Gas-Phase Reactions of Atomic Lanthanide Cations with CO\textsubscript{2} and CS\textsubscript{2}: Room-Temperature Kinetics and Periodicities in Reactivity

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Gas-phase reactions of atomic lanthanide cations (excluding Pm\textsuperscript{+}) have been surveyed systematically with CO\textsubscript{2} and CS\textsubscript{2} using an inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer. Observations are reported for reactions with Lu\textsuperscript{+}, Ce\textsuperscript{+}, Pr\textsuperscript{+}, Nd\textsuperscript{+}, Sm\textsuperscript{+}, Eu\textsuperscript{+}, Gd\textsuperscript{+}, Tb\textsuperscript{+}, Dy\textsuperscript{+}, Ho\textsuperscript{+}, Er\textsuperscript{+}, Tm\textsuperscript{+}, Yb\textsuperscript{+}, and Lu\textsuperscript{+} at room temperature (295 ± 2 K) in helium at a total pressure of 0.35 ± 0.02 Torr. The observed primary reaction channels correspond to X-atom transfer (X = O, S) and CX\textsubscript{2} addition. X-atom transfer is the predominant reaction channel with Lu\textsuperscript{+}, Ce\textsuperscript{+}, Pr\textsuperscript{+}, Nd\textsuperscript{+}, Gd\textsuperscript{+}, Tb\textsuperscript{+}, and Lu\textsuperscript{+}, and CX\textsubscript{2} addition occurs with the other lanthanide cations. Competition between these two channels is seen only in the reactions of CS\textsubscript{2} with Nd\textsuperscript{+} and Lu\textsuperscript{+}. Rate coefficient measurements indicate a periodicity in the reaction efficiencies of the early and late lanthanides. With CO\textsubscript{2} the observed trends in reactivity across the row and with exothermicity follow trends in the energy required to achieve two unpaired non-f valence electrons by electron promotion within the Ln\textsuperscript{+} cation that suggest the presence of a kinetic barrier, in a manner much like those observed previously for reactions with isoelctronic N\textsubscript{2}O. In contrast, no such barrier is evident for S-atom transfer from the valence isoelectronic CS\textsubscript{2} molecule which proceeds at unit efficiency, and this is attributed to the much higher polarizability of CS\textsubscript{2} compared to CO\textsubscript{2} and N\textsubscript{2}O. Up to five CX\textsubscript{2} molecules were observed to add sequentially to selected Ln\textsuperscript{+} and LnX\textsuperscript{+} cations.

1. Introduction

The recent experimental activity in measurements of gas-phase reactions of atomic lanthanide cations with small molecules has provided new fertile ground for the exploration of fundamental aspects of chemical reactivity.\textsuperscript{1–5} Gas-phase reactivities of isolated lanthanide cations began to be studied in the late 1980s with Fourier transform mass spectrometry and various ion-beam techniques, together with laser ablation techniques to produce the atomic cations.\textsuperscript{1,6,7} Numerous investigations over the past 20 years have made available extensive data on the gas-phase reactions of the lanthanide cations with various inorganic and organic molecules including hydrogen,\textsuperscript{8} oxygen and nitrous oxide,\textsuperscript{9} D\textsubscript{2}O,\textsuperscript{10} alkanes and cycloalkanes,\textsuperscript{1,3,7} alkynes,\textsuperscript{1,6,11} alcohols,\textsuperscript{2,4,12} benzene and substituted benzenes,\textsuperscript{13,14} phenol,\textsuperscript{15} orthoformates,\textsuperscript{13,16} ferrocene and Fe pentacarbonyl,\textsuperscript{17} methyl fluoride,\textsuperscript{18} and methyl chloride.\textsuperscript{5} Generally, these studies show that the reactivity of Ln\textsuperscript{+} varies along the 4f series in terms of both the ionic products formed and the reaction efficiencies. These variations have been related to the accessibility of excited electron configurations with two unpaired non-f electrons, that is, to the energies required to excite the ground states of the Ln\textsuperscript{+} cations, typically from 4f\textsuperscript{5}5d\textsuperscript{6}s\textsuperscript{1} to the 4f\textsuperscript{5–15}d\textsuperscript{6}s\textsuperscript{1} states. A recent bonding configuration analysis by Gibson\textsuperscript{19} suggests that two unpaired 5d valence electrons rather than a 5d and a 6s electron enable efficient bonding between the metal center and the oxygen atom in LnO\textsuperscript{2–}. The variations in the promotion energies required to achieve either 5d\textsuperscript{2} or 5d\textsuperscript{6}s\textsuperscript{1} excitation are qualitatively similar across the Ln\textsuperscript{+} family and result in similar predictions for the periodic and Arrhenius-like dependencies of the efficiencies of O-atom transfer on the electron promotion energy, except for differences in characteristic temperature. Here we add experimental observations of reactions of atomic lanthanide cations with CO\textsubscript{2} and the related CS\textsubscript{2} molecule to the database.

Surprisingly, to the best of our knowledge, there are no previous reports on the reactions of lanthanide cations with either carbon dioxide or carbon disulfide, although reactions of other metal cations with these two gases now have been surveyed by several groups,\textsuperscript{20–23} including our own.\textsuperscript{24,25} CO\textsubscript{2} and CS\textsubscript{2} are interesting reagent gases to compare in terms of their chemical activities since they are valence isoelectronic. Furthermore, CO\textsubscript{2} is isoelectronic with N\textsubscript{2}O, for which we have previously reported an experimental study of lanthanide ion chemistry.\textsuperscript{9} Measurements of the temperature dependence of rate coefficients for gas-phase reactions of neutral lanthanide atoms with CO\textsubscript{2} recently reported by Campell also are available for comparison.\textsuperscript{26} Large variations in reactivity were observed, and the reaction energy barrier was found to correlate with the energy required to promote an electron out of the filled 6s subshell. Here we shall explore the influence of electron promotion energy on the reactivities of atomic lanthanide cations at room temperature.

2. Experimental Method

The experimental results reported here were obtained with the inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer that has been described in detail previously.\textsuperscript{9,27,28} The atomic ions were generated within the ICP/SIFT) tandem mass spectrometer that has been described in detail previously.\textsuperscript{9,27,28} The atomic ions were generated within the ICP/SIFT tandem mass spectrometer that has been described in detail previously.\textsuperscript{9,27,28} The atomic ions were generated within the ICP/SIFT tandem mass spectrometer that has been described in detail previously.\textsuperscript{9,27,28}
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. The ions emerging from the ICP were injected through a differentially pumped sampling interface into a quadrupole mass filter and, after mass analysis, introduced through an aspirator-like interface into flowing helium carrier gas at 0.35 ± 0.01 Torr and 295 ± 2 K. After experiencing about 10⁵ collisions with He atoms, the ions were allowed to react with CO₂ or CS₂ added into the flow tube.

The lanthanide ions emerging from the plasma initially have a Boltzmann internal energy distribution characteristic of the plasma temperature. However, these emerging populations are expected to relax during the approximately 20 ms duration before entry into the reaction region in the flow tube. Energy degradation can occur by radiative decay as well as by collisions with argon atoms and the 10⁵ collisions with He before entry into the reaction region. Electronic states of the lanthanides, due to the presence of f electrons, are a mixture of states with both positive and negative parity. This means that there are a large number of parity allowed transitions that will occur quickly (~10⁻⁸ s), changing their original state distribution from the ICP. La⁺ itself is an exception for lanthanides in that it behaves like a transition-metal ion since it does not have any low-lying states with occupied f orbitals. The extent to which quenching of any electronically excited states of the lanthanide cations that may be formed within the ICP is complete is uncertain and could be inferred only indirectly from the observed decays of primary ion signals. The observed semilogarithmic decays of the reacting lanthanide cations were invariably linear over a range from two to as much as three decades of ion depletion and so were indicative of single-state populations (or multiple-state populations with equal reactivities). The many collisions with Ar and He between the source and the reaction region should ensure that the atomic ions reach a translational temperature equal to the tube temperature of 295 ± 2 K prior to entering the reaction region.

Reactant and product ions were sampled at the end of the flow tube with a second quadrupole mass filter, and their signals were measured as a function of added reactant. The resulting profiles provide information about reaction rate coefficients and product-ion distributions. Rate coefficients for primary reactions were determined with an uncertainty estimated to be less than ±30% from the semilogarithmic decay of the reactant ion intensity as a function of added reactant.

CS₂ (Matheson Coleman & Bell, ≥99%) was introduced into the reaction region of the SIFT as a dilute mixture of CS₂ vapor
in helium (~10%), and CO₂ was introduced into the reaction region as a pure gas (Matheson Gas Products, ≥99.9%). The influence of possible impurities in either of these gases can be neglected; all reactions measured to have low efficiencies (<10⁻² or 10⁻³) were observed to proceed exclusively by the addition of the added gases.

3. Results and Discussion

The reactions of 14 lanthanide cations were investigated with both CO₂ and CS₂. Both the primary and subsequent chemistries were monitored. Ion profiles obtained for the reactions of Ce⁺, Pr⁺, Gd⁺, and Lu⁺ with CO₂ and CS₂ are shown in Figures 1 and 2. Tables 1 and 2 summarize the measured rate coefficients and the derived reaction efficiencies as well as measured product distributions. The reaction efficiency is taken to be equal to the ratio $k/k_c$, where $k$ is the experimentally measured rate coefficient and $k_c$ is the capture or collision rate coefficient. $k_c$ was computed using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich²⁹ with $\alpha$(CO₂) = 2.91 × 10⁻²⁴ cm³ and $\alpha$(CS₂) = 8.74 × 10⁻²⁶ cm³. Figure 3 displays and compares the data in Tables 1 and 2 in a periodic table format.

Only atom transfer, reaction 1a, and adduct formation, reaction 1b, were observed as primary reaction channels (here X may be O or S).

$$\text{Ln}^+ + \text{CX}_2 \rightarrow \text{LnX}^+ + \text{CX} \quad (1a)$$

$$\text{Ln}^+ + \text{CX}_2 \rightarrow \text{Ln}^+(\text{CX}_2) \quad (1b)$$

As expected from the much lower first ionization energies (IE) of the lanthanides (all values for IE(Ln) < 6.3 eV are much lower than IE(CO₂) = 13.773 ± 0.002 eV and IE(CS₂) = 10.0685 ± 0.0020 eV),³⁰ electron transfer was not observed with any of the Ln⁺ cations.

3.1. Atom Transfer Reactions. O-atom transfer from CO₂ to Ln⁺ was observed exclusively with La⁺, Ce⁺, Pr⁺, Nd⁺, Gd⁺, Tb⁺, and Lu⁺ with rate coefficients in the range from 3.3 × 10⁻¹¹ (Lu⁺) to 4.6 × 10⁻¹⁰ (Ce⁺) cm³ molecule⁻¹ s⁻¹. The efficiencies ($k/k_c$) for O-atom transfer show a systematic decrease for the first two or three of the early and of the late lanthanides (see Figure 3). S-atom transfer from CS₂ to Ln⁺ also was observed exclusively with La⁺, Ce⁺, Pr⁺, Nd⁺, Gd⁺, Tb⁺, but to compete with CS₂ addition in the reactions of CS₂ with Nd⁺ (90%) and Lu⁺ (20%). The measured rate coefficients for the exclusive S-atom transfer reactions are all equal to 1.0 × 10⁻⁹ cm³ molecule⁻¹ s⁻¹, within experimental uncertainty, and higher than those for the corresponding O-atom transfer.
TABLE 1: Rate Coefficients (in Units of 10^{-10} cm^3 molecule^{-1} s^{-1}) and Higher Order Product Ions Measured for Reactions of Atomic Ln^+ Cations with CO₂ in Helium at 0.35 ± 0.01 Torr and 295 ± 2 K

<table>
<thead>
<tr>
<th>Ln⁺</th>
<th>k</th>
<th>k_c</th>
<th>k/k_c</th>
<th>primary products</th>
<th>PD</th>
<th>higher order productions</th>
</tr>
</thead>
<tbody>
<tr>
<td>La⁺</td>
<td>4.4</td>
<td>6.91</td>
<td>0.64</td>
<td>LaO⁺</td>
<td>100</td>
<td>LaO⁺(CO₂)</td>
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<tr>
<td>Ce⁺</td>
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<td>6.91</td>
<td>0.66</td>
<td>CeO⁺</td>
<td>100</td>
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<tr>
<td>Pr⁺</td>
<td>1.6</td>
<td>6.90</td>
<td>0.23</td>
<td>PrO⁺</td>
<td>100</td>
<td>PrO⁺(CO₂)</td>
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<tr>
<td>Nd⁺</td>
<td>0.37</td>
<td>6.89</td>
<td>5.4x10^{-2}</td>
<td>NdO⁺</td>
<td>100</td>
<td>NdO⁺(CO₂)</td>
</tr>
<tr>
<td>Sm⁺</td>
<td>0.0050</td>
<td>6.83</td>
<td>7.3x10^{-4}</td>
<td>Sm⁺(CO₂)</td>
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<td>Sm⁺(CO₂)</td>
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<tr>
<td>Eu⁺</td>
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<td>6.84</td>
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<td>Gd⁺</td>
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<td>0.50</td>
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<td>Tb⁺</td>
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<td>Er⁺</td>
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<td>8.9x10^{-4}</td>
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<td>Yb⁺</td>
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<tr>
<td>Lu⁺</td>
<td>0.33</td>
<td>6.73</td>
<td>4.9x10^{-2}</td>
<td>LuO⁺</td>
<td>100</td>
<td>LuO⁺(CO₂)</td>
</tr>
</tbody>
</table>

a Products and product distributions (PD in %) are also included along with calculated collision rate coefficients, k_c (in units of 10^{-10} cm^3 molecule^{-1} s^{-1}), and reaction efficiencies, k/k_c (see text). b Measured reaction rate coefficient with an estimated accuracy of ±30%.

TABLE 2: Rate Coefficients (in Units of 10^{-10} cm^3 molecule^{-1} s^{-1}) and Higher Order Product Ions Measured for Reactions of Atomic Ln^+ Cations with CS₂ in Helium at 0.35 ± 0.01 Torr and 295 ± 2 K

<table>
<thead>
<tr>
<th>Ln⁺</th>
<th>k</th>
<th>k_c</th>
<th>k/k_c</th>
<th>primary products</th>
<th>PD</th>
<th>higher order productions</th>
</tr>
</thead>
<tbody>
<tr>
<td>La⁺</td>
<td>10</td>
<td>9.87</td>
<td>1.00</td>
<td>LaS⁺</td>
<td>100</td>
<td>LaS⁺(CS₂)</td>
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<tr>
<td>Ce⁺</td>
<td>10</td>
<td>9.87</td>
<td>1.00</td>
<td>CeS⁺</td>
<td>100</td>
<td>CeS⁺(CS₂)</td>
</tr>
<tr>
<td>Pr⁺</td>
<td>10</td>
<td>9.87</td>
<td>1.00</td>
<td>PrS⁺</td>
<td>100</td>
<td>PrS⁺(CS₂)</td>
</tr>
<tr>
<td>Nd⁺</td>
<td>7.0</td>
<td>9.83</td>
<td>0.71</td>
<td>NdS⁺</td>
<td>100</td>
<td>NdS⁺(CS₂)</td>
</tr>
<tr>
<td>Sm⁺</td>
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<td>9.73</td>
<td>7.7x10^{-2}</td>
<td>Sm⁺(CS₂)</td>
<td>100</td>
<td>Sm⁺(CS₂)</td>
</tr>
<tr>
<td>Eu⁺</td>
<td>0.15</td>
<td>9.72</td>
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<td>1.00</td>
<td>GdS⁺</td>
<td>100</td>
<td>GdS⁺(CS₂)</td>
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<tr>
<td>Tb⁺</td>
<td>10</td>
<td>9.65</td>
<td>1.00</td>
<td>TbS⁺</td>
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<td>TbS⁺(CS₂)</td>
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<tr>
<td>Dy⁺</td>
<td>0.23</td>
<td>9.62</td>
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<td>Ho⁺</td>
<td>0.29</td>
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<td>3.0x10^{-2}</td>
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<td>Ho⁺(CS₂)</td>
</tr>
<tr>
<td>Er⁺</td>
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<td>9.58</td>
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<td>Er⁺(CS₂)</td>
<td>100</td>
<td>Er⁺(CS₂)</td>
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<tr>
<td>Tm⁺</td>
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<td>9.56</td>
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<td>Tm⁺(CS₂)</td>
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<tr>
<td>Yb⁺</td>
<td>0.060</td>
<td>9.52</td>
<td>6.3x10^{-3}</td>
<td>Yb⁺(CS₂)</td>
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<td>Yb⁺(CS₂)</td>
</tr>
<tr>
<td>Lu⁺</td>
<td>0.91</td>
<td>9.52</td>
<td>9.6x10^{-2}</td>
<td>LuS⁺</td>
<td>20</td>
<td>LuS⁺(CS₂)</td>
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</table>

a Products and product distributions (PD in %) are also included along with calculated collision rate coefficients, k_c (in units of 10^{-10} cm^3 molecule^{-1} s^{-1}), and reaction efficiencies, k/k_c (see text). b Measured reaction rate coefficient with an estimated accuracy of ±30%.

reactions. Indeed, exclusive S-atom transfer occurs with unit efficiency, within experimental uncertainty.

A second X-atom transfer was not observed with any of the Ln⁺ cations.

3.2. Influence of Exothermicity on Atom Transfer. The X-atom affinities of CO are quite high: OA(CO) = 125.75 ± 0.05 kcal mol⁻¹ and SA(CS₂) = 103.8 ± 0.9 kcal mol⁻¹. Thus, X-atom transfer from CO₂ to Ln⁺ according to reaction 1a is exothermic and can be expected to occur for those lanthanide cations with a comparable or higher X-atom affinity. The available experimental and theoretical O- and S-atom affinities listed in Table 3 indicate that 11 out of the 14 atomic lanthanide cations have O-atom affinities higher than that of CO, but we observed only seven of these to react measurably with CO₂ by O-atom transfer. The other four cations, Sm⁺, Dy⁺, Ho⁺, and Er⁺, all of which have O-atom affinities of ca. 140 kcal mol⁻¹, simply react by CO₂ addition. Figure 4 shows that, with the exception of Lu⁺, O-atom transfer actually exhibits an onset at ca. 170 kcal mol⁻¹, viz. at exothermicities larger than ca. 45 kcal mol⁻¹. An analogous onset is apparent in Figure 4 for O-atom transfer from the isoelectronic N₂O molecule for which we have previously reported measured reaction efficiencies, but no such onset is apparent in Figure 4 for the CS₂ reactions that exhibit unit efficiency for exothermic S-atom transfer. The (six) S-atom transfer reactions for which SA(Ln⁺) is known generally are less exothermic than the corresponding O-atom transfer reactions, with the exception of Lu⁺, with which both O-atom transfer and S-atom transfer are nearly thermoneutral. Apparently a kinetic barrier that decreases with increasing exothermicity operates for O-atom transfer from CO₂ and N₂O, but not for S-atom transfer from CS₂.

3.3. Role of Electron Promotion. We know from our previous studies of O-atom transfer from N₂O to Ln⁺ that electron promotion is required (for most Ln⁺ cations) to make available non-f valence electrons for covalent bonding with O in the formation of the oxide cation LnO⁺ (the orbitals of f electrons cannot extend far enough spatially to become involved in bonding). A similar requirement is expected for reactions of Ln⁺ with the isoelectronic CO₂ molecule and the valence isoelectronic CS₂ molecule. Indeed, the periodic variation of the reaction efficiency seen in Figure 3 for the early and late lanthanides is a manifestation of this requirement as it parallels the variation in promotion energy for both CO₂ and N₂O, but is restricted to fewer elements in the reactions with CO₂. Thus Gd⁺(d⁴S⁴), La⁺(d⁴), and Ce⁺(d⁴) exhibit high reactivity in their two non-f valence electron configurations, while the reactions of Pr⁺, Nd⁺, and Tb⁺ with CO₂ are less efficient due to the need to promote an f electron in their ground-state 4f⁵5d⁶6s¹ configurations to achieve two valence electrons. Lu⁺(d⁴s²) is anomalous in that a 6s rather than a 4f electron would have to
the valence isolectronic CS₂ molecule. S-atom transfer at room temperature is observed for S-atom transfer to lanthanide cations from the higher reactivity of Lu⁺ compared to other late lanthanide cations (Dy⁺, Ho⁺, Er⁺) that have similar or lower promotion energy and reaction exothermicity can be understood qualitatively in terms of the double-minimum potential energy surface sketched in Figure 5. Proceeding from left to right in Figure 5, the potential energy of the ion/molecule reactants initially decreases as they approach each other due to electrostatic interaction. The consequent kinetic energy of relative motion becomes available to surmount the energy required for electron promotion (PE). Thus the reactivity of Ln⁺ ions is expected to decrease with increasing electron promotion energy and become immeasurably small once the kinetic barrier (PE) substantially exceeds the initial energy of the reactants. Thus the reactions of Sm⁺, Dy⁺, Ho⁺, and Er⁺ with CO₂, for which be promoted to a 5d orbital to achieve a d¹s¹ configuration. Apparently such a promotion does not occur, as is evident from the higher reactivity of Lu⁺ compared to other late lanthanide cations (Dy⁺, Ho⁺, Er⁺) that have similar or lower promotion energies (PEs) but are much less reactive.

Large variations in reactivity also have been reported for gas-phase reactions of neutral lanthanide atoms with CO₂, and the reaction energy barrier was found to correlate with the energy required to promote an electron out of the filled 6s subshell.²⁶

In sharp contrast, no correspondence with electron promotion was found in ref 31 and IE(LnS) and D(Ln=S) found in ref 32. In kcal mol⁻¹, taken from ref 9. The promotion energy and accompanying error are taken as the mean and standard deviation of the energy difference between all states in the ground-state manifold transitioning to all possible states in the first excited manifold.²⁶

### TABLE 3: Summary of Available Oxygen and Sulfur Atom Affinities (in Units of kcal mol⁻¹) and Various Electronic Properties for Lanthanide Cations

<table>
<thead>
<tr>
<th>Ln⁺</th>
<th>OA(Ln⁺)</th>
<th>SA(Ln⁺)</th>
<th>Ln⁺ ground-state configuration</th>
<th>Ln⁺ term symbol</th>
<th>Promotion energy (in kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La⁺</td>
<td>206.6 ± 4.3</td>
<td>124.4 ± 2.4</td>
<td>5d²</td>
<td>⁵F₂</td>
<td>4.5 ± 3.0</td>
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<tr>
<td>Ce⁺</td>
<td>203.6 ± 5.9</td>
<td>125 ± 14</td>
<td>⁴F⁵d²</td>
<td>⁴H₀/₂</td>
<td>4.6 ± 5.7</td>
</tr>
<tr>
<td>Pr⁺</td>
<td>189.6 ± 4.3</td>
<td>⁴F⁶s¹</td>
<td>⁹/₁₂ +</td>
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<td>22.3 ± 0.8</td>
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<tr>
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<td>180.8 ± 4.3</td>
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<td>⁹/₁₂</td>
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</tr>
<tr>
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<td>⁹/₁₂</td>
<td>4.1</td>
<td>62.1 ± 5.8</td>
</tr>
<tr>
<td>Sm⁺</td>
<td>139.6 ± 4.3</td>
<td>59 ± 7</td>
<td>⁴F⁶s¹</td>
<td>⁹/₁₂</td>
<td>92.8 ± 5.0</td>
</tr>
<tr>
<td>Eu⁺</td>
<td>93.2 ± 4.3</td>
<td>106.2 ± 13.8</td>
<td>⁴F⁶s¹</td>
<td>⁹/₁₂</td>
<td>0</td>
</tr>
<tr>
<td>Gd⁺</td>
<td>180.0 ± 4.3</td>
<td>106.2 ± 13.8</td>
<td>⁴F⁶s¹</td>
<td>⁹/₁₂</td>
<td>0</td>
</tr>
<tr>
<td>Tb⁺</td>
<td>171.0 ± 5.9</td>
<td>⁴F⁶s¹</td>
<td>(15/2,1/2) +</td>
<td>0</td>
<td>9.3 ± 8.1</td>
</tr>
<tr>
<td>Dy⁺</td>
<td>143.4 ± 5.9</td>
<td>⁴F⁶s¹</td>
<td>(15/2,1/2) +</td>
<td>0</td>
<td>36.0 ± 6.1</td>
</tr>
<tr>
<td>Ho⁺</td>
<td>141.3 ± 4.3</td>
<td>⁴F⁶s¹</td>
<td>(15/2,1/2) +</td>
<td>0</td>
<td>37.8 ± 5.4</td>
</tr>
<tr>
<td>Er⁺</td>
<td>140.3 ± 4.3</td>
<td>⁴F⁶s¹</td>
<td>(15/2,1/2) +</td>
<td>0</td>
<td>34.5 ± 3.1</td>
</tr>
<tr>
<td>Tm⁺</td>
<td>116.6 ± 4.3</td>
<td>⁴F⁶s¹</td>
<td>(7/₂,1/₂) +</td>
<td>0</td>
<td>55.5 ± 7.4</td>
</tr>
<tr>
<td>Yb⁺</td>
<td>88.1 ± 5.9</td>
<td>⁵F⁶s¹</td>
<td>⁸S¹/₂</td>
<td>0</td>
<td>79.4 ± 4.0</td>
</tr>
<tr>
<td>Lu⁺</td>
<td>128.0 ± 4.3</td>
<td>107.2 ± 0.1</td>
<td>⁴F⁶s²</td>
<td>⁸S₀</td>
<td>36.6 ± 3.6</td>
</tr>
</tbody>
</table>

*XA (X = O, S) values were taken on the basis of ΔH_f(X, LnX⁺), ΔH_f(X, Ln⁺), and ΔH_f(X) found in ref 31. SA values were taken on the basis of ΔH_f( Ln⁻) and ΔH_f(S) found in ref 31 and IE(LnS) and D(Ln=S) found in ref 32. In kcal mol⁻¹, taken from ref 9.
O-atom transfer is exothermic (see Figure 4), proceed by CO2 addition because the kinetic barrier (PE) is too high; the exothermicity \((\text{PE})\) increases, viz. \(\text{OA}(\text{Ln}^+\text{X})\) increases. Since \(\Delta H = \text{OA}(\text{X}) - \text{OA}(\text{Ln}^+)\), we can express the physicochemical potential of the \(\text{Ln}^+\) to be oxidized, or the oxophilicity Ox-\(\text{Ln}^+\), as PE = OA(\(\text{Ln}^+\)) for reactions of \(\text{Ln}^+\) with \(\text{N}_2\text{O}\) pointed out that the potential energy surface for removing an oxygen atom from \(\text{N}_2\text{O}\) follows a singlet surface to yield \(\text{N}_2 + \text{O}(1\text{D})\). Thus there is a crossing between the singlet and triplet surfaces of the \(\text{N}_2\text{O}\), and by analogy \(\text{CO}_2\), molecule. The singlet–triplet splitting for O is 1.958 eV, whereas it is only 1.121 eV for S. Because the singlet–triplet splitting is smaller for the sulfur species, the coupling between these two surfaces is energetically more accessible and this could account for the relatively higher reactivity of \(\text{CS}_2\).

3.5. \(\text{CX}_2\) Addition Reactions. Primary \(\text{CX}_2\) addition, reaction 1b, was observed exclusively with \(\text{Sm}^+\), \(\text{Eu}^+\), \(\text{Dy}^+\), \(\text{Ho}^+\), \(\text{Er}^+\), \(\text{Tm}^+\), and \(\text{Yb}^+\) with measured reaction rate coefficients in the range \(5.0 \times 10^{-13} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) to \(2.7 \times 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\). \(\text{CS}_2\) addition also was observed exclusively with the same atomic ions with reaction rate coefficients in the range \(5.3 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) to \(7.4 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\), but also competed with S-atom transfer in the reactions with \(\text{Nd}^+\) and \(\text{Lu}^+\). The \(\text{CS}_2\) addition reactions are about 10 times faster than the \(\text{CO}_2\) addition reactions.

Almost all of the primary \(\text{Ln}^+(\text{CX}_2)\) cations added \(\text{CX}_2\) according to reaction 2 as did the primary \(\text{LnX}^+\) cations greater with \(\text{CS}_2\) than with \(\text{CO}_2\), \(\alpha(\text{CS}_2) = 8.74 \text{Å}^3 > \alpha(\text{CO}_2) = 2.91 \text{Å}^3\), and with \(\text{N}_2\text{O}\) \((\alpha = 3.03 \text{Å}^3, \mu = 0.167 \text{D})\). This translates into an increased availability of chemical activation energy (an enhanced well depth for \(\text{Ln}^+-\text{CS}_2\)) in the reactions with \(\text{CS}_2\) which is likely to account for the higher efficiency of S compared to O transfer that is observed. Indeed, the observed unit efficiency for S-atom abstraction implies that any kinetic barriers to S-atom transfer (PE in Figure 5) lie below the initial energy of the reactants.

An alternative explanation (offered by one of the reviewers) becomes apparent from a comparison of the \(\text{CO}_2\) results with results previously reported for the isoelectronic \(\text{N}_2\text{O}\) molecule. The first observation of a kinetic barrier to reactions of metal ions with \(\text{N}_2\text{O}\) pointed out that the potential energy surface for removing an oxygen atom from \(\text{N}_2\text{O}\) follows a singlet surface to yield \(\text{N}_2 + \text{O}(1\text{D})\). Thus there is a crossing between the singlet and triplet surfaces of the \(\text{N}_2\text{O}\), and by analogy \(\text{CO}_2\), molecule. The singlet–triplet splitting for O is 1.958 eV, whereas it is only 1.121 eV for S. Because the singlet–triplet splitting is smaller for the sulfur species, the coupling between these two surfaces is energetically more accessible and this could account for the relatively higher reactivity of \(\text{CS}_2\).
are expected to proceed in a termolecular fashion with He buffer helium bath at 0.35 Torr proceed by atom transfer or molecule and carbon disulfide in the gas phase at room temperature in a

\[ \text{Ln}^+(\text{CX}_2)_n + \text{CX}_2 \rightarrow \text{Ln}^+(\text{CX}_2)_{n+1} \]  
(2)

\[ \text{LnX}^+(\text{CX}_2)_n + \text{CX}_2 \rightarrow \text{LnX}^+(\text{CX}_2)_{n+1} \]  
(3)

Thus, secondary and higher order CO\(_2\) addition was observed for Ln\(^+\) = Sm\(^+\) (n = 1, 2) and Eu\(^+\) (n = 1) according to reaction 2 and for LnO\(^+\) = LaO\(^+\), CeO\(^+\), PrO\(^+\) (n = 0), GdO\(^+\) (n = 0, 1), TbO\(^+\) (n = 0–3), and LuO\(^+\) (n = 0–4) according to reaction 3. Secondary and higher order CS\(_2\) addition was observed for Ln\(^+\) = Nd\(^+\), Eu\(^+\), Dy\(^+\), Ho\(^+\), Lu\(^+\) (n = 1–3), Sm\(^+\), Tm\(^+\), Yb\(^+\) (n = 1, 2), and Er\(^+\) (n = 1–4) according to reaction 2 and for LnS\(^+\) = LaS\(^+\), NdS\(^+\) (n = 0–2), CeS\(^+\), PrS\(^+\), GdS\(^+\), and TbS\(^+\) (n = 0–3) according to reaction 3. All these addition reactions are expected to proceed in a termolecular fashion with He buffer gas atoms acting as the stabilizing third body.

4. Conclusions

Reactions of atomic lanthanide cations with carbon dioxide and carbon disulfide in the gas phase at room temperature in a helium bath at 0.35 Torr proceed by atom transfer or molecule addition. The kinetics of atom transfer exhibit a periodicity in reaction efficiency and, for O-atom transfer from CO\(_2\), a barrier to reaction that involves the energy required to make available two non-f valence electrons for O-atom bonding (similar to that previously observed with the isoelectronic N\(_2\)O molecule). No such barrier is operative for S-atom transfer from the valence isoelectronic CS\(_2\) molecule in which the strong initial electrostatic interaction between the reagents appears to be sufficient to overcome any intrinsic activation barrier that may be present. Secondary atom transfer does not occur. Molecule addition prevails in the absence of atom transfer and in the further reactions of the ionic products of atom transfer. Up to four molecules were observed to add sequentially to selected atomic cations and five to lanthanum oxide or sulfide cations.

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References and Notes


