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Ligation kinetics as a probe for relativistic effects in ion chemistry: Gas-phase ligation of Ni^+, Pd^+ and Pt^+ at room temperature

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Dedicated to Jose Riveros in recognition of his outstanding career in gas-phase ion chemistry.

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ABSTRACT

The kinetics of ammonia ligation for the three d^9 transition metal cations Ni^+, Pd^+ and Pt^+ were measured in an attempt to assess the role of relativistic effects in these chemical reactions. Measurements were performed at room temperature in helium bath gas at 0.35 Torr using an Inductively-Coupled Plasma/Selected-Ion Flow Tube (ICP/SIFT) tandem mass spectrometer. The atomic cations are produced at ca. 5500 K in an ICP source and are allowed to decay radiatively and to thermalize by collisions with argon and helium atoms prior to reaction. Rate coefficients are reported for ammonia and pyridine addition, the only reaction channel that was observed with these cations. A strong enhancement in the rate of addition of NH_3 to Pt^+ was observed for these cations similar to the enhancement recently reported for Au^+ in the adjacent coinage metal cation period. We attribute this rate enhancement to the enhancement in the Pt^+-NH_3 binding energy expected from relativistic effects. Comparisons are made with the periodic trends in the rates of ligation of the d^9 atomic metal cations that we also measured with pyridine and that we reported previously with O_2, D_2O, CS_2 and SF_6. Rate enhancement with Pt^+ was observed for five of the six ligands that were investigated in total and this was attributed to the relativistic stability enhancement of the ligated Pt^+. Computational studies were performed with Density Functional Theory (DFT) for M^+L, with M = Ni, Pd and Pt and L = NH_3, that predict an increase in the binding energy D_e and a decrease in equilibrium bond separation r_e in going from Pd^+L to Pt^+L when relativistic effects are included.

1. Introduction

Very recently we reported the use of kinetic measurements to probe relativistic effects in chemical reactions, specifically in the ligation of the three (d^{10}) transition metal coinage cations Cu^+, Ag^+ and Au^+ [1]. A strong rate enhancement was observed going down the period for the ligation of Au^+ with ammonia and several other small molecular ligands that could be attributed to relativistic effects that enhance the stability of the ligated Au^+ that is formed, according to density functional computations. Here we report an extension of this approach to the adjacent d^9 transition metal cations Ni^+, Pd^+ and Pt^+.

Relativistic effects in gas-phase ion chemistry are now well established and have been reviewed [2] in the context of relativistic effects in chemistry generally [3,4]. Structural properties, thermochemical data and reactivity patterns were discussed; much focus was directed to the ligation chemistry of Au^+ ($5d^{10}6s^0$). The reactivities of the atomic cations Ni^+, Pd^+ and Pt^+ were addressed recently (2013) in the context of possible relativistic effects for reactions with H_2O and H_2S with quantum chemical calculations and comparisons with a few available experimental observations, although the emphasis was on differences in the reactions of the bare metal cations Pd^+ and Pt^+ and their oxides and sulfides, for both low and high-spin states [5].

In our very recent study of the rates of ligation of the atomic coinage metal cations Cu^+, Ag^+ and Au^+ we proposed that the magnitude of the rate coefficient of ligation of an atomic ion in the gas phase is sensitive to the binding energy of the adduct ion that is formed and therefore to the presence of relativistic stabilization. In the gas phase (in a helium bath, for example), the gas-phase formation of ligated atomic cations M^+L (where L is the ligand) occurs via two steps: formation of an encounter complex and its subsequent collisional stabilization.

$$M^+ + L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (M^+ - L)^*$$

$$(M^+ - L)^* + He \xrightarrow{k_s} M^+ - L + He$$

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The third order rate constant for the overall ligation $k = k_1 k_s / k_{-1}$ can be derived when applying the steady-state assumption to the encounter complex $(M^+{-}L)^*$. For the unimolecular dissociation of the encounter complex back to reactants, k_{-1} is a frequency or the inverse of the lifetime, $\tau_1{}^{-1}$. Classical statistical theories predict that the lifetime for unimolecular decomposition τ is related to the binding energy (well depth) D of the encounter complex according to $\tau = \tau_0\ ((D + rRT)/rRT)^{s-1}$ [6]. Here τ_0 is the collision lifetime (the inverse of the vibrational frequency along the reaction coordinate), r is the number of energy square terms contributing to the internal energy of the molecule (r = 3 for non-linear and 2.5 for linear molecules when contributions of vibrational degrees of freedom are ignored), and s is the number of coupled harmonic oscillators. So the rate coefficient for ligation k is related to the binding energy. An enhanced stability due to relativistic effects will therefore be manifested by an enhanced rate coefficient for ligation; when comparisons are made down a Group of atomic metal cations attaching to the same ligand, primarily the binding energy, and not the degrees of freedom or the number of energy square terms, will be decisive and trend setting. Both k_1 and k_s (k_c) decrease with increasing mass of the cation, and only slightly, less than 10% going from Ni^+ to Pt^+ ($k_s = P\,k_c$ where k_c is the collision rate coefficient and P is the probability of stabilization which is assumed to be constant).

In the study reported here, we have probed the ligation of the Group 10 (d^9) cations Ni^+, Pd^+ and Pt^+ first with new rate coefficient measurements using ammonia as the ligand. Computations using Density Functional Theory (DFT) using relativistic Effective Core Potentials (ECPs) were performed to predict the binding energies with this ligand and these are correlated with our measured rate coefficients. Also, we have collected results obtained in our laboratory under similar experimental conditions that we reported previously for the kinetics of ligation of Ni^+, Pd^+ and Pt^+ with other ligands, selecting only those reactions in which ligation was the exclusive reaction channel. These ligands include O_2 [7], D_2O [8], CS_2 [9], SF_6 [10] and pyridine. The rate coefficients for the ligation with pyridine are reported here for the first time. Correlations are explored for H_2O and O_2 for which some information is available for computed relativistic or measured binding energies with Ni^+, Pd^+ and Pt^+.

2. Experimental procedures

The experimental results reported here were obtained with the ICP/SIFT tandem mass spectrometer that has been described in detail previously [11–14]. The atomic ions were generated within an atmospheric pressure argon plasma at 5500 K fed with a vapourized solution containing the metal salt. Solutions containing the metal salt of interest with concentration of ca. 5 μg L^{-1} were peristaltically pumped via a nebulizer into the plasma. The nebulizer flow was adjusted to maximize the ion signal detected downstream of the flow tube. 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 between 5 and 20 ppm to achieve suitable intensity of the resultant ion beam. A stabilizing agent was usually added to each solution in order to prevent precipitation: KOH for base-stabilized salts, HNO_3 or HCl for acid-stabilized salts.

Atomic ions emerge from the ICP at a nominal plasma ion temperature of 5500 K with the corresponding Boltzmann distributions. After extraction from the ICP, the plasma ions may experience electronic-state relaxations via both radiative decay and collisional energy transfer. The latter may occur by collisions with argon, as the extracted plasma cools upon sampling, and with helium in the flow tube (ca. 4×10^5 collisions with helium) prior to the reaction region. However, the exact extent of electronic relaxation is uncertain. Clues to the presence of excited electronic states of the atomic ions in the reaction region can be found in the product ions observed and in the shape of the semi-logarithmic decay of the reacting atomic ion upon addition of neutral reactants. Curvature will appear in the measured atomic-ion decay when the ground state and excited state react at different rates even when they give the same product ions. An excited-state effect cannot be seen when the products and reaction rates are the same for both the ground and excited states, but in this case the measured atomic-ion decay defines the ground-state kinetics. There were no indications of excited state effects in the measurements reported here. The many collisions experienced by the atomic cations with the quite polarizable argon atoms as they emerge from the ICP and the ca. 4×10^5 collisions with helium atoms in the flow tube (the helium buffer gas pressure was 0.35 ± 0.01 Torr) appear to be sufficient to thermalize the excited states and to ensure that the atomic ions reach a translational temperature equal to the tube temperature of 295 ± 2 K prior to entering the reaction region.

Reactions of Ni^+, Pd^+ and Pt^+ were investigated with NH_3 at a helium buffer gas pressure of 0.35 ± 0.01 Torr and temperature of 295 ± 2 K. Reaction rate coefficients were determined in the usual manner using pseudo first-order kinetics.

Highly pure NH_3 gas was obtained commercially (Semiconductor Grade 99.999%, Matheson/Linde Canada) and introduced into the reaction region of the SIFT as a dilute (15%) mixture in helium. Reactions of Ni^+, Pd^+ and Pt^+ also were measured with pyridine. The pyridine reagent for these reactions was obtained from Sigma–Aldrich (Oakville, ON, Canada) with 99.8% purity. Pyridine was mixed with helium by filling the reservoir system with pyridine vapour up to approximately 18 Torr and adding helium to a final mixture pressure of 760 Torr. Due to the larger than usual uncertainty in determining the concentration of the pyridine mixture, the rate coefficients reported here for pyridine have been assigned an uncertainty of ±50% rather than the usual ±30%. The low vapour pressure of pyridine restricted the pyridine flow range to a typical maximum flow rate of $(0.5–1.0) \times 10^{18}$ molecules s^{-1} [15].

3. Computational procedures

The adducts of Ni^+, Pd^+ and Pt^+ with ammonia were examined with DFT using relativistic Effective Core Potentials (ECPs). We used the Gaussian 03 suite of programs [16] with the B3LYP DFT method [17,18] and the SDD basis set [19] on the metals centers and the D95 basis set on hydrogen and nitrogen [20]. The SDD basis set employs a relativistically corrected effective core potential on the three metal centers studied. The Effective Core Potential (ECP) spans 60 electrons for Pt, 28 for Pd and 10 for Ni.

Stationary points for the ammonia complexes were studied starting from fully flexible C1 symmetry initial geometries. Upon geometry optimization the ammonia clusters fell into C3v symmetry structures.

An attempt also was made to assess the magnitude of the relativistic effect on bond contraction and bond strengthening. Comparing relativistic and non-relativistic effects across a broad range in atomic numbers is not a simple task; there is the matter of finding or creating two basis sets that span the three transition metal periods (and for the case of the third period, incorporates f electrons) where one basis set includes relativistic effects and the other neglects relativistic effects. Inclusion of the relativistic effect can be performed by one of several means, and is generally achieved by either incorporation of the RE in the core pseudo potential or by using a basis set formulated using the Douglas-Kroll method.