COMMUNICATION: TRANSFER IONIZATION IN A THERMAL REACTION OF A CATION AND ANION: \( \text{AR}^+ \) WITH \( \text{BR}^- \) AND \( \text{I}^- \) (POSTPRINT)

Nicholas S. Shuman, et al.

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Communication: Transfer Ionization in a Thermal Reaction of a Cation and Anion: Ar+ with Br− and I− (Postprint)

Nicholas S. Shuman, Thomas M. Miller, Rainer Johnsen, and Albert A. Viggiano

Direct dynamics simulations and selected ion flow tube (SIFT) experiments were performed to study the kinetics and dynamics of the OH- + CH3I reaction versus temperature. This work complements previous direct dynamics simulation and molecular beam ion imaging experiments of this reaction versus reaction collision energy (Xie et al. J. Phys. Chem. A 2013, 117, 7162). The simulations and experiments are in quite good agreement. Both identify the S(N)2, OH- + CH3I > CH3OH + I-, and proton transfer, OH- + CH3I CH2I- + H2O, reactions as having nearly equal importance. In the experiments, the S(N)2 pathway constitutes 0.64 +/- 0.05, 0.56-4-0.05, 0.51 +/- 0.05, and 0.46 +/- 0.05 of the total reaction at 210, 300, 400, and 500 K, respectively. For the simulations this fraction is 0.56 +/- 0.06, 0.55 +/- 0.04, and 0.50 +/- 0.05 at 300, 400, and 500 K, respectively. The experimental total reaction rate constant is (2.3 +/- 0.6) x 10(-9), (1.7 +/- 0.4) x 10(-9), (1.9 +/- 0.5) X 10-9, and (1.8 +/- 0.5) X 10-9 cm(3)s I at 300, 400, and 500 K, respectively. For the simulations this fraction is 0.56 +/- 0.06, 0.55 +/- 0.04, and 0.50 +/- 0.05 at 300, 400, and 500 K, respectively, which is approximately 25% smaller than the collision capture value. The simulation values for this rate constant are (1.7 +/- 0.2) X 10-9, (1.8 +/- 0.1) X 10-9, and (1.6 + 0.1) X 10(-9) cm3/s I at 300, 400, and 500 K. From the simulations, direct rebound and stripping mechanisms as well as multiple indirect mechanisms are identified as the atomic-level reaction mechanisms for both the S(N)2 and proton-transfer pathways. For the S(N)2 reaction the direct and indirect mechanisms have nearly equal probabilities; the direct mechanisms are slightly more probable, and direct rebound is more important than direct stripping. For the proton-transfer pathway the indirect mechanisms are more important than the direct mechanisms, and stripping is significantly more important than rebound for the latter. Calculations were performed with the OW quantum number J equal to 0, 3, and 6 to investigate the effect of OH-rotational excitation on the OH- + CH3I reaction dynamics. The overall reaction probability and the probabilities for the S(N)2 and protontransfer pathways have little dependence on J. Possible effects on the atomic mechanisms were investigated for the S(N)2 pathway and the probability of the direct rebound mechanism increased with J. However, the other atomic mechanisms were not appreciably affected by J.

s(n)2 nucleophilic-substitution; correlated molecular calculations; classical trajectory simulations; exchange-correlation functionals; gaussian-basis sets; direct dynamics; symplectic integration; atomic mechanisms; energy; hydrogen
Communication: Transfer ionization in a thermal reaction of a cation and anion: Ar+ with Br− and I−

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Communication: Transfer ionization in a thermal reaction of a cation and anion: Ar\(^+\) with Br\(^-\) and I\(^-\)

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We present experimental evidence that reactions of argon cations Ar\(^+\) with the halogen anions Br\(^-\) and I\(^-\) do not occur exclusively by mutual neutralization, but also produce the cations Br\(^+\) or I\(^+\) ions by transfer ionization (TI). The experiments were carried out in flowing-afterglow plasmas at gas temperatures between and 300 and 500 K, and employed a variant of the Variable Electron and Neutral Density Attachment Mass Spectrometry method. The measured TI rate coefficients are 1.9 \(\pm 0.6 \times 10^{-9}\) cm\(^3\) s\(^{-1}\) and 1.1 \(\pm 0.3 \times 10^{-9}\) cm\(^3\) s\(^{-1}\) for the Br\(^-\) and I\(^-\) reactions, respectively. We find that the TI rate coefficients decline with temperature as approximately T\(^{−0.5}\) to T\(^{−1}\). No indication of TI was found in the reaction with Cl\(^-\), where it is endoergic. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4828455]

The reaction of atomic cations A\(^+\) with atomic anions B\(^-\) is usually assumed to produce two neutral atoms by mutual neutralization (MN), i.e.,
\[ A^+ + B^- \rightarrow A + B, \]  
(1)
in which one or both of the product atoms may be electronically excited. However, when the total energy suffices to ionize the atom of lesser ionization potential, transfer ionization (TI) can give rise to an additional product channel that includes an ion and an electron:
\[ A^+ + B^- \rightarrow A + B^+ + e^- . \]  
(2)

Invoking TI in cation/anion reactions is not new. It has been observed in beam experiments on H\(^+\) + H\(^-\) \(\rightarrow\) H\(^+\) + H\(^-\) + e\(^-\) collisions\(^4\) and theoretical treatments have been published.\(^5\) In symmetric systems such as H\(^+\) + H\(^-\), TI is endoergic by the electron affinity of the atom and, hence, will not take place at thermal energies. In asymmetric systems TI is energetically possible at thermal energies when the recombination energy of the cation exceeds the energy required to remove two electrons from the target anion, as is the case for some pairs of rare-gas cations, Rg\(^+\), and halogen anions, X\(^-\). Whether or not TI actually occurs in such a situation is a more subtle question. TI has not been previously observed in Rg\(^+\) + X\(^-\) reactions at any energy, nor at thermal energies for any singly charged cation/anion system. Transfer ionization in fast collisions of multiply charged ions with neutrals has been extensively investigated (see, e.g., the recent paper by Voitkiv).\(^3\) In some cases it can occur at thermal energies as has been observed in thermal-energy drift tube experiments.\(^4\) Both experimental and theoretical results have been reported for He\(^2+\) + H\(^-\) \(\rightarrow\) He\(^+\) + H\(^+\)\(^-\).\(^5\)

Here, we present the results of flowing afterglow studies of three reactions of Ar\(^+\) ions with Cl\(^-\), Br\(^-\), and I\(^-\) at thermal energies using the Variable Electron and Neutral Density Attachment Mass Spectrometry (VENDAMS) technique. In the Br\(^-\) and I\(^-\) systems, TI is exoergic, we find clear evidence for TI, with the TI channel more important in the Br\(^-\) system. The reaction with Cl\(^-\), which is endoergic, was studied as a test of the experimental methods and analysis and no TI products were found. Experiments at different gas temperatures (from 300 to 500 K) indicate that the TI rate declines with temperature as approximately T\(^{−0.5} \ldots T^{−1}\), similar to the temperature dependence found for MN reactions.\(^6\) Total rate coefficients, i.e., the sum of MN and TI, are obtained in a larger study by the measured loss rate of ions, and will be presented in a separate publication.

In principle, collisions of this type can also lead to molecular products by associative ionization (AI),
\[ A^+ + B^- \rightarrow AB^+ + e^- \]  
(3)
provided that the AB\(^+\) molecule is stable. HeH\(^+\) and HeD\(^+\) formation has been observed\(^7\) in the reactions of He\(^+\) with H\(^-\) and D\(^-\). Our experiments give no evidence of molecular product ions, such as ArBr\(^+\); however, the binding energies of ions of this type tend to be rather weak,\(^5\) and even if they were formed they may not be observed due to thermal dissociation.

The VENDAMS technique has been thoroughly described elsewhere, and has been used to study numerous plasmas process that were heretofore either difficult or impossible to measure by other means.\(^9\) The current measurements employ a novel variant of the VENDAMS technique in which positive product ion abundances are monitored. Briefly, an Ar\(^+\)/e\(^-\) plasma is established in a fast helium buffer flow in a flowing afterglow – Langmuir probe (FALP) apparatus through standard techniques.\(^10\) A species (CCl\(_4\), CF\(_2\)Br\(_2\), C\(_2\)F\(_3\)I) that attaches electrons rapidly to yield a halogen anion, i.e.,
\[ XR + e^- \rightarrow X^- + R, \]  
(4)
is introduced in sufficient concentration, typically $3 \times 10^{10}$ cm$^{-3}$, to deplete the electron density within about 0.5 ms (approximately 3 cm).

The resulting anions react with Ar$^+$ through (1) and (2). After a known reaction time, typically 5–10 ms, the relative abundances of Ar$^+$ and X$^+$ (along with any other cations present, e.g., impurities related cations) are measured using a quadrupole mass spectrometer sampling the flow through a pinhole aperture at the end of the flow tube. The rate coefficient of (2) is reflected by the X$^+$ (X = Cl, Br, I) abundance as a function of the initial plasma density (Figure 1), which is determined by measuring the absolute electron concentration [$e_0$] using a cylindrical Langmuir probe stationed 1 cm upstream of the neutral reactant inlet.

Importantly, the shape of the X$^+$ curve is defined by the mechanism by which X$^+$ is produced. In the case of TI, produced by the sequence (4) followed by (2), the X$^+$ abundance will increase roughly linearly with [$e_0$] with a proportionality constant of about 1. The rate constant of (2) is reflected by the magnitude of the X$^+$ abundance. In contrast, X$^+$ formed by charge transfer from Ar$^+$ with XR will have a zero slope at low ($< 5 \times 10^9$ cm$^{-3}$) [$e_0$], and then gradually rise or fall reflecting the difference in the reaction rates of Ar$^+$ and X$^+$ with X$^-$. As such, the technique allows X$^+$ from TI to be distinguished from X$^+$ produced by other means.

In particular, while Ar$^+$ was found to react with XR to yield X$^+$ only in the case of C$_2$F$_3$I, He$^+$, present in small quantities from the manner of Ar$^+$ production, yields X$^+$ from all three precursors. The present measurements were made at increasingly higher pressures, in order to reduce the amount of He$^+$ by conversion to He$_2^+$ and subsequently Ar$^+$, until the He$^+$ concentration was sufficiently small so that the signal from TI dominated. The initial ratio of He$^+$:Ar$^+$ was not constant as a function of [$e_0$], but rather increased slowly with [$e_0$] showing a cusp at $5 \times 10^9$ cm$^{-3}$. The nascent distribution of He$^+$:Ar$^+$ was measured prior to introduction of the neutral reactants, and incorporated into modeling of the data.

A simple analytical function to extract the TI rate coefficient from these data does not exist. Instead, the rate coefficient is derived numerically by solving the coupled differential equations describing the possible chemistry occurring between all species known or inferred to be present in the flow tube from the known initial reaction conditions throughout the known reaction time. A full description of such a procedure is available elsewhere. Interestingly, the resulting TI rate coefficients are robust to a wide range of assumed values for the rate coefficients of other reactions occurring, including that of the competing MN process (1), even assuming rate coefficients as high as $10^{-6}$ cm$^3$ s$^{-1}$. Statistical uncertainty from the fitting is generally 20%–25%. Systematic uncertainty in the measurement is dominated by characterizing the mass discrimination between relevant species. Mass discrimination factors are measured through procedures described elsewhere, and have an assumed uncertainty of 10%. The convolution of these factors yields the uncertainties reported.

Figure 1 shows representative data for the Br$^-$, Cl$^-$, and I$^-$ systems. The Br$^-$ signal is observed to increase with [$e_0$] in agreement with modeling assuming TI as the dominant source of Br$^-$; note that the slope of the curve is fixed by the chemistry and essentially the only degree of freedom in the modeling is the magnitude of the rate coefficient of TI, variation of which results in a vertical translation of the Br$^-$ curve, the slope staying fixed. In contrast, the Cl$^+$ signal was roughly 1 order of magnitude smaller than the Br$^-$ and does not rise with [$e_0$] indicating TI is not occurring. Instead, the Cl$^+$ signal is well modeled by assuming dissociative charge transfer of He$^+$ with CCl$_4$ and accounting for the nascent He$^+$ distribution. Analysis of the I$^-$ system was more complex as dissociative charge transfer between Ar$^+$ and C$_2$F$_3$I was observed to have a substantial I$^+$ product channel. Fortunately, at higher [$e_0$], the I$^+$ signal from TI dominates (Figure 1), and deconvolution of the competing signals resulted in only marginally larger uncertainties than those of the Br$^-$ system. The partial rate coefficient for I$^+$ from charge transfer between C$_2$F$_3$I and Ar$^+$ was found to be $1.0 \pm 0.2 \times 10^{-10}$ cm$^3$ s$^{-1}$ at all temperatures. Results for all three systems appear in Figure 2 and Table I. Note that the TI measurement does not depend on the rate coefficient of the competing mutual neutralization channel to any appreciable extent.

A detailed theoretical description of the competition between TI and MN is difficult, even in the simpler case of the H$^+$ + H$^-$ reaction. It seems likely that the first step in the reaction consists of an “accidentally resonant” electron transfer from the anion into one or more molecular states formed by the interaction of an excited argon atom (perhaps in one of the argon 4$s$ states) with a halogen atom. If these states are antibonding they may either lead to dissociation into neutral products (MN), or, if their energies lie slightly above the ionization energy of the halogen atom, they may couple to autoionizing...
states and decay by TI. In the reactions with Br⁻ the TI channel is estimated to account for about 40% of the sum of TI and MN while the TI channel in the I⁻ reactions amounts to only about 6% of the total even though the latter process has a higher exoergicity. These estimates are based on recent data on the total rate coefficients for Ar⁺ + X⁻ (5 × 10⁻⁹ cm³ s⁻¹ and 2 × 10⁻⁸ cm³ s⁻¹ at 300 K for the Br⁻ and I⁻ systems, respectively), to be published separately. The higher TI contribution in the reaction with Br⁻ compared to that with I⁻ is probably a consequence of the energetic ordering of the MN and TI exit channels. In the Br⁻ reaction, the potential curves leading to the TI lie slightly (~0.25 eV) above those leading to Br and Ar⁺ in the lowest metastable state, while in the reaction with I⁻, the TI curve lies substantially below (~1 eV) that for dissociation in to I and Ar⁺.

Afterglow measurements of the kind described here offer high sensitivity and chemical flexibility, but they cover only a limited energy range and are not capable of measuring product energies or energy distributions of the ejected electrons. Such information may become available from merged-beam storage rings that are currently being developed. While mutual neutralization is certainly an important process in plasma processing, rare-gas halide lasers, and ionospheric chemistry, the possible effects of TI in such applications have not, to our knowledge, been investigated.

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<table>
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<th>ΔE (eV)</th>
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<tr>
<td>Br</td>
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<td>1.9 ± 0.6</td>
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