ARTICLE IN PRESS

International Journal of Mass Spectrometry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Full length article

Ligation kinetics as a probe for relativistic effects in ion chemistry: Gas-phase ligation of late atomic transition metal cations with OCS and CH_3Cl at room temperature☆

Voislav Blagojevic, Vitali V. Lavrov, 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

ARTICLE INFO

Keywords:
Ligation of Zn^+
Cd^+ and Hg^+
Relativistic effects
Periodic trends in ion kinetics
Carbonyl sulfide
Methyl chloride
ICP/SIFT technique

ABSTRACT

The kinetics of ligation with OCS and CH_3Cl were measured to assess the role of relativistic effects in these chemical reactions with the three $d^{10}s^1$ transition metal cations Zn^+, Cd^+ and Hg^+ as well as the three d^{10} coinage cations Cu^+, Ag^+ and Au^+ and the three d^9 cations Ni^+, Pd^+ and Pt^+. Measurements were performed at 295 K in helium bath gas at 0.35 Torr using an Inductively-Coupled Plasma/Selected-Ion Flow Tube (ICP/SIFT) tandem mass spectrometer. Rate coefficients are reported for OCS and CH_3Cl ligation of Zn^+, Cd^+ and Hg^+ and for OCS ligation with the adjacent d^{10} coinage metal cations. A strong rate enhancement is observed for Hg^+ and Au^+, similar to that we have reported recently for Pt^+ and Au^+ reacting with other ligands. We attribute this rate enhancement to the enhancement in the Hg^+-OCS, Au^+-OCS and Hg^+-CH_3Cl binding energies expected from relativistic effects. Comparisons are made with the measured rates of ligation of the adjacent main group $d^{10}s^2$ atomic metal cations Ga^+, In^+ and Tl^+ with OCS and CH_3Cl and which don't exhibit a relativistic effect. Further comparisons are made with the rates of ligation of Zn^+, Cd^+ and Hg^+ with CH_4, CH_3F, and D_2O that we reported previously and these also exhibit relativistic effects with Hg^+. The relativistic effect is obfuscated by electron transfer to Hg^+ with NO, NO_2, CS_2, NH_3, C_6H_6, C_6F_6 and C_5H_5N as we measured previously. Ligation with O_2, CO, CO_2, N_2O and SF_6, is immeasurably slow, too slow to exhibit a relativistic effect with Hg^+ under our experimental conditions. Furthermore, the additional new measurements with OCS and CH_3Cl provide examples of the occurrence of bimolecular channels in competition with ligation, such as S atom transfer with OCS and H_2 or HCl elimination with CH_3Cl. Finally, we compare the maximum computed relativistic contraction of the 6s shell reported for Au with the occurrence of a maximum in the rate coefficient of ligation for the third-row transition metal cations Pt^+, Au^+ and Hg^+.

1. Introduction

The interplay between the enhanced velocity and mass of electrons in heavy atoms or atomic ions and the size of their orbitals gives rise to relativistic effects in the chemistry of these atoms or ions [1–7]. For atoms, relativistic effects have been assessed across the periodic table with non-relativistic and relativistic calculations in terms of 6s-shell radii [5]. For atomic ions, a combined approach of theory and experiment has been employed to probe relativistic effects primarily with a focus on Au^+, largely because of the maximum revealed for Au in the relativistic effect in atoms [5]. Both theory [8,9] and experiment [4,10] have been used to probe relativistic effects in the binding energies of ligated gold cations, Au^+-L, the latter with qualitative bracketing measurements of ligand binding energies for eleven different small inorganic and organic ligands [10]. Very recently, we reported a new experimental probe for relativistic effect that involves the measurement of specific reaction rates of ligation of atomic cations. We performed absolute kinetic measurements for ammonia ligation of the three (d^{10}) transition metal coinage cations Cu^+, Ag^+ and Au^+ [11] and the three d^9 cations Ni^+, Pd^+ and Pt^+ [12]. A strong rate enhancement was observed going down the period for the ligation of both Au^+ and Pt^+ that could be attributed to relativistic effects that enhance the stability of the ligated cations that are formed. The relativistic effect for the adjacent $d^{10}s^1$ cations could not be assessed in a similar fashion since the ligation of Hg^+ by ammonia (IE = 10.1 eV [13]) is superceded by electron transfer [14]. In fact, the relatively high electron

---

☆ Dedicated to Terry McMahon in recognition of his outstanding career in gas-phase ion chemistry.

* Corresponding author.

E-mail address: dkbohme@yorku.ca (D.K. Bohme).

http://dx.doi.org/10.1016/j.ijms.2017.06.008
Received 11 February 2017; Received in revised form 1 June 2017; Accepted 12 June 2017

Please cite this article as: Blagojevic, V., International Journal of Mass Spectrometry (2017), http://dx.doi.org/10.1016/j.ijms.2017.06.008

recombination energy of Hg^+ (RE = 10.44 eV [13]) prevents its ligation with a large number of ligands due to the occurrence of electron transfer, as we have reported previously [14]. Hence, in the study reported here, we switched from ammonia to the higher ionization ligands OCS (IE = 11.2 eV [13]) and CH_3Cl (IE = 11.4 eV [13]), and surveyed the ligation kinetics for the three $d^{10}s^1$ transition metal cations Zn^+, Cd^+ and Hg^+ as well as the three (d^{10}) transition metal coinage cations Cu^+, Ag^+ and Au^+ and the three d^9 cations Ni^+, Pd^+ and Pt^+. Furthermore, we also reported previously the ligation kinetics for three other high ionization energy ligands, D_2O [15] (IE = 12.6 eV [13]), CH_4 [16] (IE = 12.5 eV [13]) and CH_3F [17] (IE = 12.4 eV [13]). We also include these in a more extended assessment of the operation of relativistic effects in the ligation of late atomic transition metal cations.

In our earliest exploration of the relativistic effects in ion/molecule reactions [11], we postulated that the magnitude of the rate coefficient of ligation of the atomic coinage metal cations in the gas phase responds to the binding energy of the adduct ion that is formed and therefore to the presence of relativistic stabilization. Under our gas phase conditions (in a helium bath at room temperature), the 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.

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

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

The third order rate constant for the overall ligation $k = k_1k_s/k_{-1}$ can be derived when applying the steady-state assumption to the encounter complex $(M^+\text{-}L)^*$. 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 $\tau = \tau_0\ ((D + rRT)/rRT)^{s-1}$ [18]. Here τ_0 is the collision lifetime (the inverse of the vibrational frequency along the reaction coordinate), r is the number of rotaional 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 attached 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 decrease with increasing mass of the cation, albeit slightly, not more than about 15% 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 $d^{10}s^1$ cations Zn^+, Cd^+ and Hg^+ with the new rate coefficient measurements using OCS and CH_3Cl as the ligand and compared these with similar kinetics measurements for adjacent d^9 (Ni^+, Pd^+ and Pt^+) and d^{10} (Cu^+, Ag^+, Au^+) atomic cations, as well as the adjacent closed shell $d^{10}s^2$ (Ga^+, In^+ and Tl^+) main group atomic cations for which no relativistic effect is expected. We collect results obtained previously in our laboratory under similar experimental conditions for the kinetics of ligation of Zn^+, Cd^+ and Hg^+ with other ligands, selecting only those reactions in which ligation was the exclusive reaction channel with *all three* cations, *viz.* D_2O [15], CH_4 [16] and CH_3F [17]. Finally, we compare the maximum computed relativistic contraction of the 6 s shell reported for Au with the occurrence of a maximum in the rate coefficient of ligation for the third-row transition metal cations Pt^+, Au^+ and Hg^+ with O_2 [19], D_2O [15], N_2O [20], OCS, CH_4 [16] and SF_6 [21].

2. Experimental procedures

The experimental results reported here were obtained with the ICP/SIFT tandem mass spectrometer that has been described in detail previously [22–25]. The atomic ions were generated within an atmospheric pressure argon plasma at 5500 K fed with a vaporized solution containing the metal salt. Solutions containing the metal salt of interest, with a 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. Indeed, excited state effects were not expected for Zn^+, Cd^+ and Hg^+ for which we calculated a 100% population at 5500 K of the lowest electronic states of these ions [19]. 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 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. The only indication of the presence of excited states for the d^9, d^{10} and $d^{10}s^1$ metal cations was the Pt^+ bimolecular reaction with N_2O [20], which showed enhanced reactivity for the excited spin state. The population of the excited state was experimentally estimated to be 25%, consistent with the calculated population at 5500 K.

Reactions of Ni^+, Pd^+, Pt^+, Cu^+, Ag^+ Au^+, Zn^+, Cd^+ and Hg^+, Ga^+, In^+ and Tl^+ were investigated with OCS and CH_3Cl (Matheson Gas products, > 98.0%) 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.

3. Results and discussion

3.1. Reactions with OCS

Table 1 provides a summary of the ion products observed, along with the measured rate coefficients, for the reactions of OCS with the d^9 (Ni^+, Pd^+, Pt^+), the d^{10} (Cu^+, Ag^+, Au^+) and the $d^{10}s^1$ (Zn^+, Cd^+, Hg^+) transition metal cations, and the $d^{10}s^2$ main group cations Ga^+, In^+ and Tl^+.