

# Nitric Oxide as an Electron Donor, an Atom Donor, an Atom Acceptor, and a Ligand in Reactions with Atomic Transition-Metal and Main-Group Cations in the Gas Phase

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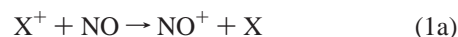
The room-temperature reactions of nitric oxide with 46 atomic cations have been surveyed systematically across and down the periodic table using an inductively-coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer. Rate coefficients and product distributions were measured for the reactions of first-row cations from  $K^+$  to  $Se^+$ , of second-row cations from  $Rb^+$  to  $Te^+$  (excluding  $Tc^+$ ), and of third-row cations from  $Cs^+$  to  $Bi^+$ . Reactions both first and second order in NO were identified. The observed bimolecular reactions were thermodynamically controlled. Efficient exothermic electron transfer was observed with  $Zn^+$ ,  $As^+$ ,  $Se^+$ ,  $Au^+$ , and  $Hg^+$ . Bimolecular O-atom transfer was observed with  $Sc^+$ ,  $Ti^+$ ,  $Y^+$ ,  $Zr^+$ ,  $Nb^+$ ,  $La^+$ ,  $Hf^+$ ,  $Ta^+$ , and  $W^+$ . Of the remaining 32 atomic ions, all but 8 react in novel termolecular reactions second order in NO to produce  $NO^+$  and the metal–nitrosyl molecule, the metal–monoxide cation and nitrous oxide, and/or the metal–nitrosyl cation.  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Ga^+$ ,  $In^+$ ,  $Tl^+$ ,  $Pb^+$ , and  $Bi^+$  are totally unreactive. Further reactions with NO produce the dioxide cations  $CaO_2^+$ ,  $TiO_2^+$ ,  $VO_2^+$ ,  $CrO_2^+$ ,  $SrO_2^+$ ,  $ZrO_2^+$ ,  $NbO_2^+$ ,  $RuO_2^+$ ,  $BaO_2^+$ ,  $HfO_2^+$ ,  $TaO_2^+$ ,  $WO_2^+$ ,  $ReO_2^+$ , and  $OsO_2^+$  and the still higher order oxides  $WO_3^+$ ,  $ReO_3^+$ , and  $ReO_4^+$ . NO ligation was observed in the formation of  $CaO^+(NO)$ ,  $ScO^+(NO)$ ,  $TiO^+(NO)$ ,  $VO^+(NO)_{1-3}$ ,  $VO_2^+(NO)_{1-3}$ ,  $SrO^+(NO)$ ,  $SrO_2^+(NO)_{1,2}$ ,  $RuO^+(NO)_{1-3}$ ,  $RuO_2^+(NO)_{1,2}$ ,  $OsO^+(NO)_{1-3}$ , and  $IrO^+(NO)$ . The reported reactivities for bare atomic ions provide a benchmark for reactivities of ligated atomic ions and point to possible second-order NO chemistry in biometallic and metal-surface environments leading to the conversion of NO to  $N_2O$  and the production of metal–nitrosyl molecules.

## Introduction

Gaseous nitric oxide has a long and extensive history of relevance in atmospheric and ionospheric chemistry and as a pollutant in combustion. But more recently, because of its biochemical activity, nitric oxide has burst upon the scene of neuroscience, particularly neurotransmission and neurobiology, as well as cardiovascular physiology, immunology, and carcinogenesis.<sup>1–4</sup> “This new role has reinvigorated research into the fundamental chemistry of this simple molecule, much to the delight of chemists, and led *Science* magazine to designate NO Molecule of the Year in 1992”.<sup>4</sup> It also prompted *Chemical & Engineering News* to assign “superstar” status to this molecule a year later.<sup>2</sup>

Metal atoms and ions are often implicated in the chemical and biochemical activity of NO. For example, the interaction of transition metals such as Ti, Pb, Zn, Fe, V, Mn, and Ni with NO may be involved in the photodissociative production of smog in highly polluted environments.<sup>5</sup> Reactions of NO on metal surfaces and zeolites doped with metals are important in the development of efficient catalysts for use in catalytic converters or for industrial applications of NO decomposition.<sup>6,7</sup> Gas-phase chemical cycles mediated by transition-metal cations and their oxides have been identified for the catalytic conversion of  $N_2O$  and CO to  $N_2$  and  $CO_2$ .<sup>8,9</sup> The binding of NO to metalloenzymes and metalloporphyrins has been implicated in the important biological functions of NO.<sup>10</sup>

Much of the chemical and biochemical activity of NO is due to the unique free radical nature of this diatomic molecule along with the relative ease of removing its unpaired electron ( $I_E(NO) = 9.264$  eV).<sup>11</sup> In this study we survey the kinetic ability of NO to transfer an electron or donate an oxygen atom to isolated atomic cations. We have accomplished this with 46 atomic cations including transition-metal and main-group cations. Previous measurements with atomic ions have demonstrated rapid electron transfer,  $k > 10^{-10}$   $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>, from NO to  $H^+$ ,  $He^+$ ,  $C^+$ ,  $N^+$ ,  $F^+$ ,  $Ne^+$  (dissociative electron transfer),  $S^+$ ,  $Cl^+$ , and  $Ar^+$  but not to  $Na^+$ ,  $K^+$ ,  $Kr^+$ ,  $O^+$ , and  $Si^+$ ,  $k < 10^{-10}$   $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>.<sup>12</sup> Of particular note is the observation of N-atom transfer, reaction 1b, proceeding in competition with electron transfer, reaction 1a, with  $X^+ = N^+$  (15%)<sup>13</sup> and  $F^+$  (10%).<sup>14</sup>



Apparently, the first measurement of a reaction of a transition-metal cation with NO in the gas phase was that with  $Ti^+$  reported in 1974 by Biondi et al.<sup>15</sup>  $Ti^+$  ions were produced with a titanium–tungsten filament. Rate coefficients for reactions with NO were measured for both  $Ti^+$  and  $Th^+$  in a drift-tube mass spectrometer over an energy range from thermal energies (300 K) to 2 eV (mean kinetic energy). In 1985, the drift tube was coupled to a zirconium-ion discharge containing  $ZrBr_4$  to measure the rate coefficient for the reaction of  $Zr^+$  with NO

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over a similar energy range.<sup>16</sup> In 1981 ion cyclotron resonance (ICR) mass spectroscopy, in which metal cations were produced by laser volatilization/ionization, provided results for go/no go experiments that indicated fast oxidation reactions of NO with  $\text{Ti}^+$ ,  $\text{Zr}^+$ , and  $\text{Nb}^+$  and nonoxidation with  $\text{V}^+$ .<sup>17</sup> Somewhat surprisingly, there appear not to have been any other previous measurements of atomic metal and main-group cation reactions with NO. In the experiments reported here the atomic cations are generated in an inductively-coupled plasma (ICP) of argon at ca. 5500 K. The ions are then injected into a flow tube to measure their reactivities with NO. This combined ICP/SIFT technique<sup>18,19</sup> was used to examine the reactivities of 46 atomic cations including 29 transition-metal and 17 main-group cations, most of which have not previously been investigated by others. The experiments were performed over a high range of NO additions, and this led to the discovery of unexpected second-order NO chemistry that has previously also not been reported. These latter results may have important implications for  $\text{NO}^+$ ,  $\text{MO}^+$ ,  $\text{N}_2\text{O}$ , and nitrosyl formation in environments containing charged metals and elevated levels of nitric oxide gas. Certainly the results reported here for the interaction of bare atomic metal ions with NO will serve as a valuable benchmark for similar interactions in the condensed phase involving ligated metal ions.

### Experimental Method

The experimental results reported here were obtained using the selected-ion flow tube (SIFT) tandem mass spectrometer in the Ion-Chemistry Laboratory at York University, described in detail elsewhere.<sup>19</sup> Recently, it has been modified to accept ions generated in an inductively coupled plasma (ICP) torch through an atmosphere/vacuum interface (ELAN series, Perkin-Elmer SCIEX). The ICP ion source and interface have also been described previously.<sup>18</sup> Solutions containing the metal salt of interest having concentration of ca.  $5 \mu\text{g L}^{-1}$  were peristaltically pumped via a nebulizer into the plasma. The nebulizer flow was adjusted to maximize the ion signal detected downstream of the SIFT. The sample solutions were prepared using atomic spectroscopy standard solutions commercially available from SPEX, Teknolab, J. T. Baker Chemical Co., Fisher Scientific Co., Perkin-Elmer, and Alfa Products. A single-isotope solution was used for  $\text{Ca}^+$  ( $m/z$  44) from readily soluble  $\text{CaCO}_3$  (>98.5% isotope purity, Oak Ridge National Laboratory (Isotope Business Office)) to avoid overlap with  $\text{Ar}^+$  ( $m/z$  40) in the ICP ion selection. Aliquots of standard solutions were diluted with highly purified water produced in the Millipore Milli-Qplus ultrapure water system. The final concentrations were varied within 5–20 ppm interval to achieve suitable intensity of the resultant ion beam. Normally, a stabilizing agent was added to each solution to prevent precipitation. That was either  $\text{HNO}_3$  or  $\text{HCl}$  for acid-stabilized salts or  $\text{KOH}$  for those base-stabilized.

Atomic ions emerge from the ICP at a nominal ion temperature of 5500 K with corresponding Boltzmann state distributions. These distributions have been derived from available optical spectra<sup>20,21</sup> and reported by us previously.<sup>22</sup> The calculations show that excited states of the main-group elemental cations except  $\text{Ba}^+$  are high in energy and contribute little (never more than 10%) to the total ion population at 5500 K. The ground  $^2\text{S}$  state of  $\text{Ba}^+$  contributes 44% and the excited  $^2\text{D}$  state 55% at 5500 K. The state distributions are more variable for the transition-metal cations. Excited states contribute 20% or less toward the populations of  $\text{Cr}^+$ ,  $\text{Mn}^+$ ,  $\text{Ni}^+$ ,  $\text{Cu}^+$ ,  $\text{Zn}^+$ ,  $\text{Rh}^+$ ,  $\text{Pd}^+$ ,  $\text{Ag}^+$ ,  $\text{Cd}^+$ ,  $\text{Re}^+$ ,  $\text{Au}^+$ , and  $\text{Hg}^+$  and 50% or more toward the populations of  $\text{Ti}^+$ ,  $\text{Y}^+$ ,  $\text{Zr}^+$ ,  $\text{Nb}^+$ ,  $\text{La}^+$ , and  $\text{Ir}^+$  with  $\text{Sc}^+$ ,  $\text{V}^+$ ,  $\text{Fe}^+$ ,  $\text{Co}^+$ ,  $\text{Mo}^+$ ,  $\text{Ru}^+$ ,  $\text{Hf}^+$ ,  $\text{Ta}^+$ ,  $\text{W}^+$ , and  $\text{Pt}^+$  having intermediate distributions.

After extraction from the ICP, the plasma ions may experience both radiative electronic-state relaxation and collisional electronic-state relaxation. The latter may occur with argon as the extracted plasma cools upon sampling and then by collisions with He atoms in the flow tube (ca.  $4 \times 10^5$  collisions) prior to the reaction region, but the actual extent of electronic relaxation (either radiative or collisional) is not known and is difficult to assess. Almost all of the electronic states of the transition-metal ions have positive parity; electric dipole transitions between states of the same parity are forbidden (Laporte rule).<sup>23a</sup> This means that radiative transitions between different states in metal cations can be achieved only by either magnetic dipole or electric quadrupole radiation. The probabilities for these transitions are very low,<sup>23b</sup> and the resulting radiative lifetimes are of the order of seconds or larger. The time interval in the ICP/SIFT experiments between the exit of the ICP source and the entrance in the reaction region is  $\sim 20$  ms, and therefore no major modification of state distributions can occur in this time interval by forbidden radiative decay. That having been said, there were no indications of excited-state effects in our previous measurements of reactions of atomic cations derived from the same ICP source with  $\text{N}_2\text{O}$ , except with  $\text{Pt}^+$ .<sup>22</sup> The many collisions experienced by the atomic cations with the quite polarizable Ar atoms as they emerge from the ICP and the ca.  $10^4$  collisions with He atoms in the flow tube (the helium buffer gas pressure was  $0.35 \pm 0.01$  Torr) appear to be sufficient to provide for the thermalization of the excited states and ensure that the atomic ions reach a translational temperature equal to the tube temperature of  $295 \pm 2$  K prior to entering the reaction region. However, the exact extent of electronic relaxation is uncertain. Clues to the presence of excited electronic states of the atomic ions in the reaction region can be found in the products observed and the shape (linearity) of the semilogarithmic decay of the reacting atomic ion upon addition of neutral reactant. All such indications, often including the observation of linearity for more than one decade of signal decay, are that the excited states are relaxed or that they react with the same rate and give the same product as the ground-state species. The semilogarithmic decay for most of the reactive cations investigated was observed to be linear for more than one decade. A decay of much more than the percentage of excited states calculated to be present within the ICP indicates cannot be attributed solely to excited states.

The NO reagent gas had a nominal purity of 99.5% (BOC Gases) within the gas tank. In situ chemical ionization experiments with atomic metal cations derived from the ICP source provided further insight into the levels of impurities *within the reaction region*. In separate experiments we have found that some metal oxide ions ( $\text{ScO}^+$ ,  $\text{ZrO}^+$ ,  $\text{LaO}^+$ ) react with  $\text{NO}_2$  to produce  $\text{NO}^+$  but do not form  $\text{NO}^+$  with NO. Therefore the failure to observe downstream  $\text{NO}^+$  with these metal oxide ions with added NO can provide an upper limit to the level of  $\text{NO}_2$  impurity in the NO. Such experiments have provided a conservative upper limit of 0.5%. An analogous approach was used to arrive at an upper limit of 1% to the level of  $\text{N}_2\text{O}$  impurity in NO. In this case  $\text{CeN}^+$  was used as the indicator because our experiments established that  $\text{Ce}^+$  reacts with  $\text{N}_2\text{O}$  to produce  $\text{CeN}^+$  with  $k = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>22</sup> No  $\text{CeN}^+$  was observed when NO was added to  $\text{Ce}^+$ . Also, failure to observe  $\text{AsO}^+$  with added NO indicated levels for possible  $\text{N}_2\text{O}$  impurities, of less than 0.1% in the reaction region because we have shown that  $\text{As}^+$  reacts with  $\text{N}_2\text{O}$  to produce  $\text{AsO}^+$  ( $k = 2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>22</sup> and it is known now that subsequent electron transfer of NO to  $\text{AsO}^+$  is

**TABLE 1: Rate Coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), Reaction Efficiencies ( $k/k_c$ ), and Higher Order Product Ions Measured for Reactions of First-Row Metal Cations with Nitric Oxide in Helium at  $0.35 \pm 0.01$  Torr and  $295 \pm 2$  K**

reaction <sup>a</sup>	$k^b$	$k_c^c$	$k/k_c$	higher order product ions
$\text{K}^+ + \text{NO} \rightarrow \text{NR}$	$\leq 1 \times 10^{-12}$	$7.8 \times 10^{-10}$	$\leq 10^{-3}$	
$\text{Ca}^+ + \text{NO} + \text{NO} \rightarrow \text{CaO}^+ + \text{N}_2\text{O}$	$7.0 \times 10^{-12}$	$7.6 \times 10^{-10}$	$9.2 \times 10^{-3}$	$\text{CaO}_2^+, \text{CaO}^+(\text{NO})$
$\text{Sc}^+ + \text{NO} \rightarrow \text{ScO}^+ + \text{N}$	$3.3 \times 10^{-11}$	$7.6 \times 10^{-10}$	0.043	$\text{ScO}^+(\text{NO})$
$\text{Ti}^+ + \text{NO} \rightarrow \text{TiO}^+ + \text{N}$	$1.2 \times 10^{-10}$	$7.5 \times 10^{-10}$	0.16	$\text{TiO}_2^+, \text{TiO}^+(\text{NO}), \text{NO}^+$
$\text{V}^+ + \text{NO} + \text{NO} \rightarrow \text{VO}^+ + \text{N}_2\text{O}$	$2.1 \times 10^{-11}$	$7.4 \times 10^{-10}$	0.028	$\text{VO}_2^+, \text{NO}^+, \text{VO}^+(\text{NO})_{1-3}, \text{VO}_2^+(\text{NO})_{1-3}$
$\text{Cr}^+ + \text{NO} + \text{NO} \rightarrow \text{CrO}^+ + \text{N}_2\text{O}$ (0.8) $\rightarrow \text{NO}^+ + \text{CrNO}$ (0.2)	$9.2 \times 10^{-12}$	$7.4 \times 10^{-10}$	0.012	$\text{CrO}_2^+$
$\text{Mn}^+ + \text{NO} + \text{NO} \rightarrow \text{NO}^+ + \text{MnNO}$ (0.7) $\rightarrow \text{MnO}^+ + \text{N}_2\text{O}$ (0.3)	$3.3 \times 10^{-12}$	$7.3 \times 10^{-10}$	0.005	
$\text{Fe}^+ + \text{NO} + \text{NO} \rightarrow \text{FeO}^+ + \text{N}_2\text{O}$	$1.8 \times 10^{-11}$	$7.3 \times 10^{-10}$	0.025	$\text{NO}^+$
$\text{Co}^+ + \text{NO} + \text{NO} \rightarrow \text{CoO}^+ + \text{N}_2\text{O}$	$4.2 \times 10^{-11}$	$7.2 \times 10^{-10}$	0.058	$\text{NO}^+$
$\text{Ni}^+ + \text{NO} + \text{NO} \rightarrow \text{NiO}^+ + \text{N}_2\text{O}$ (0.6) $\rightarrow \text{NO}^+ + \text{NiNO}$ (0.3) $\rightarrow \text{NiNO}^+ + \text{NO}$ (0.1)	$1.5 \times 10^{-11}$	$7.2 \times 10^{-10}$	0.021	
$\text{Cu}^+ + \text{NO} + \text{NO} \rightarrow \text{NO}^+ + \text{CuNO}$ (0.9) $\rightarrow \text{CuNO}^+ + \text{NO}$ (0.1)	$6.8 \times 10^{-12}$	$7.1 \times 10^{-10}$	$9.2 \times 10^{-3}$	
$\text{Zn}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{Zn}$ (0.97) $+ \text{NO} + \text{NO} \rightarrow \text{ZnO}^+$ (0.03)	$1.0 \times 10^{-10}$	$7.1 \times 10^{-10}$	0.14	
$\text{Ga}^+ + \text{NO} \rightarrow \text{NR}$	$\leq 6 \times 10^{-13}$	$7.1 \times 10^{-10}$	$\leq 8 \times 10^{-4}$	
$\text{Ge}^+ + \text{NO} + \text{NO} \rightarrow \text{NO}^+ + \text{GeNO}$ (0.6) $\rightarrow \text{GeO}^+ + \text{N}_2\text{O}$ (0.4)	$1.9 \times 10^{-11}$	$7.1 \times 10^{-10}$	0.027	
$\text{As}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{As}$	$3.2 \times 10^{-10}$	$7.0 \times 10^{-10}$	0.46	
$\text{Se}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{Se}$	$3.0 \times 10^{-10}$	$6.9 \times 10^{-10}$	0.43	

<sup>a</sup> Product distributions are given in parentheses. The branching fractions are estimated to be accurate to  $\pm 20\%$ . <sup>b</sup> Effective bimolecular rate coefficient first order in NO. The estimated uncertainty is  $\pm 30\%$ . <sup>c</sup> Collision rate coefficient calculated using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich.<sup>26</sup>

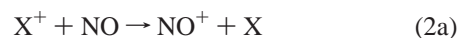
endothermic.<sup>24</sup> So we can exclude formation of significant amounts of  $\text{NO}_2$  and  $\text{N}_2\text{O}$  nitrogen oxides from reactions of NO with possible impurities such as  $\text{H}_2\text{O}$  or  $\text{O}_2$  in the inlet system, which of course is continuously flushed with NO during a reaction measurement. There was also no indication of  $(\text{NO})_2^+$  formation from  $(\text{NO})_2$  dimer in any of the experiments. The known dissociation constant of  $(\text{NO})_2$  is  $1.6 \times 10^{23}$  molecules  $\text{cm}^{-3}$  at room temperature,<sup>25</sup> and this is large enough to keep the dimer concentration below  $10^{-5}\%$  of the monomer in the flow tube.

Reaction rate coefficients were determined in the usual manner.<sup>19</sup> Primary rate coefficients are determined from the observed semilogarithmic decay of the primary reactant ion intensity using pseudo-first-order kinetics. Higher-order rate coefficients are obtained by fitting the experimental data to the solutions of the system of differential equations for sequential reactions. These fits are shown in the graphical presentations of the experimental results. The rate coefficients for the primary and consecutive reactions reported herein have an absolute accuracy of  $\pm 30\%$ . When rate coefficients are reported as an upper limit ( $\leq$ ), this indicates the statistical scatter in the data was significant compared to the slope of the data and an upper limit (based on the line of steepest slope through the data) is reported. Product distributions are obtained in the usual manner from plots of the fractional abundance of ions with added NO.

## Results and Discussion

The reactions of 46 atomic ions with NO were investigated, including 29 transition-metal and 17 main-group cations. Some (seven) atomic ions were completely unreactive with NO in the dynamic range of our measurements,  $k < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . These include the group 1 ions ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) that have a rare-gas configuration, the group 14 ions ( $\text{In}^+$ ,  $\text{Tl}^+$ ) that have a  $d^{10}s^2$  filled-orbital configuration ( $\text{Ga}^+$  was also quite unreactive),  $\text{Pb}^+$  ( $s^2p^1$ ) and  $\text{Bi}^+$  ( $s^2p^2$ ).

Two different channels, electron and O-atom transfer, were observed for bimolecular reactions known to be *exothermic* and these are indicated in reactions 2a and 2b, respectively.



Competing N-atom transfer leading to the formation of  $\text{XN}^+$ , as has been reported for  $\text{N}^+$ <sup>13</sup> and  $\text{F}^+$ ,<sup>14</sup> was not observed in our experiments, presumably due to the lower stability of the  $\text{XN}^+$  ions, viz. the nitrogen-atom affinity  $\text{NA}(\text{X}^+) < \text{NA}(\text{O}) = 150.9 \pm 0.2 \text{ kcal mol}^{-1}$ .<sup>11</sup>

Unexpectedly,  $\text{NO}^+$  and  $\text{XO}^+$  product ions were often observed even when formation by bimolecular reaction first order in NO, reactions 2a and 2b, was *endothermic* for ground-state reactants. However, we realize that formation by termolecular reactions *second order in NO*, viz. Reactions 3 and 4, can often be exothermic. Exothermicity can be achieved in



reactions 3 and 4 by bond formation in the neutral product: X–NO bond formation in reaction 3 and N–NO bond formation in reaction 4. Reaction 3 is exothermic when  $\text{IE}(\text{X}) > \text{IE}(\text{NO}) - \text{D}(\text{X–NO})$ . Reaction 4 is exothermic when the oxygen-atom affinity  $\text{OA}(\text{X}^+) > \text{OA}(\text{N}) - \text{D}(\text{N–NO}) = 36 \text{ kcal mol}^{-1}$ .<sup>11</sup> Remarkably, this is known to be the case, within experimental uncertainty, with 35 of the atomic ions investigated! Occasionally,  $\text{X}^+(\text{NO})$  also was observed to be produced with kinetics similar to reactions 3 and 4. We attribute this to the collisional stabilization with NO acting as the third body according to reaction 5. Because of its internal degrees of freedom, the NO



**TABLE 2: Rate Coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), Reaction Efficiencies ( $k/k_c$ ), and Higher Order Product Ions Measured for Reactions of Second-Row Metal Cations with Nitric Oxide in Helium at  $0.35 \pm 0.01$  Torr and  $295 \pm 2$  K**

reaction <sup>a</sup>	$k^b$	$k_c^c$	$k/k_c$	higher order product ions
Rb <sup>+</sup> + NO → NR	$\leq 1 \times 10^{-13}$	$6.8 \times 10^{-10}$	$\leq 10^{-4}$	
Sr <sup>+</sup> + NO + NO → SrO <sup>+</sup> + N <sub>2</sub> O	$6.8 \times 10^{-12}$	$6.8 \times 10^{-10}$	0.01	SrO <sub>2</sub> <sup>+</sup> , SrO <sup>+</sup> (NO), SrO <sub>2</sub> <sup>+</sup> (NO) <sub>1,2</sub>
Y <sup>+</sup> + NO → YO <sup>+</sup> + N	$7.9 \times 10^{-11}$	$6.8 \times 10^{-10}$	0.12	
Zr <sup>+</sup> + NO → ZrO <sup>+</sup> + N	$4.7 \times 10^{-10}$	$6.8 \times 10^{-10}$	0.69	ZrO <sub>2</sub> <sup>+</sup>
Nb <sup>+</sup> + NO → NbO <sup>+</sup> + N	$4.7 \times 10^{-10}$	$6.8 \times 10^{-10}$	0.69	NbO <sub>2</sub> <sup>+</sup> , NO <sup>+</sup>
Mo <sup>+</sup> + NO + NO → MoO <sup>+</sup> + N <sub>2</sub> O (0.5) → NO <sup>+</sup> + MoNO (0.25) → MoNO <sup>+</sup> + NO (0.25)	$5.9 \times 10^{-12}$	$6.7 \times 10^{-10}$	$8.8 \times 10^{-3}$	
Ru <sup>+</sup> + NO + NO → RuO <sup>+</sup> + N <sub>2</sub> O	$1.4 \times 10^{-11}$	$6.7 \times 10^{-10}$	0.021	RuO <sub>2</sub> <sup>+</sup> , NO <sup>+</sup> , RuO <sup>+</sup> (NO) <sub>1-3</sub> , RuO <sub>2</sub> <sup>+</sup> (NO) <sub>1,2</sub>
Rh <sup>+</sup> + NO + NO → NO <sup>+</sup> + RhNO (0.7) → RhNO <sup>+</sup> + NO (0.3)	$7.3 \times 10^{-13}$	$6.7 \times 10^{-10}$	$1.1 \times 10^{-3}$	RhNO <sup>+</sup> (NO)
Pd <sup>+</sup> + NO + NO → PdNO <sup>+</sup> + NO (0.45) → NO <sup>+</sup> + PdNO (0.55)	$5.0 \times 10^{-12}$	$6.7 \times 10^{-10}$	$7.4 \times 10^{-3}$	
Ag <sup>+</sup> + NO + NO → NO <sup>+</sup> + AgNO	$9.4 \times 10^{-13}$	$6.7 \times 10^{-10}$	$1.4 \times 10^{-3}$	
Cd <sup>+</sup> + NO + NO → NO <sup>+</sup> + CdNO	$1.7 \times 10^{-12}$	$6.6 \times 10^{-10}$	$2.6 \times 10^{-3}$	
In <sup>+</sup> + NO → NR	$\leq 1 \times 10^{-13}$	$6.6 \times 10^{-10}$	$\leq 10^{-4}$	
Sn <sup>+</sup> + NO + NO → NO <sup>+</sup> + SnNO (0.9) → SnO <sup>+</sup> + N <sub>2</sub> O (0.1)	$2.1 \times 10^{-11}$	$6.5 \times 10^{-10}$	0.032	
Sb <sup>+</sup> + NO + NO → NO <sup>+</sup> + SbNO (0.15) → SbO <sup>+</sup> + N <sub>2</sub> O (0.85)	$2.7 \times 10^{-11}$	$6.5 \times 10^{-10}$	$4.2 \times 10^{-2}$	
Te <sup>+</sup> + NO + NO → NO <sup>+</sup> + TeNO (0.5) → TeO <sup>+</sup> + N <sub>2</sub> O (0.5)	$1.9 \times 10^{-12}$	$6.5 \times 10^{-10}$	$2.9 \times 10^{-3}$	

<sup>a</sup> Product distributions are given in parentheses. The branching fractions are estimated to be accurate to  $\pm 20\%$ . <sup>b</sup> Effective bimolecular rate coefficient first order in NO. The estimated uncertainty is  $\pm 30\%$ . <sup>c</sup> Collision rate coefficient calculated using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich.<sup>26</sup>

**TABLE 3: Rate Coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), Reaction Efficiencies ( $k/k_c$ ), and Higher Order Product Ions Measured for Reactions of Third-Row Metal Cations with Nitric Oxide in Helium at  $0.35 \pm 0.01$  Torr and  $295 \pm 2$  K**

reaction <sup>a</sup>	$k^b$	$k_c^c$	$k/k_c$	higher order product ions
Cs <sup>+</sup> + NO → NR	$\leq 1 \times 10^{-13}$	$6.6 \times 10^{-10}$	$\leq 10^{-4}$	
Ba <sup>+</sup> + NO + NO → BaO <sup>+</sup> + N <sub>2</sub> O	$2.1 \times 10^{-11}$	$6.5 \times 10^{-10}$	0.032	BaO <sub>2</sub> <sup>+</sup> , NO <sup>+</sup>
La <sup>+</sup> + NO → LaO <sup>+</sup> + N	$2.6 \times 10^{-10}$	$6.5 \times 10^{-10}$	0.40	
Hf <sup>+</sup> + NO → HfO <sup>+</sup> + N	$5.6 \times 10^{-10}$	$6.5 \times 10^{-10}$	0.87	HfO <sub>2</sub> <sup>+</sup> , NO <sup>+</sup>
Ta <sup>+</sup> + NO → TaO <sup>+</sup> + N	$5.7 \times 10^{-10}$	$6.4 \times 10^{-10}$	0.89	TaO <sub>2</sub> <sup>+</sup> , NO <sup>+</sup>
W <sup>+</sup> + NO → WO <sup>+</sup> + N	$5.0 \times 10^{-10}$	$6.3 \times 10^{-10}$	0.79	WO <sub>2,3</sub> <sup>+</sup> , NO <sup>+</sup>
Re <sup>+</sup> + NO + NO → ReO <sup>+</sup> + N <sub>2</sub> O	$1.3 \times 10^{-11}$	$6.3 \times 10^{-10}$	0.021	ReO <sub>2-4</sub> <sup>+</sup> , NO <sup>+</sup>
Os <sup>+</sup> + NO + NO → OsO <sup>+</sup> + N <sub>2</sub> O	$1.5 \times 10^{-11}$	$6.3 \times 10^{-10}$	0.024	OsO <sub>2</sub> <sup>+</sup> , NO <sup>+</sup> , OsO <sup>+</sup> (NO) <sub>1-3</sub>
Ir <sup>+</sup> + NO + NO → IrO <sup>+</sup> + N <sub>2</sub> O (0.95) → IrNO <sup>+</sup> + NO(0.05)	$1.5 \times 10^{-11}$	$6.3 \times 10^{-10}$	0.024	NO <sup>+</sup> , IrO <sup>+</sup> (NO) IrNO <sup>+</sup> (NO)
Pt <sup>+</sup> + NO + NO → NO <sup>+</sup> + PtNO (0.9) → PtNO <sup>+</sup> + NO (0.1)	$1.2 \times 10^{-11}$	$6.3 \times 10^{-10}$	0.019	Pt <sup>+</sup> (NO) <sub>2,3</sub>
Au <sup>+</sup> + NO → NO <sup>+</sup> + Au	$1.0 \times 10^{-10}$	$6.3 \times 10^{-10}$	0.16	
Hg <sup>+</sup> + NO → NO <sup>+</sup> + Hg	$1.2 \times 10^{-10}$	$6.3 \times 10^{-10}$	0.19	
Tl <sup>+</sup> + NO → NR	$\leq 1 \times 10^{-13}$	$6.3 \times 10^{-10}$	$\leq 10^{-4}$	
Pb <sup>+</sup> + NO → NR	$\leq 1 \times 10^{-13}$	$6.3 \times 10^{-10}$	$\leq 10^{-4}$	
Bi <sup>+</sup> + NO → NR	$\leq 1 \times 10^{-13}$	$6.3 \times 10^{-10}$	$\leq 10^{-4}$	

<sup>a</sup> Product distributions are given in parentheses. The branching fractions are estimated to be accurate to  $\pm 20\%$ . <sup>b</sup> Effective bimolecular rate coefficient first order in NO. The estimated uncertainty is  $\pm 30\%$ . <sup>c</sup> Collision rate coefficient calculated using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich.<sup>26</sup>

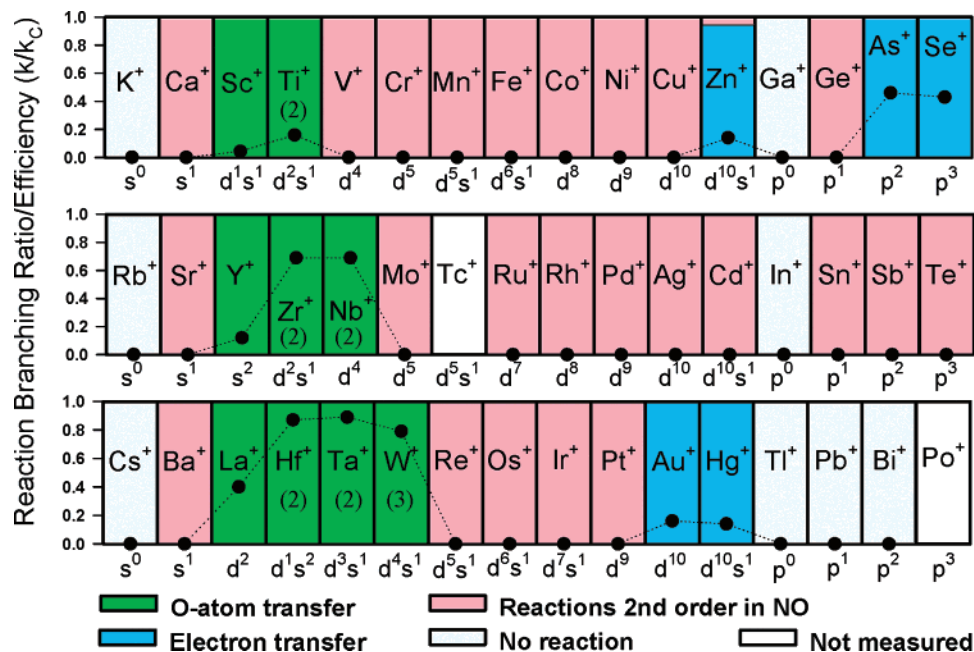
molecule is expected to be a better third body than the He atom in stabilizing the intermediate ( $X^+, \text{NO}$ )<sup>\*</sup>.

The kinetic results of our experiments are summarized in Tables 1–3 according to row in the periodic table. The tabulated effective bimolecular rate coefficients,  $k$ , apply either to exothermic bimolecular reactions of type (2a) or (2b) that are first order in NO or to exothermic termolecular reactions of type (3), (4), or (5) that are second order in NO. Ions produced by further reactions with NO are included in the listing of higher order product ions, i.e., the right-hand column, in Tables 1–3. Also included are calculated reaction efficiencies expressed as  $k/k_c$ . The collision rate coefficients,  $k_c$ , are calculated using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich<sup>26a</sup> with  $\alpha\text{-(NO)} = 1.70 \times 10^{-24} \text{ cm}^3$  and  $\mu_D = 0.161 \text{ D}$ .<sup>26b</sup>

**Bimolecular Transfer Reactions.** The kinetic results for the observed bimolecular electron transfer and O-atom transfer reactions are displayed on a periodic table in Figure 1.

**Bimolecular Electron Transfer.** Bimolecular electron transfer, reaction 2a, is exothermic and was observed for those three transition-metal ions (Zn<sup>+</sup>, Au<sup>+</sup>, Hg<sup>+</sup>) and two main-group ions (As<sup>+</sup>, Se<sup>+</sup>) with  $\text{IE}(X) \geq \text{IE}(\text{NO}) = 9.26436 \pm 0.00006 \text{ eV}^{11}$  (see Table 4). Figure 2 shows results obtained with Zn<sup>+</sup>. The electron transfer between Au<sup>+</sup> (with  $\text{IE} = 9.225 \text{ eV}^{11}$ ) and NO is essentially thermoneutral ( $\Delta\text{IE} = 0.03 \text{ eV}$ ). Figure 3 shows how the efficiency for electron transfer varies with  $\text{IE}(M^+)$ . For the most part, these electron transfer reactions are fairly rapid when exothermic with  $k = 0.97, 3.2, 3.0,$  and  $1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  but do not have unit efficiency with  $k/k_c = 0.14, 0.46, 0.43,$  and  $0.19$  for Zn<sup>+</sup>, As<sup>+</sup>, Se<sup>+</sup>, and Hg<sup>+</sup>,





**Figure 1.** Periodic variations observed in the efficiencies,  $k/k_c$  (represented as solid circles), for reactions of nitric oxide with transition-metal ions and main-group cations.  $k$  represents the measured reaction rate coefficient, and  $k_c$  is the calculated collision rate coefficient (see Tables 1–3). Also indicated are the observed reaction channels and the ground-state electronic configurations of the atomic cations. The reactions of  $Tc^+$  and  $Po^+$  were not investigated. The numbers in parentheses indicate the number of observed sequential O-atom transfer reactions.

**TABLE 4: O-Atom Affinities,  $D_0(M^+ - O)$  in kcal mol $^{-1}$ , and Ionization Energies,  $IE(M)$  in eV, for the Transition-Metal Ions Taken, with Few Exceptions, from the Review by Schröder et al.<sup>28</sup>**

first row			second row			third row		
$M^+$	OA( $M^+$ )	IE( $M$ )	$M^+$	OA( $M^+$ )	IE( $M$ )	$M^+$	OA( $M^+$ )	IE( $M$ )
$K^+$	3	4.34	$Rb^+$	7	4.18	$Cs^+$	14	3.89
$Ca^+$	77.2	6.11	$Sr^+$	71.4	5.70	$Ba^+$	92.8	5.21
$Sc^+$	$164.6 \pm 1.4^a$	6.56	$Y^+$	$167.0 \pm 4.2^b$	6.22	$La^+$	$206 \pm 4^d$	5.58
$Ti^+$	$158.6 \pm 1.6^a$	6.83	$Zr^+$	$178.9 \pm 2.5^b$	6.63	$Hf^+$	$173 \pm 5^e$	6.83
$V^+$	$134.9 \pm 3.5^a$	6.75	$Nb^+$	$164.4 \pm 2.5^b$	6.76	$Ta^+$	$188 \pm 15^e$	7.55
$Cr^+$	$85.8 \pm 2.8^a$	6.77	$Mo^+$	$116.7 \pm 0.5^b$	7.09	$W^+$	$166 \pm 10^f$	7.86
$Mn^+$	$68.0 \pm 3.0^a$	7.43				$Re^+$	$115 \pm 15^g$	7.83
$Fe^+$	$80.0 \pm 1.4^a$	7.90	$Ru^+$	$87.9 \pm 1.2^c$	7.36	$Os^+$	$100 \pm 12^h$	8.44
$Co^+$	$74.9 \pm 1.2^a$	7.88	$Rh^+$	$69.6 \pm 1.4^c$	7.46	$Ir^+$	$59^e$	8.97
$Ni^+$	$63.2 \pm 1.2^a$	7.64	$Pd^+$	$33.7 \pm 2.5^c$	8.34	$Pt^+$	$77,^i 75 \pm 2^j$	8.96
$Cu^+$	$37.4 \pm 3.5^a$	7.72	$Ag^+$	$28.4 \pm 1.2^c$	7.58	$Au^+$		9.23
$Zn^+$	$38.5 \pm 1.2^a$	9.39				$Hg^+$		10.44
$Ga^+$	5.6	6.00	$In^+$		5.79	$Tl^+$		6.11
$Ge^+$	81.8	7.90	$Sn^+$	75.1	7.34	$Pb^+$	53.2	7.42
$As^+$	$147 \pm 2^k$	9.81	$Sb^+$		8.64	$Bi^+$	41.6	7.29
$Se^+$	$92^k$	9.75	$Te^+$	96.6	9.01			

<sup>a</sup> Reference 29. <sup>b</sup> Reference 30. <sup>c</sup> Reference 31. <sup>d</sup> Reference 32. <sup>e</sup> Reference 11. <sup>f</sup> Reference 33. <sup>g</sup> Reference 34. <sup>h</sup> Reference 35. <sup>i</sup> Reference 36. <sup>j</sup> Reference 37. <sup>k</sup> Reference 38.

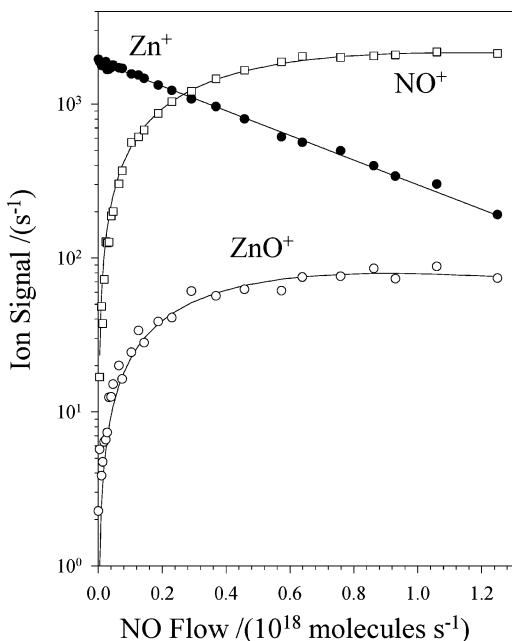
respectively. We have reported separately the extent to which energy resonance and Franck–Condon factors may be responsible for determining the magnitudes of these electron transfer efficiencies.<sup>27</sup>

**Bimolecular O-Atom Transfer.** Figure 4 provides measured profiles for the O-atom transfer reactions of  $Ti^+$ ,  $Zr^+$ ,  $Nb^+$ , and  $Ta^+$  with NO and Figure 3 shows how the efficiency for O-atom transfer varies with OA ( $X^+$ ). The bimolecular O-atom transfer channel (1b) is exothermic and was observed for those nine transition-metal ions ( $Sc^+$ ,  $Ti^+$ ,  $Y^+$ ,  $Zr^+$ ,  $Nb^+$ ,  $La^+$ ,  $Hf^+$ ,  $Ta^+$ ,  $W^+$ ) for which  $OA(X^+) > OA(N) = 150.9 \pm 0.2$  kcal mol $^{-1}$ ,<sup>11</sup> (see Table 4). Our results for  $Ti^+$  and  $Zr^+$  with  $k = (1.2 \pm 0.4) \times 10^{-10}$  and  $(4.7 \pm 1.4) \times 10^{-10}$  cm $^3$  molecule $^{-1}$  s $^{-1}$ , respectively, are in good agreement with the previously reported room-temperature values of  $(9.5 \pm 2) \times 10^{-11}$  and  $(4.8 \pm 0.6) \times 10^{-10}$  cm $^3$  molecule $^{-1}$  s $^{-1}$  obtained using a selected-ion drift apparatus coupled to a hot-filament and ion-discharge source,

respectively.<sup>15,16</sup> There is also agreement with the early qualitative ICR results that indicated oxidation with  $Ti^+$ ,  $Zr^+$ , and  $Nb^+$  but not with  $V^+$ .<sup>17</sup>

**Termolecular Reactions.** Of the 46 atomic ions investigated, 14 react with NO in an exothermic bimolecular fashion: 5 by direct electron transfer, reaction 2a, and 9 by O-atom transfer, reaction 2b. Of the remaining 32 atomic ions, all but 8 appeared to react in termolecular reactions of type (3a), (3b), or (5) that are second order in NO. The remaining 8 are totally unreactive ( $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Ga^+$ ,  $In^+$ ,  $Tl^+$ ,  $Pb^+$  and  $Bi^+$ ).

**Termolecular  $XO^+$  Formation.** Reaction 4 is exothermic when  $OA(X^+) > OA(N) - D(N-NO) = 36$  kcal mol $^{-1}$ , and this is the case for almost all of the atomic ions investigated except for  $X^+ = K^+$ ,  $Rb^+$ ,  $Pd^+$ ,  $Cs^+$ ,  $Ag^+$ , and  $Ga^+$  (see Table 4) and probably also  $Cd^+$ ,  $In^+$ , and  $Tl^+$ , whose O-atom affinities, although not known, are likely to be lower than 36 kcal mol $^{-1}$  based on the low values for  $OA(Zn^+)$  and  $OA(Ga^+)$ . Figure 5



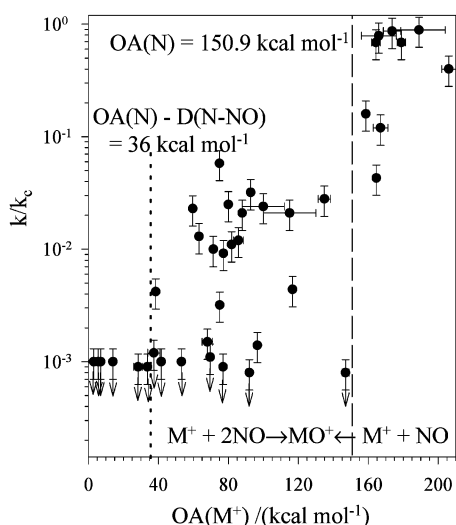
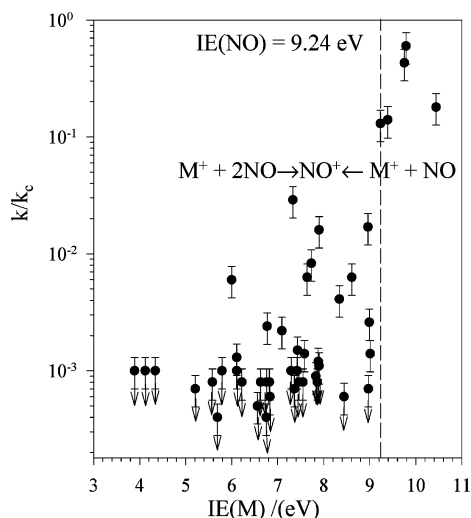
**Figure 2.** ICP/SIFT results for the reaction of  $\text{Zn}^+$  with nitric oxide in helium buffer gas at  $0.35 \pm 0.01$  Torr and  $295 \pm 2$  K.

provides measured profiles for the reactions of  $\text{V}^+$ ,  $\text{Fe}^+$ ,  $\text{Ru}^+$ , and  $\text{Os}^+$  that exhibit  $\text{XO}^+$  formation that is expected to be second order in NO.

All of the first-row cations for which direct O-atom transfer is endothermic exhibit  $\text{XO}^+$  formation except for  $\text{K}^+$  ( $s^0$ ) and  $\text{Ga}^+$  ( $p^0$ ) that do not react at all and  $\text{Cu}^+$  ( $d^{10}$ ) that forms mainly  $\text{NO}^+$  (0.9) and some  $\text{CuNO}^+$  (0.1).

All of the second-row cations for which direct O-atom transfer is endothermic exhibit  $\text{XO}^+$  formation except for  $\text{Rb}^+$  ( $s^0$ ) that does not react at all,  $\text{Rh}^+$  ( $d^8$ ) and  $\text{Pb}^+$  ( $d^9$ ) that form  $\text{NO}^+$  and  $\text{X}^+$  (NO),  $\text{Ag}^+$  ( $d^{10}$ ) and  $\text{Cd}^+$  ( $d^{10}s^1$ ) that slowly form  $\text{NO}^+$ , and  $\text{In}^+$  ( $p^0$ ) that is unreactive.

Only four third-row cations ( $\text{Ba}^+$ ,  $\text{Re}^+$ ,  $\text{Os}^+$ ,  $\text{Ir}^+$ ) for which direct O-atom transfer is endothermic exhibit  $\text{XO}^+$  formation. The others exhibit direct exothermic O-atom transfer ( $\text{La}^+$ ,  $\text{Hf}^+$ ,  $\text{Ta}^+$ ,  $\text{W}^+$ ), exothermic electron transfer ( $\text{Au}^+$ ,  $\text{Hg}^+$ ), or no reaction ( $\text{Cs}^+$  ( $s^0$ ),  $\text{Tl}^+$  ( $p^0$ ),  $\text{Pb}^+$  ( $p^1$ ),  $\text{Bi}^+$  ( $p^2$ )).  $\text{Pt}^+$  ( $d^9$ ) is the



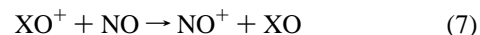
**Figure 3.** Semilogarithmic dependence of the efficiency,  $k/k_c$ , for  $\text{NO}^+$  formation on the ionization energy,  $\text{IE}(\text{M})$ , and  $\text{MO}^+$  formation on the O-atom affinity,  $\text{OA}(\text{M}^+)$ , in reactions of atomic cations with nitric oxide.  $k$  represents the measured first-order or pseudo-first-order reaction rate coefficient, and  $k_c$  is the calculated collision rate coefficient (see Table 1). Bimolecular electron transfer and O-atom transfer reactions are exothermic on the right of the dashed lines and endothermic on the left. Termolecular  $\text{MO}^+$  formation is exothermic to the right of the dotted line.

only third-row cation that exhibits  $\text{NO}^+$  formation even though direct electron transfer is endothermic.

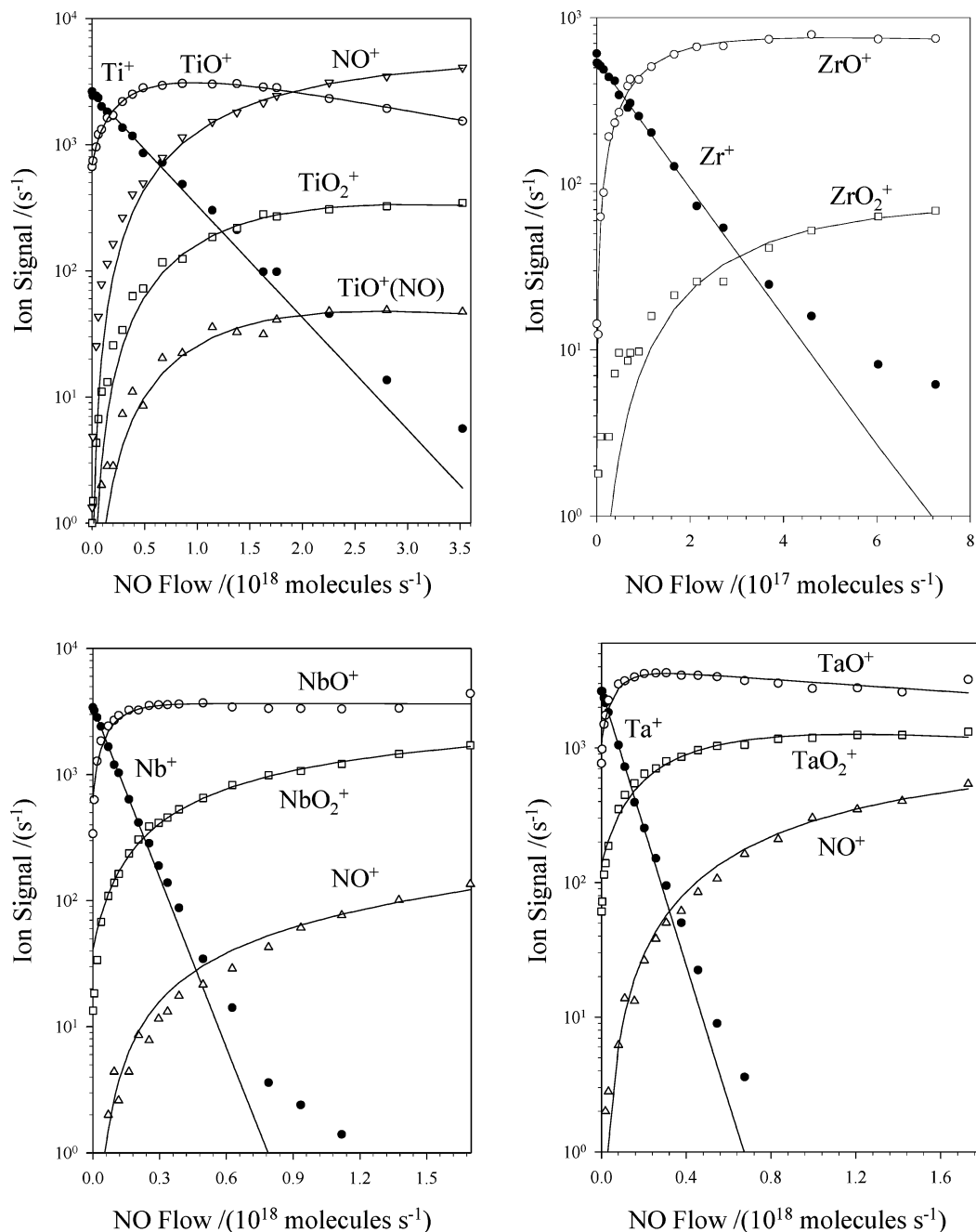
Exclusive  $\text{XO}^+$  formation was observed with the group 2 ( $s^1$ ) cations  $\text{Ca}^+$ ,  $\text{Sr}^+$ , and  $\text{Ba}^+$ , with the group 8 cations  $\text{Fe}^+$  ( $d^6s^1$ ),  $\text{Ru}^+$  ( $d^7$ ), and  $\text{Os}^+$  ( $d^6s^1$ ), with the group 7 cation  $\text{Re}^+$  ( $d^5s^1$ ), and with the group 9 cation  $\text{Co}^+$  ( $d^8$ ).

**Termolecular  $\text{NO}^+$  Formation.** Reaction 3 is exothermic when  $\text{IE}(\text{X}) > \text{IE}(\text{NO}) - D(\text{X}-\text{NO})$  or  $9.264 \text{ eV} - D_{298}(\text{X}-\text{NO})$ . The bond energies  $D_{298}(\text{X}-\text{NO})$  are generally unknown, but density-functional calculations of mononitrosyls of first-row transition-metal atoms have provided binding energies,  $D_e(\text{X}-\text{NO})$ , that decrease from Sc at 2.5 eV to Ni and Cu at about 1.3 eV, remaining almost constant at almost 2.2 eV between Ti and Fe and has a value of 2.0 eV for Co.<sup>39</sup> These values would make  $\text{NO}^+$  formation by reaction 3a exothermic for  $\text{X}^+ = \text{Mn}^+$ ,  $\text{Fe}^+$ , and  $\text{Co}^+$  and endothermic by at least 0.2 eV for  $\text{Sc}^+$  and at least 0.3 eV for  $\text{X}^+ = \text{V}^+$ ,  $\text{Cr}^+$ ,  $\text{Ni}^+$ , and  $\text{Cu}^+$  because  $D_e > D_{298}$ . The value of  $D_0(\text{Ga}-\text{NO}) = 1.6 \text{ eV}$  computed at the B3LYP/6-311+G(d) level<sup>40</sup> makes reaction 3a with  $\text{Ga}^+$  endothermic by 1.7 eV. Figure 6 provides measured profiles for the reactions of  $\text{Cu}^+$ ,  $\text{Pd}^+$ ,  $\text{Sn}^+$ , and  $\text{Pt}^+$  that exhibit  $\text{NO}^+$  formation that is expected to be second order in NO.

Five of the first-row atomic cations ( $\text{Cr}^+$ ,  $\text{Mn}^+$ ,  $\text{Ni}^+$ ,  $\text{Cu}^+$ ,  $\text{Ge}^+$ ) appear to exhibit primary  $\text{NO}^+$  formation second order in NO. However,  $\text{NO}^+$  formation always occurs in competition with another channel (see Table 1): formation of  $\text{XO}^+ + \text{N}_2\text{O}$  (reaction b in the case of  $\text{Cr}^+$ ,  $\text{Mn}^+$ ,  $\text{Ni}^+$ , and  $\text{Ge}^+$  and formation of  $\text{X}^+(\text{NO}) + \text{NO}$  (reaction c) in the case of  $\text{Cu}^+$ . The computed metal-nitrosyl binding energies predict exothermicity only for the reaction with  $\text{Mn}^+$ .  $\text{NO}^+$  also was observed in the chemistry initiated by  $\text{V}^+$ ,  $\text{Fe}^+$  (see Figure 5), and  $\text{Co}^+$ , but product-ion ratio analyses indicate secondary formation of  $\text{NO}^+$  either by reaction 6, also second order in NO, or by reaction 7, electron transfer from NO to the primary  $\text{XO}^+$  product (which may be formed with some internal energy).

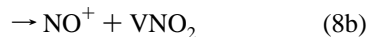
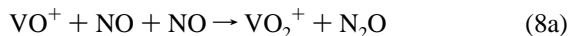


In the case of  $\text{V}^+$  for example (see Figure 7), the product-ion ratio analysis indicates the occurrence of reaction 8 in the



**Figure 4.** Composite of ICP/SIFT results for bimolecular O-atom transfer reactions (first order in NO) of nitric oxide with atomic cations in helium buffer gas at  $0.35 \pm 0.01$  Torr and  $295 \pm 2$  K.

ratio (8a)/(8b)/(8c) = 0.7/0.3/0.1. Further production of  $\text{NO}^+$  occurs by the reaction of  $\text{VO}_2^+$  with NO. There has been one



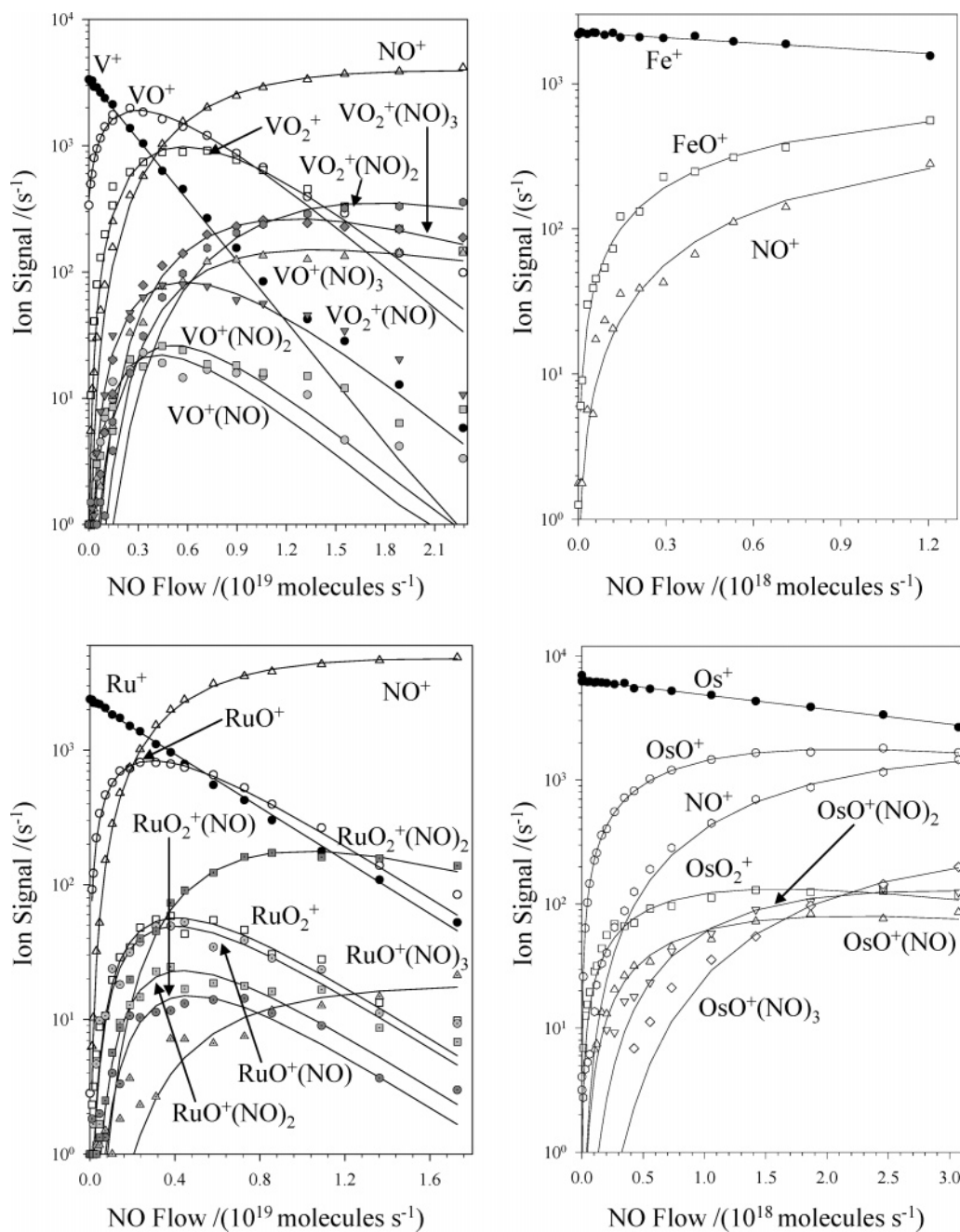
previous report of rapid  $\text{NO}^+$  formation with  $\text{Fe}^+$  (close to the collision rate), but this was attributed to the reaction of excited states of  $(\text{Fe}^+)^*$  that lie at least 1.31 eV above the  $^6\text{D}$  ground state.<sup>41</sup> The ground state was reported to be unreactive with NO. This latter result is perhaps not surprising because these experiments were performed with FT-ICR mass spectrometry at lower concentrations of NO.

Six of the second-row atomic cations ( $\text{Mo}^+$ ,  $\text{Rh}^+$ ,  $\text{Pd}^+$ ,  $\text{Sn}^+$ ,  $\text{Sb}^+$ ,  $\text{Te}^+$ ) appear to exhibit primary  $\text{NO}^+$  formation second

order in NO. In all cases, however, it occurs again in competition with other channels (see Table 2). The  $\text{NO}^+$  observed in the chemistry initiated by  $\text{Nb}^+$  and  $\text{Ru}^+$  is attributed to further reactions of the oxide cations.

Only one of the third-row atomic cations ( $\text{Pt}^+$ ) appears to exhibit primary  $\text{NO}^+$  formation second order in NO, in this case in competition with formation of  $\text{PtNO}^+ + \text{NO}$ . The  $\text{NO}^+$  observed in the chemistry initiated by  $\text{Ba}^+$ ,  $\text{Hf}^+$ ,  $\text{Ta}^+$ ,  $\text{W}^+$ ,  $\text{Re}^+$ ,  $\text{Os}^+$ , and  $\text{Ir}^+$  is attributed to further reactions of the oxide cations.

**Termolecular  $\text{X}^+(\text{NO})$  Formation.** Reaction 5 is exothermic for the  $\text{X}^+$  ions investigated here, all of which are expected to have a positive affinity for NO, but must compete with (3) and (4). Molecular NO is expected to be more effective than a He atom in the collisional deactivation of  $(\text{X}^+, \text{NO})^*$  formed in reaction 5. However, the collisional deactivation of  $(\text{X}^+, \text{NO})^*$  by NO must compete with the reaction which leads to  $\text{NO}^+$



**Figure 5.** Composite of ICP/SIFT results for termolecular formation of  $XO^+$  (second order in NO) and NO ligation in reactions of nitric oxide with atomic cations in helium buffer gas at  $0.35 \pm 0.01$  Torr and  $295 \pm 2$  K.

and  $(X,NO)$ , especially if the latter is more exothermic, viz. if  $IE(X,NO) > IE(NO)$ .

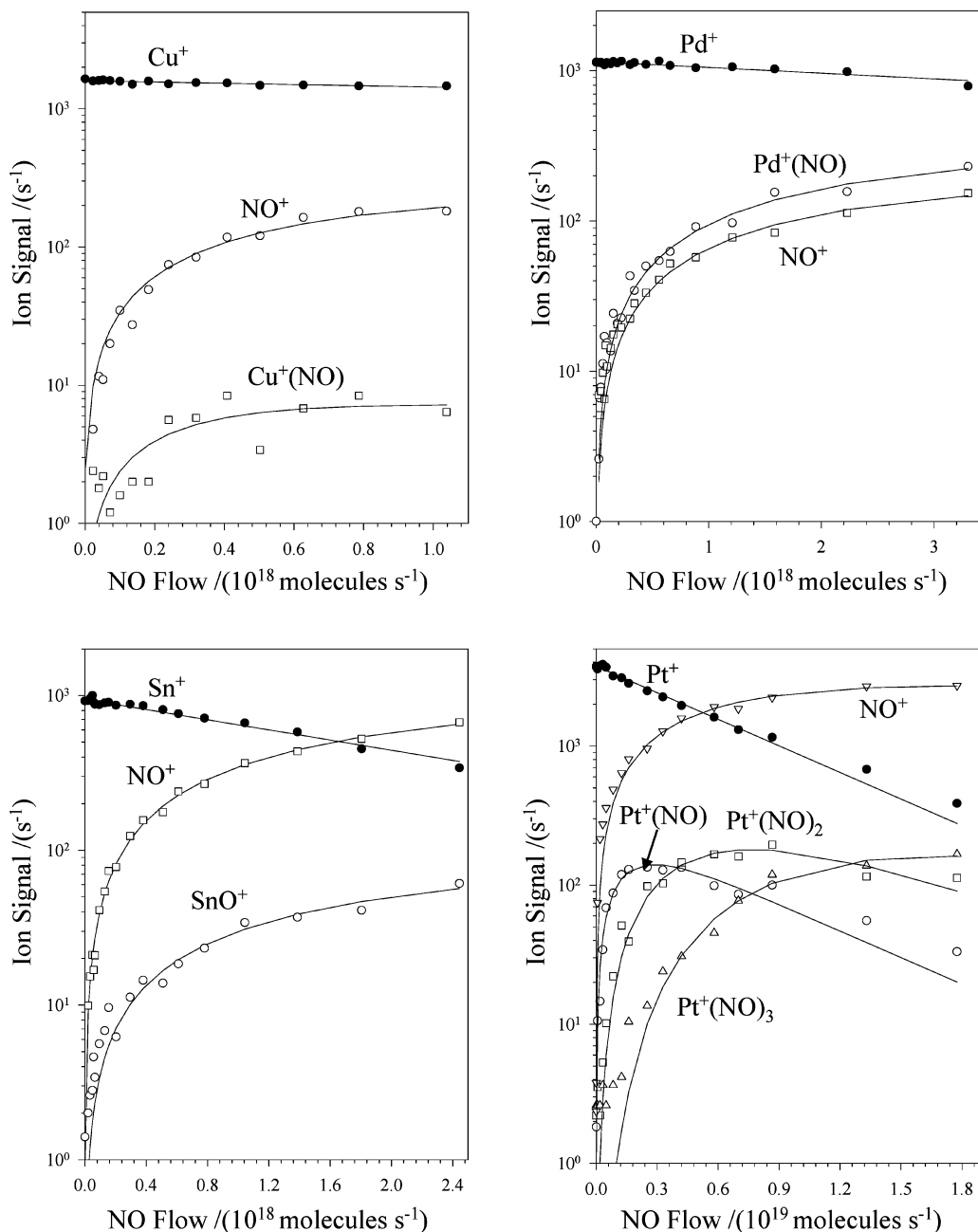
An inspection of the observed product ions indicates that formation of  $X^+(NO)$  is much less common than formation of  $(X,NO)$ . Thus minor channels leading to  $X^+(NO)$  formation were recorded for  $X = Ni$  and  $Cu$  (first row),  $X = Mo, Rh$ , and  $Pd$  (second row), and  $X = Ir$  and  $Pt$  (third row). In all these cases except  $Ir$ ,  $(X,NO) + NO^+$  formation was predominant or at least equal to  $X^+(NO)$  formation.  $IrO^+$  formation was predominant with  $Ir$ . Furthermore,  $XNO$  formation was observed with  $X = Cr$  and  $Mn$  (first row) and with  $X = Ag, Cd, Sn, Sb$ , and  $Te$  (second row). No  $(X,NO)$  formation was apparent with the third-row atomic cations.

As far as we are aware, most of these  $X^+(NO)$  cations have not been seen before. Mass spectrometric evidence for  $CuNO^+$  was first reported in 1991.<sup>42</sup> It was formed by electron impact ionization (70 eV) of anhydrous copper nitrate. More recent

experiments have demonstrated the formation of  $CuNO^+$  by the association reaction of NO to  $Cu^+$  produced by  $Ar^+$ -sputtering from a copper cathode.<sup>43</sup> Also, a bond strength of  $D_0(Cu^+ - NO) = 1.13 \pm 0.08$  eV was determined by means of guided ion beam mass spectrometry and the  $CuNO^+$  isomer was shown with calculations to be 0.4 eV more stable than the  $CuON^+$  isomer.<sup>43</sup>  $NiNO^+$  also has been observed previously and was produced by ligating  $Ni^+$  with NO in a dc discharge source.<sup>44</sup>  $CuNO^+$  and  $ZnNO^+$  have been produced previously from reactions of  $NO_2$  with  $Cu^+$  and  $Zn^+$  respectively, in a guided ion-beam mass spectrometer.<sup>45</sup>

**Overview of Second-Order NO Chemistry.** The identification of the ion chemistry that is second order in NO is an important new result that has implications for NO chemistry generally in any environment that is rich in NO. The second-order reactions with many of the ground-state atomic cations that are investigated here clearly are thermodynamically favored





**Figure 6.** Composite of ICP/SIFT results for termolecular formation of  $\text{NO}^+$  (second order in  $\text{NO}$ ) and  $\text{NO}$  ligation in reactions of nitric oxide with atomic cations in helium buffer gas at  $0.35 \pm 0.01$  Torr and  $295 \pm 2$  K.

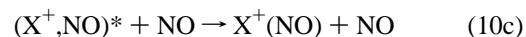
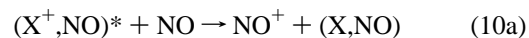
to produce  $\text{MO}^+$  and, but less so,  $\text{NO}^+$  ions that are not accessible to first-order  $\text{NO}$  chemistry. Unfortunately, the observed first- and second-order kinetics could not be distinguished on the basis of the observed shape of the  $\text{M}^+$  decay. There is a general difference in the apparent reaction rate: the reactions first order in  $\text{NO}$  have efficiencies generally  $>0.1$ , whereas the reactions second order in  $\text{NO}$  have apparent efficiencies generally  $<0.06$ .

The low apparent rate coefficients and efficiencies of the reactions second order in  $\text{NO}$ , reactions 3–5, can be understood in terms of a two-step mechanism involving the formation of a temporary adduct ion  $(\text{X}^+, \text{NO})^*$ , reaction 9, as a first step.



At high flows of  $\text{NO}$  this intermediate is more likely to encounter another  $\text{NO}$  molecule and this can result in formation

of  $\text{NO}^+$ ,  $\text{XO}^+$  and  $\text{XNO}^+$  via reactions 10a–10c. Also, a



fraction of the intermediate may be dissociated according to reaction 10d.

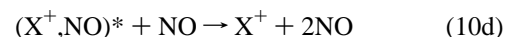
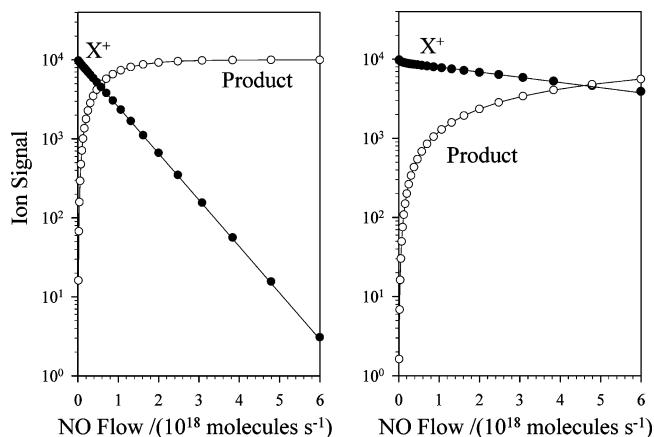


Figure 7 shows kinetic simulations using this mechanism for two cases with small apparent rate coefficients of  $7.7 \times 10^{-11}$  and  $8.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , both of which lead to linearity in the semilogarithmic decay of  $\text{X}^+$ . These results illustrate a possible origin of linearity in the primary ion decay



**Figure 7.** Simulated profiles for the second-order reaction of  $X^+$  and NO. LHS:  $k_0 = 7.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{-9} = 50 \text{ s}^{-1}$ ,  $k_{10a,b,c} = 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{10d} = 6.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and an apparent bimolecular rate coefficient of  $7.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . RHS:  $k_0 = 7.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{-9} = 50 \text{ s}^{-1}$ ,  $k_{10a,b,c} = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{10d} = 6.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and an apparent bimolecular rate coefficient of  $8.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

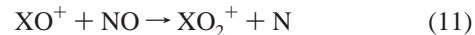
for a reaction second order in NO and so the difficulty in distinguishing second from first order (in NO) kinetics from the shape of the measured primary ion decay. The low apparent rate coefficients can be attributed mainly to rapid dissociation of the temporary adduct ion  $(X^+, \text{NO})^*$  by NO, reaction 7d.

The kinetic results for the second-order chemistry with NO are displayed on the periodic table shown in Figure 8. Both the variations in reaction efficiency and the variations in product distributions exhibit some periodic behavior. When exothermic,  $XO^+$  formation is favored for atomic ions with  $s^1$  and  $d^n s^1$  configurations, although it competes with second-order  $\text{NO}^+$  formation in the case of  $\text{Mn}^+$  and first-order electron transfer in the case of  $\text{Zn}^+$ .

**Higher Order Multiple Oxide Formation and NO Ligation.** Tables 1–3 list the higher order product ions that were observed and Table 5 indicates the reactions that are proposed

to lead to these ions, together with rate coefficients for those reactions for which they were accessible. Dioxide and, in the case of W and Re, multiple oxide formation as well as NO ligation were the main higher order reactions that were observed.

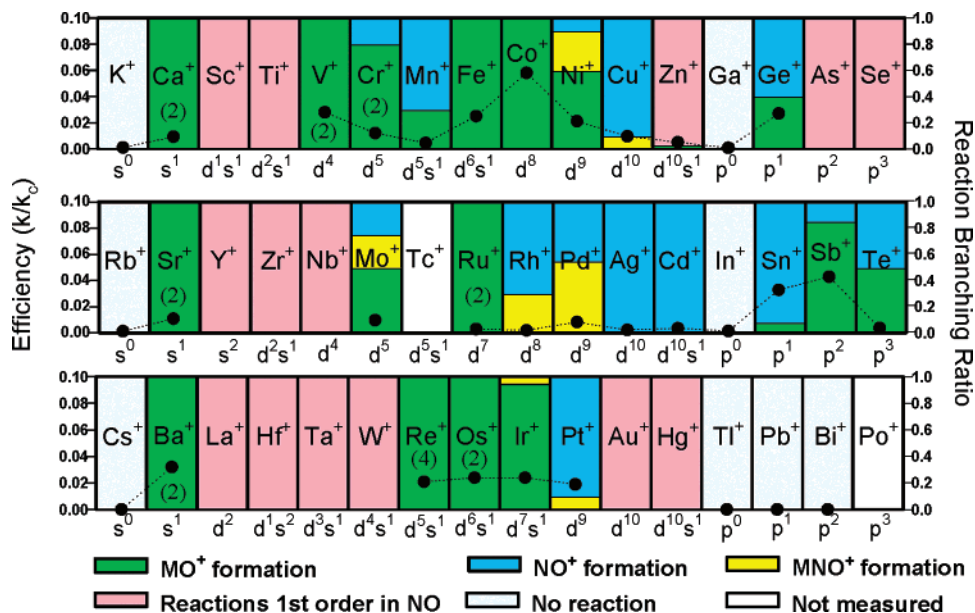
Dioxide cation formation can proceed either by bimolecular O-atom transfer to the monoxide cation, reaction 11, which is first order in NO, or by the termolecular reaction 10 that is second order in NO. For reaction 11 to be exothermic with



thermalized  $\text{XO}^+$  ions,  $\text{OA}(\text{XO}^+)$  must exceed  $\text{OA}(\text{N}) = 150.9 \pm 0.2 \text{ kcal mol}^{-1}$ .<sup>11</sup> Reaction 12 is  $115 \text{ kcal mol}^{-1}$  more exothermic than reaction 11 because it leads to the formation of the N–NO bond and so is thermodynamically more favorable.

None of the known O-atom affinities of  $\text{XO}^+$  exceed  $151 \text{ kcal mol}^{-1}$ .<sup>27</sup> The reported values for the O-atom affinities (in  $\text{kcal mol}^{-1}$ ) of the first-row oxide cations are  $\text{ScO}^+$  (40),  $\text{TiO}^+$  (81),  $\text{VO}^+$  (90),  $\text{CrO}^+$  (66),  $\text{FeO}^+$  (66), and  $\text{CuO}^+$  (99). Those for the second-row oxide cations are  $\text{YO}^+$  (41),  $\text{ZrO}^+$  (89),  $\text{NbO}^+$  (132),  $\text{MoO}^+$  (128),  $\text{RuO}^+$  (79), and  $\text{RhO}^+$  (78) whereas those for the third-row oxide cations are  $\text{LaO}^+$  (23),  $\text{TaO}^+$  (140),  $\text{WO}^+$  (132),  $\text{ReO}^+$  (65),  $\text{OsO}^+$  (105),  $\text{IrO}^+$  (125), and  $\text{PtO}^+$  (75). The least endothermic O-atom transfer reaction of any of these oxide cations is that with  $\text{TaO}^+$  which still is endothermic by  $11 \text{ kcal mol}^{-1}$ . In our measurements we have observed dioxide cation formation with  $\text{CaO}^+$ ,  $\text{TiO}^+$ ,  $\text{VO}^+$ , and  $\text{CrO}^+$ , with  $\text{SrO}^+$ ,  $\text{ZrO}^+$ ,  $\text{NbO}^+$ , and  $\text{RuO}^+$ , and with  $\text{BaO}^+$ ,  $\text{HfO}^+$ ,  $\text{TaO}^+$ ,  $\text{WO}^+$ ,  $\text{ReO}^+$ , and  $\text{OsO}^+$ . Of these, dioxide formation from monoxide cations reacting with NO have been reported only for  $\text{TiO}^+$  and  $\text{ZrO}^+$ .<sup>15,16</sup>

We propose that the plethora of dioxide formation observed in our experiments (see Tables 1–3) is predominantly due to the termolecular reaction 12, which is second order in NO. In the unlikely event that some of the exothermicity of the reactions (either first or second order in NO) leading to  $\text{XO}^+$  formation is retained before collision with another NO molecule, we cannot



**Figure 8.** Periodic variations observed in the efficiencies,  $k/k_c$  (represented as solid circles), for second-order reactions of nitric oxide with transition-metal ions and main-group cations.  $k$  represents the measured effective bimolecular reaction rate coefficient and  $k_c$  is the calculated collision rate coefficient (see Tables 1–3). Also indicated are the observed reaction channels and the ground-state electronic configurations of the atomic cations. The reactions of  $\text{Tc}^+$  and  $\text{Po}^+$  were not investigated. The numbers in parentheses indicate the number of observed sequential  $\text{MO}^+$  formation reactions.

**TABLE 5: Rate Coefficients ( $k$ ,  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and Product Distributions Measured for Reactions between Oxide Cations and Nitric Oxide in Helium at  $0.35 \pm 0.01$  Torr and  $295 \pm 2$  K**

reaction	product distribution <sup>a</sup>	$k^b$
$\text{CaO}^+ + 2 \text{NO} \rightarrow \text{CaO}_2^+ + \text{N}_2\text{O}$	0.5	$3.5 \times 10^{-12}$
$\rightarrow \text{CaO}^+(\text{NO}) + \text{NO}$	0.5	
$\text{ScO}^+ + \text{NO} \rightarrow \text{ScO}^+(\text{NO})$	1	$\leq 7 \times 10^{-12}$
$\text{TiO}^+ + 2 \text{NO} \rightarrow \text{NO}^+ + \text{TiONO}$	0.83	$2.0 \times 10^{-11}$
$\rightarrow \text{TiO}_2^+ + \text{N}_2\text{O}$	0.13	
$\rightarrow \text{TiO}^+(\text{NO}) + \text{NO}$	0.02	
$\text{VO}^+ + 2 \text{NO} \rightarrow \text{VO}_2^+ + \text{N}_2\text{O}$	0.67	$1.5 \times 10^{-11}$
$\rightarrow \text{NO}^+ + \text{VNO}$	0.27	
$\rightarrow \text{VO}^+(\text{NO}) + \text{NO}$	0.06	
$\text{VO}^+(\text{NO}) + \text{NO} \rightarrow \text{VO}^+(\text{NO})_2$	1	observed
$\text{VO}^+(\text{NO})_2 + \text{NO} \rightarrow \text{VO}^+(\text{NO})_3$	1	observed
$\text{VO}_2^+ + \text{NO} \rightarrow \text{VO}_2^+(\text{NO})$	1	observed
$\text{VO}_2^+(\text{NO}) + \text{NO} \rightarrow \text{VO}_2^+(\text{NO})_2$	1	observed
$\text{VO}_2^+(\text{NO})_2 + \text{NO} \rightarrow \text{VO}_2^+(\text{NO})_3$	1	observed
$\text{CrO}^+ + 2 \text{NO} \rightarrow \text{CrO}_2^+ + \text{N}_2\text{O}$	1	$\leq 1.8 \times 10^{-11}$
$\text{FeO}^+ + 2 \text{NO} \rightarrow \text{NO}^+ + \text{FeONO}$	1	$\leq 3.4 \times 10^{-11}$
$\text{CoO}^+ + 2 \text{NO} \rightarrow \text{NO}^+ + \text{CoONO}$	1	$\leq 3.5 \times 10^{-11}$
$\text{SrO}^+ + 2 \text{NO} \rightarrow \text{SrO}_2^+ + \text{N}_2\text{O}$	0.80	$\leq 6.4 \times 10^{-12}$
$\rightarrow \text{SrO}^+(\text{NO}) + \text{NO}$	0.20	
$\text{SrO}_2^+ + \text{NO} \rightarrow \text{SrO}_2^+(\text{NO})$	1	$\leq 1.0 \times 10^{-11}$
$\text{SrO}_2^+ + \text{NO} \rightarrow \text{SrO}_2^+(\text{NO})_2$	1	observed
$\text{ZrO}^+ + 2 \text{NO} \rightarrow \text{ZrO}_2^+ + \text{N}_2\text{O}$	1	$\leq 6.2 \times 10^{-12}$
$\text{NbO}^+ + 2 \text{NO} \rightarrow \text{NbO}_2^+ + \text{N}_2\text{O}$	1	$\leq 4.4 \times 10^{-11}$
$\text{NbO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{NbO}_2$	1	observed
$\text{RuO}^+ + 2 \text{NO} \rightarrow \text{NO}^+ + \text{RuONO}$	0.6	$2.8 \times 10^{-11}$
$\rightarrow \text{RuO}_2^+ + \text{N}_2\text{O}$	0.2	
$\rightarrow \text{RuO}^+(\text{NO}) + \text{NO}$	0.2	
$\text{RuO}^+(\text{NO}) + \text{NO} \rightarrow \text{RuO}^+(\text{NO})_2$	1	$\leq 6.5 \times 10^{-11}$
$\text{RuO}^+(\text{NO})_2 + \text{NO} \rightarrow \text{RuO}^+(\text{NO})_3$	1	$\leq 1.1 \times 10^{-10}$
$\text{RuO}_2^+ + \text{NO} \rightarrow \text{RuO}_2^+(\text{NO})$	1	$\leq 6.8 \times 10^{-11}$
$\text{RuO}_2^+(\text{NO}) + \text{NO} \rightarrow \text{RuO}_2^+(\text{NO})_2$	1	$\leq 1.8 \times 10^{-10}$
$\text{Rh}^+(\text{NO}) + \text{NO} \rightarrow \text{Rh}^+(\text{NO})_2$	1	observed
$\text{TeO}^+ + \text{NO} + \text{NO} \rightarrow \text{NO}^+ + \text{TeONO}$	1	observed
$\text{BaO}^+ + \text{NO} + \text{NO} \rightarrow \text{BaO}_2^+ + \text{N}_2\text{O}$	1	$\leq 1.4 \times 10^{-11}$
$\text{BaO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{BaO}_2$	1	observed
$\text{HfO}^+ + 2 \text{NO} \rightarrow \text{HfO}_2^+ + \text{N}_2\text{O}$	0.85	$\leq 1.8 \times 10^{-11}$
$\rightarrow \text{NO}^+ + \text{HfONO}$	0.15	
$\text{HfO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{HfO}_2^+$	1	$\leq 4.6 \times 10^{-11}$
$\text{TaO}^+ + 2 \text{NO} \rightarrow \text{TaO}_2^+ + \text{N}_2\text{O}$	1	$\leq 1.5 \times 10^{-11}$
$\text{TaO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{TaO}_2$	1	$\leq 1.2 \times 10^{-10}$
$\text{WO}^+ + 2 \text{NO} \rightarrow \text{WO}_2^+ + \text{N}_2\text{O}$	1	$\leq 1.2 \times 10^{-11}$
$\text{WO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{WO}_2$	0.9	$\leq 4.0 \times 10^{-11}$
$\text{WO}_2^+ + 2 \text{NO} \rightarrow \text{WO}_3^+ + \text{N}_2\text{O}$	0.1	
$\text{WO}_3^+ + \text{NO} \rightarrow \text{NO}^+ + \text{WO}_3$	1	observed
$\text{ReO}^+ + 2 \text{NO} \rightarrow \text{ReO}_2^+ + \text{N}_2\text{O}$	0.5	$\leq 5.4 \times 10^{-11}$
$\rightarrow \text{NO}^+ + \text{ReONO}$	0.5	
$\text{ReO}_2^+ + 2 \text{NO} \rightarrow \text{ReO}_3^+ + \text{N}_2\text{O}$	1	observed
$\text{ReO}_3^+ + 2 \text{NO} \rightarrow \text{ReO}_4^+ + \text{N}_2\text{O}$	1	observed
$\text{OsO}^+ + 2 \text{NO} \rightarrow \text{OsO}_2^+ + \text{N}_2\text{O}$	0.6	$\leq 4.1 \times 10^{-11}$
$\rightarrow \text{NO}^+ + \text{OsONO}$	0.3	
$\rightarrow \text{OsO}^+(\text{NO}) + \text{NO}$	0.1	
$\text{OsO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{OsO}_2$	1	observed
$\text{OsO}^+(\text{NO}) + \text{NO} \rightarrow \text{OsO}^+(\text{NO})_2$	1	observed
$\text{OsO}^+(\text{NO})_2 + \text{NO} \rightarrow \text{OsO}^+(\text{NO})_3$	1	observed
$\text{IrO}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{IrO}$	0.95	$\leq 2.4 \times 10^{-10}$
$\rightarrow \text{IrO}^+(\text{NO})$	0.05	
$\text{Ir}^+(\text{NO}) + \text{NO} \rightarrow \text{Ir}^+(\text{NO})_2$	1	observed
$\text{Pt}^+(\text{NO}) + \text{NO} \rightarrow \text{Pt}^+(\text{NO})_2$	1	$\leq 2.9 \times 10^{-11}$
$\text{Pt}^+(\text{NO})_2 + \text{NO} \rightarrow \text{Pt}^+(\text{NO})_3$	1	observed

<sup>a</sup> Product distribution with an accuracy estimated to be 20% for the individual branching fractions. <sup>b</sup> Effective bimolecular rate coefficient first order in NO. The estimated uncertainty is  $\pm 30\%$ .

completely rule out some  $\text{XO}_2^+$  formation resulting from  $(\text{XO}^+)^*$  for  $\text{X} = \text{V}, \text{Ru}, \text{Ta}$ , and  $\text{Os}$  for which the exothermicity of  $\text{XO}^+$  formation exceeds the endothermicity for  $\text{XO}_2^+$  formation from reaction 11.

Still higher order oxides were observed with tungsten,  $\text{WO}_3^+$ , and rhenium,  $\text{ReO}_3^+$  and  $\text{ReO}_4^+$ . Presumably, these are also formed by the thermodynamically-favored termolecular reactions second order in NO.

A number of the oxide cations demonstrated an affinity for NO under the experimental operating conditions employed here. NO ligation was observed in the formation of  $\text{CaO}^+(\text{NO})$ ,  $\text{ScO}^+(\text{NO})$ ,  $\text{TiO}^+(\text{NO})$ ,  $\text{VO}^+(\text{NO})_{1-3}$ ,  $\text{VO}_2^+(\text{NO})_{1-3}$ ,  $\text{SrO}^+(\text{NO})$ ,  $\text{SrO}_2^+(\text{NO})_{1,2}$ ,  $\text{RuO}^+(\text{NO})_{1-3}$ ,  $\text{RuO}_2^+(\text{NO})_{1,2}$ ,  $\text{OsO}^+(\text{NO})_{1-3}$ , and  $\text{IrO}^+(\text{NO})$ . These ligations are expected to take place by termolecular addition in which either He or NO acts as the stabilizing third body.

Also, three atomic cations exhibit an affinity for two NO molecules in the formation of  $\text{Rh}^+(\text{NO})_2$ ,  $\text{Ir}^+(\text{NO})_2$ , and  $\text{Pt}^+(\text{NO})_2$ . Again, these ions are expected to be formed by termolecular addition of NO to the  $\text{XNO}^+$  nitrosyl cation in which either He or NO acts as the stabilizing third body.

### Conclusions

The substantial kinetic results obtained in this study clearly demonstrate that atomic cations initiate a very rich chemistry in their reactions with nitric oxide in the gas phase at room temperature. We have shown that this chemistry can proceed via bimolecular reactions first order in NO and termolecular reactions second order in NO. NO can donate an electron, donate an O-atom in the sequential formation of metal–oxide cations, or simply act as a ligand for some atomic cations and many metal–oxide cations. In some of the ion chemistry NO accepts N atoms leading to the conversion of NO to  $\text{N}_2\text{O}$  or accepts a metal atom leading to the production of metal–nitrosyl molecules. Also, insight is provided into the dependence of the chemistry on the electronic structure of the atomic cation and into the periodic variation in reactivity across and down the periodic table.

Our measurements indicate that the occurrence of bimolecular electron transfer and O-atom transfer from NO to atomic cations is thermodynamically controlled and that NO is not a good N atom donor.

These experiments have demonstrated remarkable termolecular ion chemistry with atomic cations, as well as their oxides, that is second order in NO. We suppose that such chemistry is favorable with NO because of its radical nature that facilitates bond formation, leading to nitrous oxide and metal–nitrosyl molecules. The second-order chemistry with atomic cations is analogous to that which we have reported recently for the diradical oxygen molecule in which a termolecular reaction of  $\text{Os}^+$  second order in oxygen was observed to produce  $\text{O}_2^+$  and osmium dioxide along with  $\text{OsO}^+$  and ozone.<sup>46</sup>

The results with the isolated atomic ions provide *intrinsic* reactivities that may serve as a benchmark for the reactivities of ligated atomic cations toward NO. Our gas-phase measurements also point toward the possibility that metal ions ligated to biological molecules can react in a second-order fashion with NO, perhaps in “pockets” of enhanced NO concentrations that may be present locally in the vicinity of ligated metal ions in biological systems. Such chemistry could produce  $\text{N}_2\text{O}$  and metal nitrosyl molecules *in vivo*. Analogies also can be drawn with atomic metal ion chemistry occurring on metal surfaces.

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