM^+-O)$  and  $D_0^0(OM-O)$  from the threshold energies for reactions (1) and (2) via the relations

$$D_0^0(OM^+-O) = D_0^0(ON-O) - E_0(1) \quad (5)$$

Table 1  
Metal oxide thermochemistry (in eV) at 0 K

M	$D^0(\text{MO})^{\text{a)}}$	$D^0(\text{M}^+-\text{O})^{\text{b)}}$	$\text{IE}(\text{MO})^{\text{c)}}$	$\Delta_f H_0(\text{MO})^{\text{d)}}$	$\Delta_f H_0(\text{MO}^+)^{\text{e)}}$
Sc	7.01(0.12)	7.14(0.11) <sup>f)</sup>	6.43(0.16) <sup>f)</sup>	-0.55(0.13)	5.88(0.14) <sup>f)</sup>
Y	7.41(0.12)	7.78(0.19)	5.85(0.15)	-0.49(0.12)	5.36(0.19)
La	8.27(0.12)	8.95(0.16)	4.90(0.1)	-1.24(0.12)	3.66(0.16)
ScO	3.95(0.33) <sup>g)</sup>	1.72(0.19) <sup>g)</sup>	8.66(0.20) <sup>g)</sup>	-1.94(0.35)	6.72(0.40)
YO	4.14(0.22) <sup>g)</sup>	1.76(0.16) <sup>g)</sup>	8.23(0.16) <sup>g)</sup>	-2.07(0.25)	6.16(0.30)
LaO	4.20(0.33) <sup>g)</sup>	0.99(0.31) <sup>g)</sup>	8.11(0.35) <sup>g)</sup>	-2.88(0.35)	5.23(0.49)
Ti	6.92(0.10)	6.92(0.10)	6.819(0.006) <sup>h)</sup>	0.50(0.10)	7.32(0.10)
Zr	8.00(0.13)	8.74(0.33)	6.1(0.3)	0.80(0.13)	6.9(0.3)
Ce	8.30(0.14)	8.94(0.17)	4.9(0.1)	-1.36(0.14)	3.54(0.17)
TiO	6.14(0.16) <sup>i)</sup>	3.42(0.19)	9.54(0.1)	-3.08(0.19)	6.46(0.21)
ZrO	6.3(0.5) <sup>j)</sup>	2.9(0.7)	9.5(0.3)	-2.9(0.5)	6.6(0.6)
CeO	6.8(0.5) <sup>k)</sup>	2.0(0.7)	9.7(0.5) <sup>k)</sup>	-5.6(0.5)	4.1(0.7)

<sup>a)</sup> Unless otherwise stated,  $D^0(\text{MO})$  values are from ref. [1].

<sup>b)</sup> Unless otherwise stated, values are derived from  $D^0(\text{M}^+-\text{O}) = D^0(\text{MO}) + \text{IE}(\text{M}) - \text{IE}(\text{MO})$ . Other ionization energies (in eV) needed are  $\text{IE}(\text{Y}) = 6.22$ ,  $\text{IE}(\text{La}) = 5.58$ ,  $\text{IE}(\text{Ti}) = 6.82$ ,  $\text{IE}(\text{Zr}) = 6.84$ , and  $\text{IE}(\text{Ce}) = 5.54$  from ref. [3].

<sup>c)</sup> Values are from ref. [3] unless otherwise noted.

<sup>d)</sup>  $\Delta_f H_0(\text{MO}) = \Delta_f H_0(\text{M}) + \Delta_f H_0(\text{O}) - D_0^0(\text{MO})$ , where  $\Delta_f H_0(\text{O}) = 2.558$  eV from ref. [4]. Other necessary values (in eV) are  $\Delta_f H_0(\text{Sc}) = 3.90$ ,  $\Delta_f H_0(\text{Y}) = 4.36$ ,  $\Delta_f H_0(\text{La}) = 4.47$ ,  $\Delta_f H_0(\text{Ti}) = 4.86$ ,  $\Delta_f H_0(\text{Zr}) = 6.24$ , and  $\Delta_f H_0(\text{Ce}) = 4.38$  from ref. [3].

<sup>e)</sup>  $\Delta_f H_0(\text{MO}^+) = \Delta_f H_0(\text{MO}) + \text{IE}(\text{MO})$ .

<sup>f)</sup> Ref. [17].

<sup>g)</sup> This study.

<sup>h)</sup> Ref. [23].

<sup>i)</sup> Value derived from the atomization energy of  $\text{TiO}_2 = 13.06 \pm 0.12$  eV given in ref. [24].

<sup>j)</sup>  $D_0^0(\text{OZr-O}) = \Delta_f H_0(\text{ZrO}) + \Delta_f H_0(\text{O}) - \Delta_f H_0(\text{ZrO}_2)$ .

<sup>k)</sup> Values are from ref. [13].

Table 2  
Summary of parameters of eq. (4) used to fit cross sections <sup>a)</sup>

Products	$E_0(\text{eV})$	$\sigma_0$	$n$	$E_D(\text{eV})$
$\text{ScO}_2^+ + \text{NO}$	1.40(0.19)	0.7(0.3)	2.4(0.5)	3.1(0.1)
$\text{YO}_2^+ + \text{NO}$	1.36(0.16)	1.1(0.5)	2.9(0.4)	3.1(0.1)
$\text{LaO}_2^+ + \text{NO}$	2.13(0.31)	0.4(0.2)	2.8(0.9)	3.1(0.1)
$\text{ScO}_2 + \text{NO}^+$	2.00(0.29)	1.0(0.6)	2.1(0.8)	
$\text{YO}_2 + \text{NO}^+$	2.39(0.16)	1.4(0.5)	2.5(0.7)	
$\text{LaO}_2 + \text{NO}^+$	3.28(0.31)	0.5(0.1)	1.4(0.8)	

<sup>a)</sup> Uncertainties in parentheses.

and

$$D_0^0(\text{OM-O}) = D_0^0(\text{ON-O}) + \text{IE}(\text{NO}) - \text{IE}(\text{MO}) - E_0(2), \quad (6)$$

respectively, where  $\text{IE}(\text{NO}) = 9.26436 \pm 0.00006$  eV [3] and  $\text{IE}(\text{MO})$  is the ionization energy of the metal monoxide given in table 1. Combined with the values of  $E_0$  in table 2, these equations yield the  $\text{OM}^+-\text{O}$  and  $\text{OM-O}$  bond energies for the group 3 metals

listed in table 1.

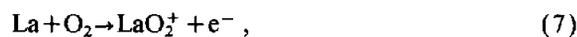
The difference in the thresholds for reactions (1) and (2),  $\Delta E_0 = E_0(2) - E_0(1)$ , can be used to determine values for the ionization energy of  $\text{MO}_2$ , since  $\text{IE}(\text{MO}_2) = \text{IE}(\text{NO}) - \Delta E_0$ . The average differences between the thresholds for each independent data set are  $\Delta E_0 = 0.60 \pm 0.20$ ,  $1.03 \pm 0.16$  and  $1.15 \pm 0.35$  eV for the Sc, Y and La systems, respectively. Combining these values with  $\text{IE}(\text{NO})$  gives

the IEs for the group 3 metal dioxides listed in table 1.

The OM–O bond energies measured here are grossly different than the estimates made by Kordis and Gingerich (KG) [5]. As noted in section 1, they assumed that  $D^0(\text{OM–O}) + D^0(\text{M–O})$  would be 1.9 times  $D^0(\text{M–O})$ , based on comparisons with other metal dioxides. We find instead that the sums of the first and second metal oxide bond energies average only 1.54 times the first bond energy for the three group 3 metals. Likewise, our value for  $\text{IE}(\text{LaO}_2)$  is substantially lower than the estimate of Cockett et al. [12,13],  $9.5 \pm 1.5$  eV, also cited in section 1. Both KG and Cockett et al. made their estimates by comparison with metals than can support a +4 oxidation state (and thus bond strongly to two  $\text{O}^{2-}$  ligands). Since the group 3 metals have a maximum valence oxidation state of only +3, the difference between our thermochemistry and the estimates are easily justified, as discussed in more detail in section 4.2.

#### 4.2. Comparison to chemiionization results

The one experimental observation in the literature that can provide thermochemical information concerning the group 3 metal dioxides is a chemiionization experiment of Cockett et al. [12]. They observed  $\text{LaO}^+$  and  $\text{LaO}_2^+$  formation by crossing an effusive La beam (evaporated from a heated furnace at 1600 K) with an effusive beam of  $\text{O}_2$  in the reaction region of an electron spectrometer. They attributed formation of the dioxide ion to the chemiionization reaction,



which they believed was exothermic by  $1.08 \pm 1.95$  eV, based on the thermochemistry of Kordis and Gingerich and their IE estimate. This exothermicity was apparently confirmed by the observation that the maximum kinetic energy of the chemielectrons was  $1.5 \pm 0.1$  eV (although no such correspondence between the exothermicity of the chemiionization reaction and the maximum kinetic energy of the chemielectrons was found in the case of Ce).

If the chemiionization reaction (7) is truly exothermic, this means that  $E_0(1)$  must be less than  $1.37 \pm 0.16$  eV, and if the reaction is exothermic by

1.5 eV, then reaction (1) with  $\text{M}=\text{La}$  should be exothermic. The lowest threshold consistent with our cross sections for this reaction is 1.8 eV, clearly inconsistent with an exothermic reaction and or a threshold of 1.37 eV. While it is possible that reaction (1) with  $\text{M}=\text{La}$  is exhibiting an activation barrier (this cannot be ruled out unequivocally), such a barrier (especially one of 1.8 eV) is unusual for ion–molecule reactions unless the reaction involves a restriction of spin or orbital angular momentum. No such restrictions are apparent for reaction (1) <sup>#4</sup>.

Another possibility that we have considered in order to rationalize the discrepancies between our results and those of Cockett et al. [12] is that the structures of the  $\text{MO}_2^+$  ions formed here are different from the products of the chemiionization experiment. It is possible that our thermochemistry corresponds to a  $\text{M}^+-\text{O}_2$  structure instead of the metal dioxide ion. This assumption leads to  $D^0(\text{La}^+-\text{O}_2) = 4.82 \pm 0.35$  eV <sup>#5</sup>, which is much too large to be reasonable. The thermochemistry from Cockett et al. leads to an even higher value for  $D^0(\text{La}^+-\text{O}_2)$  such that this structure can be ruled out.

Our thermochemistry predicts that reaction (7) is endothermic by  $0.76 \pm 0.39$  eV. While this value is actually consistent with the estimated thermochemistry for reaction (7) of  $-1.08 \pm 1.95$  eV, it implies that  $\text{LaO}_2^+$  is formed by some other pathway in their experiment. This could involve excited electronic species of La, although the population of such states should be very small under the conditions of their experiment. More complex pathways to the production of  $\text{LaO}_2^+$  are also possible since formation of  $\text{LaO}^+$ , a more prevalent product than  $\text{LaO}_2^+$  at low  $\text{O}_2$  pressures, requires two sequential reactions,  $\text{La} + \text{O}_2 \rightarrow \text{LaO} + \text{O}$  and  $\text{La} + \text{O} \rightarrow \text{LaO}^+ + e^-$  [12],

<sup>#4</sup> Reaction (1) involves interaction of a singlet species,  $\text{LaO}^+$ , with a doublet,  $\text{NO}_2$ , and thus must proceed along a potential energy surface that has doublet spin. Such a surface can then evolve into products,  $\text{NO}$ , which has doublet spin, and  $\text{LaO}_2^+$ , which could be either a singlet or a triplet species. If  $\text{LaO}_2^+$  has a singlet ground state, reaction (1) clearly conserves spin. If  $\text{LaO}_2^+$  has a triplet ground state, its interaction with doublet  $\text{NO}$  will lead to doublet and quartet potential energy surfaces and thus also allows spin to be conserved in the overall reaction.

<sup>#5</sup> This value is calculated from  $D^0(\text{La}^+-\text{O}_2) = D^0(\text{MO}^+) + D^0(\text{ON–O}) - D^0(\text{O}_2) - E_0(1)$  and the thermochemical values listed in tables 1 and 2.

both of which are exothermic by over 3 eV, table 1. While the reaction sequence leading to  $\text{LaO}_2^+$  formation is not obvious, it is possible that it involves excited states of products formed in these strongly exothermic reaction channels.

#### 4.3. Trends in OM–O bonding

In order to help gauge whether the thermochemistry measured in the present experiments is more reasonable than the estimates of Kordis and Gingerich and Cockett et al., it is useful to consider the bonding in these species. As we have discussed previously [2,29], the large values for the group 3 neutral and cationic monoxide bond energies (table 1) can be rationalized as two covalent M–O bonds (since oxygen atoms have two unpaired electrons) enhanced by donation of electron density from the lone pair of 2p electrons on the oxygen atom into an empty metal s or d orbital (a dative bond). The net result is essentially a triple bond between the metal and the oxygen for both the neutral and ionic monoxides and leads to ground electronic states that are doublets and singlets, respectively. The similarity of  $D^0(\text{MO})$  and  $D^0(\text{MO}^+)$  for the group 3 metals is consistent with this picture. Alternatively, the bonding can be viewed in the ionic limit as interaction of  $\text{O}^{2-}$  with  $\text{M}^{2+}$  and  $\text{M}^{3+}$ , respectively, again predicting doublet ground states for MO and singlet ground states for  $\text{MO}^+$ .

For the neutral group 3 dioxides, both covalent and dative interactions are possible for bonding MO to O. Since the neutral group 3 monoxides have a single unpaired electron, one covalent bond to the second oxygen atom is possible and this can be augmented by dative interactions. This type of bonding implies that the group 3 dioxides have doublet spin ground states since one oxygen electron is left unpaired. In the ionic bonding limit,  $\text{M}^{3+}$  interacts with  $\text{O}^{2-}$  and  $\text{O}^-$ , again to form a doublet ground state. In either bonding model, these ideas suggest that  $D^0(\text{OM–O})$  should be much less than  $D^0(\text{M–O})$ . Such ideas contrast with the estimate that  $D^0(\text{OM–O}) \approx 0.9D^0(\text{M–O})$  [5], but this was based on a comparison with other rare earth metals. Indeed, table 1 shows that the dioxides of the group 4 metals (Ti and Zr) and Ce have second metal oxide bond energies that are similar to their monoxide bond energies. This is

clearly because the group 4 metals and Ce (as well as other rare earth elements) have four valence electrons and thus can bond (either covalently or ionically) two oxygen atoms in an equivalent manner. It is useful to note that  $\text{TiO}_2^+$ ,  $\text{ZrO}_2^+$  and  $\text{CeO}_2^+$ , species that are isoelectronic with  $\text{ScO}_2$ ,  $\text{YO}_2$ , and  $\text{LaO}_2$ , also have much weaker second bond energies,  $D^0(\text{OM}^+–\text{O})$ , than their very strong first bond energies,  $D^0(\text{M}^+–\text{O})$ , table 1.

An indirect observation that illustrates that the group 3 metal dioxides are less stable than the group 4 metal dioxides is that the dioxides of Ti, Zr, and the rare earth elements, Ce, Pr, Nd, Gd, Tb, and Ho, have been observed in high temperature [6,30] and matrix [31,32] studies and their thermochemistry measured. The dioxides of Sc, Y and La have not been observed, even though the experimental conditions are similar [5,33,34]. According to thermochemistry listed in table 1 and in the compilation of Cockett et al. [13], these eight metal dioxides have atomization energies,  $D^0(\text{MO}) + D^0(\text{OM–O})$ , above 13.1 eV (the value for Ti). According to the estimates of Kordis and Gingerich and Cockett et al. [5,13], all other rare earths have lower atomization energies, *except* La, which has the highest value of  $15.6 \pm 0.5$  eV, and Lu, which is borderline at  $13.4 \pm 1.1$  eV. If this thermochemistry for  $\text{LaO}_2$  were correct, it seems hard to reconcile why this molecule would not be observed. In contrast, our thermochemistry yields an atomization energy for  $\text{LaO}_2$  of  $12.35 \pm 0.35$  eV, a value that is more consistent with the failure to observe  $\text{LaO}_2$  previously. Overall, it seems clear that accurate thermochemistry for the group 3 metal dioxides cannot be obtained by simple comparisons with metals having additional electrons.

For the ionic group 3 dioxides, bonding between  $\text{MO}^+$ , which has no unpaired valence electrons, and an additional oxygen atom can be achieved with only dative interactions whether the bonding is covalent or ionic<sup>#6</sup>. These ideas suggest that the  $\text{MO}_2^+$  molecules could have either a singlet or triplet spin ground states and that  $D^0(\text{OM}^+–\text{O})$  should be much

<sup>#6</sup> Of course, once the  $\text{MO}_2^+$  molecule is formed, the two metal–oxygen bonds are equivalent and essentially double bonds (one covalent and one dative bond for each O atom). As  $\text{MO}_2^+$  dissociates to  $\text{MO}^+ + \text{O}$ , the remaining metal–oxygen bond increases in strength as it becomes a triple bond, thus lowering the dissociation energy of  $\text{OM}^+–\text{O}$ .

less than  $D^0(M^+-O)$  and less than  $D^0(OM-O)$ . These relative bond energies are consistent with both our measurements and with the thermochemistry for  $LaO_2^+$  estimated by Cockett et al. [12,13]. Indeed, their estimates suggest that  $D^0(OLa^+-O) - D^0(OLa-O) = IE(LaO_2) - IE(LaO) = 4.5 \pm 0.5$  eV, while we find that this difference is  $3.21 \pm 0.36$  eV. Their estimate of the *absolute* value of  $D^0(OLa^+-O)$ ,  $3.0 \pm 1.2$  eV [13], is substantially higher than ours, however, because their estimates for  $D^0(OLa-O)$  are much higher than our value, as discussed above.

At this point, there is no obvious rationale for explaining the discrepancies between our measurements and the observations of the chemiionization experiment. Simple considerations of the nature of the bonding in these metal dioxides help rationalize the bond energies measured here and do not appear to be consistent with the previously estimated thermochemistry. It would clearly be beneficial for additional experimental and theoretical work to be performed to help clarify the nature and strength of the bonding in these interesting chemical species.

### Acknowledgement

This work is supported by the National Science Foundation Grant No. CHE-8917980. We would also like to thank Professor John Dyke for useful discussions and for providing a copy of his work before publication.

### References

- [1] J.B. Pedley and E.M. Marshall, *J. Phys. Chem. Ref. Data* 12 (1983) 967.
- [2] E.R. Fisher, J.L. Elkind, D.E. Clemmer, R. Georgiadis, S.K. Loh, N. Aristov, L.S. Sunderlin and P.B. Armentrout, *J. Chem. Phys.* 93 (1990) 2676.
- [3] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, *J. Phys. Chem. Ref. Data* 17 Suppl. 1 (1988) 1.
- [4] M.W. Chase, C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald and A.N. Syverud, *J. Phys. Chem. Ref. Data* 14 Suppl. 1 (1985) (JANAF Tables).
- [5] J. Kordis and K.A. Gingerich, *J. Chem. Phys.* 66 (1977) 483.
- [6] L. Brewer and G.M. Rosenblatt, *Chem. Rev.* 61 (1961) 257.
- [7] P.N. Walsh, H.W. Goldstein and D. White, *J. Am. Ceram. Soc.* 43 (1960) 229.
- [8] B.F. Yudin, V.I. Mogilenskii, Yu.A. Polonskii and S.A. Lapshin, *Zh. Prikl. Khim.* 49 (1974) 776; R.J. Ackermann and E.G. Rauh, *J. Chem. Thermodyn.* 3 (1971) 445.
- [9] P.N. Walsh, D.F. Dever and D. White, *J. Phys. Chem.* 65 (1961) 1410.
- [10] J.L. Gole and C.L. Chalek, *J. Chem. Phys.* 65 (1976) 4384.
- [11] C.L. Chalek and J.L. Gole, *J. Chem. Phys.* 19 (1977) 59.
- [12] M.C.R. Cockett, J.M. Dyke, A.M. Ellis, M. Feher and T.G. Wright, *J. Electron Spectry.* 51 (1990) 529.
- [13] M.C.R. Cockett, L. Nyulaszi, T. Veszpremi, T.G. Wright and J.M. Dyke, *J. Electron Spectry.*, in press.
- [14] R. Georgiadis and P.B. Armentrout, *Intern. J. Mass Spectrom. Ion Processes* 89 (1989) 227.
- [15] S.K. Loh, E.R. Fisher, L. Lian, R.H. Schultz and P.B. Armentrout, *J. Phys. Chem.* 93 (1989) 3159.
- [16] L.S. Sunderlin and P.B. Armentrout, *J. Phys. Chem.* 94 (1990) 3589.
- [17] D.E. Clemmer, J.L. Elkind, N. Aristov and P.B. Armentrout, *J. Chem. Phys.* 95 (1991) 3387.
- [18] D.E. Clemmer, N.F. Dalleska and P.B. Armentrout, *J. Chem. Phys.* 95 (1991) 7263.
- [19] D.E. Clemmer, N.F. Dalleska, S.K. Loh and P.B. Armentrout, work in progress.
- [20] K.M. Ervin and P.B. Armentrout, *J. Chem. Phys.* 83 (1985) 166.
- [21] R.H. Schultz and P.B. Armentrout, *Intern. J. Mass Spectrom. Ion Processes* 107 (1991) 29.
- [22] D.E. Clemmer, N. Aristov and P.B. Armentrout, in preparation.
- [23] A.D. Sappey, G. Eiden, J.E. Harrington and J.C. Weisshaar, *J. Chem. Phys.* 90 (1989) 1415.
- [24] G. Balducci, G. Gigli and M. Guido, *J. Chem. Phys.* 83 (1985) 1909.
- [25] Y.-M. Chen, D.E. Clemmer and P.B. Armentrout, *J. Chem. Phys.* 95 (1991) 1228.
- [26] P.B. Armentrout, in: *Advances in gas phase ion chemistry*, Vol. 1, eds. N.G. Adams and L.M. Babcock (JAI Press, Greenwich), in press.
- [27] M.E. Weber, J.L. Elkind and P.B. Armentrout, *J. Chem. Phys.* 84 (1986) 1521.
- [28] P.B. Armentrout, in: *Structure/reactivity and thermochemistry of ions*, eds. P. Ausloos and S.G. Lias (Reidel, Dordrecht, 1987) p. 97.
- [29] P.B. Armentrout and D.E. Clemmer, in: *Energetics of organometallic species*, ed. J.A.M. Simoes (Kluwer, Dordrecht), submitted for publication.
- [30] V. Piacente, G. Bardi, L. Malaspina and A. Desideri, *J. Chem. Phys.* 59 (1973) 31.
- [31] R.L. DeKock and W. Weltner Jr., *J. Phys. Chem.* 75 (1971) 514.
- [32] S.D. Gabelnick, G.T. Reedy and M.G. Chasanov, *J. Chem. Phys.* 60 (1974) 1167.
- [33] W. Weltner Jr., D. McLeod Jr. and P.H. Kasai, *J. Chem. Phys.* 46 (1967) 3172.
- [34] S. Smoes, J. Drowart and G. Verhaegen, *J. Chem. Phys.* 43 (1965) 732.