The High-Pressure Segmented Quadrupole Collision Cell (HP-SQCC) as an Ion Molecule Reactor

Yuzhu Guo and K.W. Michael Siu

Department of Chemistry and Centre for Research in Mass Spectrometry, York University, Toronto, Ontario, Canada

Vladimir I. Baranov

MDS SCIEX, Concord, Ontario, Canada

A high-pressure 20-segment quadrupole collision cell (HP-SQCC), which replaces a collision cell in a modified triple-quadrupole mass spectrometer is investigated in this work as an ion-molecule reactor with an inherent heat source. The highest working pressure achievable is 20 mTorr. The 20 quadrupole segments permit superimposition of linear axial electric field over the conventional quadrupole field in the radial direction. The axial and radial fields are employed to control ion temperature. Heat is transferred to the reactants through ion frictional heating. The HP-SQCC utilizes a combination of several physicochemical phenomena and an attempt is made to examine a range of ion-molecule reactions. Due to a sufficiently large number of reactive collisions, the reactor is used to promote sequential exothermic ion-molecule reactions. To characterize the performance of the HP-SQCC, the various ion-molecule reactions between the fragment ions of ferrocene (Cp_2Fe), cobaltocene (Cp_2Co) and nitrogen, oxygen, water and carbon monoxide are investigated. (*J Am Soc Mass Spectrom* 2005, 16, 957–966) © 2005 American Society for Mass Spectrometry

Ion-molecule reactions have captured the fascination of mass spectrometrists for a number of decades and have been probed using a variety of instrumentation, including Fourier-transform ion cyclotron resonance spectrometry, ion-trap mass spectrometry, triple-quadrupole mass spectrometry and the selected-ion flow tube technique [1]. The conventional triple-quadrupole mass spectrometer is a less than perfect instrument for an examination of ion-molecule reactions due to the relatively low pressure achievable in its second quadrupole (Q_2), which restricts the number of ion-molecule collisions, and to the limited control of ion energy within Q_2 . Nevertheless, reactions that lead to novel products have been discovered; one such reaction is the ligand-exchange reaction between $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ and water to give $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ and acetonitrile [2]. This was the first observation of $[\text{Pb}(\text{H}_2\text{O})]^{2+}$; Pb^{2+} had previously been described as to be among “a select group of doubly charged metal ions that will not form stable complexes in the gas phase with water” [3].

Here we report the first ion-molecule reaction results obtained on a high-pressure 20-segment quadrupole collision cell (HP-SQCC) that functions as the Q_2 in a modified triple-quadrupole mass spectrometer. The

highest working pressure achievable is 20 mTorr with neon, about 4 times higher than that achievable on a standard triple-quadrupole instrument. The 20 quadrupole segments permit superimposition of an axial electric field, typically linear, over the conventional quadrupole field in the radial direction [4–6]. The HP-SQCC was originally developed for ion-mobility measurements [5, 7], where the goal is to maintain the drift field low enough that the ion temperature is not increased significantly. In this study, we are exploring the use of the HP-SQCC as an efficient apparatus for utilizing ion-molecule reactions as an analytical method. The axial and radial fields are employed to control the ion temperature.

To characterize the performance of the HP-SQCC, we have elected to use as probes the various ion-molecule reactions between the fragment ions of ferrocene (Cp_2Fe) as well as cobaltocene (Cp_2Co) and neutrals such as nitrogen, oxygen, water and carbon monoxide. These systems have been much studied [8–13] and will serve well as probes for evaluating the HP-SQCC.

Experimental

A high-pressure 20-segment quadrupole collision cell (HP-SQCC) was used in this work as an ion molecule reactor, which was installed on a PE SCIEX API 365 triple quadrupole mass spectrometer (Concord, Canada), re-

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Address reprint requests to Vladimir I. Baranov, 71 Four Valley Drive, Concord, Ontario, L4K 4V8, Canada. E-mail: vladimir.baranov@sciex.com.

Figure 1. Schematics representation of the experimental setup: Q_0 : RF-only ion guide (-7V normally); RO_1 and RO_3 : DC offset of quadrupole mass analyzers (normally $RO_1 = -8.4\text{ V}$, $RO_3 = U_{20} - 5\text{V}$ for MS/MS scan); IQ_1 , IQ_2 and IQ_3 : electrostatic lenses ($IQ_1 = -7.5\text{V}$, $IQ_2 = -27\text{V}$ and $IQ_3 = U_{20} - 5\text{V}$); IL_2 , IL_3 : additional HP-SQCC enclosure lenses ($IL_2 = -7\text{V}$; $IL_3 = U_{20} - 5\text{V}$); ST : short RF-only prefilter (-7V); E_{lab} : ion energy defined in lab frame; RO_2 : DC offset of HP-SQCC (-7V); ΔU : DC potential between the first and last segments equally distributed along 20 segments; U_1 , U_{20} : DC offset of the first and last segment ($U_1 = RO_2 = -7\text{V}$; $U_{20} = U_1 - \Delta U$).

placing the original Q_2 collision cell (see Figure 1). The radio-frequency (RF-only) segmented quadrupole has been described elsewhere [5, 7]. Briefly, the HP-SQCC was enclosed by two extra lenses, IL_2 and IL_3 , and could be pressurized up to 20 mTorr with Ne. An additional Leybold TW250 turbo pump (Concord, Germany) was employed to evacuate the main vacuum chamber to preserve optimum operational pressure in the Q_3 region. The reagent gas was directly introduced into the cell through a high-vacuum needle valve. The pressure inside the HP-SQCC was measured directly using an MKS Baratron 627B absolute pressure transducer (Wilmington, MA), with a stated accuracy of 0.25%. The reagent gas was premixed in a home-built gas mixer.

The RF-only quadrupole offset was set at -7 V . Using a potential divider, an axial drift field, $\Delta U = U_1 - U_{20}$, was applied axially across the reaction cell (U_1 was set equal to RO_2). A standard API 365 collision cell does not have a drift field nor the lenses IL_2 and IL_3 that bracket the collision cell; IQ_3 and RO_3 (the Q_3 rod offset voltage) are set normally attractive with respect to the collision cell. In the present modified version, IL_3 , IQ_3 and RO_3 were all referenced to the potential of the last HP-SQCC segment, U_{20} to keep field the same after ions leave the collision cell. The DC offset on the first segment, U_1 , was equal to the RO_2 (normally -7V) on a standard instrument. A DC power supply from Spectrum Solutions Inc. (Russellton, PA) was used to provide offset voltages for IL_2 and IL_3 . A Kepco Power Supply (Flushing, NY) supplies the floating ΔU .

As in a standard instrument, each segment of the HP-SQCC was capacitively coupled to Q_3 . The quadrupole field was decoupled from the axial field in this configuration and assured high ion transmission because of its strong focusing effect [5, 7].

Ion-molecule reactions were monitored in the product ion scan mode. Q_1 was set to mass-select the reagent ion for reaction in the HP-SQCC. The initial energy of the reagent ion was kept as low as possible by adjusting

the E_{lab} , defined as $Q_0 - U_1$, to 0 V. Q_3 was used to monitor the unreacted precursor and all product ions. The HP-SQCC could be operated as a standard collision cell by assigning appropriate voltages on IL_2 and IL_3 (equal to IQ_2 and IQ_3 , respectively), and setting $\Delta U = 0$.

The translational energy for ions exiting HP-SQCC was estimated by biasing Q_3 offset relative to the last segment U_{20} offset. If Q_3 offset voltage (RO_3) is higher than that of U_{20} , a barrier is formed between Q_3 and U_{20} . Only ions with translational energy above the barrier can be detected downstream by CEM. The barrier height versus ion current diagram (stopping curve) was used to evaluate ions' translational energy and its distribution.

Materials

Ferrocene and cobaltocene (Cp_2Fe and Cp_2Co) were purchased from Sigma-Aldrich (St. Louis, MO). One mM stock solution of these compounds were prepared by dissolving the required amounts of solid in methanol. Working solutions were 100 μM in 1/1 methanol/acetonitrile. Sample solutions were electrosprayed at a flow rate of 2 $\mu\text{L}/\text{min}$. Ultra High-Purity neon was purchased from Praxair (Danbury, CT). High-purity CO was purchased from BOC Canada (Mississauga, Canada).

Results and Discussion

Influence of the RF Field on the Ion Energy

The average the radial ion energy E_r in the presence of the RF field can be expressed as follows [14, 15]:

$$E_x = \frac{m\omega^2 x^2}{8} v_{21}^2(a, q) + \frac{m}{4\gamma_1^2} v_{22}^2(a, q),$$

$$E_y = \frac{m\omega^2 y^2}{8} v_{21}^2(-a, -q) + \frac{m}{4\gamma_1^2} v_{22}^2(-a, -q), \quad (1)$$

$$E_r = E_x + E_y.$$

Here, $r^2 = x^2 + y^2$ represents radial location of an ion in

the RF driven quadrupole field, which is a combination of two terms: spatial (U) and periodic (V) trapping potentials. The dimensionless parameters $\frac{4eU}{m\omega^2 r_0^2} = a$, $\frac{2eV}{m\omega^2 r_0^2} = q$ were also introduced, where r_0 is the electrode separation (inscribed radius), Ω is the main trapping RF angular frequency for an ion with mass m and charge e . The most probable ion thermal speed $\frac{1}{\gamma_\perp}$ is related to the translational kinetic temperature $T_\perp$ in the radial direction as follows:

$$\gamma_\perp = \frac{1}{\sqrt{2RT_\perp}}; \quad R = k_B/m. \quad (2)$$

Here, k_B is Boltzmann's constant. Two dimensionless parameters $v_{21}^2(a, q)$ and $v_{22}^2(a, q)$ depend only on the field properties and their values were tabulated in [14, 15].

In our configuration of the experimental setup (see Figure 1), the HP-SQCC is capacitively coupled to Q_3 , which divides the RF voltage by a factor 1.75, effectively placing the ion selected by Q_3 ($a = 0.236994$, $q = 0.705996$) into "the RF-only" ion guide stability condition ($a = 0$, $q = 0.4$). In this case, eq 1 can be simplified to:

$$E_r = \frac{m\omega^2 r_i^2}{8} v_{21}^2(0, q) + \frac{m}{2\gamma_\perp^2} v_{22}^2(0, q), \quad (3)$$

because $v_{21}^2(0, q) = v_{21}^2(0, -q)$ and $v_{22}^2(0, q) = v_{22}^2(0, -q)$. Let us consider the iron cyclopentadienyl ion's (CpFe^+ , $m/z = 121$) reaction with CO. As was observed previously [16, 17] and confirmed in this work, CpFe^+ reacts with CO sequentially:

Under typical conditions of our experiment, dependence of the averaged radial ion energy versus its position (r_0, q) in the RF field is presented in Figure 2. Highest averaged radial ion energy is observed in vicinity of the stability boundaries [4] and close to r_0 . Assuming that Q_3 is adjusted to pass the third CO cluster, $\text{CpFe}(\text{CO})_3^+$, in the HP-SQCC the stability parameters for this ion are $a = 0$, $q = 0.4$. Simultaneously, the precursor ion, the first and the second clusters are under the conditions of $q = 0.678$, 0.55, and 0.463, respectively ($a = 0$ for all ions in Q_2). Because of sequential character of this ion molecule reaction, all ions should be considered, not only immediate precursor. Collisions with reaction/collision gas (reactive as well as non-reactive collisions) lead to some energy transfer between the axial and radial translational degrees of freedom [18]. It is expected that collisions

Figure 2. (a) Average radial ion energy in the quadrupole RF field versus q parameter and radial position r/r_0 . n is the number of CO molecules in the $\text{CpFe}(\text{CO})_n^+$ cluster. The following parameters were used in the calculations: $\Omega = 5.1$ Mrad/s, $\frac{1}{\gamma_\perp} = 828.9$ m/s and $r_0 = 4.1$ mm. The overall structure for the dependence of the ion radial energy from the q parameter is somewhat expected: the field contribution increases with increasing distance from the quadrupole axis and increasing q value. (b) Average radial ion energy as a function of the ion radial position in the HP-SQCC quadrupole field for simultaneously present products in Reaction 4. Q_3 is adjusted to pass the third cluster.

should result in a collapse of the ion beam around the cell's axis [19, 20]. In this case, the potential energy portion of the average radial ion energy ($\frac{m\omega^2 r_i^2}{8} v_{21}^2(0, q)$, see eq 3) is negligible. However, the kinetic energy portion ($\frac{m}{2\gamma_\perp^2} v_{22}^2(0, q)$) will not diminish. As can be seen in Figure 2b, in the vicinity of the central axis, where the strength of the RF field is minimal, the RF field contribution to the average energy is also minimal. In the presence of collisions, the radial and axial degrees of freedom cannot be considered as independent. Under usual experimental conditions, the initial axial translational energy is higher than the radial one due to the collimation of the ion beam in Q_0 . However, the temperatures of all translational degrees of freedom might be the same. Collisions with a target gas lead initially to energy transfer from the axial to the radial direction that follows by thermal equilibration. After thermal

equilibration the RF field's contribution to ion frictional heating is equally distributed among all translational degrees of freedom.

The axial drift field ΔU results in some increase of the ion beam's cross-section (due to the collisional energy transfer from axial to radial direction) as well as in increase of the ion axial temperature, thus contributing also to both components of the radial ion energy through collisions with target gas. Therefore, the axial field's contribution to the enthalpy of the ion-molecule reaction is direct as well as indirect by increase of the RF-field input.

Influence of the Axial Drift Field on the Ion Energy

The axial field affects ion-molecule reactions through change of the reaction time and contribution to the enthalpy of reaction. The collisions between the ion and the neutrals have been viewed as a "slow" heating event [21]. The effects of an axial drift field in a segmented quadrupole have been described in detail [22]. The residence time of the ions under a given field strength within the low-field limit are described by the ions' mobilities that are related to the ions' orientation-averaged collision cross-sections [23]. Collisions limit the drift velocities and direct some of the drift energy into heat contributing to the enthalpy of reaction. The frictional ion heating rate Q_i is:

$$Q_i = n\mu\nu v_D^2 \quad (5)$$

where n is the ion number density, μ is the reduced mass, ν is the collisional frequency, and v_D is the ion drift velocity. If thermodynamic equilibrium is reached with the gas of Maxwellian particles, the frictional ion heating rate is equal to ion cooling rate [24]:

$$Q = 3k_B \frac{nm}{m + m_n} \cdot (T_n - T) \quad (6)$$

where m_n is the collision/reaction gas mass and T_n is its temperature. In this case:

$$3k_B(T_n - T) = -m_n v_D^2 \quad (7)$$

Because the drift velocity is proportional to $\Delta U/L$ (L is the HP-SQCC length), the temperature difference is proportional to $(\Delta U/L)^2$. A simple estimation reveals that for a field of 0.5 V/cm, the ion temperature could reach several thousand degrees, which might significantly contribute to the enthalpy of the ion-molecule reaction or can lead to thermal dissociation of the drifting ions. However, drift velocity is inversely proportional to the collision/reaction gas number density. Thermodynamic equilibrium can be reached only under certain experimental conditions; the unfavorable combination of short ion residence time for high axial drift

Figure 3. Thermal dissociation of the CpCo^+ ion due to frictional ion heating: dependence of normalized ion intensities versus drift field, ΔU , and Ne collision gas pressure. Signal normalization was conducted on the sum of all ion intensities. Water adducts were formed from residual water vapor as a result of association reaction. The CpCo^+ ion was mass-selected by Q_1 .

fields and low gas number density reduces frictional ion heating. Therefore, one should expect that the efficiency of thermal dissociation should be low for low gas pressure, it should increase under intermediate pressures and should decrease again for high pressure. This trend was observed experimentally in the case of CpCo^+ ions colliding with Ne in the presence of the drift field (see Figure 3). Two dissociation channels are apparent:

These products are detected under all three Ne pressures (2.1, 5.5 and 19.6 mTorr). However, the most efficient dissociations are observed around 5.5 mTorr where the ion cooling rate is not sufficient to prevent dissociation and the ion residence time is not sufficiently short to reduce resultant heating. In this experiment, Q_1 was adjusted for CpCo^+ ; the RF field coupled to Q_3 additionally contributed to the ion frictional heating in the radial direction. When Q_3 is adjusted for Co^+ , the precursor CpCo^+ ion is in the RF field characterized by $q = 0.19$. For this q value, $v_{21}^2(0,1.19) =$

0.0378 and $v_{22}^2(0,0.19) = 1.035$, which for $r_o = 0.1 r$ and $T_{\perp} = 500$ K corresponds to $E_r = 0.071$ eV, rather insignificant in comparison to the axial drift field's contribution. It is interesting to note that the water cluster CpCoH_2O^+ , an electrostatically-bonded complex, produced as a result of residual water vapor in neon is expected to be less stable than CpCo^+ or $\text{C}_3\text{H}_3\text{Co}^+$. When Q_3 is adjusted to pass $\text{CpCo}(\text{H}_2\text{O})^+$, the precursor CpCo^+ ion is in the RF field characterized by $q = 0.458$. For this q value $v_{21}^2(0,0.458) = 0.028$ and $v_{22}^2(0,0.458) = 1.25$, which for $r_o = 0.1 r$ and $T_{\perp} = 500$ K corresponds to $E_r = 0.25$ eV (0.035 eV in the center-of-mass coordinates). However, as can be seen in Figure 3, even this condition is not sufficiently energetic to prevent complexation with water without the help of the axial drift field.

Investigation on the Ion Translational Energy Upon Exiting the HP-SQCC with a Q_3 Offset

This section dwells on the translational energy of ions exiting the HP-SQCC as measured using different Q_3 offsets. It is well known that the quadrupole rod offset is far from being an ideal energy barrier [25]. For example, it would be beneficial to install a three-grid energy analyzer between the cell and Q_3 . Such an arrangement will facilitate more precise measurements of the ion energy by employing a repulsive electrostatic field that is spatially uniform. Additionally, a well-characterized reaction/collision gas flow controlling system similar to that described in references [26, 27] is bound to improve the reproducibility of reaction profiles and minimize occurrence of unwanted reactions from impurities. Although these and additional improvements seem reasonable, they could hardly be expected to be implemented in practical (easy-to-use) analytical instrumentation. The goal of this paper is to characterize the HP-SQCC as an ion-molecule reactor in its simplest configuration. This same reason compels us to defer intriguing ion drift studies [5, 7, 23] involving reactive mixtures for future investigations.

Despite limited capabilities of Q_3 as an energy analyzer, change the Q_3 offsets offers valuable insight into ion relaxation processes [28, 29] which are discussed here. Typical stopping curves (graphs of ion intensities versus the Q_3 offsets) for constant Co^+ and Cp_2Co^+ ion beams are presented in Figure 4 and Figure 5, respectively. These ions were produced from Cp_2Co and mass-selected by Q_1 ; they traversed the HP-SQCC filled with Ne and overcame the Q_3 offset barrier for detection. The stopping curve is characteristic of the integral distribution of the axial ion energy: only ions with axial energy above the Q_3 offset can be successfully detected. More accurately, the detector registers only ions that passed Q_3 . It has been described previously (references [30–32], for example), that ion transmission through a quadrupole assembly (which usually includes aperture at exit) depends on the ion beam energy (along with

Figure 4. Stopping curves (graphs of ion intensities versus Q_3 offsets) for the Co^+ ion beam produced from Cp_2Co sample. Fitted curves were plotted employing three parameters sigmoid:

$$y = \frac{a}{1 + e^{-\left(\frac{x-x_0}{b}\right)}}, \text{ where } y \text{ is the normalized ion intensity, } x \text{ is the } Q_3 \text{ offset, and } a, b \text{ and } x_0 \text{ are adjustable parameters. The lower graph shows plots that are the differentials of the fitted curves for } \frac{d}{dx} \left(\frac{a}{1 + e^{-\left(\frac{x-x_0}{b}\right)}} \right) = \frac{a}{2b} \left(1 + \cosh\left(\frac{x-x_0}{b}\right) \right)^{-1}.$$

other parameters). An attractive offset leads to periodic focusing of ions (fluctuation of the ion beam intensity) versus their axial energy. Moreover, this effect is mass dependent. As a consequence, resultant stopping curves are not sigmoidal, as one would expect from the integral of the second momentum of normal distribution of the ion axial velocity. Therefore, the stopping curves were subjectively cut somewhere in the attractive part of the Q_3 offset. This procedure does not affect the position or the width of the distribution on the energy scale. In spite of these reservations, it can be clearly seen that by increasing Ne pressure, the ion beam's axial energy and its temperature decreases. The fitted curves were drawn employing three parameters sigmoid to make this trend clear.

The practical value of differentiating experimental

Figure 5. Stopping curves (graphs of ion intensities versus Q_3 offsets) for the Cp_2Co^+ ion beam produced from Cp_2Co sample. Fitted curves were drawn employing three parameters sigmoid (see Figure 4). The lower graph shows plots that are the differentials of the fitted curves.

data is always debatable and this is also true in our case. However, in order to support the semi-quantitative nature of our investigation it was found to be beneficial to differentiate fitted curves. Despite its oversimplification, such a procedure provides powerful insight into relaxation processes. As can be seen in Figure 4 and Figure 5, the maximum of the energy distribution shifts from -6.5 V to -7 V with increasing Ne pressure. The width of the distribution also decreases with increasing Ne pressure due to collisional relaxation of all translational degrees of freedom. Under the conditions of our experiment, the Q_0 offset is equal to -7 V; therefore, one can observe that the Co^+ ions are nearly thermalized with a Ne pressure above ~10 mTorr. Additionally, according to eq 3, under thermalized conditions, the ion temperature is expected to be similar in all directions because $v_{22}^2(0,0.4) = 1.18$ [15] and the RF field contribution should be minimal. This similar trend is also observed in the case of Cp_2Co^+ ions colliding with Ne

Figure 6. Stopping curves (graphs of ion intensities versus Q_3 offsets) for the Co^+ ion beam produced from Cp_2Co sample under different drift fields, ΔU . Fitted curves were drawn employing three parameters sigmoid (see Figure 4). The lower graph shows plots that are the differentials of the fitted curves.

(Figure 5). As these ions have a larger cross-section and mass, they collide more often with Ne but require more collisions to dissipate their axial translational energy. However, even in this case, 10 mTorr of Ne is sufficient to achieve reasonable equilibrium among all translational degrees of freedom.

Such near thermalization (although desirable to control the enthalpies of ion molecule reactions) is achievable under our experimental conditions, but should be considered of limited value as it simultaneously involves the loss of directional axial movement. To deliver ions from the entrance to the exit of the HP-SQCC reproducibly (independent of the total ion current and the Q_3 state), it was found [5, 22, 33] to be of benefit to utilize the axial drift field. In the presence of the drift field ΔU , ions collide, drift and are trapped by the RF field simultaneously. The design of the HP-SQCC ensures that, without collisions, the ion energy distribution (axial as well as radial) remains the same before and after the cell. One can also expect that the many collisions in the HP-SQCC under a ΔU should shift the laboratory ion energy from its original near $Q_0\text{-RO}_2$. Lack of collisional relaxation will further contribute to

Figure 7. Stopping curves (graphs of ion intensities versus Q_3 offsets) for the Cp_2Co^+ ion beam produced from Cp_2Co sample under different drift fields, ΔU . Fitted curves were drawn employing three parameters sigmoid (see Figure 4). The lower graph shows plots that are the differentials of the fitted curves.

the laboratory ion energy. It was observed experimentally and is demonstrated in Figure 6 and Figure 7 in the case of Co^+ and Cp_2Co^+ ions colliding with Ne. Successful relaxation of the Cp_2Co^+ ions can be achieved under 11.5 mTorr pressure of Ne for $\Delta U = 5\text{V}$. It is interesting to observe that under intermediate pressure (1.43 mTorr) ions have an elevated temperature in comparison with both “no drift field” (19.1 mTorr, $\Delta U = 0\text{V}$) and “drift field, many collisions” (11.5 mTorr, $\Delta U = 5\text{V}$) conditions. The same phenomenon was observed for higher drift field $\Delta U = 10\text{V}$. Total relaxation of the ion temperature was not observed even under 19.1 mTorr of Ne.

It is also possible to distinguish between exothermic and endothermic reactions by analyzing the differential stopping curves of the product ions. For example, as seen in Figure 8, the differential distribution (and temperature) is narrower for products CpCoO_2^+ of the ligand switching reaction in comparison with the distribution of the reactant (precursor) ions because this reaction occurs only on the “low energy tail” of the precursor ion (CpCoN_2^+) energy distribution. This ef-

Figure 8. Differential stopping curves of the precursor CpCoN_2^+ ; the product of ligand switching reaction, CpCoO_2^+ ; and the product of thermal dissociation, CpCo^+ , for the same Ne pressure of 1.42 mTorr. The curves are normalized and re-centered.

fect is related to the anti-Arrhenius dependence of the rate constants of some exothermic reactions on temperature (see below). On the contrary, the product of endothermic dissociation reaction CpCo^+ is produced from the “high energy tail” of the precursor ion (CpCoN_2^+) energy distribution and its distribution is wider than that of the precursor.

Ion Molecule Reactions in the HP-SQCC

Under mild interface conditions of low orifice voltage (OR), molecular ions of ferrocene and cobaltocene Cp_2Fe^+ and Cp_2Co^+ , are observable. Increasing the OR induced the dissociation of these molecular ions and allowed fragment ions and adducts to be seen, which include CpFe^+ (or CpCo^+) and its H_2O , O_2 , N_2 adducts. These adducts formed because N_2 and air were used as the curtain and nebulizer gas, respectively.

CpFe^+ reacts rapidly with H_2O [16]. Twenty mTorr of neon does not promote Ne adducts, but some water adducts can be observed. Without the collision/reaction gas only parent ions are observed. Unfortunately, the amount of water introduced together with neon cannot be controlled without an exceptional effort. Therefore, in addition to the source, the HP-SQCC can also produce water clusters.

It is important to remember that clusters (for example, CpCoH_2O^+ , see Figure 3), if they are not selected by Q_1 from the source, are formed in the HP-SQCC. We observed that an additional enthalpy provided by the drift or RF field prevents clusters from forming. Therefore, reported data suggests an anti-Arrhenius dependence of the rate constants for the cluster formation on temperature. A decrease of ion-molecule reaction rate with increasing temperature is quite common for exothermic association reactions. As a result, there is a shift of the equilibrium toward the reactants due to a tem-

Figure 9. Thermal dissociation of the CpCoN_2^+ ion due to frictional ion heating: dependence of normalized ion intensities versus drift field, ΔU , and Ne collision gas pressure. Signal normalization was conducted on the sum of all ion intensities. Water and oxygen adducts were formed from residual gases as a result of cluster-switching reaction. The CpCoN_2^+ ion was mass-selected by Q_1 .

perature increase. In special cases, even entropy effects were considered to be responsible for this trend [34]. These effects allow an additional suppression of cluster formation in the HP-SQCC without significant alteration of more exothermic ion molecule reactions.

Alternatively, some clusters of the metallocenes can be obtained from the ion source. For example, CpCoN_2^+ cluster forms readily in the ion source employing nitrogen as a curtain gas. This cluster undergoes ligand-switching reactions with water and oxygen, which are present in neon as residual gases (see Figure 9). It was noticed [17, 34] that ions of half-sandwich metallocenes react with electron-donating ligands with rate constants that are inversely proportional to the ligand ionization energies (IEs). In general, bond energies are also inversely proportional to the ligand IEs. Consequently, N_2 (IE = 15.6 eV) should be substituted by H_2O (IE = 12.6 eV) and O_2 (IE = 12.07 eV). These reactions were observed in the HP-SQCC and the results are presented in Figure 9. Even under a very low Ne pressure (0.2 mTorr), frictional ion heating slowed down the ligand-switching reaction and significantly suppressed water-cluster formation under drift fields $\Delta U > 10\text{V}$. Under a moderate Ne pressure (12.1 mTorr), the nitrogen cluster fully exchanged with water and oxygen (for $\Delta U = 0\text{V}$); upon larger ΔU values, frictional heating largely suppressed these reactions. In addition,

Figure 10. Reactions of CpFe^+ ions with CO under different reactant gas pressures (10% CO in Ne) and under two drift field conditions, $\Delta U = 0$ (upper) and $\Delta U = 2\text{V}$.

frictional heating also decomposes the nitrogen cluster to CpCo^+ for $\Delta U \geq 5\text{V}$.

An anti-Arrhenius dependence of the cluster formation rate constant is also apparent in reactions between CpM^+ and CO, despite the fact that the $\text{CpM}^+\text{-CO}$ bond is much stronger than those between CpM^+ and the aforementioned ligands due to its electron donor-acceptor nature [16]. The CpFe^+ ion reacts with CO according to eq 4 (see Figure 10). Even a relatively moderate axial drift field ($\Delta U = 2\text{V}$) dramatically slows the ion-molecule reactions down. The results are a combined effect of an anti-Arrhenius dependence of the rate constants and a reduction of the ions' residence times inside the HP-SQCC. The ion's residence time is inversely proportional to $\sqrt{\Delta U}$. Increasing the reactant gas pressure at a ΔU of 2V results in more abundant complexes, including $\text{CpFe}(\text{H}_2\text{O})^+$. This is a combined effect of increasing ions' residence times and increasing thermalization.

Conclusions

The results presented here demonstrate that the high-pressure segmented quadrupole collision cell is a valuable ion-molecule reactor with an inherent heat source.

Heat is transferred to the reactants through ion frictional heating. There are two major sources of the ion frictional heating under typical HP-SQCC conditions: the radial RF-trapping field and the axial drift field. Both sources are closely interconnected. The contribution from the trapping field depends on the radial position of the colliding ions. The axial drift field results in an increase of the ion axial temperature. However, collisions with the target gas lead to an increase of the ion beam cross-section thus contributing to radial heating. Therefore, the axial drift field contributes directly to the enthalpy of the ion-molecule reaction as well as indirectly by increasing the RF field input. The HP-SQCC utilizes a combination of several physicochemical phenomena and permits examination of a range of ion-molecule reactions. In the future, it would be interesting to see if it can be used to promote selected endothermic reactions (via frictional heating) as well as to suppress unwanted reactions with impurities. In addition, the same reactor can be used to promote sequential exothermic ion-molecule reactions provided there are sufficiently large numbers of collisions and sufficiently long ion residence times.

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