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Bond-Forming Reactions of Gas-Phase Molecular Dications

Stephen D. Price,[⊥] Michelle Manning,[†,§] and Stephen R. Leone[*,‡,§]

Contribution from the Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom and Joint Institute for Laboratory Astrophysics, National Institute of Standards and Technology and University of Colorado, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440

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Abstract: We observe a series of novel reactions involving the formation of chemical bonds in a comprehensive study of the reactivity of eight dications, CF^{2+}, CF_2^{2+}, CF_3^{2+}, SF_4^{2+}, SF_3^{2+}, SF_2^{2+}, CO_2^{2+}, and OCS^{2+}, with the neutral collision partners Xe, D_2, O_2, N_2, NO, and CO. The reactions are detected in a crossed beam apparatus at laboratory-frame collision energies between 30 and 50 eV. The mass-selected dication beam interacts with a pulsed beam of the neutral reactant in a collision region and the ionic products are monitored by a time-of-flight mass spectrometer. The major reactions for each system are charge transfer processes. However, reactions involving the formation of new chemical bonds contribute significantly to the ion yield (1–20%) for several of the collision systems studied. Two classes of bond-forming reactions are observed, one involving negative ion transfer to the dication and the other involving positive ion transfer from the dication to the neutral reactant. An example of the former is the production of DCF_2^+ from the reaction between CF_2^{2+} and D_2; an example of the latter is the production of XeF^+ from the reaction between CF_2^{2+} and Xe. Estimates of the appropriate curve-crossing radii for the negative ion transfer reactions give values consistent with a Landau–Zener curve-crossing mechanism. Charge transfer products and collision-induced neutral loss channels are also reported in this study.

Introduction

In the past decade there has been increasing experimental and theoretical interest in the gas-phase physics and chemistry of small molecular dications.[1,2] During this period, the majority of the investigations of reactivity of molecular dications[3–13] were performed at high (keV) energies; only a few studies were conducted at thermal collision energies in drift tubes.[14,15] More recently, attention has focused on molecular dication/neutral collisions at intermediate (1–200 eV) kinetic energies.[10–12,16,17] However, almost without exception, these investigations of molecular dication reactivity probed dication collisions with atomic rare gases, not molecular species.

Previous investigations of the reactivity of molecular dications, employing rare gas atoms (Rg) as the neutral collision partners, focused on two types of reactivity: charge transfer and collision-induced dissociation.[3–13,16,17] The charge transfer reactions may be nondissociative (eq 1a) or dissociative (eq 1b) and involve the exchange of a single (eq 1) or a double (eq 2) charge. Collision-induced (CI) dissociation reactions commonly result in charge separation (CICS) products (eq 3), but recently collision-induced neutral loss processes (CINL) have also been observed (eq 4).[17] A similar collision-induced reactivity is observed for doubly charged cluster ions[18]

$$ABC^{2+} + Rg \rightarrow ABC^+ + Rg^+ \tag{1a}$$

$$ABC^{2+} + Rg \rightarrow AB^+ + C + Rg^+ \tag{1b}$$

$$ABC^{2+} + Rg \rightarrow ABC + Rg^{2+} \tag{2}$$

$$ABC^{2+} + Rg \rightarrow A^+ + BC^+ + Rg \tag{3}$$

$$ABC^{2+} + Rg \rightarrow AB^{2+} + C + Rg \tag{4}$$

The present study was undertaken to search for an additional class of molecular dication reaction which involves the breaking and forming of chemical bonds with simultaneous charge separation. Bond-forming reactions of *atomic* transition metal dications have been observed in low-energy collisions with hydrocarbon molecules. These bond-forming reactions, involving hydride transfer from the hydrocarbon, can compete effectively with charge-transfer.[19,20] Dehydrogenation reactions involving ligand coupling have been reported for gas-phase substituted transition metal dications.[19–21] For example, $NbCH_2^{2+}$ undergoes sequential dehydrogenation reactions with CH_4 to yield $NbC_6H_6^{2+}$ and $NbC_6H_8^{2+}$ as the highest order products.[19] Bond-forming

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[*] Address correspondence to this author at the Department of Chemistry, University of Colorado.

[†] Current Address: Chemistry Department, University of Wisconsin, Madison, WI 53706.

[‡] Staff Member, Quantum Physics Division, National Institute of Standards and Technology.

[§] University of Colorado.

[⊥] University College London.

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(1) Mathur, D. *Phys. Rep.* **1993**, *225*, 193.

(2) Larsson, M. *Comments At. Mol. Phys.* **1993**, *29*, 39.

(3) Reid, C. J.; Ballantine, J. A.; Harris, F. M. *Int. J. Mass Spectrom. Ion Proc.* **1989**, *93*, 23.

(4) Reid, C. J.; Harris, F. M.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Proc.* **1988**, *82*, 151.

(5) Curtis, J. M.; Boyd, R. K. *J. Chem. Phys.* **1984**, *80*, 1150.

(6) Herman, Z.; Jonathan, P.; Brenton, A. G.; Beynon, J. H. *Chem. Phys. Lett.* **1989**, *141*, 433.

(7) Hamdan, M.; Brenton, A. G. *J. Phys. B* **1989**, *22*, L45.

(8) Mathur, D.; Kingson, R. G.; Harris, F. M.; Brenton, A. G.; Beynon, J. H. *J. Phys. B* **1987**, *20*, L577.

(9) Koslowski, H. R.; Lebius, H.; Staemmler, V.; Fink, R.; Wiesemann, K.; Huber, B. A. *J. Phys. B* **1991**, *24*, 5023.

(10) Pedersen, J. O. K.; Hvelplund, P. *J. Phys. B* **1987**, *20*, L317.

(11) Rogers, S. A.; Price, S. D.; Leone, S. R. *J. Chem. Phys.* **1993**, *98*, 280.

(12) Price, S. D.; Rogers, S. A.; Leone, S. R. *J. Chem. Phys.* **1993**, *98*, 9455.

(13) Dejarme, L. E.; Cooks, R. G.; Ast, T. *Org. Mass Spectrom.* **1992**, *27*, 667.

(14) Jones, J. D. C.; Raouf, A. S. M.; Lister, D. G.; Birkenshaw, K.; Twiddy, N. D. *Chem. Phys. Lett.* **1981**, *78*, 75.

(15) Chatterjee, B. K.; Johnsen, R. *J. Chem. Phys.* **1989**, *91*, 1378.

(16) Manning, M.; Price, S. D.; Leone, S. R. *J. Chem. Phys.* **1993**, *99*, 8695.

(17) Price, S. D.; Manning, M.; Leone, S. R. *Chem. Phys. Lett.* **1993**, *214*, 553.

(18) Leiter, K.; Kreisle, D.; Echt, O.; Märk, T. D. *J. Phys. Chem.* **1987**, *91*, 2583.

(19) Roth, L. M.; Freiser, B. S. *Mass Spectrom. Rev.* **1991**, *10*, 303.

(20) Tonkyn, R.; Weisshaar, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7128.

(21) Weisshaar, J. C. *Acc. Chem. Res.* **1993**, *21*, 213.

0002-7863/94/1516-8673$04.50/0

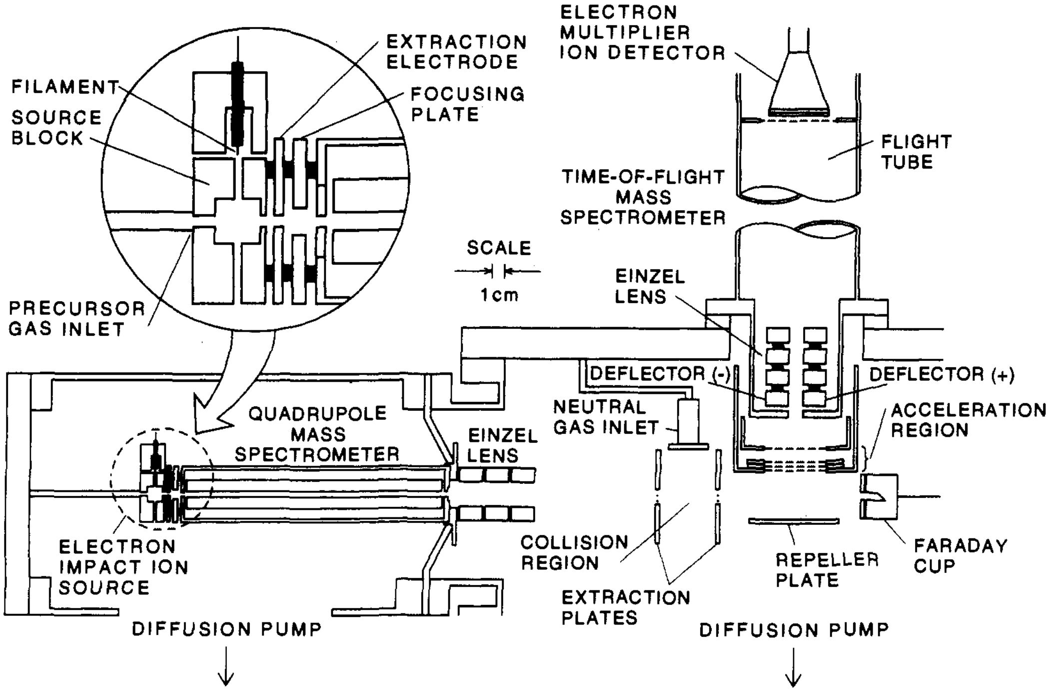

Figure 1. Schematic diagram of the crossed beam apparatus used to study the bond-forming reactivity of molecular dications.

reactions of C_{60}^{2+} have also been reported in the literature.[22] In these experiments the most commonly encountered product channels involve the association of the dication with the neutral reactant, but reactions involving the transfer of hydroxide ions from small primary alcohols to C_{60}^{2+} are also observed. However, to our knowledge, only one other bond-forming reaction of a small molecular dication has been reported before in the literature.[15] In this paper we present a study of the reactivity of 44 molecular dication/neutral systems at a laboratory kinetic energy of 30–50 eV. We focus in the discussion on those reactions in which chemical bonds are broken and formed between the reactants.

The neutral reactants used in this investigation are the small diatomic molecules D_2, O_2, N_2, NO, and CO and as well as Xe atoms. The dications with which these neutral species interact are CF^{2+}, CF_2^{2+}, CF_3^{2+}, SF_4^{2+}, SF_3^{2+}, SF_2^{2+}, CO_2^{2+} and OCS^{2+}. Our results show that charge transfer is the major reactive pathway in these collisions, but there are several systems for which characteristic reactions involving the breaking and forming of chemical bonds contribute significantly to the ion yield. Results are also presented on the charge transfer and collision-induced neutral loss pathways.

Experimental Section

The experimental apparatus is shown in Figure 1. More detailed descriptions of the experiment and procedure have been reported.[11,12] The dication reactants are generated in an ion source where a continuous jet of the precursor gas is intersected by a beam of ~150 eV electrons. The source is biased between 20 and 30 V to define the kinetic energy of the reactant ions accurately. The precursor molecules employed are CF_4, SF_6, CO_2, and OCS. All the positive ions are extracted from the source and a mass selected dication beam (>99%) is generated using a quadrupole mass spectrometer. The resulting dication beam is then focused into the collision region (Figure 1) using three electrostatic lenses. Appropriate electrical potentials are applied to the collision region to define the kinetic energy of the collision system under study. The neutral reaction partner is introduced into the collision region through a pulsed valve. The backing pressure of the neutral gas is carefully controlled so that single-collision conditions are maintained in the interaction region. The product ions resulting from any collisions and the unreacted dications are extracted from the collision region into the source region of a time-of-flight mass spectrometer (TOFMS) by an electric field. One cycle of the experiment involves pulsing the source field of the TOFMS 1.2 ms after the pulsed valve is triggered to release the neutral molecule. This time delay, due principally to the mechanical operation of the valve, was determined experimentally to be the time necessary for the product ions to reach the TOFMS source region after the voltage pulse is sent to open the valve. Each product ion mass spectrum recorded in this study was accumulated at a repetition rate of 10 Hz over 15 000 to 50 000 such cycles in order to achieve a satisfactory signal-to-noise ratio for all the product ions.

A set of deflectors in the ion flight tube of the TOFMS (Figure 1) is used to correct for the lateral velocity of the ions, enabling them to reach the microchannel plate detector. Unfortunately, these deflectors introduce some mass discrimination into the final product ion mass spectra.[11,12] In the investigations presented in this paper, the deflectors were set to transmit efficiently the product ions containing new bonds. As a result, the other product ions may be discriminated against to a small extent. In all cases where we observe bond-forming reactivity, we performed extensive tests to ensure that the associated product ion signals were not due to contaminants or background gases.

One drawback of the current experimental arrangement is that the quadrupole imparts a significant angular divergence to the dication beam. This divergence, despite the focusing optics (Figure 1), introduces extremely large ion beam losses when the collision energy is reduced below 30 eV in the laboratory frame. Previous work has indicated that bond-breaking and bond-forming reactions of gas-phase dications are most likely to be observed at low collision energies.[19–21] Hence, most of the collisions in this study were carried out at a laboratory kinetic energy of 30 eV. This laboratory-frame energy restriction means the center-of-mass kinetic energy is not the same for all the collision systems investigated. For the interaction of an effectively stationary neutral species with an ion moving at a given laboratory frame energy, the ratio of the center-of-mass kinetic energy to the laboratory kinetic energy is equal to the ratio of the reduced mass of the collision system to the mass of the ion. Hence, for example, the center-of-mass kinetic energies for the interaction of CF_2^{2+} at 30 eV laboratory kinetic energy with Xe, D_2, and O_2 are 21.7, 2.2, and 11.7 eV, respectively, while for the interaction of CF_3^{2+} the center-of-mass energies decrease to 19.7, 1.6, and 9.5 eV. However, as the present study is intended to be an initial survey of dication reactivity, we considered it most important to work at the lowest possible collision energy for each system. Such an approach allows a qualitative investigation to determine whether bond-forming reactions are important

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[22] Javahery, G.; Petrie, S.; Wincel, H.; Bohme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 6296.

[23] Jonathan, P.; Hamdan, M.; Brenton, A. G.; Whillett, G. D. *Chem. Phys.* **1988**, *119*, 159.

[24] Masuoka, T.; Koyano, I. *J. Chem. Phys.* **1991**, *95*, 909.

Table 1. Ionic Products Observed from Molecular Dication/Neutral Collision Systems in Which Products Involving the Formation of New Chemical Bonds Are Detected

reactants	charge transfer products[a]	CINL products[b]	unassigned products[c]	products of bond-forming reactions[d]	ion yield of bond-forming reactions (%)[e]
CF_3^{2+} + Xe	CF^+, CF_2^+	CF_2^{2+}		XeF^+	<1
CF_2^{2+} + Xe	CF^+, C^+		F^+	XeF^+	<1
SF_4^{2+} + Xe	SF_3^+, SF_2^+, SF^+	SF_2^{2+}		XeF^+	<1
SF_3^{2+} + Xe	SF_2^+, SF^+	SF_2^{2+}		XeF^+	<1
SF_2^{2+} + Xe	SF_2^+, SF^+, S^+			XeF^+	<1
CO_2^{2+} + Xe	CO^+		O^+	XeO^+	<1
CF_3^{2+} + D_2	CF_3^+, CF_2^+, CF^+	CF_2^{2+}		DCF_2^+	12
CF_2^{2+} + D_2	CF_2^+, CF^+			DCF_2^+, DCF^+	9, <1
CF^{2+} + D_2	CF^+, C^+			CD^+	12
CO_2^{2+} + D_2	CO_2^+, CO^+		O^+	DCO^+, DCO_2^+, OD^+	9, <1, 2
OCS^{2+} + D_2	OCS^+		CO^+, S^+	SD^+	21
CF_3^{2+} + O_2	CF_3^+, CF_2^+, CF^+	CF_2^{2+}		OCF^+	<1
CF_2^{2+} + O_2	CF_2^+, CF^+			OCF^+, CO^+	1, <1
CF^{2+} + O_2	CF^+, C^+		F^+	CO^+	3
SF_4^{2+} + CO	SF_3^+, SF_2^+	SF_3^{2+}, SF_2^{2+}	F^+	OCF^+	<1

[a] Charge transfer and dissociative charge transfer products. Although not listed explicitly here, the corresponding singly charged product ions formed from the neutral reactant by charge transfer (e.g Xe^+ in the Xe/dication systems) are observed in each case. [b] Collision-induced neutral loss products. [c] Products which cannot be definitely assigned to a specific reactive channel. See text for details. [d] All ions identified that involve the formation of new chemical bonds. Several of the collision systems involve more than one bond-forming product channel; in these cases each product is listed. See text for details. [e] Yield of ions detected from the bond-forming channels expressed as a percentage of the total number of product ions for each system. For systems involving more than one bond-forming product channel, values are given for each channel in the same order as the list of products in the previous column.

Table 2. Ionic Products Observed from Molecular Dication + Neutral Collision Systems in Which Products Involving the Formation of New Chemical Bonds Are Not Detected

reactants	charge transfer[a]	CINL products[b]	unassigned products[c]
CF^{2+} + Xe	C^+, CF^+		F^+
OCS^{2+} + Xe	S^+		CO^+
SF_4^{2+} + D_2	SF_2^+		
SF_3^{2+} + D_2	SF_3^+, SF_2^+	SF_2^{2+}	
SF_2^{2+} + D_2	SF_2^+, SF^+		
SF_4^{2+} + O_2	SF_3^+, SF_2^+, S^+	SF_3^{2+}	
SF_3^{2+} + O_2	SF_3^+, SF_2^+, SF^+, S^+	SF_2^{2+}	
SF_2^{2+} + O_2	SF_2^+, SF^+, S^+		
CF_3^{2+} + N_2	CF_3^+, CF_2^+, CF^+	CF_2^{2+}	F^+
CF_2^{2+} + N_2	CF_2^+, CF^+		
CF^{2+} + N_2	CF^+, C^+		
SF_4^{2+} + N_2	SF_3^+, SF_2^+	SF_3^{2+}, SF_2^{2+}	F^+
SF_3^{2+} + N_2	SF_3^+, SF_2^+, SF^+	SF_2^{2+}	
SF_2^{2+} + N_2	SF_2^+, SF^+	SF^{2+}	F^+
CO_2^{2+} + N_2	O^+, CO^+		
OCS^{2+} + N_2	OCS^+		CO^+, S^+
CF_3^{2+} + NO	CF_3^+, CF_2^+, CF^+	CF_2^{2+}	F^+
CF_2^{2+} + NO	CF_2^+, CF^+, C^+		F^+
CF^{2+} + NO	CF^+		C^+, F^+
SF_4^{2+} + NO	SF_3^+, SF_2^+		
SF_3^{2+} + NO	SF_3^+, SF_2^+, SF^+	SF_2^{2+}	
SF_2^{2+} + NO	SF_2^+, SF^+, S^+		
CO_2^{2+} + NO	CO_2^+, C^+		CO^+, O^+
OCS^{2+} + NO	OCS^+		CO^+, S^+
CF_3^{2+} + CO	CF_3^+, CF_2^+, CF^+	CF_2^{2+}	F^+
CF_2^{2+} + CO	CF_2^+, CF^+, C^+		
CF^{2+} + CO	CF^+, C^+		F^+
SF_3^{2+} + CO	SF_3^+, SF_2^+, SF^+	SF_2^{2+}	
SF_2^{2+} + CO	SF_2^+, SF^+		

[a] Charge transfer and dissociative charge transfer products. Although not listed explicitly here, the corresponding singly charged product ions derived from the neutral reactant (e.g. Xe^+ in the Xe/dication systems) are observed in each case. [b] Collision-induced neutral loss products. [c] Products which cannot be definitely assigned to a specific reactive channel. See text for details.

for a given collision system, but it does not provide a determination of detailed collision energy dependencies and cross section estimates. For one molecular dication, CF^{2+}, the reactant ion current was so small that experiments at E_{lab} = 30 eV were not possible, hence the CF^{2+}/neutral reactions were carried out at E_{lab} = 50 eV.

Results

Tables 1 and 2 list the ionic products observed for all the collision systems studied. Table 1 gives the ionic products from the systems in which bond-forming reactivity is observed and Table 2 lists the ionic products from systems where only charge transfer and collision-induced dissociation reactions are observed. Where possible, Tables 1 and 2 also indicate the mechanism (e.g. charge transfer) by which a particular product is formed. Due to the mass discrimination effects discussed above, the ion yields of the bond-forming reactions presented in Table 1 are upper limits. A brief discussion of the assignment of the various charge transfer (eq 1) and collision-induced dissociation (eqs 3 and 4) reactions is given below. However, since several recent studies of these classes of reactions between dications and neutrals have been reported,[3-13,16,17] the principal focus of this paper will be on the reactive processes in which new chemical bonds are formed.

The occurrence of neutral loss reactions is easily identified by the observation of daughter dications (eq 4). Tables 1 and 2 show that the formation of daughter dications, via neutral F atom loss, is an important process in the collision of CF_3^{2+}, SF_4^{2+}, SF_3^{2+}, and SF_2^{2+} with the neutral reaction partners employed in this experiment. More detailed studies of such neutral loss reactions of fluorinated molecular dications have recently been discussed;[17] such reactions are also observed following collisions of doubly charged metal clusters.[18] The present investigation provides further evidence that, for certain fluorinated molecular dications, neutral loss processes contribute significantly to the ion yield at intermediate collision energies.

For every system studied in the present investigation, charge transfer reactions populating either stable (eq 1a) or dissociative (eq 1b) states of the singly charged product ion are important reaction pathways (Tables 1 and 2). Recent work has shown that at intermediate collision energies these charge transfer processes can be successfully modeled by a Landau–Zener avoided crossing between a weakly attractive reactant potential and a repulsive product potential.[8-12,16] The assignment of ions as the products of charge transfer processes is more involved than for neutral loss reactions. Singly charged ions formed directly from the parent molecular dication, such as SF_2^+ from the SF_2^{2+}/D_2 collision system, are obviously products of nondissociative charge transfer (eq 1a). In addition, the assignment of a fragment singly charged ion as the product of a dissociative charge transfer pathway (eq 1b), such as CF_2^+ in the CF_3^{2+}/D_2 collision system, is usually straightforward. If the CF_2^+ ion from this system was a product of CICS (eq 3) an approximately equal number of partner ions (F^+) should be observed in the mass spectrum, after

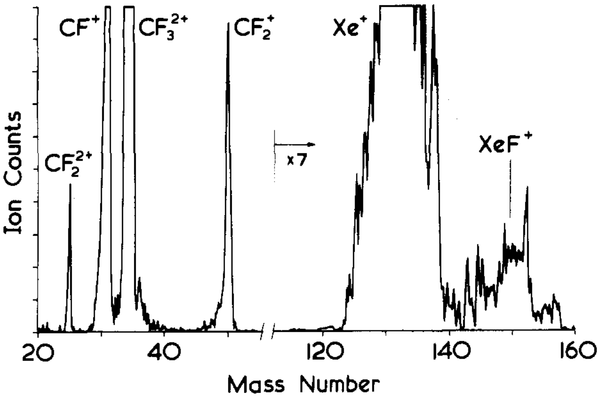

Figure 2. Mass spectrum recorded following collisions of CF_3^{2+} with Xe at a laboratory collision energy of 30 eV.

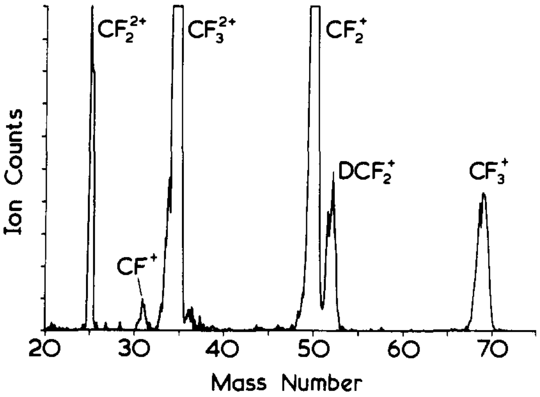

Figure 3. Mass spectrum recorded following collisions of CF_3^{2+} with D_2 at a laboratory collision energy of 30 eV.

allowing for mass discrimination effects. In many of the collision systems studied, a partner ion is not observed and the dissociative charge transfer mechanism (eq 1b) can be assigned definitively. In many cases where the partner CICS ion is observed, for example F^+ in the CF^{2+}/O_2 system, its intensity is many times smaller than that of the ion of interest, in this case the C^+ ion. In this situation, even allowing for mass discrimination effects, it is clear the majority of the C^+ signal is due to dissociative charge transfer, but we cannot distinguish between the charge transfer and CICS mechanisms for the formation of the F^+ ion. In a few cases, such as the OCS^{2+}/N_2 system where the CO^+ and S^+ product ions are observed in approximately equal amounts, the above logic does not allow us to distinguish the charge transfer and CICS mechanisms for either of the fragment singly charged ions. These cases are clearly indicated in Tables 1 and 2.

In the present study, the simplest collisional systems that yield ionic products with new bonding arrangements involve the reactions of CF_3^{2+}, CF_2^{2+}, SF_4^{2+}, SF_3^{2+}, SF_2^{2+}, and CO_2^{2+} with Xe atoms. Although the signals for these products are weaker than some others, we consider these simple positive ion transfer reactions first. In the product mass spectra recorded following these collisions, a signal is observed corresponding to XeF^+ formation (or XeO^+, in the case of CO_2^{2+}). Figure 2 shows a sample mass spectrum recorded following collisions of CF_3^{2+} with Xe at a laboratory frame collision energy of 30 eV. A weak XeF^+ signal is observed, with characteristic isotopic broadening due to Xe, centered at mass 151. In each case where XeF^+ or XeO^+ ions are observed, they comprise less than 1% of the ionic products (Table 1). Collisions of OCS^{2+} and CF^{2+} with Xe at intermediate laboratory collision energies did not result in any observable bond-forming reactions (Table 2). Upon qualitative inspection, the reactions with Xe atoms listed in Table 1 all appear to involve positive ion transfer (F^+ or O^+) from the molecular dication to the Xe atom.

Of the other reactive systems investigated, collisions involving the deuterium molecule are the most effective at forming new bonds with molecular dications. Deuterium is chosen as the neutral species rather than hydrogen because of its greater mass, yielding product ions which are easily distinguished in the TOFMS. The observed high reactivity of D_2 is partly because this molecule is the lightest neutral reactant employed, and hence it has the lowest experimental center of mass kinetic energy. In addition, the small polarizability of D_2 may play a role, as discussed further below. The deuterium molecule reacts to create new bonds with CF_3^{2+}, CF_2^{2+}, CF^{2+}, CO_2^{2+}, and OCS^{2+}. The products of these reactions are listed in Table 1.

The only product ion resulting from new bond formation in the CF_3^{2+}/D_2 system is DCF_2^+, which shows up as a strong peak in the product mass spectrum (Figure 3). The DCF_2^+ ion signal in this product mass spectrum is comparable (10% of the total) to the CF_3^+ signal that occurs by nondissociative charge transfer (eq 1a). The mass spectrum resulting from collisions of CF_2^{2+} and D_2 also shows a significant DCF_2^+ signal with a weak signal due to DCF^+ also present. The reaction of CF^{2+} with D_2, which for the intensity reasons described above was carried out at 50 eV collision energy, forms a C–D bond to produce CD^+ ions. The reaction of $CO_2^{2+} + D_2$ includes three products with new bonds. The mass spectrum shows an appreciable DCO^+ peak and weak OD^+ and DCO_2^+ signals. The SD^+ ion is the sole product ion due to a new bond formed in the OCS^{2+}/D_2 reaction system. Although the SD^+ ion is formed in significantly smaller yields than the charge transfer product OCS^+, it is a substantial signal, comprising 21% of the total product ions detected, with an intensity comparable to the S^+ and CO^+ signals, which are also observed in the product mass spectrum. Bond-forming reactions between D_2 and SF_4^{2+}, SF_3^{2+}, or SF_2^{2+} are not observed at 30 eV laboratory-frame collision energy. Mechanistically, the reactions with D_2 appear to result from D^- transfer to the dication, usually accompanied by fragmentation of the resulting singly charged molecular ion. A mechanism may be:

$$CF_3^{2+} + D_2 \rightarrow [DCF_3^+]^* + D^+ \qquad (5)$$

$$[DCF_3^+]^* \rightarrow DCF_2^+ + F \qquad (6)$$

A more detailed consideration of the mechanisms of these reactions is presented below.

Reactions of CF_3^{2+}, CF_2^{2+}, and CF^{2+} with O_2 are similar to the corresponding reactions involving D_2; although stable and dissociative charge transfer are the primary processes observed, weaker signals for bond-forming reactions are clearly present. These bond-forming reactions are also listed in Table 1. At a collision energy of 30 eV the CF_3^{2+}/O_2 system yields only one product ion resulting from new bond formation: OCF^+. The product ion mass spectrum of the $CF_2^{2+} + O_2$ reaction (Figure 4) includes weak signals from both OCF^+ and CO^+ ions. A small CO^+ signal is also present in the mass spectrum following 50 eV collisions between CF^{2+} and O_2. In the cases where CO^+ is observed, tests were conducted to ensure that this signal was not due to background N_2^+. The percentage product ion yields for the bond-forming reactions that take place between the molecular dications and O_2 (Table 1) are markedly smaller than those for D_2. However, the qualitative picture of the first step of the reactivity is the same, appearing to involve negative ion transfer, O^- in this case, from the neutral molecule to the doubly charged species.

Like D_2, the oxygen molecule does not appear to form new bonds with SF_4^{2+}, SF_3^{2+}, and SF_2^{2+} at intermediate collision energies. The collision systems involving the interaction of OCS^{2+} and CO_2^{2+} with O_2 were not investigated due to the difficulty in distinguishing the reactive processes from charge transfer reactions.

The only neutral molecule that demonstrates any propensity to break and reform bonds with SF_4^{2+} is the heteronuclear diatomic

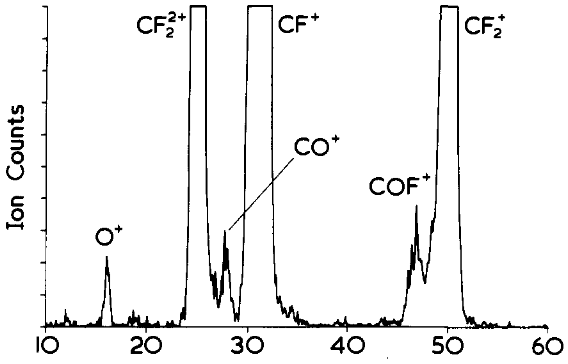

Figure 4. Mass spectrum recorded following collisions of CF_2^{2+} with O_2 at a laboratory collision energy of 30 eV.

CO, which reacts to give a weak OCF^+ signal (Table 1). The OCF^+ peak is similar in magnitude to the weak SF_3^{2+} and SF_2^{2+} peaks resulting from neutral atom loss, which are also observed in the product mass spectrum. In contrast to the reactivity observed with D_2 and O_2, this reaction may involve positive ion transfer from the dication to the neutral species in a manner similar to the reactions with Xe. There is no evidence for reactions that form new bonds following 30 eV collisions of CO with any of the other dications generated in this work. Similarly, none of the dication/N_2 or dication/NO collision systems investigated in this study (Table 2) have detectable yields of product ions involving the formation of new bonds.

Discussion

As described above, a significant number of bond-forming reactions between molecular dications and neutral species are observed at intermediate collision energy. However, it is important to note that charge transfer reactions still account for the majority of the product ions in these collision systems. The charge transfer reactivity of molecular dications at intermediate collision energies has been the subject of several recent experimental investigations.[9-12,16] Hence, the discussion here focuses on the new bond-forming reactivity observed.

We are aware of one previous report of a bond-forming reaction for a small molecular dication. In a drift tube study of the reactivity of O_2^{2+}, Chatterjee and Johnsen[15] observed an apparent "ion transfer reaction" between the molecular dication and the nitric oxide molecule (eq 7). This reaction could be viewed as either N^- transfer from the neutral molecule or O^+ transfer from the dication:

$$O_2^{2+} + NO \rightarrow NO_2^+ + O^+ \qquad (7)$$

Bond-forming reactions are also known to be important in the thermal reactivity of gas-phase *atomic* dications.[19-21] In fact, reactions involving hydride ion transfer, similar to those observed here between molecular dications and D_2, are well documented for transition metal atomic dications and small hydrocarbons (eq 8):

$$Nb^{2+} + C_2H_6 \rightarrow NbH^+ + C_2H_5^+ \qquad (8)$$

As noted above, the bond-forming reactivity observed in this investigation can be classified into two categories. First, reactions can occur by negative ion transfer (eqs 5 and 6) from the neutral species to the molecular dication. This class of bond-forming reaction appears to have the largest cross section and to occur with O_2 and D_2. The second class of reaction observed with Xe and CO involves positive ion transfer from the molecular dication to the neutral species (eq 9):

$$CF_3^{2+} + Xe \rightarrow XeF^+ + CF_2^+ \qquad (9)$$

Each is considered in more detail below, with the negative ion transfer discussed first, since a greater proportion of previous work has addressed this mechanism.

Negative Ion Transfer Reactions

The competition between hydride (deuteride) transfer reactions and charge transfer reactions in collisions of atomic transition metal dications with hydrocarbons has been rationalized using a curve-crossing approach based on Landau–Zener theory.[19-21] As shown in Figure 5a, the collision can be modeled by the reactants approaching each other along a potential energy curve which is slightly attractive due to ion-induced polarization forces. Following the reaction, the two positively charged products move apart along a surface dominated by Coulomb repulsion. For reaction, a curve crossing must occur from the reactant surface to one of the product potentials. As demonstrated by the analysis of Landau and Zener, the probability of this crossing depends, in large part, on the radius of the intersection of the potential energy curves. Curve crossings at small internuclear distances are too strongly avoided and hence unreactive, while crossings at large internuclear distance, due to the distance over which the electron or hydride ion must hop, are also unreactive. This dependence of the reactivity on internuclear distance leads to a so called "reaction window" of internuclear distances in which a particular reaction channel is favored. As expected, due to the differing masses of an electron and the hydride ion, the reaction windows for electron transfer and hydride transfer are not identical; the hydride transfer window lies at smaller reactant separations than the electron transfer window.[21] Changing the identity of the reaction partners changes the relative energies of the reactant and product asymptotes, and hence the radii of the avoided crossings, thus moving the crossings in and out of the respective reaction windows. Changing the identity of the reactants can result in marked changes in reactivity.

Analysis of the differing reactivity of a range of transition metal dications with a variety of alkanes has allowed an estimate to be made of the reaction window for hydride transfer of 0.4–0.6 nm. Experimentally it is apparent that the probability for hydride transfer is high if the energetics of a particular reactant pair place the electron transfer crossing at large internuclear distance, outside the appropriate reaction window, but position the hydride transfer curve crossing in its reaction window (Figure 5a).[21] This situation allows a significant proportion of the encounters to achieve the "critical distance" required for hydride transfer.

Table 3 shows the exothermicities and calculated curve-crossing radii for a selection of the negative ion transfer reactions observed here. The curve crossing radii are calculated by analytically finding the intersection point of a polarization-attraction potential which converges to the energy of the separated reactants with a Coulomb repulsion potential which converges to the energy of the separated ionic products (Figure 5a).[11] Clearly for this procedure we require the heats of formation of the reactants and products. All the thermodynamic data used in Table 3 have been taken from standard literature sources, except the double ionization potentials. Data are scarce concerning the values of the double ionization potentials for several of the molecules whose dication reactions have been investigated in this study. In Table 3 we have used reliable literature values[23,24] for the double ionization potentials of OCS and CO_2, as well as estimates of the double ionization potentials of CF and CF_2 obtained in a recent study of their charge transfer reactivity.[16] No information is available regarding the double ionization potentials of CF_3 and the SF_n species, hence curve-crossing radii for these species cannot be evaluated. For all the reactions shown in Table 3 we have indicated that the reaction involves the formation of a corresponding positive ion atomic fragment (e.g. D^+ or O^+) derived

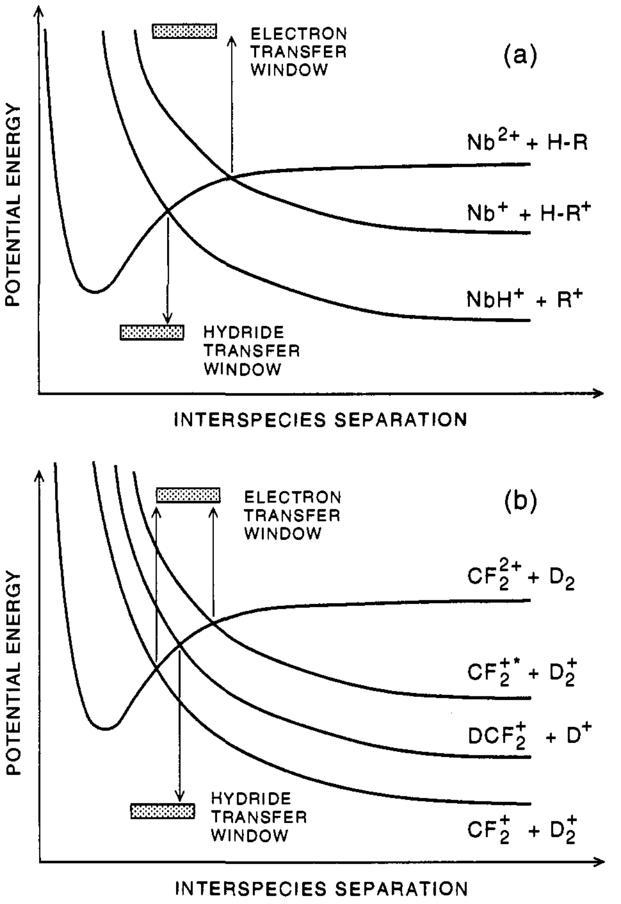

Figure 5. Schematic potential energy surfaces for electron and hydride transfer reactions of (a) Nb^{2+} with alkanes and (b) CF$_2^{2+}$ with D$_2$.

Table 3. Reaction Exothermicities and Calculated Curve-Crossing Radii for the Observed Negative Ion Transfer Reactions

reactants	products	exothermicity (eV)	crossing radius (nm)
CF^{2+} + D$_2$	CD^{+} + D^{+} + F	4.6	0.33
CF$_2^{2+}$ + D$_2$	DCF$_2^{+}$ + D^{+}	8.2	0.21
CF$_2^{2+}$ + D$_2$	DCF^{+} + D^{+} + F	2.1	0.69
CO$_2^{2+}$ + D$_2$	DCO$_2^{+}$ + D^{+}	11.5	0.17
CO$_2^{2+}$ + D$_2$	DCO^{+} + D^{+} + O	6.0	0.26
CO$_2^{2+}$ + D$_2$	OD^{+} + D^{+} + CO	5.3	0.29
OCS^{2+} + D$_2$	SD^{+} + D^{+} + CO	3.0	0.49
CF$_2^{2+}$ + O$_2$	CO^{+} + O^{+} + F$_2$	1.4	1.03
CF$_2^{2+*}$ + O$_2$[a]	CO^{+} + O^{+} + F$_2$	5.4	0.30
CF$_2^{2+}$ + O$_2$	OCF^{+} + O^{+} + F	6.5	0.26
CF^{2+} + O$_2$	CO^{+} + O^{+} + F	8.3	0.22

[a] The asterisk indicates an excited state (see text).

from the neutral diatomic reactant. This conclusion is drawn from the fact that we observe D^{+} signals in our product ion mass spectra from the reaction of CF$_n^{2+}$ with D$_2$ but no signals corresponding to F^{+}. Indeed, observation of DCF$_2^{+}$ from the reaction of CF$_2^{2+}$ with D$_2$ strongly supports this conclusion, since the DCF$_2^{+}$ ion must be formed together with a D^{+} ion. As has been discussed before, the crossed beam arrangement employed here is not very sensitive to ions that are formed from the slow neutral species.[11,12] However, when the relevant ion peaks are not masked by other signals, the observed product ion mass spectra never contradict the conclusion that one of the ions formed in a negative ion transfer reaction is an atomic ion derived from the neutral reactant.

Apart from one value, the calculated crossing radii (Table 3) of the observed negative ion transfer reactions are grouped between 0.17 and 0.69 nm. It is important to realize that the crossing radii given in Table 3 are all calculated assuming the interaction of ground state reactants to form the given product ions in their ground states. Hence, the values reported in Table 3 give lower limits on the crossing radii for the reaction of ground state dications, since the product ions can be formed in excited electronic states.[11,12] The product ion excitation is limited, however, because if large excitations occur, the ion itself (e.g. CF$_2^{+}$) would dissociate and a different ion would be observed in the product ion mass spectrum. Considering the uncertainties in the thermodynamic data involved in the calculations and the possibility of the formation of excited product ion states, the values of the crossing radii are similar to the 0.4–0.6 nm "reaction window" determined for the reactions of the atomic transition metal dications.[21] Our data therefore are in qualitative agreement with the Landau–Zener model of the hydride transfer reaction.

Table 4. Reaction Exothermicities and Curve-Crossing Radii for the Nondissociative Charge Transfer Reactions of the Systems Listed in Table 3

reactants	products	exothermicity (eV)	crossing radius (nm)
CF^{2+} + D$_2$	CF^{+} + D$_2^{+}$	10.9	0.17
CF$_2^{2+}$ + D$_2$	CF$_2^{+}$ + D$_2^{+}$	5.6	0.28
CO$_2^{2+}$ + D$_2$	CO$_2^{+}$ + D$_2^{+}$	8.4	0.20
OCS^{2+} + D$_2$	OCS^{+} + D$_2^{+}$	4.4	0.34
CF$_2^{2+}$ + O$_2$	CF$_2^{+}$ + O$_2^{+}$	9.1	0.21
CF^{2+} + O$_2$	CF^{+} + O$_2^{+}$	14.3	0.17

The lower limit on the crossing radius of 1.03 nm determined for the CF$_2^{2+}$ + O$_2$ reaction (Table 3) is significantly *larger* than the reaction window. This value can be rationalized by assuming the reaction may occur with an excited state of the dication reactant. In fact, a recent study has suggested that an excited state of CF$_2^{2+}$ lies ~4 eV above the ground electronic state of the dication and that this state is populated in the CF$_2^{2+}$ beam.[16] Table 3 shows that the lower limit on the curve-crossing radius for the negative ion transfer reaction of O$_2$ with this excited dication state is 0.3 nm, a value much more in accord with the position of the reaction window. The wider spread of the nominal curve-crossing radii listed in Table 3 compared with the radii determined for the reactions of atomic dications may be due to several reasons: the uncertainty concerning the molecular dication energetics, the possibility of excited states of product ion being formed, the considerable anisotropy of the molecular dication/neutral potential energy surface, which is not reflected in the simple one-dimensional Landau–Zener model, or the lower polarizabilities of small diatomic molecules in comparison with large alkane molecules.

Some important differences are apparent between our observations and those involving transition metal dications. In this study we do not observe a situation where bond-forming reactivity dominates the ion yield, whereas for reactions of metal dications, bond formation can be the dominant reactive channel.[19–21] This contrast arises because of the markedly different energetics of transition metal atomic dications and molecular dications. In the case of the transition metal atomic dications, the hydride transfer reaction is often the most exothermic channel available to the reacting system. Hence, the electron transfer curve-crossing radius can be too large for efficient transfer, yet the crossing corresponding to hydride ion transfer can be located in the appropriate reaction window (Figure 5a). Table 4 shows the exothermicities and calculated electron transfer crossing radii for the molecular dication collision systems that exhibit bond-forming reactivity. Except in one case (CO$_2^{2+}$ + D$_2$ → DCO$_2^{+}$ + D^{+}), the electron transfer process is more exothermic than the corresponding hydride transfer reaction. Thus, as shown in Figure 5b, electron transfer can usually compete directly with hydride transfer. Also indicated in Figure 5b, these electron transfer processes may involve excited electronic product ion states. In the specific case of the CO$_2^{2+}$ + D$_2$ system, although electron transfer is less exothermic than nondissociative D^{-} transfer, both processes are sufficiently exothermic to allow their direct competition, which is observed experimentally. These energetic differences between the molecular and atomic systems explain qualitatively why bond-forming reactivity does not dominate the product ion yield for the molecular systems investigated in this study.

As mentioned above, the smaller product ion yield for the bond-forming reactions of molecular dications with O_2 compared with D_2 at 30 eV laboratory collision energy is probably due to the larger center-of-mass collision energy in the systems involving the heavier neutral molecule. This suggests that the cross sections for bond-forming reactions may increase at lower collision energies, a conclusion supported by the fact that reactions of molecular dications at higher collision energies do not exhibit bond-forming reactivity.[3-13]

The Landau–Zener model of electron transfer reactions has a powerful predictive capability for the charge transfer reactions of molecular dications.[6,8,10-12] However, the qualitative Landau–Zener model for negative ion transfer cannot always identify when there are no bond-forming reactions (Table 2). For example, the collision system involving the interaction of OCS^{2+} with NO exhibits no bond-forming reactivity, yet several possible reactive channels (e.g. $NS^+ + CO + O^+$) have exothermicities which would place a curve crossing for negative ion transfer at a favorable radius. There is a lack of bond-forming reactivity for a significant number of the collision systems investigated. This clearly indicates that the details of the energetics and reaction dynamics of each collision system play a significant role in determining the nature of the overall reactive scheme. Hence, at present, the Landau–Zener model, while permitting a rationalization of the negative ion transfer reactions that are observed, has little merit as a predictive tool.

The Landau–Zener approach to negative ion transfer is used to model the reaction as an interaction between two structureless species. However, the arguments presented above indicate that more complex negative ion transfer mechanisms may in fact be operating. A few qualitative observations can be made. One possible mechanism for negative ion transfer could involve collision-induced charge separation (CICS, eq 3) of the molecular dication, with concomitant reaction of one of the resulting fragment ions with the neutral species. Note that the same neutral species must be involved in both steps since the experiments are performed under single collision conditions. This mechanism might be illustrated by eqs 10 and 11:

$$CF_3^{2+} + D_2 \rightarrow [CF_2^+ + F^+ + D_2]^* \tag{10}$$

$$[CF_2^+ + F^+ + D_2]^* \rightarrow DCF_2^+ + F^+ + D \tag{11}$$

This mechanism does not agree, however, with the experimental observations, since it was concluded from the data above that one of the positive ions formed by the negative ion transfer reaction most likely derives from the neutral molecule. This mechanism (eqs 10 and 11) also seems distinctly improbable since the ion yields observed for negative ion transfer are significantly larger than those associated with CICS, the first step of this mechanism.[11]

Another possible stepwise negative ion transfer mechanism involves dissociative electron transfer followed by an appropriate ion–neutral reaction. Again, these reactions must occur within the same reactant pair:

$$OCS^{2+} + D_2 \rightarrow [OC^+ + S + D_2^+]^* \tag{12}$$

$$[OC^+ + S + D_2^+]^* \rightarrow OC^+ + SD^+ + D \tag{13}$$

Note that this mechanism (eqs 12 and 13) requires that one of the product ions is derived from the neutral species formed in the dissociative electron transfer step (for example, S in eq 12). In the majority of cases, the ionic products observed from negative ion transfer reactions (Table 1) are also not consistent with this scheme. For example, the formation of DCF_2^+ from $CF_3^{2+} + D_2$ by such a mechanism is unlikely since the product ion data show that dissociative charge transfer to form $D_2^+ + F^+ + CF_2$ is not favored (Table 1). The mechanism illustrated in eqs 12 and 13 would also imply a positive correlation between charge transfer reactivity and bond-forming reactivity. Such a correlation is not obvious from the data since systems which exhibit strong charge transfer reactivity often do not exhibit any bond-forming reactivity (Table 2).

In light of the above, the simplest mechanism which seems consistent with the experimental data involves negative ion transfer followed by fragmentation, as illustrated for CF_3^{2+} in eqs 5 and 6. The first step of this mechanism involves simple hydride ion transfer, which is consistent with the success of the qualitative Landau–Zener analysis presented above. Of course, given the experimental data, we cannot completely rule out other alternative mechanisms for these negative ion transfer reactions. Hydride ion transfer reactions are well-known in the chemistry of singly charged molecular ions. In these cases, where more detailed dynamical information is available, microscopic models based on complexation are often proposed.[25] The participation of more chemically specific mechanisms than envisaged by the Landau–Zener model of negative ion transfer may explain the variations in reactivity observed between different molecular dications. However, to evaluate the applicability of a more detailed negative ion transfer mechanism, further experimental and theoretical information concerning the reaction dynamics is required. A study of differences in the reactive cross sections of D_2 and H_2 may prove valuable since transfer of the lighter H^- ion should occur more readily at larger distances given the Landau–Zener model of the reaction. However, with the current TOFMS it is difficult to resolve the signals of ions formed by H^- transfer from those of ions formed by electron transfer. This difficulty, coupled with the complication that the product ions from H^- transfer occur at the same *m*/*z* values as the signals of ions containing ^{13}C, makes such isotopic experiments impractical on the current apparatus.

Positive Ion Transfer Reactions

As described above, several less efficient reactions are detected which appear to involve transfer of a positive ion from the molecular dication to the neutral species (Table 1). In all but two cases, these reactions involve F^+ transfer to Xe giving XeF^+. These positive ion transfer reactions have product intensities that are markedly weaker than those from many of the negative ion transfer reactions (Table 1). Several mechanisms can be proposed for these positive ion transfer reactions. Analogous to negative ion transfer, the reaction could occur at a curve crossing between an attractive reactant potential and a repulsive product ion potential. The available thermodynamic data permit calculation of the curve-crossing radius for F^+ transfer in the case of the reaction of CF_2^+ with Xe. In this case, the crossing radius is 0.27 nm. This value should be compared with an electron transfer radius for this system of 0.25 nm. The only conclusion from these values is that they do not preclude the operation of a curve-crossing mechanism. Alternative positive ion transfer mechanisms can also be proposed. One possibility involves CICS induced by the Xe atom followed by reaction with the same Xe species in the complex (eqs 14 and 15)

$$CF_3^{2+} + Xe \rightarrow [CF_2^+ + F^+ + Xe]^* \tag{14}$$

$$[CF_2^+ + F^+ + Xe]^* \rightarrow CF_2^+ + XeF^+ \tag{15}$$

Another possibility is dissociative charge transfer followed by

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[25] Farnik, M.; Dolejsek, Z.; Herman, Z. *Chem. Phys. Lett.* **1993**, *216*, 458.

reaction of the resulting neutral fragment with the Xe^+ ion in the complex (eqs 16 and 17)

$$CF_3^{2+} + Xe \rightarrow [CF_2^+ + F + Xe^+]^* \tag{16}$$

$$[CF_2^+ + F + Xe^+] \rightarrow CF_2^+ + XeF^+ \tag{17}$$

The present experimental data provide little information to distinguish conclusively between the above reaction mechanisms. Intuitively, the first mechanism (eqs 14 and 15) is perhaps less probable, since charge transfer from F^+ to Xe can compete effectively with reaction 15 because the ionization potential of F is much higher than that of Xe. In contrast, in the second mechanism (eqs 16 and 17) competition of reaction 17 with charge transfer is not possible since the charge resides on the xenon atom. The laboratory frame kinetic energy restrictions of the current apparatus make the center-of-mass kinetic energies for dication interactions with the heavy Xe atoms markedly higher than those for D_2. Further investigations of these positive ion transfer reactions at lower collision energies may provide valuable insights.

Conclusions

We report several new reactions involving the formation of chemical bonds in a study of the reactivity of eight dications, CF^{2+}, CF_2^{2+}, CF_3^{2+}, SF_4^{2+}, SF_3^{2+}, SF_2^{2+}, CO_2^{2+}, and OCS^{2+}, with the neutral collision partners Xe, D_2, O_2, N_2, NO, and CO. Two classes of bond-forming reactions are observed, one involving negative ion transfer to the dication and the other involving positive ion transfer from the dication to the neutral reactant. Estimates of the appropriate curve-crossing radii are consistent with the participation of a Landau–Zener style negative ion transfer mechanism. The survey of molecular dication reactivity presented in this paper indicates that the low-energy reactivity of molecular dications may differ substantially from the reactivity previously observed at high collision energies.

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