THE JOURNAL OF PHYSICAL CHEMISTRY Letters

pubs.acs.org/JPCL

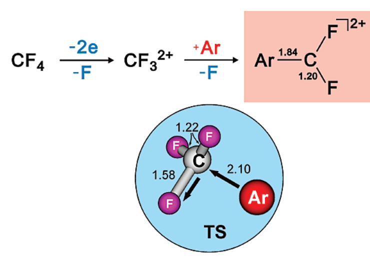
Generation of the $ArCF_2^{2+}$ Dication

Jessica F. Lockyear,[†] Kevin Douglas,[†] Stephen D. Price,[†] Małgorzata Karwowska,[‡] Karol J. Fijalkowski,[‡] Wojciech Grochala,[‡,§] Marek Remeš,[#,⊥] Jana Roithová,[#,⊥] and Detlef Schröder*[,⊥]

[†]Department of Chemistry, Universizty College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom, [‡]Faculty of Chemistry, University of Warsaw, Pasteur 1, 02093 Warsaw, Poland, [§]University of Warsaw, ICM, Pawinskiego 5a, 02106 Warsaw, Poland, [#]Department of Organic and Nuclear Chemistry, Faculty of Sciences, Charles University in Prague, 12843 Prague 2, Czech Republic, and [⊥]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic

ABSTRACT Thermal reactions of the CF_3^{2+} dication with argon lead to the formation of an $ArCF_2^{2+}$ dication, a new type of metastable species with an argon−carbon bond. None of the other rare gases undergo a similar reaction with CF_3^{2+}. For the lighter rare gases (He and Ne), no reactions with CF_3^{2+} other than those due to electronically excited reactant ions are observed, whereas for the heavier rare gases (Kr and Xe), the prevailing reactive pathways involve single-electron transfer. At elevated collision energies, single-electron transfer predominates for collisions with all rare gases (He−Xe).

SECTION Molecular Structure, Quantum Chemistry, General Theory



The formation of rare-gas compounds, first discovered in 1962,[1] is an attractive field for chemical research, which recently experienced additional stimuli by the photochemical generation of several new rare-gas compounds in matrix isolation experiments.[2−4]

$$SiF_3^{2+} + Ar \rightarrow ArSiF_2^{2+} + F^{\bullet} \quad (1)$$

Inspired by the recent observation of the gaseous dication $ArSiF_2^{2+}$, having an argon−silicon bond, formed in thermal collisions of the mass-selected SiF_3^{2+} dication with argon (reaction 1),[5] we decided to follow an earlier prediction that halocarbene dications should also form reasonably stable adducts with rare gases.[6] In this context, an important conclusion from the investigation of reaction 1 was that the chances for the successful observation of bond-forming reactions of molecular dications[7,8] are particularly large at low collision energies, preferentially, in the thermal regime. For example, earlier studies of SiF_3^{2+} + Ar failed to observe reaction 1 due to the elevated experimental collision energies.[9] Accordingly, we felt it worthwhile to reinvestigate the analogous low-energy collisions of the CF_3^{2+} dication with the rare gases He−Xe. The reactions of CF_3^{2+} with the rare gases have been the subject of several previous investigations at elevated (few eV) collision energies,[10,11] as have the reactions of CF_3^{2+} with deuterium molecules.[12,13]

The CF_3^{2+} dication can be easily generated by (dissociative) double ionization of tetrafluoromethane with energetic electrons or photons.[14−16] It has a very high single-electron recombination energy to form CF_3^+, RE(CF_3^{2+}) = 26.3 eV,[17,18] and a weak C−F bond, $D(F_2C^{2+}-F)$ = (1.1 ± 0.4) eV,[14,19,20] which can be attributed to the presence of a localized hole in the σ-bonding C−F orbital. Accordingly, in bimolecular encounters, more strongly bonding substituents might be induced to replace this weakly bound fluorine atom as we have recently demonstrated for the reactions of the heavier analogue SiF_3^{2+}.[5,21]

$$CF_3^{2+} + Ar \rightarrow ArCF_2^{2+} + F^{\bullet} \quad (2)$$

$$CF_3^{2+} + Ar \rightarrow CF_2^{2+} + F^{\bullet} + Ar \quad (3)$$

$$CF_3^{2+} + Ar \rightarrow CF_3^{+} + Ar^{+} \quad (4)$$

$$CF_3^{2+} + Ar \rightarrow CF_2^{+} + F^{\bullet} + Ar^{+} \quad (5)$$

$$CF_3^{2+} + Ar \rightarrow CF^{+} + 2F^{\bullet} + Ar^{+} \quad (6)$$

Our experiments reveal that the interaction of mass-selected CF_3^{2+} with neutral argon generates $ArCF_2^{2+}$ formed via the substitution reaction 2. Additional processes observed (Figure 1) correspond to dication dissociation (reaction 3), either collision-induced or arising from metastable states, and charge separations according to reactions 4−6, of which the latter has previously been assigned to an excited state of CF_3^{2+}.[10] Reactions 3, 5, and 6 have been clearly observed before at collision energies of 1.8 and 4.4 eV, and weak contributions from reaction 4 can be traced at a collision energy of 3.0 eV.[11] However, the $ArCF_2^{2+}$ product and strong signals due to CF_3^+, reactions 2 and 4, are only observed following the low-energy collisions studied in this work. This increase in the $ArCF_2^{2+}$ signals at low collision energy is demonstrated by the energy dependence of the $ArCF_2^{2+}$

Received Date: November 16, 2009
Accepted Date: December 2, 2009

DOI: 10.1021/jz900274p | *J. Phys. Chem. Lett.* **2010**, *1*, 358–362

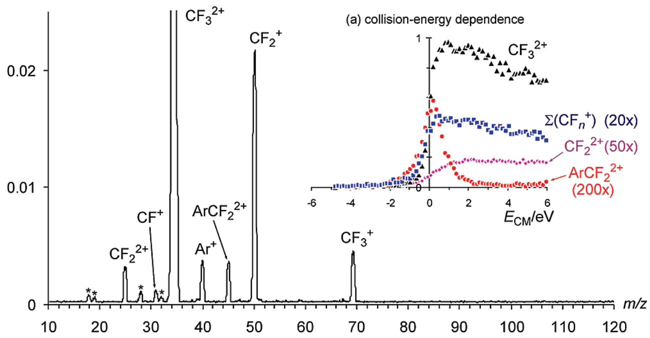


Figure 1. Reaction of mass-selected CF_3^{2+} dications with argon at an octopole voltage of U_{oct} = −2 V and p(Ar) = 2 × 10^{-4} mbar; these conditions correspond to a nominal laboratory energy of reactant ions set close to zero. The vertical scale refers to the precursor dication with an intensity of 1.00 (off-scale). The signals denoted with asterisks are due to reactions with background moisture and air (i.e., H_2O^+, H_3O^+, N_2^+, and O_2^+). Inset (a) shows the energy dependences of the major channels in the center-of-mass scale. Note that the sum of CF_n^+ monocations is shown for the sake of clarity in the graph; also, the Ar^+ trace is omitted.

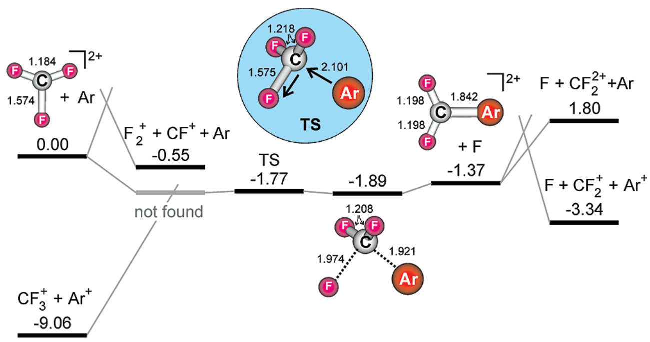


Figure 2. Minima on the potential energy surface of the CF_3^{2+} dication reacting with argon according to B3LYP/6-311+G(2d,p) calculations and a representation of the bonding C−Ar orbital. Energies are expressed in eV relative to the reactant asymptote. The selected bond lengths are given in Å.

signal in inset (a) of Figure 1, which shows a sharp maximum near a nominal collision energy of 0 eV. We note in passing that Figure 1 of ref 10 taken at a collision energy of 3.3 eV shows some elevated noise at m/z 45, perhaps corresponding to the $ArCF_2^{2+}$ product, which is consistent with the energy dependence shown in Figure 1. Similarly, the yield of the CF_3^+ monocation (not separately shown in the inset of Figure 1) also has a maximum at E_{CM} = 0 eV with a rapid decline at elevated collision energies.

The experimental results described above are further supported by theoretical calculations using density functional theory (Figure 2). The precursor dication CF_3^{2+} has C_{2v} symmetry with two short (r_{CF} = 1.184 Å) and one long (r_{CF} = 1.574 Å) C−F bond; the bond dissociation energy is computed as $D_{calc}(CF_2^{2+}-F)$ = 1.80 eV and is thus somewhat larger than the experimental estimate quoted above. The initial interaction of CF_3^{2+} with neutral argon should lead to an encounter complex, but all attempts to localize this structure led to charge separation into CF_3^+ and Ar^+. However, we have found a transition structure (TS, E_{rel} = −1.77 eV; see inset structure in Figure 2) for the substitution of fluorine, as a leaving group, by argon, as a nucleophile, and also located the corresponding complex of the $ArCF_2^{2+}$ product with a fluorine atom (E_{rel} = −1.89 eV). The C−Ar bond length in the transition structure amounts to 2.101 Å. The crossing between the Coulomb-repulsion potential energy curve and that of the dication/induced dipole interaction is located at ∼2.35 Å.[22] Hence, single-reference calculations at geometries expected for the encounter complex, that is, the C−Ar bond most probably larger than 2.3 Å, lead to the dissociation along the CF_3^+−Ar^+ coordinate, and therefore, the encounter complex cannot be localized at this level of theory.

The final product $ArCF_2^{2+}$ is formed by the elimination of a fluorine atom from the product complex and lies 1.37 eV below the entrance channel. The C−Ar bond length in $ArCF_2^{2+}$ is calculated to be 1.842 Å. Both the single-bond and double-bond covalent radii of Pyykkö and Atsumi predict a C−Ar distance of about 1.7 Å,[23] which is significantly shorter than the value found here. According to natural bond analysis, the σ Ar−C bond is formed by the overlap $2p_C$ and $3p_{Ar}$ orbitals along the axis of the bond with an occupancy of 1.98 e. This bond however is weakened by the 0.20 e occupancy of the antibonding Ar−C orbital, where predominantly the lone pairs of the fluorine atoms contribute to the Ar−C interactions. Thus, upon analysis of the bonding, we expect the Ar−C bond to be indeed slightly longer than a "typical" Ar−C σ bond.

A major difference between the CF_3^{2+}/Ar collision system compared with the homologous SiF_3^{2+}/Ar interaction is that, due to the much higher single-electron recombination energy (RE) of CF_3^{2+}, nondissociative electron transfer (reaction 4) as well as dissociative electron transfer (reactions 5 and 6) are much more pronounced in the CF_3^{2+}/Ar system. The competing, very exothermic electron-transfer processes to yield pairs of monocations explain the low yield of the substitution product $ArCF_2^{2+}$. The significant exothermicity of the electron-transfer process between CF_3^{2+} and Ar also accounts for the dominance of dissociative electron transfer with two major pathways, formation of CF_2^+ + F + Ar^+ via dissociation of an energized CF_3^+ product of a primary electron transfer event (reaction 5) and via the primary reaction 2 followed by the subsequent dissociation of the $ArCF_2^{2+}$ product.[10] Conceptually, our results also imply that mere electrophilicity (i.e., the recombination energy) is by no means the sole criterion for a chemically useful superelectrophile in the gas phase. In this case, precisely the opposite is true; the extreme electrophilicity of CF_3^{2+} appears to lead to the suppression of bond-forming processes due to competition with single-electron transfer (particularly for the heavier rare gases; see below). For a more successful rationalization of the bond-forming processes of molecular dications, a larger set of characteristic parameters has to be considered, as recently demonstrated for the silicon analogue of the title species.[5]

More generally, the experimental evidence (Figure 1) in conjunction with the theoretical data (Figure 2) is clear proof for the existence of the metastable $ArCF_2^{2+}$ dication, a new kind of organo-argon species in the gas phase.[24] In this context, a brief comparison to the recently studied SiF_3^{2+}/Ar system[5] is quite instructive. For the silicon analogue, reaction 1 is indeed the major channel at thermal energies,

DOI: 10.1021/jz900274p | J. Phys. Chem. Lett. 2010, 1, 358–362

Table 1. Product Ions and Abundances (given in % of the parent ion) Observed in the Reactions of Mass-Selected CF_3^{2+} Dications with Rare Gases at an Octopole Voltage of U_{oct} = −2 V, Which Corresponds to a Nominal Laboratory Collision Energy of ∼0 eV

	$RgCF_2^{2+}$	CF_2^{2+}	Rg^{+} [a]	CF^{+}	CF_2^{+}	CF_3^{+}
He [b,c]		0.3		< 0.1	0.4	0.3
Ne [b,c]		1.6		< 0.1	0.5	0.6
Ar [d]	0.3	0.2	0.3	0.1	2.2	0.4
Kr	– [e]	< 0.1	1.8	0.3	2.1	0.1
Xe [c,f]		0.1	6.8	1.2	1.8	0.1

[a] Sum over all isotopes. [b] The observed products are not corrected for collisions with background gases, and for helium and neon, the charge separation yields are likely to have major contributions from this source. [c] Despite a careful search, no significant signals due to $RgCF_2^{2+}$ were observed. [d] In addition, traces of ArF^{+} (≪0.1 %) are formed. [e] Only for the major isotope $^{84}KrCF_2^{2+}$ could a signal significantly above the noise level be detected. [f] Given the large amount of electron transfer, the single-collision regime was not strictly maintained in the case of xenon.

whereas the maximal branching of the $ArCF_2^{2+}$ channel in the CF_3^{2+}/Ar system amounts to only about 10 % of all product channels and, hence, is only a minor pathway. However, reaction 2 is still a much more efficient process than earlier examples of argon−carbon species generated in ion/molecule collisions, ArC^{2+},[25,26] $ArCH_2^{+}$,[27] and ArC_2H^{2+}.[28] The differences between CF_3^{2+}/Ar and SiF_3^{2+}/Ar can be ascribed to the much larger exothermicities of the charge-transfer reactions of CF_3^{2+} (RE = 26.3 eV) with argon (IE = 15.76 eV) as compared to those of SiF_3^{2+} (RE = 22.4 eV),[29] such that most of the transient $ArCF_2^{2+}$ species formed in reaction 2 will rapidly undergo charge-separation reactions. Indeed, coincidence experiments of the corresponding reaction 3 gave no evidence for the formation of long-lived intermediate complexes.[11]

We also briefly explored the reactions of the other rare gases with mass-selected CF_3^{2+} in order to probe if other organo rare-gas bonds can be made via this approach (Table 1). Except for a very weak signal which might correspond to $KrCF_2^{2+}$, none of the other rare gases undergo a bond-forming process analogous to reaction 2. This observation can be rationalized by the operation of two different effects. For the heavier rare gases, electron transfer leading to charge-separation reactions is more and more favored due to the lower ionization energies of krypton (IE = 14.00 eV) and xenon (IE = 12.13 eV). This is not the case for the two lighter rare gases, helium (IE = 24.59 eV) and neon (IE = 21.56 eV), which are resistant to one-electron oxidation by CF_2^{2+}. On the other hand, helium and neon clearly do not have potential for formation of strong donor−acceptor complexes with CF_2^{2+}, as indicated by their inability to replace the fluorine atom in CF_3^{2+}. These experimental results suggest that $D(Rg{-}CF_2^{2+})$ < $D(F_2C^{2+}{-}F)$ for Rg = He and Ne, which may be traced to a poor overlap between the contracted ns-valence orbitals of these rare gases and the relatively diffuse sp-hybrid on carbon.

In conclusion, we have demonstrated that the open-shell molecular dication CF_3^{2+} can serve as a suitable reagent for the generation of novel gaseous rare-gas−carbon species in thermal ion−molecule reactions. The efficiency of this superelectrophile[30] with respect to Ar−C bond formation is limited by the competing charge-transfer reactions. Accordingly, formation of $RgCF_2^{2+}$ is suppressed for Rg = Kr and Xe, while the lighter rare gases He and Ne cannot serve as Lewis bases of sufficient strength toward CF_2^{2+} and consequently cannot replace the fluorine atom in the CF_3^{2+} precursor. As a result of these different effects, among all $RgCF_2^{2+}$ species, only $ArCF_2^{2+}$ is formed in significant yields in CF_3^{2+} + Rg collisions. In a more general sense, the present results underline the importance of low-energy collisions in attempts to understand the bimolecular reactivity of gaseous dications.[7,8,31]

Experimental Methods

The experiments were performed with a TSQ Classic mass spectrometer[32,33] equipped with an ion source for electron ionization (EI) and an analyzer of QOQ configuration (Q stands for quadrupole and O for octopole), which permits a variety of MS/MS experiments. The octopole, serving as a collision cell, has a separate housing which limits the penetration of gases admitted to the octopole to the ultrahigh vacuum of the manifold. The kinetic energy of the ions entering the octopole can be varied, which allows the investigation of ion/molecule reactions at quasi-thermal conditions or at elevated kinetic energies.[34−37] The CF_3^{2+} dications generated by EI of CF_4 were mass-selected by means of the first quadrupole (Q1) at a mass resolution fully sufficient to select only dicationic species. The mass-selected dications were then reacted with rare gases admitted to the octopole at pressures of typically 2×10^{-4} mbar. The collision energy was adjusted by changing the offset between the first quadrupole and the octopole, while the offset of Q2 was locked to the sum of the offsets of Q1 and O. The zero point of the kinetic energy scale, as well as the width of the kinetic energy distribution, was determined by means of retarding potential analysis; for the dicationic species reported here, the beam width at half-maximum amounts to (2.2 ± 0.2) eV in the laboratory frame. The bimolecular reactions reported below were recorded at a nominal laboratory collision energy of the reactant ions close to zero, that is, at the point of inflection of the curve obtained by retarding potential analysis of the reactant,[38] that is, U_{oct} = (1.8 ± 0.2) V in the present experiments. Ionic products emerging from the octopole were then mass-analyzed by scanning Q2 at unit mass resolution. Ion abundances were determined using a Daly-type detector operating in the counting mode. Because the reactions of CF_3^{2+} with rare gases have been previously investigated in quite some detail and multipole arrangements are not ideally suited to investigate the reaction kinetics of ion/molecule reactions,[39] we neither convert the relative reactivities revealed by our experiments to absolute rate constants nor make corrections for the differences in the transmission of the light and heavy product ions to the detector.[40]

For the (spin-unrestricted) calculations, we used the density functional methodology B3LYP[41−44] in conjunction with a 6-311+G(2d,p) triple-ζ basis set as implemented in the Gaussian 03 suite;[45] BSSE was not accounted for. Frequency

DOI: 10.1021/jz900274p | J. Phys. Chem. Lett. 2010, 1, 358–362

analysis at the same level of theory was performed for all optimized structures in order to assign stationary points on the potential energy surface as genuine minima or transition structures, as well as to calculate zero-point vibrational energies (ZPVEs).

SUPPORTING INFORMATION AVAILABLE Calculated total energies and geometries as well as a NBO analysis of $ArCF_2^{2+}$ This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. Fax: 00420 220 183 462. E-mail: schroeder@uochb.cas.cz.

ACKNOWLEDGMENT This work was supported by the Czech Academy of Sciences (Z40550506), the Grant Agency of the Czech Republic (203/09/1223), and the Ministry of Education of the Czech Republic (MSM0021620857, RP MSMT 14/63). The cooperation between London and Prague was additionally supported by a grant of the Royal Society (London). The visit of K. F. and M.K. for a summer internship with the Prague team was supported by the University of Warsaw.

REFERENCES

(1) Bartlett, N. Xenon Hexafluoroplatinate(V) $Xe^+[PtF_6]^-$. *Proc. Chem. Soc.* **1962,** 218.

(2) Gerber, R. B. Formation of Novel Rare-Gas Molecules in Low-Temperature Matrices. *Annu. Rev. Phys. Chem.* **2004,** *55*, 55–78.

(3) Grochala, W. Atypical Compounds of Gases, which have been Called 'Noble'. *Chem. Soc. Rev.* **2007,** *36*, 1632–1655.

(4) Khriachtchev, L.; Räsänen, M.; Gerber, R. B. Noble Gas Hydrides: New Chemistry at Low Temperatures. *Acc. Chem. Res.* **2009,** *42*, 183–191.

(5) Roithová, J.; Schröder, D. Silicon Compounds of Neon and Argon. *Angew. Chem., Int. Ed.* **2009,** *48*, 8788–8790.

(6) Roithová, J.; Žabka, J.; Herman, Z.; Thissen, R.; Schröder, D.; Schwarz, H. Reactivity of the $CHBr^{2+}$ Dication Toward Molecular Hydrogen. *J. Phys. Chem. A* **2006,** *110*, 6447–6453.

(7) Price, S. D. Investigating the Gas-Phase Chemical Reactions of Molecular Dications. *Phys. Chem. Chem. Phys.* **2003,** *5*, 1717–1729.

(8) Roithová, J.; Schröder, D. Bimolecular Reactions of Molecular Dications: Reactivity Paradigms and Bond-Forming Processes. *Phys. Chem. Chem. Phys.* **2007,** *9*, 2341–2349.

(9) Lee, Y.-Y.; Leone, S. R.; Champkin, P.; Kaltsoyannis, N.; Price, S. D. Laser Photofragmentation and Collision-Induced Reactions of SiF_2^{2+} and SiF_3^{2}. *J. Chem. Phys.* **1997,** *106*, 7981–7994.

(10) Tafadar, N.; Kaltsoyannis, N.; Price, S. D. Electron-Transfer and Neutral-Loss Reactions in Collisions of CF_3^{2+} with Argon. *Int. J. Mass Spectrom.* **1999,** *192*, 205–214.

(11) Hu, W. P.; Harper, S. M.; Price, S. D. The Dynamics and Kinematics of the Electron Transfer Reactions of CF_3^{2+} with Ar. *Mol. Phys.* **2005,** *103*, 1809–1819.

(12) Lambert, N.; Kaltsoyannis, N.; Price, S. D.; Žabka, J.; Herman, Z. Bond-Forming Reactions of Dications with Molecules: A Computational and Experimental Study of the Mechanisms for the Formation of HCF_2^+ from CF_3^{2+} and H_2. *J. Phys. Chem. A* **2006,** *110*, 2898–2905.

(13) Tafadar, N.; Price, S. D. Bond-Forming Reactivity Between CF_3^{2+} and H_2/D_2. *Int. J. Mass Spectrom.* **2003,** *223*, 547–560.

(14) Masuoka, T.; Okaji, A.; Kobayashi, A. Fragmentation of CF_4^{2+} Dication from Threshold to 120 eV. *Int. J. Mass Spectrom.* **2002,** *218*, 11–18.

(15) Torres, I.; Martinez, R.; Castano, F. Electron-Impact Dissociative Ionization of Fluoromethanes CHF_3 and CF_4. *J. Phys. B* **2002,** *35*, 2423–2436.

(16) Kobayashi, A.; Okaji, A.; Masuoka, T. Dissociative Single and Double Photoionization of CF_4 and Ionic Fragmentation of CF_4^+ and CF_4^{2+} from 23 to 120 eV. *Chem. Phys.* **2004,** *298*, 107–117.

(17) Proctor, C. J.; Porter, C. J.; Ast, T.; Beynon, J. H. Evidence of Long-Lived Electronically Excited-States of Some Simple Halocarbon Ions. *Int. J. Mass Spectrom. Ion Phys.* **1982,** *41*, 251–263.

(18) Hrušák, J.; Sändig, N.; Koch, W. Structure and Stability of the CF_3^{2+} Dication. *Int. J. Mass Spectrom.* **1999,** *185—187*, 701–706.

(19) Stephan, K.; Deutsch, H.; Märk, T. D. Absolute Partial and Total Electron-Impact Ionization Cross-Sections for CF_4 from Threshold uo to 180 eV. *J. Chem. Phys.* **1985,** *83*, 5712–5720.

(20) This figure derived from the appearance energies of CF_3^{2+} and CF_2^{2+} should be taken with some caution because the absolute values in ref 14 and 19 differ by about 1 eV.

(21) Roithová, J.; Schwarz, H.; Schröder, D. The SiF_3^{2+} Dication: Chemistry Counts!. *Chem.—Eur. J.* **2009,** *15*, 9995–9999.

(22) The crossing point R_{cross} has been estimated from the equation $(1/R_{cross}) - \Delta E_{ET} = -4\alpha_{Ar}/(R_{cross})^4$, where ΔE_{ET} is the calculated exothermicity of electron transfer between CF_3^{2+} and Ar (9.1 eV) and the polarizability α_{Ar} is taken as 1.586 Å^3.

(23) (a) Pyykkö, P.; Atsumi, M. Molecular Single-Bond Covalent Radii for Elements 1−118. *Chem.—Eur. J.* **2009,** *15*, 186–197. (b) Pyykkö, P.; Atsumi, M. Molecular Double-Bond Covalent Radii for Elements Li−E112. *Chem.—Eur. J.* **2009,** *15*, 12770–12779.

(24) A reviewer (and also some of the authors) raised the question of whether isolated dications generated and probed in a mass spectrometer can correctly be termed "compounds". While the IUPAC definition of "molecular entities" (http://goldbook.iupac.org/M03986.html) explicitly includes isolated ions, we have decided not to use this term in referring to species such as $ArCF_2^{2+}$.

(25) Tosi, P.; Lu, W. Y.; Correale, R.; Bassi, D. Production of the Molecular Dication ArC^{2+} by Ion−Molecule Reactions. *Chem. Phys. Lett.* **1999,** *310*, 180–182.

(26) Lu, W. Y.; Tosi, P.; Bassi, D. Bond-Forming Reactions of Molecular Dications with Rare Gas Atoms: Production of ArC^{2+} in the Reaction CO^{2+} + Ar. *J. Chem. Phys.* **2000,** *112*, 4648–4651.

(27) Ascenzi, D.; Tosi, P.; Roithová, J.; Schröder, D. Gas-Phase Synthesis of the Rare-Gas Carbene Cation $ArCH_2^+$ Using Doubly Ionised Bromomethane as a Superelectrophilic Reagent. *Chem. Commun.* **2008,** 4055–4057.

(28) Ascenzi, D.; Tosi, P.; Roithová, J.; Ricketts, C. L.; Schröder, D.; Lockyear, J. F.; Parkes, M. A.; Price, S. D. Generation of the Organo-Rare Gas Dications $HCCRg^{2+}$ (Rg = Ar and Kr) in the Reactions of Acetylene Dications with Rare Gases. *Phys. Chem. Chem. Phys.* **2008,** *10*, 7121–7128.

(29) Champkin, P.; Kaltsoyannis, N.; Price, S. D. A Theoretical Investigation of the Electron-Transfer Reactions of the SiF_3^{2+}

DOI: 10.1021/jz900274p | J. Phys. Chem. Lett. 2010, 1, 358–362

Dication with the Rare Gases Neon, Argon, Krypton and Xenon. *Int. J. Mass Spectrom. Ion Processes* **1998,** *172*, 57–69.
(30) Olah, G. A.; Klumpp, D. A. *Superelectrophiles and Their Chemistry*; Wiley: Hoboken, NJ, 2007.
(31) Roithová, J.; Schröder, D. Bond-Forming Reactions of Molecular Dications as a New Route to Polyaromatic Hydrocarbons. *J. Am. Chem. Soc.* **2006,** *128*, 4208–4209.
(32) Roithová, J.; Schröder, D. Bond-Forming Reactions Versus Electron Transfer: C−C-Coupling Reactions of Hydrocarbon Dications with Benzene. *Phys. Chem. Chem. Phys.* **2007,** *9*, 731–738.
(33) Roithová, J.; Schröder, D.; Míšek, J.; Stará, I. G.; Starý, I. Chiral Superbases: The Proton Affinities of 1- and 2-Aza[6]helicene in the Gas Phase. *J. Mass Spectrom.* **2007,** *42*, 1233–1237.
(34) Schröder, D.; Schwarz, H.; Schenk, S.; Anders, E. A Gas-Phase Reaction as a Functional Model for the Activation of Carbon Dioxide by Carbonic Anhydrase. *Angew. Chem., Int. Ed.* **2003,** *42*, 5087–5090.
(35) Feyel, S.; Schröder, D.; Schwarz, H. Gas-Phase Oxidation of Isomeric Butenes and Small Alkanes by Vanadium-Oxide and -Hydroxide Cluster Cations. *J. Phys. Chem. A* **2006,** *110*, 2647–2654.
(36) Schröder, D.; Engeser, M.; Schwarz, H.; Rosenthal, E. C. E.; Döbler, J.; Sauer, J. Degradation of Ionized $OV(OCH_3)_3$ in the Gas Phase. From the Neutral Compound All the Way down to the Quasi-terminal Fragments VO^+ and VOH. *Inorg. Chem.* **2006,** *45*, 6235–6245.
(37) Schröder, D.; Roithová, J.; Schwarz, H. Electrospray Ionization as a Convenient New Method for the Generation of Catalytically Active Iron-Oxide Ions in the Gas Phase. *Int. J. Mass Spectrom.* **2006,** *254*, 197–201.
(38) Herman, Z. Dynamics of Charge Transfer and Chemical Reactions of Doubly-Charged Ions at Low Collision Energies. *Int. Rev. Phys. Chem.* **1996,** *15*, 299–324.
(39) Jagoda-Cwiklik, B.; Jungwirth, P.; Rulíšek, L.; Milko, P.; Roithová, J.; Lemaire, J.; Maitre, P.; Ortega, J. M.; Schröder, D. Nicro-Hydrtion of the $MgNO_3^+$ Cation in the Gas Phase. *ChemPhysChem* **2007,** *8*, 1629–1639.
(40) Ricketts, C. L.; Schröder, D.; Roithová, J.; Schwarz, H.; Thissen, R.; Dutuit, O.; Žabka, J.; Herman, Z.; Price, S. D. Competition of Electron Transfer, Dissociation, and Bond-Forming Processes in the Reaction of the CO_2^{2+} Dication with Neutral CO_2. *Phys. Chem. Chem. Phys.* **2008,** *10*, 5135–5143.
(41) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin-Density Calculations — A Critical Analysis. *Can. J. Phys.* **1980,** *58*, 1200–1211.
(42) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle−Salvetti Correlation-Energy Formulation into a Functional of the Electron-Density. *Phys. Rev. B* **1988,** *37*, 785–789.
(43) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988,** *38*, 3098–3100.
(44) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation-Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989,** *157*, 200–206.
(45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.;Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*, revision C.02 ; Gaussian, Inc.: Wallingford, CT, 2004.

DOI: 10.1021/jz900274p | *J. Phys. Chem. Lett.* **2010,** *1*, 358–362