Noble Gas Compounds

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Silicon Compounds of Neon and Argon**

Jana Roithová and Detlef Schröder**

Dedicated to Professor Konrad Seppelt on the occasion of his 65th birthday

Noble gas compounds, which were first discovered in 1962,[1] still receive continuous interest. In recent years, this field of research experienced an additional boost by the generation of a variety of new noble gas compounds by photochemical reactions in low-temperature matrices.[2–4] Challenges in noble gas chemistry that still remain are the formation of new noble gas heteroatom bonds, in which silicon has been raised as a particularly interesting case, and the generation of new compounds of the lighter noble gases argon and neon.[4,5] Herein, we address both issues by the use of the SiF_3^{2+} dication as a superelectrophilic reagent[6,7] with particularly favorable properties for the generation of noble gas compounds.

It is obvious that the involvement of the inert noble gases in covalent chemical bonds requires strong oxidation agents, such as F_2; in 2006, we suggested that gaseous dications may be used for this purpose.[8] Although we indeed managed to generate the organonoble gas compounds $ArCH_2^+$ and ArC_2H^{2+} recently using this approach, the chemical yields were disappointingly low.[9,10] Similarly, small amounts of the diatomic dication ArC^{2+} had been observed in collisionally driven reactions of neutral CO with Ar^{2+} and of neutral argon with CO^{2+}.[11,12] A more efficient dicationic reagent for the attack of noble gases must not only be a potent superelectrophile, but it also needs to meet the following requirements: 1) It should possess a potential leaving group that can be replaced by a noble gas atom without a significant kinetic barrier being involved, such as a homolytic bond cleavage; 2) the preferred oxidation states of noble gases[13] mean that increased stabilities can be expected for even-electron compounds; for homolytic cleavage, the dicationic reagent should be a radical; 3) to prevent electron transfer processes during homolysis of the bond to the leaving group, which would afford an open-shell noble gas compound, the leaving group should have a high ionization energy (IE); and 4) the superelectrophilic dication should be accessible in quantities that suffice for reactivity studies in the gas phase.[14,15]

The SiF_3^{2+} dication is a promising candidate that may fulfill these requirements: it can be readily generated by dissociative double ionization of SiF_4 as a stable, neutral precursor,[16] it has a very high recombination energy RE(SiF_3^{2+}) of about 22.4 eV,[17] which allows it to be classified as a superelectrophile, it has one surprisingly weak Si−F bond, with $D(F_2Si^{2+}{-}F) = 1.97$ eV, and the IE of fluorine as the potential leaving group is exceptionally large (17.4 eV).

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

In a tandem mass spectrometric experiment,[22] mass-selected SiF_3^{2+} can indeed attack neutral argon atoms to yield the $ArSiF_2^{2+}$ dication concomitant with loss of a neutral fluorine atom [Reaction (1)] as the major product channel at low collision energies (Figure 1). Other reactions are associated with charge separation (Ar^+, SiF_n^+ with $n = 1$–3) and dication dissociation ($SiF_2^{2+} + F$). The identity of the $ArSiF_2^{2+}$ ion is unambiguously established by a neutral gain scan (see inset in Figure 1a), which agrees well with the expected isotope pattern.[20] Furthermore, the peaks spacing $\Delta m = 0.5$ amu in Figure 1a excludes any overlapping monocations in the product ion signals.

Mechanistic insight is provided by the dependence of the yield of $ArSiF_2^{2+}$ from the octopole voltage (Figure 1b) which reveals a sharp maximum at low collision energies; Reaction (1) is thus an exothermic process via a long-lived collision complex. The very low yield of $ArSiF_2^{2+}$ at larger collision energies also explains why previous studies at elevated collision energies failed to observe this channel.[23]

The experimental findings are fully confirmed by a theoretical investigation of Reaction (1). A fluorine atom can be lost from the initially formed $ArSiF_3^{2+}$ intermediate in a process that is overall exothermic by 0.81 eV. The strength of the $Ar{-}SiF_2^{2+}$ bond is considerable (2.78 eV), and the bonding orbital is consistent with a covalent Ar−Si bond (Figure 2). For a predominantly electrostatic bonding of argon to a dication, a significantly lower bond energy would be expected; for example, $D(Mg^{2+}{-}Ar) = 1.27$ eV.[24] Conceptually, Reaction (1) may thus be regarded as a substitution reaction in which neutral argon reacts as a nucleophile and atomic fluorine as a leaving group. Although the dissociation of $ArSiF_2^{2+}$ into a pair of monocations ($Ar^+ + SiF_2^+$) is exothermic by 0.72 eV, the Coulomb barrier inherently associated with charge separation[14,15,25] renders $ArSiF_2^{2+}$ a metastable dication and thus the first example of a covalent argon–silicon compound. The only related experimental report on gaseous noble gas silicon compounds deals with

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[*] Dr. J. Roithová
Department of Organic Chemistry, Charles University in Prague
Hlavova 8, 12843 Prague 2 (Czech Republic)
E-mail: roithova@natur.cuni.cz
Dr. J. Roithová, Dr. D. Schröder
Institute of Organic Chemistry and Biochemistry
Academy of Sciences of the Czech Republic
Flemingovo náměstí 2, 16610 Prague 6 (Czech Republic)
Fax: (+42) 220-183-462
E-mail: schroeder@uochb.cas.cz

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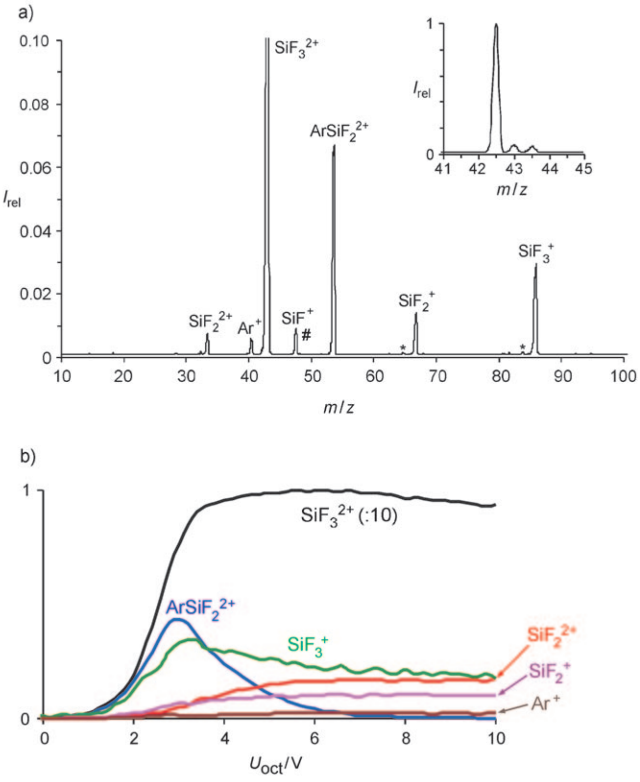

Figure 1. a) Reaction of mass-selected SiF_3^{2+} dications with argon at a collision energy circa 0 eV (that is, octopole voltage U_{oct} adjusted to 2 V) and $p(Ar) = 5\times10^{-4}$ mbar. The vertical scale refers to the precursor dication with an intensity of 1.00 (off-scale). The signals denoted with an asterix are due to consecutive reactions of SiF_n^+ monocations with background water.[18] Part of the signal assigned to SiF^+ is overlapped by $N_2SiF_2^{2+}$ (#) formed from SiF_3^{2+} and background nitrogen in analogy to reaction (1).[19] Inset in (a) shows a neutral gain spectrum[20,21] of the SiF_3^{2+} isotopes with an offset $\Delta m = 10.5$ amu of the second quadrupole analyzer to detect the corresponding precursor isotope pattern of the $^{40}ArSiF_2^{2+}$ product formed at $U_{oct} = 2$ V. b) The dependence of the most important channels from the voltage applied to the octopole collision cell; note the offset of U_{oct} is such that the zero of the E_{lab} scale is at U_{oct} = ca. 2 V.

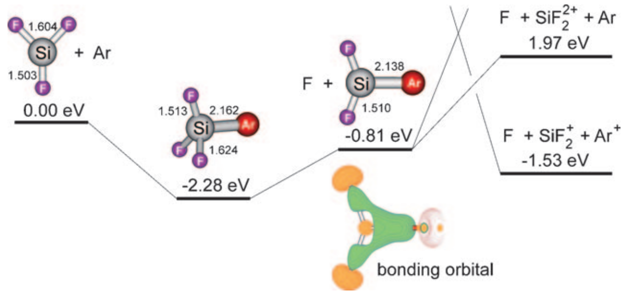

Figure 2. Minima on the potential energy surface of the SiF_3^{2+} dication upon reaction with argon according to B3LYP/6-311+G(2d,p) calculations, and a representation of the bonding silicon–argon orbital.

the electrostatic complexes Rg–SiF_3^+ (Rg = Ar, Kr, Xe) and circumstantial evidence for the formation of $FXeSiF_2^+$;[26] the existence of neutral FXeSiF has been predicted theoretically.[27]

Once the formation of $ArSiF_2^{2+}$ was established, detection of the analogous process for neon was an obvious challenge. As demonstrated in Figure 3, small signals for the isotopes $^{20}NeSiF_2^{2+}$ and $^{22}NeSiF_2^{2+}$ can indeed be observed experimentally. In conjunction with the neutral gain scan (see inset in Figure 3a), these findings show unambiguously the formation of a silicon–neon compound, and the energy behavior of the $NeSiF_2^{2+}$ product is again consistent with a thermal ion–molecule reaction (Figure 3b). The yield of the neon compound is low, however, and does not increase proportionally with the neon pressure. Furthermore, calculations (not shown) predict the formation of $NeSiF_2^{2+}$ from the ground states of SiF_3^{2+} and neon to be endothermic by 1.17 eV. Therefore, we conclude that $NeSiF_2^{2+}$ is most probably formed from an excited state of the SiF_3^{2+} precursor dication; such states are known to be formed upon electron ionization of SiF_4.[17] We will address the reactivity of ground and excited states of SiF_3^{2+} in future studies using reactive monitoring with synchrotron radiation.[28]

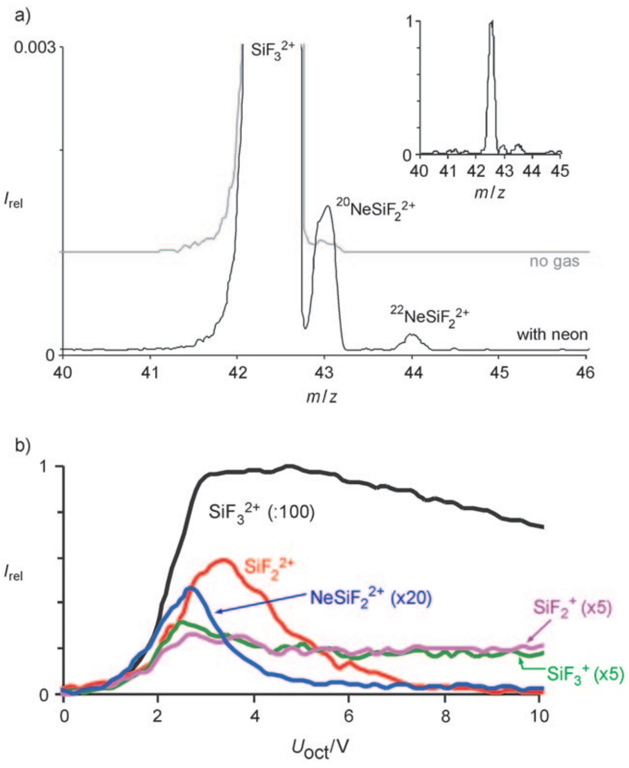

Figure 3. Parent-ion region of mass spectra showing the reaction of mass-selected SiF_3^{2+} dications with neon ($p(Ne) = 9\times10^{-4}$ mbar, black trace) and without gas (gray trace; shifted vertically by 0.001) at a collision energy circa 0 eV (that is, octopole voltage U_{oct} adjusted to 2 V). The vertical scale refers to the precursor dication with an intensity of 1.00 (off-scale); note the different scaling compared to Figure 1. The small remaining signal at m/z 43.0 in the gray trace is either due to a small amount of $^{29}SiF_3^{2+}$ co-selected with the first quadrupole, or to residual neon in the analyzer from the previous experiment. Inset in (a) shows a neutral-gain spectrum of the SiF_3^{2+} isotopes with an offset of $\Delta m = 1.5$ amu of the second quadrupole analyzer to detect the corresponding precursor isotope pattern of the $^{22}NeSiF_2^{2+}$ product, which is one order of magnitude less abundant than the ^{20}Ne isotope. b) The dependence of the most important channels from the voltage applied to the octopole collision cell.

In conclusion, we have demonstrated that the molecular dication SiF_3^{2+} can serve as a suitable superelectrophilic reagent for the generation of new noble gas silicon compounds in thermal ion–molecule reactions. For argon, the $ArSiF_2^{2+}$ dication is even formed as the major reaction product and has an argon–silicon bond of considerable strength (2.78 eV) and clearly covalent character. The discovery of these $RgSiF_2^{2+}$ dications certainly has a component of fortune, but as outlined in the introduction, the particular choice of SiF_3^{2+} as the superelectrophilic reagent was inspired by plausibility considerations derived from earlier work,[8–15,22,29] and similar strategies are likely to afford other new noble gas compounds in the future.[30]

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[1] N. Bartlett, *Proc. Chem. Soc.* **1962**, 218.

[2] R. B. Gerber, *Annu. Rev. Phys. Chem.* **2004**, *55*, 55–78.

[3] W. Grochala, *Chem. Soc. Rev.* **2007**, *36*, 1632–1655.

[4] L. Khriachtchev, M. Räsänen, R. B. Gerber, *Acc. Chem. Res.* **2009**, *42*, 183–191.

[5] L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, M. Räsänen, *Nature* **2000**, *406*, 874–876.

[6] G. A. Olah, *Angew. Chem.* **1995**, *107*, 1519–1532; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1393–1405.

[7] D. A. Klumpp, *Chem. Eur. J.* **2008**, *14*, 2004–2015.

[8] J. Roithová, J. Žabka, Z. Herman, R. Thissen, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **2006**, *110*, 6447–6453.

[9] D. Ascenzi, P. Tosi, J. Roithová, D. Schröder, *Chem. Commun.* **2008**, 4055–4057.

[10] D. Ascenzi, P. Tosi, J. Roithová, C. L. Ricketts, D. Schröder, J. F. Lockyear, M. A. Parkes, S. D. Price, *Phys. Chem. Chem. Phys.* **2008**, *10*, 7121–7128.

[11] P. Tosi, W. Y. Lu, R. Correale, D. Bassi, *Chem. Phys. Lett.* **1999**, *310*, 180–182.

[12] W. Y. Lu, P. Tosi, D. Bassi, *J. Chem. Phys.* **2000**, *112*, 4648–4651.

[13] Even oxidation states are strongly preferred for noble gases, although also ground-state transient compounds with noble gases in the oxidation state +1 exist; see, for example: D. Schröder, J. N. Harvey, M. Aschi, H. Schwarz, *J. Chem. Phys.* **1998**, *108*, 8446–8455.

[14] S. D. Price, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1717–1729.

[15] J. Roithová, D. Schröder, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2341–2349.

[16] R. Basner, M. Schmidt, E. Denisov, K. Becker, H. Deutsch, *J. Chem. Phys.* **2001**, *114*, 1170–1177.

[17] P. Champkin, N. Kaltsoyannis, S. D. Price, *Int. J. Mass Spectrom. Ion Processes* **1998**, *172*, 57–69.

[18] A. E. Ketvirtis, V. I. Baranov, A. C. Hopkinson, D. K. Bohme, *J. Phys. Chem. A* **1998**, *102*, 1162–1169.

[19] J. Roithová, H. Schwarz, D. Schröder, *Chem. Eur. J.* **2009**, *15*, 9995–9999

[20] In a neutral gain spectrum, two mass analyzers are scanned independently with a fixed mass offset (Δm) between them, such that only ions which experience the respective transformation in the intermediate collision region can reach the detector. In the present case with $\Delta m = 10.5$, only dications are detected which take up ^{40}Ar whilst losing a ^{19}F radical; any other reactive ions would lead to deviations from the natural isotope pattern of SiF_3^{2+}. See also Ref. [21].

[21] D. Schröder, H. Schwarz, S. Schenk, E. Anders, *Angew. Chem.* **2003**, *115*, 5241–5244; *Angew. Chem. Int. Ed.* **2003**, *42*, 5087–5090.

[22] J. Roithová, D. Schröder, *Phys. Chem. Chem. Phys.* **2007**, *9*, 731–738.

[23] Y.-Y. Lee, S. R. Leone, P. Champkin, N. Kaltsoyannis, S. D. Price, *J. Chem. Phys.* **1997**, *106*, 7981–7994.

[24] A. W. K. Leung, R. R. Julian, W. H. Breckenridge, *J. Chem. Phys.* **1999**, *110*, 8443–8447.

[25] a) D. Schröder, H. Schwarz, *J. Phys. Chem. A* **1999**, *103*, 7385–7394; b) D. Mathur, *Phys. Rep.* **2004**, *391*, 1–118; c) D. Schröder, *Angew. Chem.* **2004**, *116*, 1351–1353; *Angew. Chem. Int. Ed.* **2004**, *43*, 1329–1331.

[26] A. Cunje, V. I. Baranov, Y. Ling, A. C. Hopkinson, D. K. Bohme, *J. Phys. Chem. A* **2001**, *105*, 11073–11079.

[27] J. Lundell, J. Panek, Z. Latajka, *Chem. Phys. Lett.* **2001**, *348*, 147–154.

[28] a) C. L. Ricketts, D. Schröder, C. Alcaraz, J. Roithová, *Chem. Eur. J.* **2008**, *14*, 4779–4783; b) J. Roithová, D. Schröder, *Chem. Listy* **2009**, *103*, 636–640.

[29] J. Roithová, Z. Herman, D. Schröder, H. Schwarz, *Chem. Eur. J.* **2006**, *12*, 2465–2471.

[30] For the related synthesis of $FXeBF_2$, see: a) C. T. Goetschel, K. R. Loos, *J. Am. Chem. Soc.* **1972**, *94*, 3018–3021; see also: b) T. Jayasekharan, T. K. Ghanty, *J. Chem. Phys.* **2006**, *125*, 234106.