Oxidation Reactions of Lanthanide Cations with N_2O and O_2: Periodicities in Reactivity

Gregory K. Koyanagi and Diethard K. Bohme*

Department of Chemistry, Centre for Research in Mass Spectrometry and Centre for Research in Earth and Space Science, York University, Toronto, Ontario M3J 1P3, Canada

Received: April 30, 2001; In Final Form: July 18, 2001

The oxidation reactions of all of the lanthanide cations (except Pm^+) with N_2O and O_2 have been investigated using the inductively coupled plasma selected-ion flow tube (ICP/SIFT) technique. Lanthanide cations were generated in an inductively coupled plasma (ICP) ion source. Observations are reported for the reactions of La^+, Ce^+, Pr^+, Nd^+, Sm^+, Eu^+, Gd^+, Tb^+, Dy^+, Ho^+, Er^+, Tm^+, Yb^+, and Lu^+ with N_2O and O_2 at room temperature (295 ± 2 K) in helium at a total pressure of 0.35 ± 0.02 Torr. Measured reaction rates varied from close to the predicted ion–molecule collision rate down to less than 0.1% efficiency. Observations are rationalized in terms of reaction thermodynamics and electronic structure effects. The efficiency for the reactions with N_2O was found to decrease as the energy required to promote the metal-ion electron from the $4f^n5d^06s^1$ to the $4f^{n-1}5d^16s^1$ configuration increases. Remarkable and different Arrhenius-like correlations are found in the N_2O reactivity of the early and late lanthanide cations with this electron promotion energy.

Introduction

The periodic behavior of physical and chemical properties of the elements has long fascinated chemists. During the early 1980s, periodic patters in the intrinsic chemical reactivity of early first-row and second-row transition-metal ions also became of interest, particularly toward hydrocarbons because of the importance of C–H and C–C bond activation.[1–5] Gas-phase reactivities of isolated lanthanide cations began to be measured in the late 1980s using Fourier transform mass spectrometry and various ion-beam techniques, together with laser ablation/ionization to produce the ions. Measurements were reported for reactions of La^+ with linear, branched, and cyclic alkanes up to C_6[6] for reactions of Pr^+, Eu^+, and Gd^+ with alkanes, cycloalkanes and alkenes,[7] and for reactions of La^+ and Lu^+ with methane and ethane,[8] and it was found that the electronic configuration of the lanthanide cation plays an important role in determining chemical reactivity. For example, Shilling and Beauchamp proposed that a minimum of two non-f valence electrons are required in the lanthanide cation for C–H and C–C bond activation to proceed effectively.[7] The first systematic study of all of the lanthanide cations (except Pm^+) reacting with the same molecule, in this case 1,3,5-tri-*tert*-butylbenzene, was reported in 1994 by Yin et al.[9] Reactivities and product distributions were found generally to depend on the electronic promotion energies for the $4f^n5d^06s^1$ to the $4f^{n-1}5d^16s^1$ transitions of the lanthanide series. Systematic measurements across the lanthanide series were extended by the group of Schröder and Schwarz to reactions with alkanes, cyclopropane, and alkenes,[10] to fluorocarbons,[11] and to buta-1,3-diene[12] in further investigations of C–H and C–C, as well as C–F, bond activation.

In the study reported here, we move into a new direction of lanthanide ion chemistry and systematically explore the periodic oxidation of lanthanide cations, Ln^+. We have employed a novel inductively coupled plasma/selected-ion flow tube (ICP/SIFT) instrument[13,14] to measure rate coefficients and product distribu-

tions for the reactions of all of the lanthanide cations (except Pm^+) with N_2O and O_2. Formation of LnO^+ in most of these reactions is thermodynamically allowed so that the periodic behavior in kinetic reactivity can be scrutinized and any influence on reaction rates of electronic promotion energies in f^nd^0 to $f^{n-1}d^1$ transitions required for oxide formation can be readily examined. Only the reactivities of Ce^+ and Nd^+ with N_2O and O_2 appear to have been measured previously.[15] Very recently, Campbell has reported temperature-dependent rate coefficients for the gas-phase reactions of neutral lanthanide atoms with N_2O.[16] Large variations were observed in reactivity, and the reaction energy barrier was found to correlate with the energy required to promote an electron out of the filled 6s subshell.

Our measurements with the lanthanide cations were also initiated in part by a desire in the ICP mass spectrometry community to remove spectral interferences using ion–molecule reactions, viz. by "chemical resolution".[13,14]

Experimental Section

The selected-ion flow tube (SIFT) mass spectrometer in the Ion-Chemistry Laboratory at York University, described in detail elsewhere,[17,18] 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.[13,14] Lanthanide-salt solutions having a concentration of 5 μg L^{-1} were peristatically pumped via a nebulizer into the plasma. The nebulizer flow was adjusted to maximize the ion signal detected downstream of the SIFT. The Ln^+ ions emerge from the plasma at a nominal plasma temperature of 5500 K and may then 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 extent of this is not known. The collisions with He ensure that the ions reach a translational temperature equal to the tube temperature of 295

* Corresponding author. E-mail: dkbohme@yorku.ca.

Reactions of Lanthanide Cations with N$_2$O and O$_2$

J. Phys. Chem. A, Vol. 105, No. 39, 2001 **8965**

TABLE 1: Oxygen Atom Affinities and Electronic Properties for Lanthanide Ions

Ln$^+$ species	OA(Ln$^+$)^a (kcal mol^{-1})	Ln$^+$ ground state valence configuration	Ln$^+$ term symbol	promotion energy to first 5d^{1}6s^1 configuration
La	206.6 ± 3.4	5d^2	^{3}F$_2$	4.5 ± 3.0
Ce	203.6 ± 5.9	4f^{1}5d^2	^{4}H$_{7/2}{}^0$	4.6 ± 5.7
Pr	189.6 ± 4.3	4f^{3}6s^1	(9/2,1/2)$_4{}^0$	22.3 ± 0.8
Nd	180.8 ± 4.3	4f^{4}6s^1	^{6}I$_{7/2}$	34.8 ± 8.3
Pm	–	4f^{5}6s^1	^{7}H$_2{}^0$	46.4 ± 7.2
Sm	139.6 ± 4.3	4f^{6}6s^1	^{8}F$_{1/2}$	62.1 ± 5.8
Eu	93.2 ± 4.3	4f^{7}6s^1	^{9}S$_4{}^0$	92.8 ± 5.0
Gd	180.0 ± 4.3	4f^{7}5d16s^1	^{10}D$_{5/2}{}^0$	0.0
Tb	171.0 ± 5.9	4f^{9}6s^1	(15/2,1/2)$_8{}^0$	9.3 ± 8.1
Dy	143.4 ± 5.9	4f^{10}6s^1	(8,1/2)$_{17/2}$	36.0 ± 6.1
Ho	141.3 ± 4.3	4f^{11}6s^1	(15/2,1/2)$_8{}^0$	
Er	140.3 ± 4.3	4f^{12}6s^1	(6,1/2)$_{13/2}$	34.5 ± 3.1
Tm	116.6 ± 4.3	4f^{13}6s^1	(7/2,1/2)$_4{}^0$	35.5 ± 7.4
Yb	88.1 ± 5.9	4f^{14}6s^1	^{2}S$_{1/2}$	79.4 ± 4.0
Lu	128.0 ± 4.3	4f146s^2	^{1}S$_0$	36.6 ± 3.6

^{a} On the basis of values for $\Delta H_f{}^o$(LnO) tabulated in ref 19 and values for $\Delta H_f{}^o$(Ln), $\Delta H_f{}^o$(O), IE(Ln), and IE(LnO) found in ref 20.

± 2 K prior to entering the reaction region. The helium buffer gas pressure was 0.35 ± 0.02 Torr. Reagent gases had purities better than 99.5%.

Reaction rate coefficients were determined in the usual manner using pseudo-first-order kinetics.[17,18] When rate coefficients are reported as an upper limit (≤), this indicates that 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.

Results and Discussion

The lanthanide cations all have positive affinities for O atoms and are summarized in Table 1. Values for OA(Ln$^+$) in Table 1 are based on values for $\Delta H_f{}^o$(LnO) tabulated in ref 19 and values for $\Delta H_f{}^o$(Ln), $\Delta H_f{}^o$(O), IE(Ln), and IE(LnO) found in ref 20. They range from 88.1 ± 5.9 kcal mol^{-1} for Yb$^+$ to 206.6 ± 3.4 kcal mol^{-1} for La$^+$ and exceed (OA)N$_2$ = 40.0 ± 0.1 kcal mol^{-1} and also, for the most part, OA(O) = 119.1 ± 0.1 kcal mol^{-1}. Thus, most of the O atom-transfer reactions of the lanthanide cations with N$_2$O and O$_2$ are thermodynamically allowed. Table 2 summarizes the reaction rate coefficients, k_{obs}, measured for in units of cm^3 molecule^{-1} s^{-1}, for reactions of Ln$^+$ ions with N$_2$O and O$_2$ proceeding at 295 ± 2 K in He at 0.35 ± 0.01 Torr. Also, reaction probabilities, k_{obs}/k_c, are determined with collision rate coefficients, k_c, computed using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich.[21] For the reactions with N$_2$O, k_c is in the range 7.2−7.0 × 10^{-10} cm^3 molecule^{-1} s^{-1}, and for the reactions with O$_2$, k_c is in the range 5.8−5.7 × 10^{-10} cm^3 molecule^{-1} s^{-1}.

Reactions with N$_2$O

Data representative of the chemistry observed with N$_2$O are shown in Figure 1 for the reactions of La$^+$ and Lu$^+$. The primary reactions with N$_2$O generally proceed via O atom transfer from N$_2$O to the bare atomic cation (reaction 1). This is not unexpected since the O atom

$$Ln^+ + N_2O \rightarrow LnO^+ + N_2 \qquad (1)$$
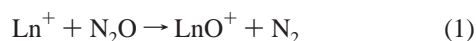
affinity of N$_2$ of 40.0 kcal mol^{-1} is much lower than the known values for OA(Ln$^+$) given in Table 1. In two instances, however, with La$^+$ and Ce$^+$, N atom transfer to form the LnN$^+$ cation,

TABLE 2: Measured Reaction Rate Coefficients, k_{obs}, in Units of cm^3 molecule^{-1} s^{-1}, for Reactions of Ln$^+$ Ions (the most abundant isotope) with N$_2$O and O$_2$ at 295 ± 2 K and 0.35 ± 0.01 Torr of He and Computed Reaction Probabilities, $k_{obs}/k_c{}^a$

Ln$^+$	N$_2$O $k_{obs}{}^b$	k_{obs}/k_c	O$_2$ $k_{obs}{}^b$	k_{obs}/k_c
La$^+$	5.9 × 10^{-10}	0.82	4.3 × 10^{-10}	0.75
Ce$^+$	5.2 × 10^{-10}	0.72	5.1 × 10^{-10}	0.88
Pr$^+$	2.8 × 10^{-10}	0.39	4.3 × 10^{-10}	0.75
Nd$^+$	2.9 × 10^{-10}	0.40	3.3 × 10^{-10}	0.57
Pm$^+$	–		–	
Sm$^+$	1.4 × 10^{-10}	0.19	2.8 × 10^{-10}	0.48
Eu$^+$	6.9 × 10^{-11}	0.097	2.6 × 10^{-13}	≤0.0006
Gd$^+$	5.3 × 10^{-10}	0.75	4.9 × 10^{-10}	0.86
Tb$^+$	1.2 × 10^{-10}	0.17	3.8 × 10^{-10}	0.67
Dy$^+$	2.7 × 10^{-11}	0.038	2.7 × 10^{-10}	0.47
Ho$^+$	1.7 × 10^{-11}	0.024	2.4 × 10^{-10}	0.42
Er$^+$	1.3 × 10^{-11}	0.018	2.5 × 10^{-10}	0.44
Tm$^+$	4.4 × 10^{-12}	0.0062	1.7 × 10^{-12}	≤0.0006
Yb$^+$	6.5 × 10^{-13}	0.000 93	3.6 × 10^{-13}	≤0.0006
Lu$^+$	2.6 × 10^{-10}	0.37	7.7 × 10^{-11}	0.014

^{a} k_c is the collision rate coefficient computed for the most abundant isotope using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich.[21] ^{b} The uncertainty in the reaction rate coefficient is less than ±30%.

reaction 2, was observed to compete with O atom transfer. The N atom transfer channel

$$Ln^+ + N_2O \rightarrow LnN^+ + NO \qquad (2)$$
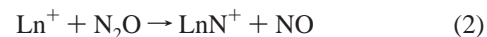
amounted to 2% and 25% for the reactions with La$^+$ and Ce$^+$, respectively. The Ce$^+$ result is in agreement with the 25% value obtained previously by Cornehl et al.[15] Using the FT-ICR technique, these authors also obtained rate coefficients of 7.4 × 10^{-10} and 3.4 × 10^{-10} cm^3 molecule^{-1} s^{-1} (deduced from the relative reaction rates reported in Table 2 of ref 15) for the reactions with Ce$^+$ and Nd$^+$, respectively. These are more than 40% higher than those obtained here. The observations of N atom transfer channels suggest that these are exothermic, or nearly so, and consequently that the N atom affinities NA(La$^+$) and NA(Ce$^+$) ≥ NA(NO) = 111 ± 1 kcal mol^{-1}. Electron transfer was not observed with any of the Ln$^+$ cations since their ionization energies, all < 6.3 eV, are much lower than IE(N$_2$O) = 12.886 eV.[20]

In some instances, trace water impurities present in the helium buffer gas were observed to add to LnO$^+$, presumably by termolecular association (with He acting as the third body) according to reaction 3. Also, N$_2$O was observed to add to most of the LnO$^+$ cations according to reaction 4. A second N$_2$O molecule was observed to add to LuO$^+$·N$_2$O (see Figure 1). These

$$LnO^+ + H_2O + He \rightarrow LnO^+ \cdot H_2O + He \qquad (3)$$

$$LnO^+ + N_2O + He \rightarrow LnO^+ \cdot N_2O + He \qquad (4)$$

N$_2$O addition reactions did not proceed rapidly ($k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}) and so are assumed to form weakly bound adduct ions. Figure 1 shows the occurrence of reactions of types 3 and 4 in the case of lutetium, along with a minor further O atom transfer with LuO$^+$ to from LuO$_2{}^+$ proceeding in competition with N$_2$O addition to LuO$^+$.

Periodicity in the reactivity with N$_2$O. The rate-coefficient measurements indicated a considerable variation in the rate of reaction 1 despite the fact that all the O atom transfer reactions
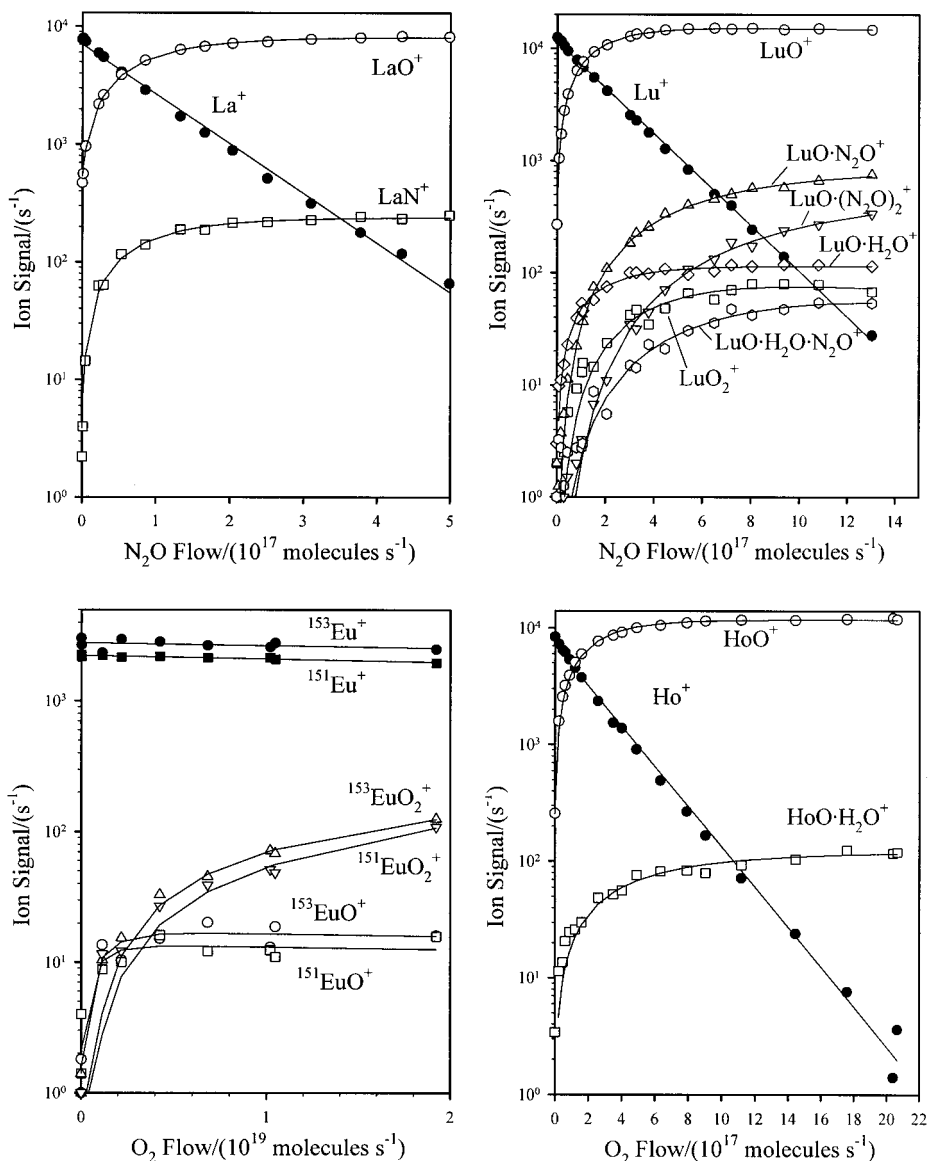
Figure 1. ICP/SIFT results for the reactions of La$^+$ and Lu$^+$ with N$_2$O and of Eu$^+$ and Ho$^+$ with O$_2$ in helium buffer gas at 0.35 ± 0.01 Torr and 295 ± 2 K.

investigated are exothermic by more than 50 kcal mol^{-1}. The O atom affinities in Table 1 indicate a variation in the exothermicity of reaction 1 from 52.6 to 167.6 kcal mol^{-1}. Some O atom transfer reactions were observed to proceed only slowly, suggesting that barriers to reaction exist with these lanthanide ions. An overview of the variation in rate across the lanthanide series is presented in Figure 2.

Formation of LnO$^+$ involves the donation of two unpaired electrons by Ln$^+$ to O(1s^2,2s^2,2p^4). These can be made available in most cases by promoting one electron in Ln$^+$ from the 4f^{n}5d^{0}6s^1 configuration in which the f orbitals do not extend far enough spatially to become involved in bonding to the 4f^{n-1}5d^{1}6s^1 configuration. In the case of La$^+$ and Ce$^+$, the promotion is from 5d^2 to the 5d^{1}6s^1 configuration. The ground state 4f^{n}5d^{1}6s^1 configuration of Gd$^+$ already satisfies the proposed bonding configuration. Energies, E_p, associated with the promotion from 4f^{n}5d^{0}6s^1 to 4f^{n-1}5d^{1}6s^1 (and from 5d^2 to the 5d^{1}6s^1 in the case of La$^+$ and Ce$^+$) and the valence configuration of the ground states of the lanthanide cations are given in Table 1. These were estimated based on spectroscopic data from a consideration of the ground-state and first 4f^{n-1}5d^{1}6s^1 manifolds. Specifically, the mean and standard deviation were

computed for the matrix of all the possible transitions between these manifolds. We have selected for the Er$^+$ excited-state manifold the closely grouped energy levels at 10667, 11309, 12388, 12815, and 13028 cm^{-1}. Atomic cation energy levels were taken from the "NIST Atomic Spectra Database".[22]

Figure 2 shows clearly that the variation in the rate of reaction 1 is mimicked by the variation in the promotion energy for the transition from the 4f^{n}5d^{0}6s^1 to the 4f^{n-1}5d^{1}6s^1 configuration. This suggests that Ln$^+$ reactions with the closed-shell nitrous oxide molecule proceed first via excitation of the lanthanide cation to the 4f^{n-1}5d^{1}6s^1 electron configuration, followed by two electron donation and LnO$^+$ bond formation with the electronic promotion energy introducing a barrier to the O atom transfer reaction. Indeed, Figure 3 demonstrates in an Arrhenius-like plot that the reaction efficiency of the Ln$^+$ reactions with N$_2$O at constant temperature exhibits an exponential dependence on the promotion energy according to eq 5. Here reactivity is expressed as the ratio k_{obs}/k_c, where k_{obs} is the measured reaction rate

$$k_{obs}/k_c = \exp(-XE_p) \tag{5}$$

Reactions of Lanthanide Cations with N₂O and O₂

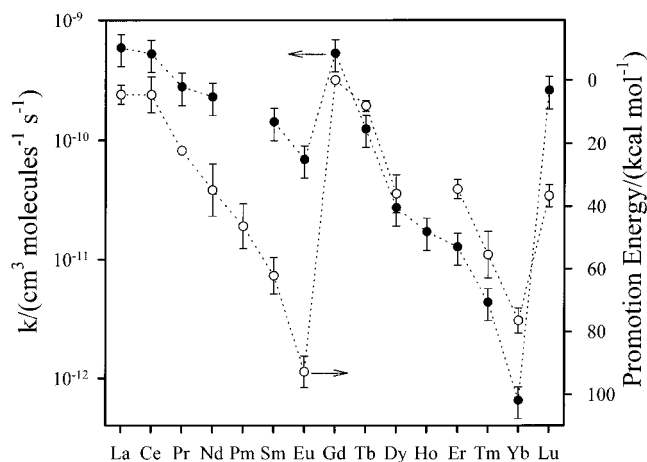*J. Phys. Chem. A, Vol. 105, No. 39, 2001* **8967**

Figure 2. Reaction rate coefficient (solid circles and left ordinate axis) and electron-promotion energy of the Ln^+ cation (open circles and right ordinate axis) plotted vs element for lanthanide cations reacting with N_2O. There is an apparent correlation between reaction rate and electron-promotion energy.
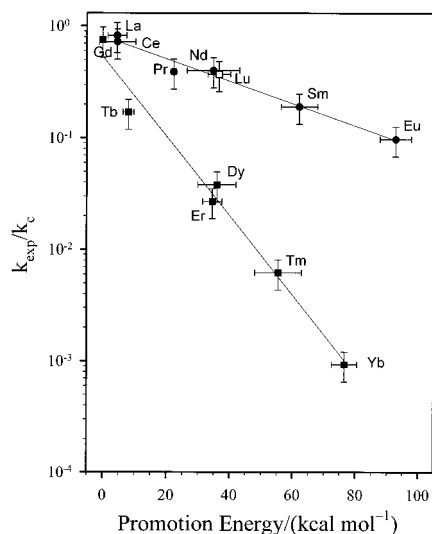

Figure 3. Correlation of reaction efficiency with the electron promotion energy that is proposed to be required for $Ln-O^+$ bond formation in the reactions of early (solid circles) and late (solid squares) Ln^+ ions with N_2O. Lu^+ (open square) clearly is an exception to the trend observed for the late Ln^+ ions.

coefficient and k_c is the collision rate coefficient. (We note here parenthetically that this may well be the first time that the Arrhenius equation has been used in this way with the activation energy rather than T as the independent variable). A remarkable aspect of these results is the distinct difference in this dependence between the early and late lanthanide ions. (If X is interpreted as $1/RT_{eff}$, the slopes of the semilogarithmic plots in Figure 3 indicate effective temperatures of ca. 22 000 and 6100 K for the early and late lanthanide ions, respectively.) We postulate that this difference in effective temperature can be attributed to the energy associated with the electron promotion. Electron promotion in the early lanthanide ions involves an unpaired f electron while that in the late lanthanide ions involves a paired f electron. Thus, electron promotion in the late lanthanide ions can be expected to be more effective and so exhibit a lower effective temperature. Lu^+ appears anomalous in Figure 2 in that its reactivity is abnormally high. However, as has been previously noted by Cornehl,[23] Lu^+ should be regarded as an exception to the lanthanide cation series in that a 6s electron rather than a 4f electron is promoted to a 5d orbital.
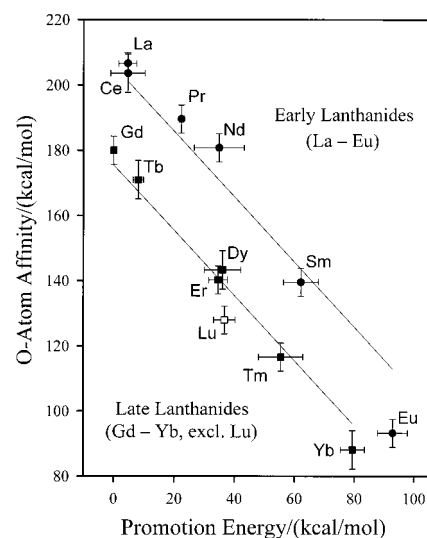

Figure 4. Correlation of O atom affinity with the electron promotion energy that is proposed to be required for $Ln-O^+$ bond formation in the reactions of early and late Ln^+ ions with N_2O. A unit slope has been imposed on the fits.

Figure 3 allows the f to d electron promotion energy of Ho^+ not available from spectroscopic data to be estimated at 37.8 ± 5.4 kcal mol^{-1}. This value compares favorably with the value of 35 kcal mol^{-1} estimated previously by Cornehl on the basis of reactivity measurements for reactions of lanthanide cations with a variety of hydrocarbons.[23]

The linear correlations shown in Figure 4 of O atom affinity with the electron promotion energy that is proposed to be required for $Ln-O^+$ bond formation are also of interest. It turns out that there is a separate correlation between the early and late lanthanides and that (when unit slope is imposed on the fits) the energy difference between the two (ca. 30 kcal mol^{-1}) expressed as RT corresponds to an effective temperature of 15 000 K. Curiously, this number coincides with the difference in the effective temperatures obtained from the correlations presented in Figure 3.

Reactions with O₂

Figure 1 includes data obtained for the reactions of Eu^+ and Ho^+ with O_2. The reactions with O_2 generally exhibited O atom transfer according to reaction 6, but with a variation in rate

$$Ln^+ + O_2 \rightarrow LnO^+ + O \qquad (6)$$
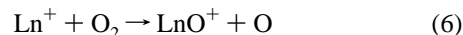
much different than that observed with N_2O. The reactions with O_2 were observed to proceed either near the collision rate or very slowly, $k < 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (see Table 1). This behavior correlates with reaction enthalpy based on OA(O) $= 119.1 \pm 0.1$ kcal mol^{-1}, viz. Reaction 6 is fast when exothermic and slow when endothermic. A similar result has been reported previously by Cornehl as a qualitative observation of background reactions with molecular oxygen in an FT-ICR mass spectrometer.[21] This author also suggested that kinetic barriers to reaction 6 are not expected since bond cleavage of the open-shell $^3\Sigma_g^-$ ground state of molecular oxygen can lead to several spin-allowed transitions between hypersurfaces of different multiplicities.[21]

According to the O atom affinities listed in Table 1, the slow reactions with Eu^+, Tm^+, and Yb^+ are endothermic by 15.9 ± 4.4, 3.5 ± 4.4, and 31.0 ± 6.0 kcal mol^{-1}, respectively. The fast reactions with the remaining La^+ cations are exothermic
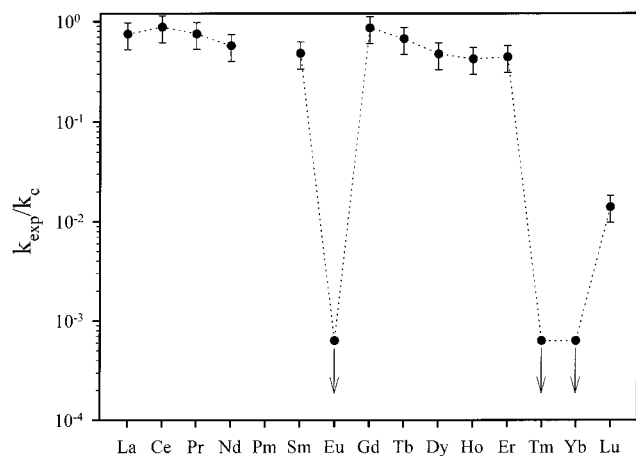
Figure 5. Reaction efficiency vs element for lanthanide cations reacting with O_2.

by at least 10 kcal mol^{-1} and proceed near the collision rate. An overview of the periodic behavior in the reaction efficiency of reaction 6 is shown in Figure 5.

For the three Ln$^+$ ions for which reaction 6 is endothermic (Eu$^+$, Tm$^+$ and Yb$^+$), some O_2 addition, reaction 7, was observed at very high oxygen flows of O_2, $\geq 1 \times 10^{19}$ molecules s^{-1}

$$Ln^+ + O_2 + He \rightarrow Ln^+{\cdot}O_2 + He \qquad (7)$$
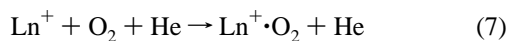
Also, O atom transfer, reaction 9, was observed in some instances due to the presence of a

$$(Ln^+)^* + O_2 \rightarrow LnO^+ + O \qquad (8)$$
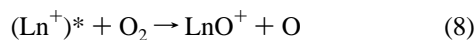
small fraction of excited states, <1%, that are generated in the high-temperature plasma and not efficiently deactivated with He collisons. This is evident, for example, in the data shown in Figure 1 for the reaction of Eu$^+$ from the early rise of very small amounts of EuO$^+$.

No secondary reactions were observed between LnO$^+$ and O_2, $k \leq 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Neither LnO$_2^+$ nor LnO$_3^+$ were formed in secondary reactions. The failure to observe the formation of LnO$_2^+$ implies that OA(LnO$^+$) $\leq$ OA(O) = 119 kcal mol^{-1} for each of the lanthanide oxide ions. The failure to observe the formation of LnO$_3^+$ is expected if the bonding of O_2 to LnO$^+$ is weak. Reactions with background water were again observed as simple H_2O addition reactions.

Conclusions

Reactions of the lanthanide cations with N_2O and O_2 have been surveyed using our new ICP/SIFT technique. O atom transfer dominates these reactions, and rate coefficient measurements indicate an obvious difference in the periodicity of the

reactivity with N_2O and O_2 that can be attributed to a difference in reaction mechanism. Closed shell nitrous oxide requires electron promotion from a nonbonding 4f to a bonding 5d or 6s valence orbital, whereas triplet oxygen appears to react readily using one or more of the unpaired electrons to initiate bond formation. For the reactions with nitrous oxide, an Arrhenius-like dependence was established for the variation in reactivity with the electron-promotion energies in the lanthanide cations from the $4f^n5d^06s^1$ to the $4f^{n-1}5d^16s^1$ configuration, and a remarkable, but enigmatic, difference was observed between the early and late lanthanides.

References and Notes

(1) Armentrout, P. B. *Annu. Rev. Phys. Chem.* **1990**, *41*, 313.
(2) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.
(3) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.
(4) Weisshaar, J. C. *Acc. Chem. Res.* **1993**, *26*, 213.
(5) Freiser, B. S. Acc. *Chem. Res.* **1994**, *27*, 353.
(6) Huang, Y.; Wise, M. B.; Jacobson, D. B.; Freiser, B. S. *Organometallics* **1987**, *6*, 346.
(7) Schilling, J. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 15.
(8) Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 3845.
(9) Yin, W. W.; Marshall, A. G.; Marcalo, J.; Pires de Matos, A. *J. Am. Chem. Soc.* **1994**, *116*, 8666.
(10) Cornehl, H. H.; Heinemann, C.; Schröder, D.; Schwarz, H. *Organometallics* **1995**, *14*, 992.
(11) Cornehl, H. H.; Hornung, G.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 9960.
(12) Cornehl, H. H.; Wesendrup, R.; Harvey, J. N.; Schwarz, H. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2284.
(13) Koyanagi, G. K.; Lavrov, V. V.; Baranov, V. I.; Bandura, D.; Tanner, S. D.; McLaren, J. W.; Bohme, D. K. *Int. J. Mass Spectrom.* **2000**, *194*, L1.
(14) Koyanagi, G. K.; Baranov, V. I.; Tanner, S. D.; Bohme, D. K. *J. Anal. At. Spectrom.* **2000**, *15*, 1207.
(15) Cornehl, H. H.; Wesendrup, R.; Diefenbach, M.; Schwarz, H. *Chem. Eur. J.* **1997**, *3*, 1083.
(16) Campbell, M. L. *J. Chem. Phys.* **1999**, *111*, 562.
(17) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36,* 259.
(18) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1983/84**, *55*, 69.
(19) Murad, E.; Hildenbrand, D. L. *J. Chem. Phys* **1980**, *73,* 4005.
(20) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1 (Suppl. 1).
(21) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.
(22) NIST Standard Reference Database 78 available on the World Wide Web at http://physics.nist.gov/cgi-bin/AtData/main_asd.
(23) Cornehl, H. H. "Gas-Phase Ion Chemistry of f-Elements". Shaker Verlag: Aachen, Germany, 1997.