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ICP-SIFT/MS study of gas-phase reactions of lanthanide cations with benzene: Room-temperature kinetics and periodicities in reactivity

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ABSTRACT

The gas-phase reactivity of atomic lanthanide cations (excluding Pm^+) has been surveyed systematically with benzene using an Inductively-Coupled Plasma/Selected-Ion Flow Tube (ICP/SIFT) tandem mass spectrometer with an added facility for collisional dissociation of product ions. Observations are reported with La^+, Ce^+, Pr^+, Nd^+, Sm^+, Eu^+, Gd^+, Tb^+, Dy^+, Ho^+, Er^+, Tm^+, Yb^+ and Lu^+ at room temperature (295 ± 2 K) in helium at a total pressure of 0.35 ± 0.02 Torr. All the Ln^+ ions were observed to add benzene exclusively and rapidly with efficiencies $\geq$28%. Sequential addition of C_6H_6 was seen to saturate with the formation of $Ln^+(C_6H_6)_3$. Measured onset energies were high (>33 kcal mol^{-1}) for the dissociation of $La^+C_6H_6$, $Ce^+C_6H_6$, $Pr^+C_6H_6$, $Gd^+C_6H_6$ and $Tb^+C_6H_6$ and low (<20 kcal mol^{-1}) for the dissociation of the remaining $Ln^+C_6H_6$ cations.

The reaction efficiency for the formation of $Ln^+C_6H_6$ and the measured onset of benzene removal from $Ln^+C_6H_6$ by collisional dissociation were seen to correlate with the electron promotion energy required to achieve a two non-f electron configuration in Ln^+. These results are interpreted in terms of schematic triple minimum potential energy profiles in which the electron promotion energy can act as a "gate" for the conversion between an electrostatically bound adduct, an adduct of the sd-hybridized lanthanide cation and one achieved by a C—H bond insertion of Ln^+. The ICP/SIFT results are compared with results of FT/ICR measurements at low pressure.

1. Introduction

The Inductively-Coupled Plasma/Selected Ion Flow Tube (ICP/SIFT) tandem mass spectrometer assembled in our laboratory and described in 2000 [1] has proven to be an extremely versatile and useful means to explore the chemistry initiated by atomic metal cations and to measure their gas-phase reactivity at room temperature [2]. One focus in the use of this instrument has been the systematic measurement of rate coefficients for atom-transfer reactions of all the lanthanide cations, except Pm^+, and all of them generated in the ICP source. Experimental results have been reported for reactions with N_2O [3], O_2 [3], CH_3F [4], CH_3Cl [5], NO [6], D_2O [7], SF_6 [8], CO_2 [9], CS_2 [9], NH_3 [10] and NO_2 [11].

Gas-phase reactivities of isolated lanthanide cations began to be studied already in the late 1980s using Fourier transform mass spectrometry and various ion-beam techniques, together with laser ablation to produce the cations [12–14]. Distinct differences in reaction kinetics, mechanism, and product distributions were observed along the 4f lanthanide row. For example, in their investigations of reactions of Pr^+, Eu^+ and Gd^+ with several hydrocarbons and oxygen-containing molecules, Schilling and Beauchamp [13] surmised that only lanthanide cations possessing at least two non-f valence electrons in their electronic ground state configuration give rise to C—H and C—C bond activation processes. The first systematic study of all the lanthanide cations (except Pm^+) with the same molecule, 1,3,5-tri-tert-butlybenzene, was reported by Yin et al. [15] in 1994 and these authors reported addition, C—H and C—C bond insertion chemistry. Extensive measurements also have been reported for gas phase reactions of the lanthanide cations with various organic, organometallic and inorganic ligands [16–18].

The previous measurements in our laboratory have been restricted to reactions of Ln^+ cations with many small, mainly inorganic, molecules [3–11]. Generally these reactions are bimolecular, bond-breaking and bond-making and exhibit a periodic behavior in reactivity, a correlation of the reactivity with the energy required to promote an f-electron to an s- or d-orbital in the Ln^+, producing a s^1d^1 configuration (referred to as the promotion energy). Reactivity of Ln^+ cations exhibited an Arrhenius-like dependence on this promotion energy [18].

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Here we focus on the measurement of gas-phase interactions of Ln^+ with benzene. There has been a previous brief report of sequential addition of two benzene molecules to most of the lanthanide cations: "the formation of bis(arene)species was verified from Pr^+ to Lu^+ in the case of benzene" [16], but no details or rate measurements were included or referenced. A preliminary report by Leal et al. [19] of results obtained with FT-ICR spectrometers using laser desorption/ionization indicated both bimolecular C—H bond activation products (dehydrogenation) for La^+, Ce^+ and Gd^+ and adduct formation with Pr^+, Nd^+, Sm^+, Eu^+, Tb^+, Dy^+, Ho^+, Er^+, Tm^+, Yb^+ and Lu^+ (rate coefficient measurements were not reported). The related substituted benzene, 1,3,5-tri-tert-butlybenzene, studied by Yin et al. using FT/ICR mass spectrometry [15] showed a dependence of reactivity and product distribution on the electronic 4f to 5d promotion energy of the lanthanide cation. Sandwich complex ions, ML_2^+ with L = 1,3,5-tri-tert-butlybenzene, were observed to be formed exclusively in efficient radiative association reactions with M = Sm^+, Eu^+, Tm^+ and Yb^+ (the four Ln^+ cations with the highest promotion energy), while the remaining lanthanide ions efficiently activated C—H and C—C bonds in the *tert*-butyl substituents to form bimolecular product ions with concomitant elimination of H_2, CH_4 and other neutrals.

Benzene was chosen as a reagent in our study with the intent to explore cation–π interactions characterized largely by electrostatic ion-quadrupole attraction [20] with a view to the occurrence of C—H bond activation leading to dehydrogenation, given the results previously reported by others. In our studies Ln^+ cations were produced in an Inductively-Coupled Plasma (ICP) at atmospheric pressure, injected into a flow tube, and allowed to thermalize in flowing He buffer gas before reacting with added benzene vapor. The buffer gas pressure was held at 0.35 Torr and so is substantially higher than the low operating pressures of FT-ICR measurements. Effective bimolecular reaction rate coefficients were measured in a manner described previously for reactions of other atomic metal cations with C_6H_6 [21] and C_6F_6 [22].

2. Experimental

The experiments were performed with the ICP/SIFT tandem mass spectrometer that has been described in detail previously [1,23]. The atomic ions were generated within an atmospheric-pressure argon plasma at 5500 K fed with a vaporized solution containing the lanthanide salt of interest. 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 Torr and 295 ± 2 K. After experiencing about 10^5 collisions with He atoms, the ions were allowed to react with C_6H_6 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 be down-graded 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 10^5 collisions with He before entry into the reaction region. 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 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 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 semi-logarithmic decay of the reactant ion intensity as a function of added reactant.

The collision-induced dissociation (CID) of sampled $Ln^+(C_6H_6)_n$ product ions was investigated in the manner described previously [23] with Ar as the collision gas. In the implementation of the triple quadrupole mass spectrometer, the sampled ions are assumed to have near-zero translation energy in $q0$ and the collision energy CE is taken to be the potential difference between $q0$ and $q2$. Thresholds for dissociation were obtained from plots of relative ion intensities as a function of CE and these provide crude estimates of binding energy. In our comparative study of the elimination of C_6H_6 from $Ln^+(C_6H_6)$, relative binding energies should be reasonably accurate. Absolute values are less definitive as the dissociation does not proceed under single collision conditions. Center-of-mass (CM) onset energy, OE, is calculated as the *x*-axis intercept of the extrapolated linear portion of the product ion rise in the CID profile.

Standard ICP calibration solutions (Spex Certiprep, Metuchen, NJ) were diluted to about. 10 ppm before injection into the argon plasma; single isotope salts (Nd (143), Sm (152), Gd (160), Dy (164), Er (166), Yb (174)) were obtained from the Oak Ridge National Laboratory. Benzene obtained from Sigma Aldrich (Oakville, Ontario, 99.9%) was introduced into the reaction region of the flow tube as a dilute mixture in helium (10%).

3. Theoretical method

Ion structures and reaction enthalpies were computed for selected reactions of lanthanum cations with benzene. Computations were performed using Gaussian 03 suite of programs [24]. The density functional method denoted as B3LYP consisting of Becke's three-parameter exchange functional [25] combined with the correlation functional of Lee, Yang and Parr was utilized [26]. The D95 basis set was used for H and C and the SDD basis set was used on La centers [27,28]. Computed harmonic vibrational frequencies were utilized un-scaled.

4. Results and discussion

4.1. Observed reactions and measured rate coefficients

The reactions of 14 lanthanide cations were investigated with C_6H_6. Both the primary and higher-order chemistries were monitored. All the Ln^+ ions were observed to react exclusively by sequential addition of C_6H_6 that appeared to saturate with the formation of $Ln^+(C_6H_6)_3$ with the buffer He gas acting as the stabilizing third body. Ion profiles measured for the reactions of La^+, Gd^+, Yb^+ and Lu^+ are shown in Fig. 1. Effective bimolecular rate coefficients measured for the first addition of C_6H_6, reaction (1), at 0.35 ± 0.01 Torr and 295 ± 2 K are summarized in Table 1. The rate coefficients were determined from the initial linear decays; the curvature in the measured decays at higher flows is due to the occurrence of the reverse of the addition reaction (1).

$$Ln^+ + C_6H_6 + He \rightarrow Ln^+(C_6H_6) + He \quad (1)$$

The primary addition reactions generally were quite fast proceeding at more than 28% of the collision rate (for Tm^+). Rate coefficients were not measured as a function of helium pressure; it was not possible to vary this pressure over a significant range.