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Bond-Forming Reactions of Small Triply Charged Cations with Neutral Molecules

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In memory of Detlef Schröder

Abstract: Time-of-flight mass spectrometry reveals that atomic and small molecular triply charged cations exhibit extensive bond-forming chemistry, following gas-phase collisions with neutral molecules. These experiments show that at collision energies of a few eV, I^{3+} reacts with a variety of small molecules to generate molecular monocations and molecular dications containing iodine. Xe^{3+} and $CS_2{}^{3+}$ react in a similar manner to I^{3+}, undergoing bond-forming reactions with neutrals. A simple model, involving relative product energetics and electrostatic interaction potentials, is used to account for the observed reactivity.

Keywords: electron transfer • gas-phase reactions • iodine • multiply charged ions • ion–molecule reactions

Introduction

Investigations of the properties of isolated small multiply charged cations in the gas phase, that is, ions free from any stabilizing interactions with solvent molecules, might be thought to reside firmly within the remit of physicists. However, such a view is mistaken. Doubly charged ions are the lowest-charged class of multiply charged cations and, as articles in this journal and elsewhere show, the chemical (bond-forming) reactivity of small gas-phase dications is varied and extensive.[1] Indeed, recent studies have shown that gas-phase dication-neutral chemistry can provide pathways to new species, such as rare gas compounds, or highly efficient routes to the formation of specific bonds.[2] In contrast to dications, little, if anything, is known of the bimolecular chemistry of small (ten atoms or fewer) gas-phase trications in collisions with neutral molecules. This paucity of information is in spite of the fact that these small gas-phase trications already find applications in etching,[3] radiology (Ne^{3+})[4] and structural imaging,[5] as well as providing targets to probe subtle details of ionization phenomena.[6] This paper reports the first investigation of the bimolecular chemistry of small gas-phase trications with neutral molecules and reveals an extensive bond-forming reactivity competing with electron transfer.

The lack of available information on the gas-phase reactivity of small trications with neutral molecules is in contrast to extensive data characterizing the gas-phase chemistry of large multiply charged biomolecules. This contrast arises because electrospray ionization has provided a convenient way to generate larger (high mass) multiply charged ions of biomolecules in the gas phase. The primarily dissociative unimolecular chemistry of such multiply charged biomolecules, often promoted by collisions, has received significant attention due to its value for characterization and sequencing.[7] In recent years, an extensive literature has also emerged concerning the bimolecular ionic reactions between these multiply charged biological ions and single or multiply charged species of the opposite charge. These interactions, between pairs of oppositely charged species, can result in a variety of bond-forming reactions including proton transfer, metal-ion transfer, electron transfer and covalent modification.[8] In contrast to this bond-forming ionic chemistry of large multiply charged biomolecules, the experiments reported herein investigate the reactivity of small (atomic and tri-atomic) trications with neutral molecules. In the gas phase, these small trications will generally have much larger charge densities than comparably charged biomolecules and should perhaps be considered a different class of ionic reactant.

Unsolvated small gas-phase trications can be formed following encounters with a variety of ionizing agents (photons, electrons, protons) of an appropriate energy.[9] Cross-sections for triple ionization of atoms, or non-dissociative triple ionization of molecules, are typically significantly smaller than those for single ionization, with Auger-style processes contributing significantly to the tricationic yield.[9a,10] A wide variety of atomic trications are potentially accessible through dissociative multiple ionization (e.g., [Eq. (1) and (2)]), which is the source of the I^{3+} beam employed in this study:

$$I_2 + e^- \rightarrow I_2{}^{3+} + 4e^- \qquad I_2{}^{3+} \rightarrow I^{3+} + I \tag{1}$$

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$$I_2 + e^- \rightarrow I_2^{4+} + 5e^-, \qquad I_2^{4+} \rightarrow I^{3+} + I^+ \tag{2}$$

The low yield of such triply charged atomic fragments, in studies of the ionization of a variety of small molecules, indicates that the cross-sections for such dissociative multiple ionization processes are much smaller than those for dissociative double ionization.[10d,e,11] However, the present study shows that, despite these small cross-sections, viable beams of small trications can be generated for experimental studies.

Long-lived molecular triply charged ions, which are stable on the microsecond time scales of mass spectrometry, have been known for many years, with trications of multi-atomic organic species perhaps the first to be systematically identified.[12] The long-lived nature of diatomic trications was first noted in 1984;[13] these ions can be formed through photoionization, using short-pulse lasers or more conventional photon sources, as well as by electron ionization, charge stripping and sputtering.[6b,14] This paper reports the results of an investigation of the consequences of low-energy collisions of triply charged atomic and triatomic ions with other neutral molecules. These experiments reveal a complex and varied reactivity involving the formation of new chemical bonds.

Results and Discussion

Figure 1a shows a section of a representative mass spectrum recorded following collisions of I^{3+} with CO. Clear signals due to bond-forming reactions generating IC^{2+} and IO^{2+} are observed.

Figure 1b shows a section of a mass spectrum recorded following collisions of I^{3+} with SO_2. Clear signals due to both monocations and dications of IO and IS are visible. Table 1 lists all the I^{3+}/molecule collision systems that we have investigated and quantifies the product ions generated which involve the formation of new chemical bonds. The only collision system investigated, in which we do not observe any bond-forming reactivity is I^{3+}/H_2S; however, in this collision system the intense I^+ and I^{2+} product peaks could easily mask weak HI^+/HI^{2+} signals. As can be seen clearly in Figure 1, electron transfer to I^{3+} from the neutral molecule (to form I^+ and I^{2+}) provides the bulk of the product ion yield in these I^{3+} collision systems; typically, I^{2+}/I^+ intensity ratios $R(I^{2+})$ vary between 3 and 11 (Table 1). Thus, the bond-forming reactivity in these collision systems is a significant, but minor process, which clearly involves a competition between the formation of monocationic and dicationic iodine-containing molecules (Table 1). Indeed, all the reactive collision systems in Table 1 form both dicationic and monocationic iodine-containing products, except for the I^{3+}/CO and I^{3+}/CS_2 systems; the only iodine-containing molecular ions formed with CO are dicationic, whilst with CS_2 all the I-containing molecular ions, which we detected, are singly charged.

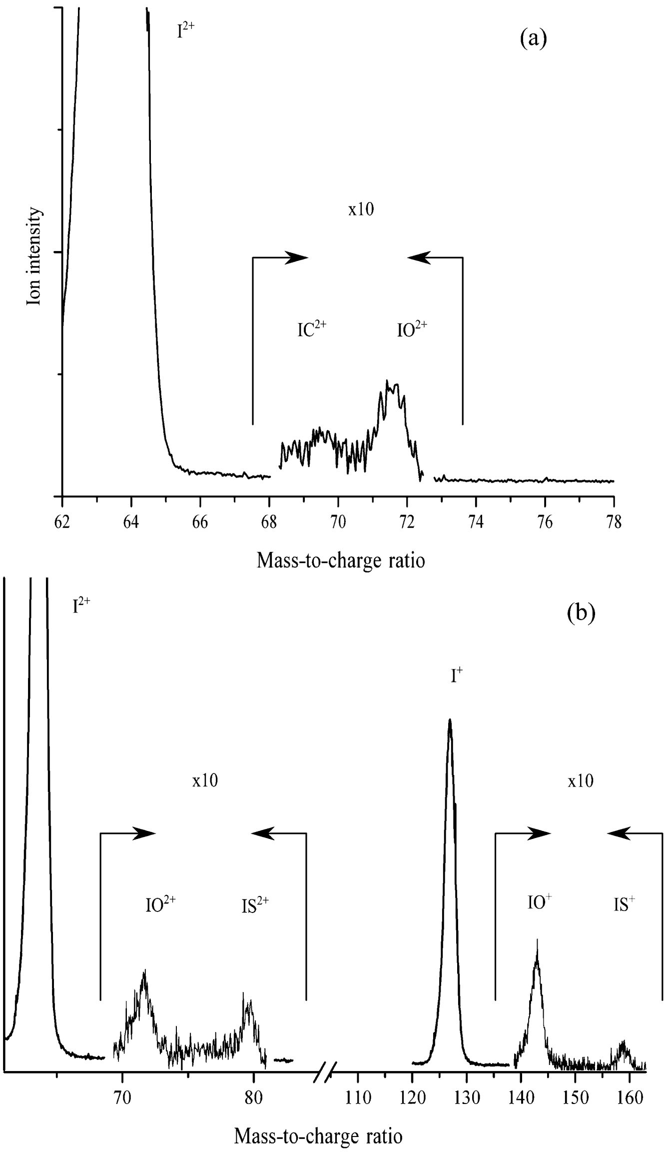

Figure 1. Sections of representative mass spectra recorded following collisions of I^{3+} with a) CO at a centre-of-mass collision energy $T_{cm}=4$ eV and b) and SO_2 at $T_{cm}=2$ eV.

Table 1. Product ions from the bond-forming and electron-transfer reactions of I^{3+} with a variety of small neutral molecules.

Reactant	T_{cm} [eV][a]	Product ion (yield, 10^3R)[b]	$R(I^{2+})$
SO_2	4.0	IO^{2+}(14.0), IS^{2+} (15.5), IO^+ (19.4), IS^+ (4.8)	2.8
CS_2	4.5	IC^+ (8.2), IS^+ (1.7)	4.6
H_2S	2.5	–	9.6
CH_3Cl	3.4	ICl^{2+}(10.4), IC^+ (8.7), ICl^+ (6.3)	6.1
CHF_3	4.3	IF^{2+} (16.0), IF^+ (52.5)	3.0
N_2O	3.1	IN^{2+}/IO^{2+} (43.7)[c], IN^+ (21.3), IO^+ (7.4)	4.3
CO_2	3.1	IO^{2+} (26.2), IO^+ (16.5)	5.7
CO	2.2	IC^{2+} (8.4), IO^{2+} (18.1)	11.0

[a] Centre of mass collision energy. [b] See the Experimental Section for details of yield determination. [c] Due to the substantial overlap between signals for IN^{2+} (m/z 70.5) and IO^{2+} (m/z 71.5), a combined yield is reported for these two products.

To rationalize the observed reactivity of I^{3+}, we have adapted a model originally developed by Herman et al. to explain the bond-forming reactivity of dications.[15] Their model accounts for the competition between dicationic bond-forming and electron-transfer reactivity and emphasizes the importance of a collision complex in the reactive pathway. Such collision complexes, although short lived at these collision energies, have been shown experimentally to be critical in many bond-forming reactions of dications.[1c]

Our model is illustrated in Figure 2, in which the I^{3+} ion initially approaches the neutral on a potential energy surface (PES) dominated by polarization attraction (trajectory A, Figure 2). To form a collision complex, allowing the close-range interactions required to generate the bond-forming products, the reactive system must successfully negotiate a series of curve crossings in the entrance channel that lead to electron transfer, to form either I^{+} or I^{2+}. For small trications, considering the magnitudes of single, double and triple ionization energies, single- and double-electron-transfer reactions are almost certain to be very strongly exothermic. Thus, it is extremely probable (as indicated in Figure 2) that charge transfer to populate some combination of excited electronic states of these electron transfer products will have an exoergicity lying in the so-called "reaction window" for efficient electron transfer (2–6 eV).[1c,15–16] In other words, electron-transfer curve crossings allowing access to certain excited states of the electron-transfer products will almost certainly lie at an interspecies separation (2–6 Å), in which the coupling is appropriate for charge transfer to be efficient (Figure 2).[16] These "windows" of efficiency arise because for efficient electron transfer, the coupling between reactant and product potentials must be neither too weak or too strong; too weak—and the electron is not transferred, too strong—and the electron is transferred on both approach and departure of the collision partners, and no net electron transfer results.[1c,15–16] In summary, because electron transfer in these trication systems is significantly exothermic, there is always likely to be an electron-transfer-product asymptote that can be reached efficiently, and so electron transfer should always be a major product channel, as was observed experimentally (Table 1). This analysis was also supported by the observation of efficient electron transfer in dication-neutral collision systems, if electron transfer has an exothermicity greater than 2 eV.[16]

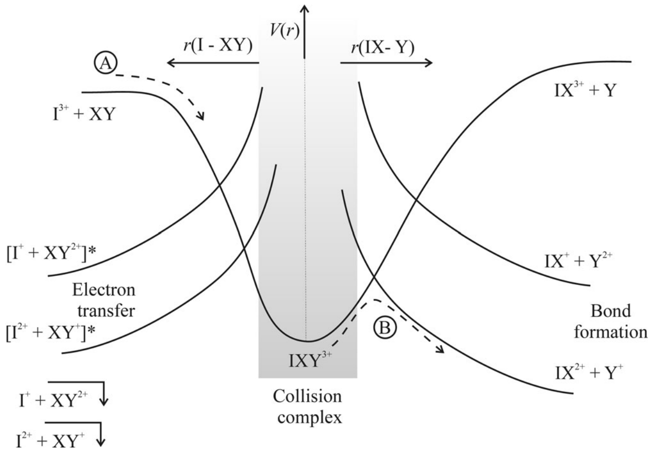

Figure 2. Schematic potential energy surfaces for bond-forming reactivity in trication-neutral collisions. As was discussed in the text, the significant exothermicity for the single- and double-electron-transfer processes means that the favored channels for these reactions are likely to populate excited states of the products, as indicated on the left-hand side of the figure. See text for further details.

The I^{3+}/neutral trajectories (Figure 2) that pass through the electron-transfer-curve crossings and manage to form a "collision complex" have the opportunity to separate with new connectivity, along a different reaction coordinate, to generate "bond-forming" products (trajectory B, Figure 2). As these bond-forming products separate, the reactive system has the opportunity to cross onto a series of product potentials, dominated by Coulomb repulsion, leading to asymptotes involving a dication and a monocation. In general, as shown in Figure 2, these product asymptotes involving charge separation will lie markedly lower in energy than the trication+neutral product asymptote ($IX^{3+}+Y$, Figure 2). The coupling at these exit channel-curve crossings decreases strongly with increasing interspecies separation of the crossing. Critically, because the separating complex is only passing through the curve crossing once (when the products separate), the majority of the bond-forming flux should flow into the most exothermic bond-forming channels, as illustrated in Figure 2; these channels are the most strongly coupled. This analysis readily explains our experimental observations. For the I^{3+}/CO collision system, the competing bond-forming reactions involve a diatomic and an atomic product (Figure 2). Energetic considerations show that the asymptotes involving an iodine-containing molecular dication (IC^{2+} or IO^{2+}) and the appropriate atomic monocation (O^{+} or C^{+}) will lie significantly lower in energy that those involving an iodine-containing molecular monocation (IC^{+} or IO^{+}) and the appropriate atomic dication (C^{2+} or O^{2+}) due to the markedly larger second ionization energy of a first- or second-row atom in comparison with a molecule containing a heavy atom, such as iodine. Thus, we would expect to detect IC^{2+} and IO^{2+} and little IO^{+} and IC^{+}, exactly as we observe (Table 1).

For the collision systems involving I^{3+} reacting with a polyatomic molecule, both of the products are molecular (Y in Figure 2 is then a molecule). In this situation, the product asymptotes for $IX^{+}+Y^{2+}$ and $IX^{2+}+Y^{+}$ should lie at comparable energies and compete effectively for the bond-forming flux. Hence, we predict that I^{3+}/polyatomic collision systems should form both monocationic and dicationic iodine-containing ions in bond-forming reactions. Table 1 shows that this is indeed the case, apart from for the I^{3+}/CS_2 collision system, which gives iodine-containing monocations, but not dications. However, in the I^{3+}/CS_2 system, a different reactive pathway may well be operating. For example, if the collision complex initially charge separates by losing an S^{+} ion, the resulting dicationic intermediate $[ICS]^{2+}$ will only have access to the $IS^+ + C^+$ and $IC^+ + S^+$ asymptotes, and only iodine-containing monocations would be expected, again, as we observe.

Of course, in the reaction mechanism described above, there is the possibility that the collision complex can “back dissociate” to form products that simply involve electron transfer (Figure 2). Such a back dissociation should, in principle, be observable in an angularly resolved experiment. Specifically, the scattering of the electron-transfer products formed through the complex will be distributed over a large range of scattering angles, due to the finite complex lifetime. This range of angular scattering should be markedly broader than that of the direct electron-transfer pathway, which does not involve complexation.[1c] To date, our on-going attempts to measure the angular scattering in these trication collision systems using a coincidence technique have been thwarted due to the low flux of the trication beams.[17]

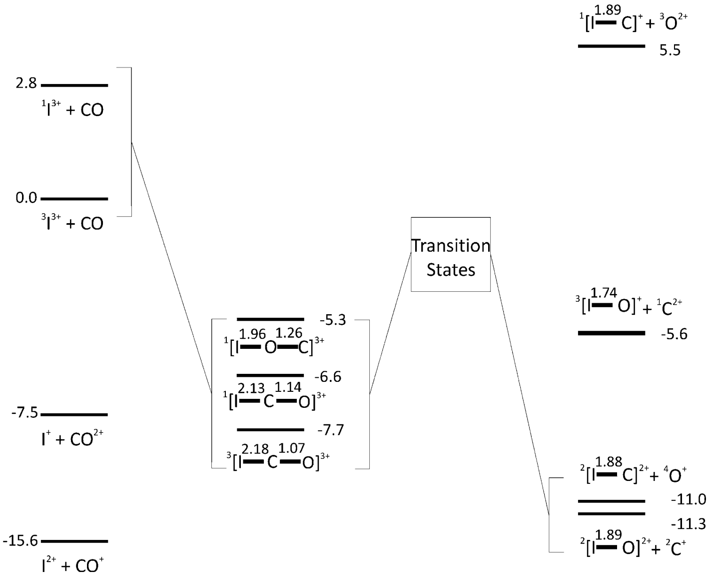

Figure 3. Calculated stationary points on the $I^{3+} + CO$ potential energy surface. Energies [eV] are expressed relative to the $I^{3+}(^3P) + CO$ asymptote and include zero-point energies. All species are linear, and bond lengths are indicated in Å. Note that the vertical axis is not to scale. The relative energies, from standard data, of the thermodynamic asymptotes for single-and double-electron transfer are marked on the left-hand side of the diagram.[18]

The rationalization presented above for the bond-forming chemistry observed in the I^{3+} collision systems was founded on the involvement of a collision complex in the bond-forming pathway. At first glance, the bond-forming products we observe (Table 1) could also be formed by a direct negative-ion-transfer process. For example:

$$I^{3+} + OCO \rightarrow I^{3+}{-}O^{-}{-}CO^{+} \rightarrow IO^{2+} + CO^{+} \qquad (3)$$

Whilst not being able to definitively rule out negative-ion transfer as the reaction mechanism, we feel that several observations favour the reaction mechanism involving a collision complex. Firstly, the formation of a product monocation containing iodine (e.g., IO^+ from I^{3+}/CO_2) by negative-ion transfer would require the transfer of a di-anion, an energetically expensive process. Secondly, several of the product ions we observe, for example, IS^{2+} from the reaction of I^{3+} with SO_2, involve considerable rearrangement in the bonding of the collision system. Such major rearrangements are not usually associated with a direct reaction mechanism, such as negative-ion transfer; this form of reactivity is far more plausible if the mechanism involves complexation. Thirdly, the thermodynamic rationalization of the reactivity we observe, as presented above, indicates that the most exothermic product pathway is favoured. Such thermodynamic control is not necessarily a likely consequence of a direct reaction mechanism, such as negative-ion transfer, but is more likely to arise from complexation.

Based on the success of computational chemistry in rationalizing the reactivity of dications,[1a,d,2a] we have performed an exploratory series of electronic structure calculations to probe the $I^{3+} + CO$ PES to support the applicability of the model presented in Figure 2. The calculations employ the MP2(fc)/aug-ccVTZ methodology to identify stationary points on the PES, relative energies of which are then given by a CCSD(T) calculation with the same basis.[19] As can be seen in Figure 3, our calculations support the general form of the PES deduced in Figure 2. The observed bond-forming product channels lie lowest in energy, well below the limits of the $IX^+ + Y^{2+}$ products. Viable collision complexes are present on the PES, at energies below that of the reactants. A search for transition states linking the collision complexes to the product asymptotes revealed several potential stationary points. However, further investigations indicated that these structures would be better modelled by a multi-configurational wavefunctions, an approach beyond the scope of this, primarily experimental, study.

Also shown in Figure 3 are the thermodynamic asymptotes for single- and double-electron transfer. As was predicted above, these electron-transfer processes are strongly exothermic meaning that, given the reaction window concept,[16] electron transfer to populate exited product states (as indicated schematically in Figure 2) is the likely source of the observed I^{2+} and I^+ products. Clearly, the relative intensity of I^{2+} to I^+ depends on subtle details of the coupling between the reactant ($I^{3+} + CO$) state and the available product potentials that lie in the reaction window. However, as was described above, due to the density of available product electronic states, suitable curve crossings for single- and double-electron transfer are almost certain to be available. Intrinsically, one would then expect transferring a single electron between the reactants to be more favorable than transferring two, and we would expect I^{2+} to dominate over I^+, as we observe.

To determine if the tricationic reactivity reported above is a unique property of the I^{3+} ion, or a more general phenomenon, we have also investigated reactions of Xe^{3+} and CS_2^{3+}. Figure 4 shows representative mass spectra recorded following the collisions of these ions with polyatomic neutral

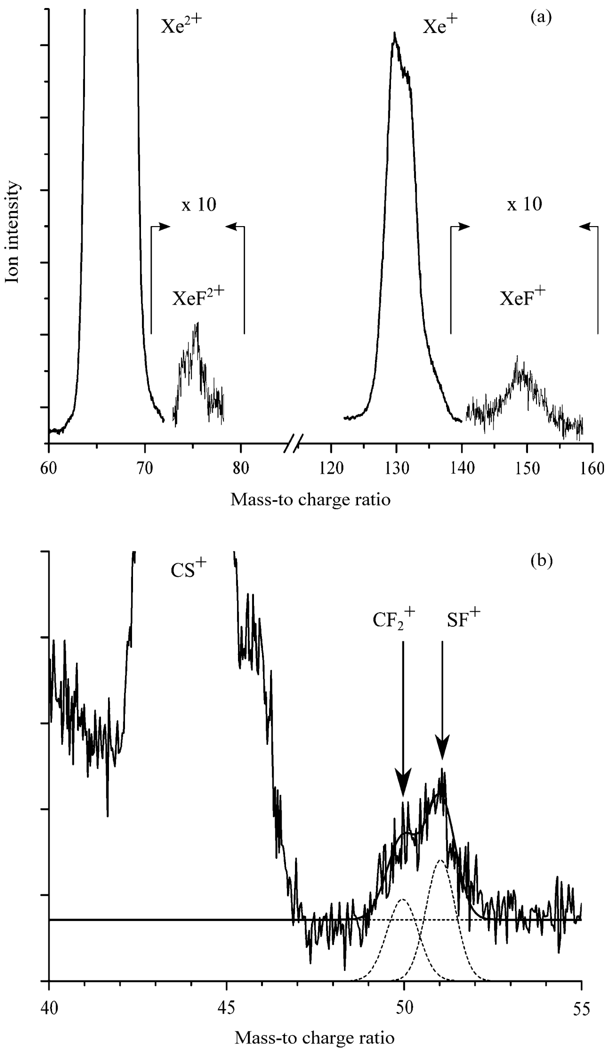

Figure 4. Mass spectra recorded following collisions of a) Xe^{3+} with CF_4 at $T_{cm} = 1.8$ eV and b) CS_2^{3+} with CF_3I at $T_{cm} = 12.5$ eV. A deconvolution to distinguish the CF_2^+ and SF^+ products is also show in (b).

targets. Following Xe^{3+} collisions with CF_4, we observed the formation of dicationic and monocationic xenon-containing molecular ions, a similar style of reactivity to that observed for I^{3+} (Figure 4a). Beams of CS_2^{3+} are harder to generate and the product ion mass spectra resulting from these weak beams have poorer statistics. However, Figure 4b clearly indicates that SF^+ is generated following interactions of CS_2^{3+} with CF_3I.

Conclusion

Bond-forming reactivity of atomic and molecular trications in low-energy supra-thermal collisions with neutral molecules seems to be a general chemical phenomenon, generating both molecular monocations and dications. This first investigation reveals a new branch of the chemistry of small multiply charged ions to explore, both experimentally and computationally.

Experimental Section

The chemical reactions reported herein were studied by using a crossed-beam mass spectrometer, which has been described before in the literature.[20] Triply charged ions were generated by electron ionization (200 eV) of a relevant precursor molecule in a low-pressure ion source. To generate I^{3+} ions, I_2 vapour, taken from above a sample of solid I_2 held at RT, was employed as a precursor. For Xe^{3+} and CS_2^{3+}, triple ionization of Xe and CS_2 vapour was performed. Typical precursor gas pressures in the ion source were of the order of 10^{-4}–10^{-3} Torr. Ions were extracted from the ion source, collimated and passed into a velocity filter, which selected the trication of interest. The ions were then electrostatically decelerated to collision energies of a few eV in the laboratory frame and entered the interaction region of a time-of-flight mass spectrometer (TOF-MS). Here, they crossed an effusive jet of the neutral collision partner under single-collision conditions. Typical I^{3+} beam currents were estimated, from the ion counts, to be of the order of a few tenths of a picoAmp. The TOF-MS periodically (50 kHz) extracts and identifies any ions present in the interaction region to quantify any reaction products. Mass spectra were recorded in the presence and absence of the neutral collision partner to allow the subtraction of any ion signals due to impurities in the ion beam or the reaction of the trications with any background gases. To quantify the yield R of bond-forming product ions in these spectra, we expressed their averaged mass-spectral intensity relative to that of the I^+ product of electron transfer. Such product ion ratios are insensitive to variations in the target gas pressure or reactant trication flux over the experimental run time.

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