

Superelectrophilic chemistry in the gas phase*

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Abstract: Superelectrophilic chemistry in the gas phase is driven by the high intrinsic reactivity of dications. The formation of new doubly charged products proceeds via highly internally excited intermediates. Conditions for the formation of the doubly charged intermediates and a “cooling principle” in the reactivity of dications are explained. The reactivity is demonstrated with several examples.

Keywords: dications; gas phase; ionization; mass spectrometry; superelectrophiles.

INTRODUCTION

Chemistry in the interstellar space or planetary atmospheres is often driven by ionic reactants. The reason stems from the fact that neutral reactants must usually overcome an energy barrier in order to form products (Fig. 1). The energy required for the activation of the reactants can be easily added in the condensed media by increasing the temperature of the reaction mixture. In contrast, such activation is not easily achieved in the above-mentioned environments, which are characterized by low pressures and low temperatures. The potential energy can be, however, supplied by ionization of one of the reactants. The interaction between an ion and a neutral reactant leads to a stabilized intermediate, and the excess energy is stored as an internal energy of the intermediate. This amount of energy is then available for surmounting the energy barrier for the formation of products. Note that contrary to the condensed phase, the excess energy does not dissipate to the media, if the reactants are isolated in the highly diluted gas phase.

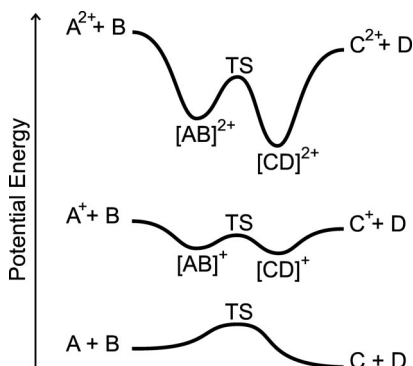


Fig. 1 Schematic representation of potential-energy surfaces for neutral, singly, and doubly ionized reactants.

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As a rule of thumb, we can say that the internal energy of the intermediate gained from the ion–dipole or ion-induced dipole interaction between the reactant partners decreases with increasing molecular size of the ionized reactant. Consequently, the atmospheric chemistry of small ions with only a few atoms is very rich, but, for example, hydrocarbons with five or six carbon atoms react considerably slower than the smaller hydrocarbons [1]. There are certainly exceptions and some larger reactive ions exist, as, for example, naphthylm ion [2]. In general, however, larger molecules better stabilize the positive charge by its delocalization, and the interaction with a neutral partner does not bring a further major stabilization.

As a logical consequence, the reactivity of larger molecules should be further promoted by a second ionization event. Interaction of a dication with a neutral reaction partner brings even more stabilization, and thus more energy is available for the following various reactivity pathways. The reactivity of many dications is, however, limited by a possible electron-transfer event, which can occur as the doubly charged and neutral reactant partners are approaching. Research on dications was for many years concentrated on their stability with respect to charge-separation upon fragmentation and on electron-transfer reactions with neutral reactants. Only recently, the favorable conditions for observing the bond-forming reactions of dications with maintenance of the charge were discovered [3], which opened a door to superelectrophilic chemistry in the gas phase. It should be noted that classical superelectrophilic chemistry in the condensed phase, associated with George A. Olah, was established already many years ago [4]. The concept is based on the same strategy: Reactants are exposed to very acidic conditions, which leads to their double protonation [5]. The so-formed dications are very reactive and can couple with nonactivated, unreactive molecules. In the following section, the principles of gaseous super-electrophilic chemistry will be described, and several examples of how the dicationic reactivity can be employed will be shown.

COOLING PRINCIPLE IN BOND-FORMING REACTIONS OF DICATIONS

Investigation of charge-separation reactions (often referred to as Coulomb explosions) brought a deep insight into the stability of molecular dications and also to their reactivity [6,7]. Charge separations are the most abundant pathways for fragmentations of most small metastable dications [6]. It has been shown, however, that for medium-sized hydrocarbon dications often eliminations of atomic or molecular hydrogens strongly prevail over the charge-separation processes [8]. For example, metastable toluene dications fragment exclusively via the eliminations of H_2 molecules [9]. The potential energy surface for the rearrangements and fragmentations of the toluene dication shows that dehydrogenation leading to the cycloheptatrienylidene dication requires only 1.2 eV of internal energy (Fig. 2).

The potential energy surface of toluene dication has been experimentally explored also from the side of the fragmentation products. The $C_7H_6^{2+}$ dication generated by dissociative electron ionization of toluene was reacted with D_2 . While the adduct $C_7H_6D_2^{2+}$ was not detected, a clear hydrogen scrambling with deuterium atoms was observed (inset in Fig. 2). The detected products $C_7H_5D^{2+}$ and $C_7H_4D_2^{2+}$ demonstrate that a doubly charged intermediate $C_7H_6D_2^{2+}$ was actually formed and underwent a series of rearrangements during which the hydrogen atoms were scrambled. The internal energy of the intermediate was, however, larger (or equal) to the dissociation limit, and therefore the reaction was terminated by a backward elimination of H_2 , HD, or D_2 .

The evidence for the formation of doubly charged intermediates in the reaction of $C_7H_6^{2+}$ with D_2 stimulated further experiments. The $C_7H_6^{2+}$ dication was reacted with acetylene [3]. Next to the products of electron and proton transfers, the doubly charged products $C_9H_6^{2+}$ and $C_9H_7^{2+}$ were indeed observed. The reaction of the perdeuterated dication $C_7D_6^{2+}$ and acetylene revealed again a complete scrambling of H and D atoms in the products, which suggested a similar mechanistic rationale as given above: The reactants $C_7H_6^{2+}$ and C_2H_2 form an intermediate $C_9H_8^{2+}$ with a life time sufficient for a series of rearrangements and the reaction ends with the elimination of either atomic or molecular hydrogen [10].

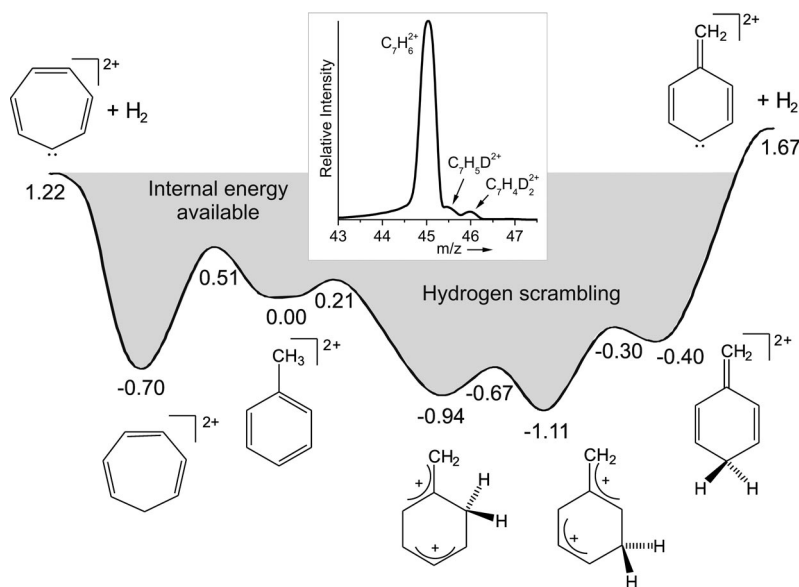


Fig. 2 Potential-energy surface for dehydrogenation of dications generated from toluene and cycloheptatriene calculated at the level B3LYP/6-311+G(2d,p) of theory. The inset shows the H/D exchange in the reaction of $C_7H_6^{2+}$ with D_2 and the gray filling depicts the internal energy available to the reactants. Energies are given in eV.

Analogous mechanisms were later observed in many other bond-forming reactions of medium-sized hydrocarbon dications with acetylene [3], benzene [11], or methane [12,13]. This general reactivity pattern can be formulated as a “cooling principle” (Fig. 3). Doubly charged intermediates formed in *thermal* interactions of molecular dications and neutral molecules contain large internal energy. These “hot” intermediates can be “cooled” by “evaporation” of a small molecule or an atom and thus form new doubly charged products. The elimination of a small molecule/atom can even occur several times until a doubly charged product with sufficiently low internal energy is formed [12]. The competing electron transfer between the reactants is suppressed, if the dissociation pathway for the elimination of a neutral fragment is lying lower in energy than the Coulomb barrier [14] for the charge separation. On the other hand, the electron-transfer channel can be enhanced by increasing the collision energy of the reactant partners, which leads to a shorter interaction time of the reactants and thus suppression of the formation of the intermediate.

This concept is not only limited to the reactions of hydrocarbon dications, but can be also found for other dications. For example, in the reaction of CO_2^{2+} with CO_2 , a “hot” intermediate $C_2O_4^{2+}$ is formed, the cooling step is accomplished by the elimination of an oxygen atom, and, finally, the dicationic product $C_2O_3^{2+}$ can be observed [15]. In comparison to other dications, however, the bond-forming reactions of hydrocarbon dications are more often reported. The reasons stem from the possibility of H or H_2 eliminations, which represents a convenient “cooling” channel and a possible relevance of such reactions for the chemistry of hydrocarbons in planetary atmospheres or interstellar space.

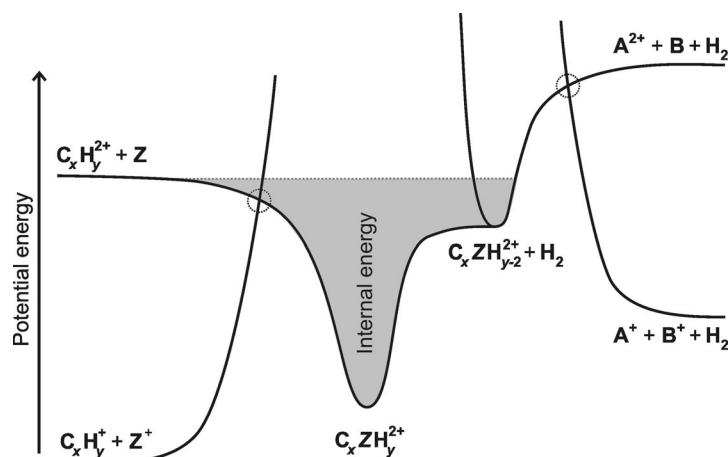


Fig. 3 Cooling principle in the thermal reactions of hydrocarbon dications with neutral molecules. Dotted circles point out surface crossings for the charge-transfer reactions, and at the same time the so-called Coulomb barriers. $A^{2+/+}$ and $B^{0/+}$ are arbitrary fragments of $C_xZH_{y-2}^{2+}$.

BOND-FORMING REACTIONS OF HYDROCARBON DICATIONS IN THE ATMOSPHERE OF TITAN

The atmosphere of Titan contains a large number of hydrocarbon ions. The current models of reactivity can nicely explain the growth of hydrocarbons up to six carbon atoms [16], but the formation of most of the larger hydrocarbons under the conditions of the atmosphere remains so far unexplained. As outlined in the Introduction, the reactivity of dications can provide a possible explanation. In order to show their relevance, the medium-sized hydrocarbons $C_xH_y^{2+}$ ($x = 7-11$, $y = 6-12$) were reacted with methane (after nitrogen, the second most abundant gas in the atmosphere of Titan). All of the studied reactions led to the growing of the dications via “hot” intermediates $C_{x+1}H_{y+4}^{2+}$, which eliminated one or two H_2 molecules to yield the observed products [12].

The mechanism of a model reaction between $C_7H_6^{2+}$ and CH_4 perfectly follows the “cooling principle” [17]. The reactant partners form an intermediate, which bears more than 1.5 eV of internal energy (3^{2+} in Fig. 4a). This amount of energy is sufficient for many rearrangements, which are terminated by elimination of H_2 . The suggested product 6^{2+} still contains an internal energy of 1.3 eV, and therefore even a second elimination of H_2 is observed to some extent. Other possible reaction pathways are electron transfer, proton transfer from the dication to methane, and a formal hydride transfer from methane to the dication. All these channels are associated with Coulomb barriers (CB in Fig. 4a) presumably much larger than the energy barriers for the rearrangements and dehydrogenation of the $C_8H_{10}^{2+}$ intermediate. The only effectively competing channel is hydride transfer to $C_7H_7^+ + CH_3^+$. In the experiment with perdeuterated methane, it has been shown that not only dicationic products, but also products of the hydride transfer show substantial scrambling of hydrogen atoms. This finding demonstrates that the hydride transfer also leads via formation of the $C_8H_{10}^{2+}$ intermediate.

Increasing the collision energy between the reactants $C_7H_6^{2+}$ and CH_4 proceeds to a suppression of the formation of $C_8H_x^{2+}$ products, and instead the products of the hydride transfer, $C_7H_7^+$ and CH_3^+ , start to dominate. The labeling experiments also show that the scrambling of hydrogen atoms in the products of the hydride transfer decreases with increasing collision energy. Both findings demonstrate that the formation of the $C_8H_{10}^{2+}$ intermediate and/or its life time drop with increasing collision energy. Similar effect is found for the internal energy of the reactants. The dications are usually generated by electron ionization, which leads to ions with an undetermined internal energy. The effect of the internal energy can be followed, if dications are generated by photoionization with synchrotron radiation (see

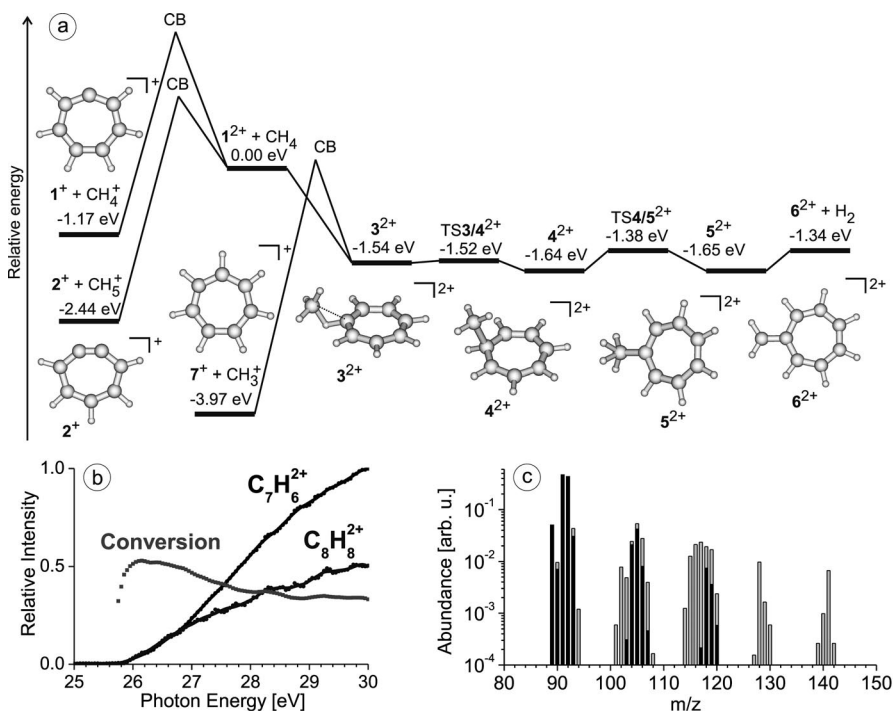


Fig. 4 (a) Potential-energy surface for the reaction of $C_7H_6^{2+}$ with methane calculated at the B3LYP/6-311+G(2d,p) level of theory; CB stands for a Coulomb barrier. (b) Monitoring of the dependence of the $C_8H_8^{2+}$ product from the $C_7H_6^{2+} + CH_4$ reaction on the photon energy used for generation of $C_7H_6^{2+}$ by dissociative photoionization of toluene. The gray curve shows the conversion ($I(C_8H_8^{2+})/(I(C_7H_6^{2+}) + \sum I(\text{fragment}))$). (c) Result of a kinetic modeling of hydrocarbon growth in the reaction with methane. Reactions were initiated by singly charged ions $C_7H_x^+$ (in black) or both, singly and doubly charged ions $C_7H_x^+/C_7H_x^{2+}$ ions (in gray) generated by electron ionization of toluene.

Fig. 4b). The photons used for the ionization determine the largest possible energy available to the system. Such an experiment with $C_7H_6^{2+}$ shows that the highest yield of the bond-forming product $C_8H_8^{2+}$ is achieved at the lowest internal energy of the reactants.

The conditions of very low collision energy and very low internal energy will certainly be fulfilled in the atmosphere of Titan, and therefore the bond-forming reactions of dications can be an interesting mechanistic variant. As to the probability of the formation of dications, the atmosphere of Titan is exposed to energetic electrons from Saturn's magnetosphere, which can transfer large energies to the present molecules [18], or a sequential ionization of molecules to singly charged ions and then to doubly charged ions can be proposed. The second ionization energies of hydrocarbon molecules decrease with their increasing molecular size. The second ionization energy of toluene (C_7H_8) amounts to 14.8 ± 0.1 eV [19]; in comparison, the ionization energy of N_2 amounts to 15.58 eV [20]. The possible relevance of the reactions of dications is shown in Fig. 4c. A simple kinetic modeling of reactions of singly and doubly charged cations generated from toluene with methane shows how the dicationic reactivity can enrich the spectrum of products and prolong the chain growth (details can be found in ref. [12]).

BOND-FORMING REACTIONS OF DICATIONS LEADING TO NEW RARE-GAS SPECIES

Another interesting example of superelectrophilic chemistry in the gas phase represents reactivity of the small dication SiF_3^{2+} . This dication is specially designed for efficient bond-forming reactions, because it is a radical and therefore it can be expected that a fluorine atom could be easily lost in a cooling process of a potential intermediate. The reactivity of SiF_3^{2+} was first probed in interaction with nitrogen molecules at nominally zero collision energy (Fig. 5a) [21]. The doubly charged intermediate $\text{SiF}_3\text{N}_2^{2+}$ lies 3.14 eV lower in energy than the reactants (Fig. 5b). As predicted, the intermediate is cooled by expulsion of a fluorine atom, which leads to $\text{SiF}_2\text{N}_2^{2+}$ as the dominant product of the reaction. The major competing pathway corresponds to electron transfer and is exothermic by 7.18 eV. Crossing of the potential energy curves corresponding to the ion-induced dipole interaction of the reactants and Coulomb repulsion between the singly charged products appears at a distance of ca. 2.7 Å, which is according to the reaction-window theory [22] favorable for electron transfer. The reaction of SiF_3^{2+} with N_2 thus demonstrates that bond-forming reactivity of dications can prevail even if electron transfer for given reaction partners is viable.

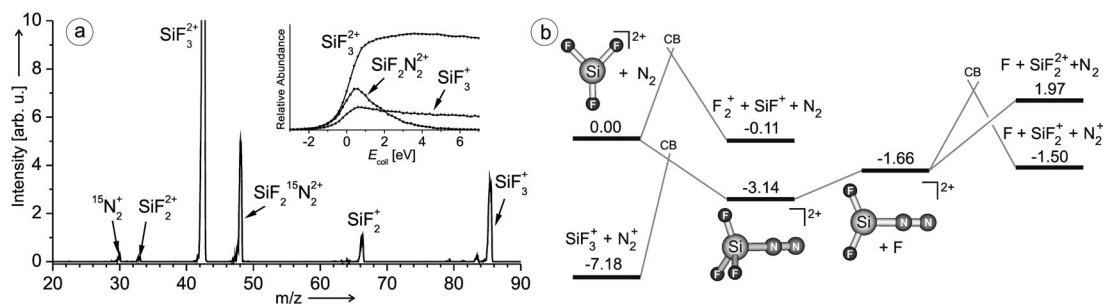


Fig. 5 (a) Mass spectrum of the products from the reaction $\text{SiF}_3^{2+} + \text{N}_2$ (the intensity of the parent ion is normalized to 100); the inset shows the abundance of the parent ions and yields of the major products as a function of collision energy. (b) Potential-energy surface associated with the reaction $\text{SiF}_3^{2+} + \text{N}_2$ calculated at the level B3LYP/6-311+G(2d,p) of theory; energies are given in eV.

The SiF_3^{2+} dication can also activate rare gases [23]. The reaction with argon proceeds very similarly to that with nitrogen (Fig. 6). The intermediate $\text{SiF}_3\text{Ar}^{2+}$ is formed with 2.28 eV of internal energy (inset in Fig. 6). The elimination of a fluorine atom yields a dominant product $\text{SiF}_2\text{Ar}^{2+}$, which represents the first experimentally prepared species with a covalent bond between argon and silicon. The competing electron transfer is again suppressed at low collision energies. The reaction proceeds also with neon, but the energy gain from the formation of the doubly charged intermediate $\text{SiF}_3\text{Ne}^{2+}$ is much smaller and the formation of $\text{SiF}_2\text{Ne}^{2+}$ is an endothermic process. Accordingly, the yield of $\text{SiF}_2\text{Ne}^{2+}$ is very small (inset in Fig. 6).

In comparison with superelectrophilic chemistry in the gas phase and in the condensed phase, we can say that the double ionization always serves as an activation event, which promotes formation of unusual intermediates. However, the subsequent “cooling” step proceeding in the gas phase is not necessary in the condensed phase, because the excess of the internal energy is dissipated to the medium. Experiments in the gas phase, which are conducted at a higher pressure, also allow a collisional thermalization of the “hot” intermediates as it happens in the condensed phase and can therefore be considered as borderline cases between the gas- and condensed-phase superelectrophilic chemistry. As an example, recent preparations of rare-gas species BaRg^{2+} from the reaction of Ba^{2+} with Rg (Rg = He, Ar, Kr, Xe) in a helium bath can be named [24].

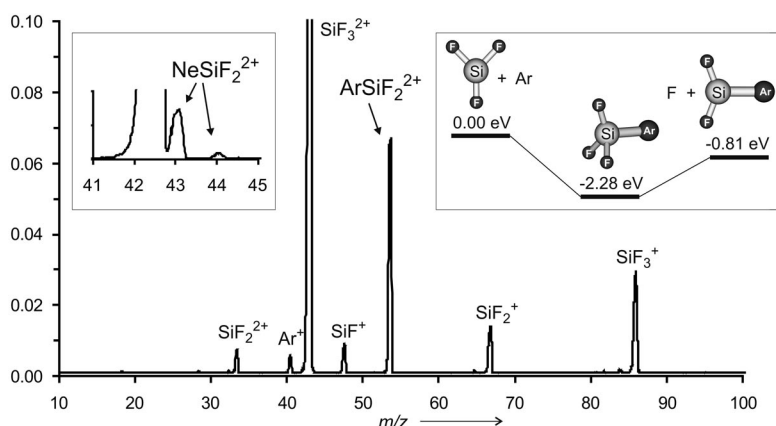


Fig. 6 Mass spectrum of the products from the reaction $\text{SiF}_3^{2+} + \text{Ar}$ (the intensity of the parent ion is normalized to 1); the right inset shows the potential-energy surface associated with the formation of $\text{SiF}_2\text{Ar}^{2+}$ calculated at the level B3LYP/6-311+G(2d,p) of theory, and the left inset shows the signals of the neon analog $\text{SiF}_2\text{Ne}^{2+}$.

CONCLUSION

Our knowledge of the intrinsic properties of dications has grown tremendously during the last decade. From an initial situation, in which mostly electron-transfer and charge-separation processes of these very energetic species were studied, we have achieved a point at which dications are employed as well-behaved reagents in designed reactions in the gas phase. The key conditions in the bond-forming reactions of dications with neutral molecules consist (i) in keeping the collision energy of the reaction partners low enough in order to allow formation of doubly charged intermediates and (ii) in the existence of a suitable “cooling process” for the intermediate, i.e., a low-energy pathway for elimination of an atom or a molecule from the intermediate. This knowledge provides exciting perspectives for super-electrophilic chemistry in the gas phase. Dications, due to their superelectrophilicity, are capable to activate otherwise unreactive substrates such as methane. Moreover, several new covalently bound rare-gas species were prepared via dications [25] and we may expect other unusual species in future.

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