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International Journal of Mass Spectrometry 249–250 (2006) 385–391

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Gas-phase reactions of nitric oxide with atomic lanthanide cations: Room-temperature kinetics and periodicity in reactivity

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Received 28 October 2005; received in revised form 16 November 2005; accepted 28 November 2005

Abstract

An inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer has been employed in a systematic survey of the room-temperature kinetics of reactions of NO with 13 atomic lanthanide cations from Ce^+ to Lu^+ (excluding Pm^+). The atomic ions are produced at ca. 5500 K in an ICP source and are allowed to decay radiatively and to thermalize by collisions with Ar and He atoms prior to reaction in helium buffer gas at 0.35 ± 0.01 Torr and 295 ± 2 K. All lanthanide cations were observed to exhibit some reactivity towards NO, almost exclusively resulting in LnO^+ formation. Reactions were observed that are both first and second order in NO. Periodic trends in the measured reaction efficiencies for direct exothermic O atom transfer correlate with trends in the energy required to promote an electron in Ln^+ to achieve either a d^1s^1 or a d^2 excited electronic configuration in which two non-f-electrons are available for bonding. No such correlation is apparent for the remaining reactions.

Keywords: Lanthanide cations; Nitric oxide; O-atom transfer; Electron promotion

1. Introduction

Our recent laboratory measurements of reactions of atomic lanthanide cations with the oxygen-containing gases N_2O and O_2 have shown that the unique electronic configurations of lanthanide cations lead to unique trends in the kinetics of oxidation of these cations across the periodic table [1]. As early as 1988, Schilling and Beauchamp [2] had proposed that electron promotion from the $4f^n6s^1$ ground state to the $4f^{n-1}5d^16s^1$ excited state was required for these cations to be effective in C–H and C–C bond activation and insertion and this has been borne out by the plethora of investigations into lanthanide hydrocarbon ion chemistry that followed [3]. Our results with N_2O have shown that electron promotion also is required (to provide two unpaired non-f-electrons) for bonding with atomic oxygen in the formation of LnO^+ in reactions of lanthanide cations with N_2O [1]. Triplet oxygen in comparison reacts more readily, apparently by using one or more of the unpaired electrons to initiate binding. The electron promotion that is clearly required with N_2O gives rise to a periodic dependence of the efficiency of O-atom transfer on the electron promotion energy and intriguing Arrhenius-like dependencies of the efficiency on the electron promotion energy which exhibit different characteristic temperatures for the early and late lanthanide cations. A recent bonding configuration analysis by Gibson [4] suggests that two unpaired 5d valence electrons rather than a 5d and a 6s electron affect the bonding between the metal centre and the oxygen atom in lanthanide oxide cations. The variations in the promotion energies required to achieve either $5d^2$ or $5d^16s^1$ excitation are qualitatively similar across the lanthanides and so give rise to similar predictions of the periodic and Arrhenius-like dependencies of the efficiencies of O-atom transfer on the electron promotion energy.

Here we report results of reactions of lanthanide cations with another oxygen gas, nitric oxide. We shall see that the radical nature and high bond energy of NO gives rise to new kinetic insight into the lanthanide cation chemistry of oxygen-containing gases.

We present a room-temperature survey of gas-phase reactions of NO with all the lanthanide cations (except Pm^+ which does

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doi:10.1016/j.ijms.2005.11.025

not have a stable isotope) as part of a more extensive study of the reactions of atomic cations with NO [5,6]. We are aware of only one previous investigation of lanthanide cation reactions with NO. Ion beam studies in 1988 [2] provided cross-sections of 4.8 and 16 Å^2 at a centre-of-mass energy of approximately 0.25 eV for the reactions of Gd^+ and Pr^+ with NO to produce GdO^+ and PrO^+, respectively. There appear to be no previous room-temperature studies of the kinetics of any of the 13 lanthanide–cation reactions with NO reported here (other than our study of the reaction with La^+ [6]).

2. 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 [7,8]. 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 [9,10]. Solutions containing the metal salt of interest having concentration of ca. 5 μg l^{-1} were peristaltically pumped via a nebulizer into the plasma. The plasma gas 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 Company, Perkin-Elmer and Alfa Products. Aliquots of standard solutions were diluted with highly purified water produced in the Millipore Milli-Qplus ultra-pure 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 HNO_3 or HCl for acid-stabilized salts or KOH for those base-stabilized.

Atomic ions are initially formed within the ICP at a nominal ion temperature of 5500 K with Boltzmann state 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. 4×10^5 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. The time interval in the ICP/SIFT experiments between the exit of the ICP source and the entrance in the reaction region is ∼10 ms and there is enough time for major modifications to the original state distributions to occur by radiative decay. Electronic states of the lanthanides, due to presence of f-electrons, are a mixture of states with both positive and negative parity. This means that there is a large number of parity allowed transitions that will occur quickly ($\sim 10^{-8}$ s), and change the original state distribution from the ICP. La^+ itself is an exception in that it behaves like a transition-metal ion since it does not have any low-lying states with occupied f-orbitals.

The extent of electronic relaxation by collisions with the quite polarizable Ar atoms is uncertain, but collisions with Ar and He ensure that the atomic ions reach a translational temperature equal to the tube temperature of 295 ± 2 K prior to entering the reaction region. The helium buffer gas pressure was 0.35 ± 0.01 Torr. Clues to the presence of excited electronic states of the atomic ions in the reaction region can be found in the products observed and in the shape of the semi-logarithmic decay of the reacting atomic ion measured upon addition of neutral reactant.

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 [5] we have found that some metal oxide ions (ScO^+, ZrO^+ and LaO^+) react with NO_2 to produce NO^+ but do not form NO^+ with NO. Therefore, the failure to observe downstream NO^+ with these metal oxide ions with added NO can provide an upper limit to the level of 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 N_2O impurity in NO. In this case CeN^+ was used as the indicator since our experiments established that Ce^+ reacts with N_2O to produce CeN^+ with $k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [10]. No CeN^+ was observed when NO was added to Ce^+. Also, failure to observe AsO^+ with added NO indicated levels for possible N_2O impurities, of less than 0.1% in the reaction region since we have shown that As^+ reacts with N_2O to produce AsO^+ ($k = 2.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) [11] and it is known now that subsequent electron transfer from NO to AsO^+ is endothermic [S. Petrie, private communication. The adiabatic IE(AsO) has been determined to be 8.290 eV at the CCSD(T)/AUG-cc-pV5Z//CCSD/AUG-cc-pVTZ level of theory, with ZPE calculated at B3-LYP/AUG-cc-pVTZ, with correlation of electrons other than O 1s and As 1s through 3p]. So we can exclude formation of significant amounts of NO_2 and N_2O nitrogen oxides from reactions of NO with possible impurities such as H_2O or O_2 in the inlet system which of course is continuously flushed with NO during a reaction measurement. There was also no indication of $(NO)_2{}^+$ formation from $(NO)_2$ dimer in any of the experiments. The known dissociation constant of $(NO)_2$ is 1.6×10^{23} molecules cm^{-3} at room temperature [12] and this is large enough to keep the dimer concentration below 10^{-5}% of the monomer in the flow tube. In situ chemical ionization experiments with $Ar_2{}^+$ derived from the ICP source (which is expected to undergo electron transfer with N_2O and NO_2) and As^+ (which we have found to react rapidly with N_2O to produce AsO^+ with $k = 2.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) indicated levels for these two possible impurity gases of less than 0.1%.

Reaction rate coefficients were determined in the usual manner using pseudo-first-order kinetics [7,8]. The rate coefficients for the primary and consecutive reactions reported herein have an absolute accuracy of ±30%.

3. Experimental results

All lanthanide cations were observed to exhibit some reactivity towards NO, almost exclusively resulting in LnO^+

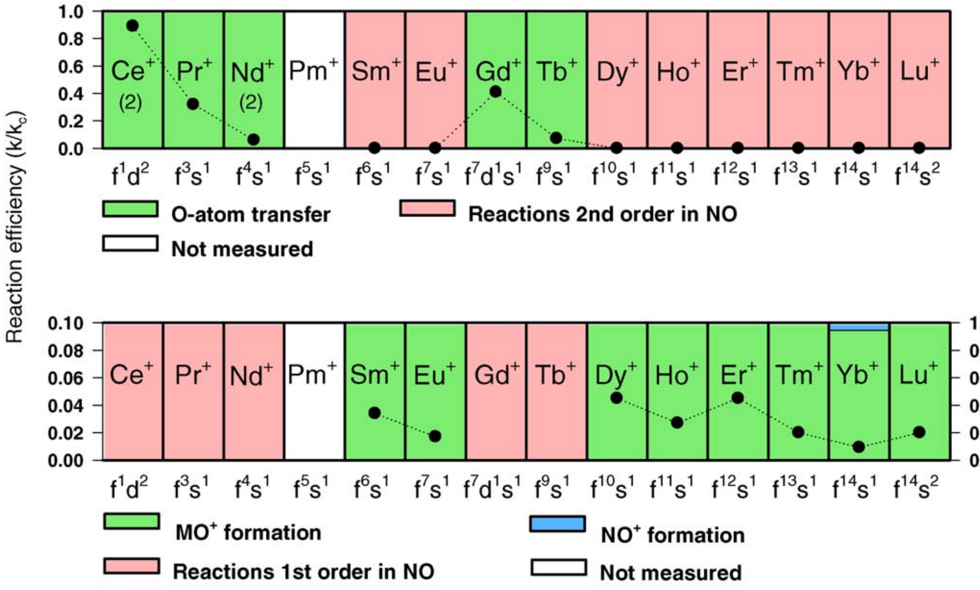

Fig. 1. Summary of results for reactions of lanthanide cations with NO. Reactions first order in NO (top) and reactions assumed to be second order in NO (bottom) are indicated separately. The right-hand scale (bottom) is a measure of the branching ratio of the reaction products (for Yb^+ only). The numbers in parentheses represent the number of sequential O-atom transfer reactions that were observed.

formation. Only Yb^+ exhibits NO^+ formation in addition to YbO^+ formation, but only as a minor channel (5%). The overview of the chemistry surveyed is given in Fig. 1, while the summary of the rate coefficients and product distributions is given in Table 1. Also included in Table 1 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 [13] with $\alpha(NO) = 1.70 \times 10^{-24}\,cm^3$ and $\mu_D = 0.161$ Debye [14]. We have reported previously a value of $k = 2.6 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$ ($k/k_c = 0.40$) for the reaction of La^+ with NO to produce LaO^+ [6].

Our results for Gd^+ and Pr^+ with $k = (2.6 \pm 0.8) \times 10^{-10}$ and $(2.1 \pm 0.6) \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$, respectively, are consistent with the previously reported ion beam results at higher energies [2], but we did not observe the enhanced (×3) reactivity of Pr^+ compared to that of Gd^+. Perhaps the reaction with Pr^+ has a stronger positive energy dependence than that with Gd^+.

Lanthanide cations appear to be oxidized by NO under our experimental operating conditions in two distinctly different ways. Cations with O-atom affinity higher than that of N, $OA(Ln) \geq 150.9 \pm 0.2\,kcal\,mol^{-1}$ [15], react by first-order O-atom transfer in NO according to reaction (1). These include La^+, Ce^+, Pr^+, Nd^+, Gd^+ and Tb^+ (see Table 2). Examples of

Table 1
Rate coefficients ($cm^3\,molecule^{-1}\,s^{-1}$), reaction efficiencies (k/k_c) and higher order product ions measured for reactions of lanthanide cations with nitric oxide in helium at 0.35 ± 0.01 Torr and 295 ± 2 K

Reaction	k^a	$k_c{}^b$	k/k_c	Higher order product ions
$La^+ + NO \rightarrow LaO^+ + N$	2.6×10^{-10}	6.5×10^{-10}	0.40	
$Ce^+ + NO \rightarrow CeO^+ + N$	5.8×10^{-10}	6.5×10^{-10}	0.89	$CeO_2{}^+$
$Pr^+ + NO \rightarrow PrO^+ + N$	2.1×10^{-10}	6.5×10^{-10}	0.32	
$Nd^+ + NO \rightarrow NdO^+ + N$	3.8×10^{-11}	6.5×10^{-10}	0.060	$NdO_2{}^+$, $NdO_2{}^+(NO)$
$Sm^+ + NO + NO \rightarrow SmO^+ + N_2O$	2.2×10^{-11}	6.4×10^{-10}	0.034	
$Eu^+ + NO + NO \rightarrow EuO^+ + N_2O$	1.1×10^{-11}	6.4×10^{-10}	0.017	
$Gd^+ + NO \rightarrow GdO^+ + N$	2.6×10^{-10}	6.4×10^{-10}	0.41	NO^+
$Tb^+ + NO \rightarrow TbO^+ + N$	4.6×10^{-11}	6.4×10^{-10}	0.072	NO^+, $TbO^+(NO)$
$Dy^+ + NO + NO \rightarrow DyO^+ + N_2O$	2.9×10^{-11}	6.4×10^{-10}	0.045	NO^+
$Ho^+ + NO + NO \rightarrow HoO^+ + N_2O$	1.7×10^{-11}	6.4×10^{-10}	0.027	
$Er^+ + NO + NO \rightarrow ErO^+ + NO$	2.9×10^{-11}	6.4×10^{-10}	0.027	NO^+
$Tm^+ + NO + NO \rightarrow TmO^+ + NO$	1.3×10^{-11}	6.4×10^{-10}	0.020	NO^+
$Yb^+ + NO + NO \rightarrow YbO^+ + NO$ (0.95)	5.9×10^{-12}	6.4×10^{-10}	0.0092	
$Yb^+ + NO + NO \rightarrow NO^+ + YbNO$ (0.05)				
$Lu^+ + NO + NO \rightarrow LuO^+ + NO$	1.3×10^{-11}	6.4×10^{-10}	0.020	

[a] Effective bimolecular rate coefficient first order in NO. The estimated uncertainty is ±30%.

[b] Collision rate coefficient calculated using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich [13].

Table 2
Thermodynamic and electronic properties for lanthanide cations

Ln^+ ground	Ln^+ state valence configuration	Ln^+ term symbol	Promotion energy[a] to $5d^1\ 6s^1$	IE(Ln)[b] (eV)	IE(LnO)[b] (eV)	$OA(Ln^+)$[c] ($kcal\ mol^{-1}$)
La^+	$5d^2$	$^3F_2$	4.5 ± 3.0	5.58	4.90	206.6 ± 3.4
Ce^+	$4f^1 5d^2$	$^4H_{7/2}{}^0$	4.6 ± 5.7	5.54	4.90	203.6 ± 5.9
Pr^+	$4f^3 6s^1$	$(9/2, 1/2)_4{}^0$	22.3 ± 0.8	5.47	4.90	189.6 ± 4.3
Nd^+	$4f^4 6s^1$	$^6I_{7/2}$	34.8 ± 8.3	5.53	4.97	180.8 ± 4.3
Pm^+	$4f^5 6s^1$	$^7H_2{}^0$	46.4 ± 7.2	5.58	–	–
Sm^+	$4f^6 6s^1$	$^8F_{1/2}$	62.1 ± 5.8	5.64	5.55	139.6 ± 4.3
Eu^+	$4f^7 6s^1$	$^9S_4{}^0$	92.8 ± 5.0	5.67	6.48	93.2 ± 4.3
Gd^+	$4f^7 5d^1 6s^1$	$^{10}D_{5/2}{}^0$	0.0	6.15	5.75	180.0 ± 4.3
Tb^+	$4f^9 6s^1$	$(15/2, 1/2)_8{}^0$	9.3 ± 8.1	5.86	5.62	171.0 ± 5.9
Dy^+	$4f^{10} 6s^1$	$(8, 1/2)_{17/2}$	36.0 ± 6.1	5.94	6.08	143.4 ± 5.9
Ho^+	$4f^{11} 6s^1$	$(15/2, 1/2)_8{}^0$	37.8 ± 5.4	6.02	6.17	141.3 ± 4.3
Er^+	$4f^{12} 6s^1$	$(6, 1/2)_{13/2}$	34.5 ± 3.1	6.11	6.30	140.3 ± 4.3
Tm^+	$4f^{13} 6s^1$	$(7/2, 1/2)_4{}^0$	55.5 ± 7.4	6.18	6.44	116.6 ± 4.3
Yb^+	$4f^{14} 6s^1$	$^2S_{1/2}$	79.4 ± 4.0	6.25	6.55	88.1 ± 5.9
Lu^+	$4f^{14} 6s^2$	$^1S_0$	36.6 ± 3.6	5.43	6.79	128.0 ± 4.3

[a] In $kcal\ mol^{-1}$ from Reference [1] with the correct value for Tm^+ which had been wrongly assigned in Reference [1].

[b] From Reference [15]. The error on all numbers is quoted as ±0.1 eV.

[c] Based on values for $\Delta H_f^\circ(LnO)$, $\Delta H_f^\circ(Ln)$, $\Delta H_f^\circ(O)$, IE(Ln) and IE(LnO) found in Reference [15].

this observed chemistry are shown in Fig. 2.

$$Ln^+ + NO \rightarrow LnO^+ + N \tag{1}$$

LnO^+ formation was also seen in the reactions of NO with Ln^+ cations for which direct O-atom transfer is endothermic, often highly endothermic. We have attributed this formation to reactions second order in NO (reaction (2)).

$$Ln^+ + 2NO \rightarrow LnO^+ + N_2O \tag{2}$$

A similar situation was encountered in our study of NO reactions with many other atomic cations on the periodic table [6] and we have demonstrated that these reactions are second order in NO, driven by exothermic N_2O formation, according to reactions (3a) and (3b).

$$M^+ + NO \rightarrow (MNO^+)^* \tag{3a}$$

$$(MNO^+)^* + NO \rightarrow MO^+ + N_2O \tag{3b}$$

Examples of such chemistry observed with atomic lanthanide cations are given in Fig. 3. Reaction (2) is exothermic when $OA(Ln^+) > OA(N)–D(N–NO) = 36\ kcal\ mol^{-1}$ and this is the case for all of the atomic ions investigated (see Table 2).

Yb^+ shows an additional small (5%) NO^+ formation channel that is endothermic by 3 eV for direct electron transfer from NO to ground-state Yb^+. It is highly unlikely that electron transfer can be attributed to the presence of excited Yb^{+*} states since only a very minute percentage of the Yb^+ cations (<0.1%) coming out of the plasma at 5500 K will have energies higher than 3 eV. We

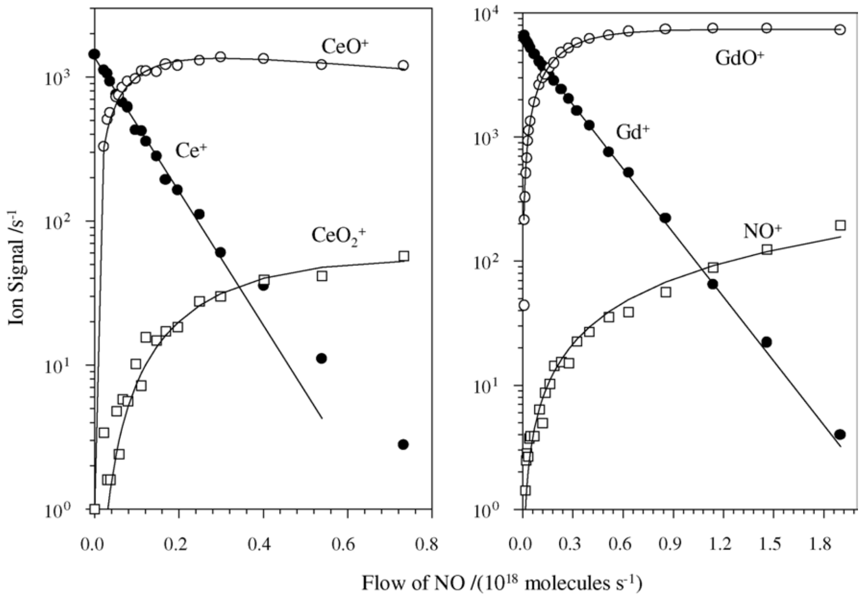

Fig. 2. ICP/SIFT results for the reaction of Ce^+ and Gd^+ with nitric oxide in helium buffer gas at 0.35 ± 0.01 Torr and 295 ± 2 K.

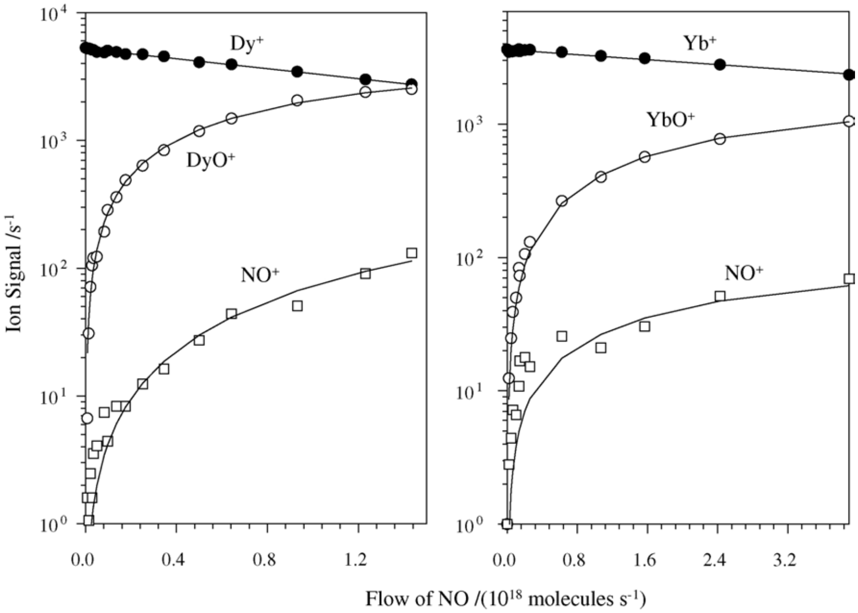

Fig. 3. ICP/SIFT results for the reaction of Dy^+ and Yb^+ with nitric oxide in helium buffer gas at 0.35 ± 0.01 Torr and 295 ± 2 K.

therefore attribute the formation of NO^+ to a second-order reaction (reaction (4b)), again as we have done previously for NO^+ production observed with other atomic cations on the periodic table for which direct electron transfer with NO is endothermic.

$$Yb^+ + 2NO \rightarrow YbO^+ + N_2O\,(0.95) \tag{4a}$$

$$Yb^+ + 2NO \rightarrow NO^+ + YbNO\,(0.05) \tag{4b}$$

The 3 eV energy difference in this case would be provided by the formation of the neutral metal nitrosyl bond. Reaction (4b) is exothermic when $IE(X) > IE(NO)–D(X–NO)$ or $9.264\,eV–D_{298}(X–NO)$. With $IE(Yb) = 6.25\,eV$ (see Table 2), Yb has the highest ionization energy of all the lanthanides. This means that NO^+ formation would be energetically most favourable with Yb^+ among all the lanthanide cations investigated if D(Ln–NO) remains unchanged across the lanthanide series as might be expected if f-electrons are not involved in Ln–NO bonding.

3.1. First-order primary chemistry

Table 1 shows that the exothermic O-atom transfer reactions of La^+, Ce^+, Pr^+, Nd^+, Gd^+ and Tb^+ with NO exhibit a large range in the magnitude of the reaction rate coefficient (from 5.8×10^{-10} to $3.8 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$) and reaction efficiency (0.89–0.060). The rate drops across the lanthanide row in the case of both the early and late lanthanides (see Fig. 1). Also, the reaction rate or efficiency correlates with the electron promotion energy from the $4f^n6s^1$ ground state to the $4f^{n-1}5d^16s^1$ excited state as we have observed previously with N_2O [1] or to the $5d^2$ excited state. The reaction efficiency falls with increasing promotion energy.

Fig. 4 displays the dependence of the measured reaction efficiency on the exothermicity of O-atom transfer when $OA(Ln^+) > OA(N)$. A rough, yet systematic, increase in efficiency is apparent with increasing $OA(Ln^+)$ and this may reflect an inverse dependence of the O-atom affinity on the electron promotion energy of Ln^+ to either $5d^16s^1$ or $5d^2$ (see Table 1 and Reference [4]).

Fig. 5(left) shows the dependence of the reaction efficiency (k/k_c) on the $5d^16s^1$ electron promotion energy in an Arrhenius-like plot. Unlike the similar dependency that we have explored with N_2O [1], this data set is very limited: four cations for the early and two for the late lanthanides. Despite these limitations, the reduction in reaction efficiency with increasing d^1s^1 elec-

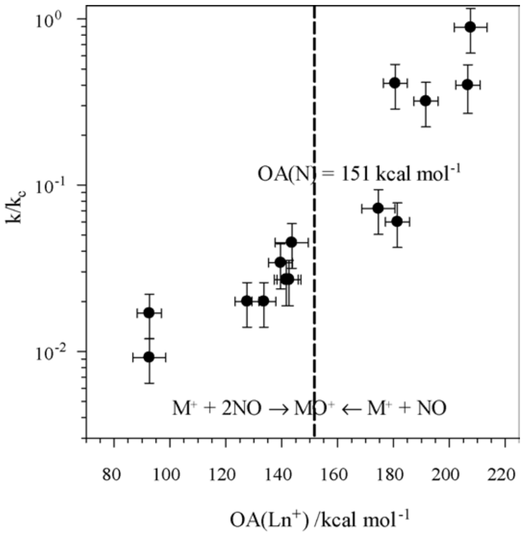

Fig. 4. Semi-logarithmic dependence of the efficiency, k/k_c, for LnO^+ formation on the O-atom affinity, $OA(Ln^+)$, in reactions of atomic cations with nitric oxide. k represents the measured first-order or pseudo-first-order reaction rate coefficient and k_c is the calculated collision rate coefficient (see Table 1). Bimolecular O-atom transfer reactions are exothermic on the right of the dashed line and endothermic on the left. Termolecular LnO^+ formation is exothermic to the left of the dashed line.

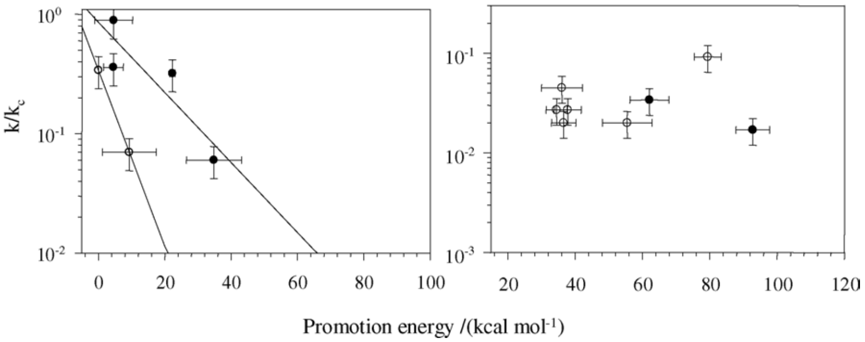

Fig. 5. Dependence of the reaction efficiency on the promotion energy from the ground to the $f^ns^1d^1$ electronic state. Shown are dependencies for the XO^+ formation that is first order in NO (left) and second order in NO (right). Solid circles represent early, while open circles represent late lanthanide cations. (Left) The two slopes provide characteristic temperatures of 7500 K (early Ln) and 3000 K (late Ln), respectively.

tron promotion energy appears to follow the same Arrhenius-like dependence with "characteristic temperatures" in this case of ca. 7500 K (early Ln) and 3000 K (late Ln), respectively. The plot for the d^2 electron promotion energy again is of similar quality and yields characteristic temperatures of 9000 and 4500 K, respectively. Both sets of temperatures are lower than the values of 22,000 and 6100 K that we obtained with N_2O but their uncertainties are much higher and a comparison is probably not warranted.

3.2. Second-order primary chemistry

Fig. 4 also displays the dependence of the measured reaction efficiency on OA(Ln^+) when OA(Ln^+) < OA(N). In this case there is a mild increase in efficiency with increasing exothermicity. The standard enthalpy change for the reactions second order in NO is given by $\Delta H^\circ_{298} = \text{OA(N)–D(N–NO)–OA(Ln}^+)$ or $\Delta H^\circ_{298} = 36\,\text{kcal mol}^{-1}\text{–OA(Ln}^+)$.

Unlike the Ln^+ cations that exhibit chemistry first order in NO, the cations leading to product ions attributed to reactions second order in NO do not exhibit an Arrhenius-like dependence of reaction efficiency on electron promotion energy (see Fig. 5(right)). This is understandable, since LnO^+ or NO^+ formation is achieved through an intermediate molecular $(LnNO^+)^*$ species rather than directly by the atomic lanthanide cation. The electron promotion in the lanthanide cation therefore loses its importance in determining reaction efficiency.

3.3. Higher order chemistry

Many of the LnO^+ cations undergo further reaction with NO to produce either ${LnO_2}^+$ or NO^+, but the observed decay in LnO^+ was insufficient to assign a rate coefficient, or even a limiting value. The observed higher order products are included in Table 1. ${LnO_2}^+$ formation was observed with the oxides of the early lanthanides CeO^+ and NdO^+ while the NO^+ formation was observed with the oxides of the late lanthanides GdO^+, TbO^+, DyO^+, ErO^+ and TmO^+. NO addition was observed to compete (0.5/0.5) only in the reaction with TbO^+ and was also seen with ${NdO_2}^+$.

Understanding the mechanism of NO^+ formation under our experimental conditions is not straightforward. Table 2 shows that IE(LnO) < 6.8 eV which is less than IE(NO) = 9.26436 ± 0.00006 eV [15] so that electron transfer from NO to ground-state LnO^+ is quite endothermic in all cases. If electron transfer from NO is to occur with excited LnO^{+*} cations, the excess of energy possessed by the LnO^+ cations would have to range from 2.45 eV (for LuO^+) to 3.5 eV (for GdO^+). This is possible for some of the cations (DyO^+, ErO^+ and TmO^+) but it would require that a large proportion (65–85%) of the excess energy in the LnO^+ formation reaction (between Ln^+ and two NO molecules) is retained by the LnO^+ cation until it collides with another NO molecule. The formation of NO^+ from LnO^+ by reaction (5) which is second order in NO may be more likely, but we cannot completely discount electron transfer from NO to excited LnO^{+*} ions.

$$LnO^+ + 2NO \rightarrow NO^+ + LnONO \qquad (5)$$

4. Conclusions

All of the 13 atomic lanthanide cations that were investigated are oxidized by NO to form LnO^+ in reactions with either one or two NO molecules, the latter being driven by the formation of N_2O molecules. The efficiency of the direct exothermic O-atom transfer from one NO molecule to Ln^+ correlates with the energy required to promote an electron in Ln^+ to achieve either a d^1s^1 or a d^2 excited electronic configuration in which two non-f-electrons are available for bonding. The electron promotion in the lanthanide cation loses its importance in determining the observed efficiency of the oxidation of the remaining eight lanthanide cations that is proposed to be second order in NO and so to proceed through an $(LnNO)^{+*}$ intermediate. The very limited data set for direct exothermic O-atom transfer (four early, including La^+, and two late lanthanide cations) shows an Arrhenius-like dependence of O-atom transfer efficiency on electron promotion energy similar to, but much less well defined than, that found previously with N_2O.

The observed higher order chemistry proceeds either by formation of ${LnO_2}^+$ from early lanthanide oxide cations or the formation of NO^+ from late lanthanide oxide cations. These cations are most likely the products of termolecular reactions with two NO molecules, although contributions from bimolecular electron transfer to excited LnO^+ cations in several cases cannot be excluded (DyO^+, ErO^+ and TmO^+). The work reported here, to our knowledge, represents the first experimental kinetic study of room-temperature reactions of lanthanide cations with NO.

Acknowledgements

Continued financial support from the Natural Sciences and Engineering Research Council of Canada is greatly appreciated. Also, we acknowledge support from the National Research Council, the Natural Science and Engineering Research Council and MDS SCIEX in the form of a Research Partnership grant. As holder of a Canada Research Chair in Physical Chemistry, Diethard K. Bohme thanks the Canada Research Chair Program for its contributions to this research.

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