

# Competition of Proton and Electron Transfers in Gas-Phase Reactions of Hydrogen-Containing Dications $\text{CHX}^{2+}$ ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) with Atoms, Nonpolar and Polar Molecules

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*Dedicated, with admiration, to George A. Olah*

**Abstract:** The competition between proton and electron transfer in reactions of mass-selected dications  $\text{CHX}^{2+}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$ ) with rare gas atoms (Ne, Ar, Kr, and Xe) and selected molecular reagents ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{HCl}$ ) is studied in the gas phase. In the ion–molecule reactions of  $\text{CHX}^{2+}$  dications with atoms and non-

polar molecules, it is the energy balance of electron transfer that acts as the decisive factor: when the exothermicity of electron transfer exceeds

2 eV, this process predominates at the expense of bond-forming proton transfer. In marked contrast, the reactions between these triatomic dications and polar molecules are governed for the benefit of the thermochemically more favored products resulting from proton transfer.

**Keywords:** ab initio calculations • dications • electron transfer • proton transport • superelectrophiles

## Introduction

Small molecular dications represent a challenging research topic for several reasons. They are attractive from fundamental points of view related to questions about characteristic features of bonding relations in dications, their stability with respect to Coulomb explosion,<sup>[1,2]</sup> and their unique electrophilic properties,<sup>[3]</sup> just to mention a few. Furthermore, small gaseous dications represent models for reactive intermediates with superelectrophilic or superacidic features, and several detailed investigations on the reactivity of molecular dications have been conducted recently.<sup>[4]</sup> The bimolecular reactivity of most small dications with neutral molecules or atoms is mostly dominated by electron transfer, because the recombination energies of dications usually greatly exceed the ionization energies of neutrals, such that electron transfer from the neutral reagent to the dication is

often rather exothermic.<sup>[2]</sup> Electron transfer to dications has been studied in some detail, and it is generally accepted that the probability of electron transfer can be described by the so-called reaction-window concept.<sup>[5]</sup> In small, hydrogen-containing dications, however, proton transfer may compete with the electron-transfer process,<sup>[6]</sup> because dications containing hydrogen are evidently also strong Brønsted acids.<sup>[7]</sup> A systematic approach to the investigation of proton transfer from dications, as has been pursued extensively for monocationic species, is severely complicated by the competing occurrence of electron transfer. Nevertheless, proton transfer from molecular dications deserves particular attention, because small hydrogen-containing dications may be regarded as models for reactive intermediates formed in superacidic solutions.<sup>[8]</sup> In the present work, we aim to compare the probability of proton transfer versus that of electron transfer for the triatomic halocarbene dications  $\text{CHX}^{2+}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$ ) with a series of atomic and molecular reagents to probe whether or not some more general guidelines for the competition of proton and electron transfer in the chemistry of gaseous dications can be derived.

## Experimental Section and Computational Details

The experiments were performed with the Berlin tandem SIFT-GIB apparatus,<sup>[9]</sup> which consists of a multifunctional ion source, a selected-ion

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flow tube (SIFT), and a quadrupole–octopole–quadrupole (QOO) unit. In the present study, the QOO part was only used as a regular guided-ion-beam mass spectrometer. For ionization, an additional electron-ionization source, situated directly in front of the QOO unit, was used. The  $\text{CHX}^{2+}$  ( $X = \text{F, Cl, Br, I}$ ) dications were formed by dissociative electron ionization (100 eV) of the respective methyl halide precursor molecules and mass-selected by means of the first quadrupole. The reactions were conducted in an octopole reaction cell at variable collision energies as defined by the voltage applied to the octopole ( $U_{\text{oct}}$ ); the pressure of the collision gas was kept in the order of  $10^{-4}$  mbar. Products of the reactions were detected and mass-analyzed by means of the second quadrupole. Throughout these studies Q1 and Q2 were both kept at mass resolutions of  $m/\Delta m \geq 200$ , ensuring proper mass selection and permitting the analysis of ions with a different number of hydrogen atoms, that is,  $\text{CX}^{2+}$ ,  $\text{CHX}^{2+}$ , and  $\text{CH}_2\text{X}^{2+}$ . By and large, the dication reactions discussed here were found to be only modestly dependent on the collision energy (see below). As we are more concerned with a general study here, we refrain from a detailed discussion of the energy dependence. The branching ratios between proton and electron transfer given below are derived as averages from separate mass spectra accumulated at  $U_{\text{oct}} = 0, 16$  and  $33.5$  eV, to achieve better signal-to-noise ratios. Data acquisition was carried out by using Merlin Automation Software (ABB Extrel). Usually, 100–300 scans were accumulated for a single spectrum, and three to seven spectra were recorded for a given reaction to minimize the experimental error. The intensity of a signal ( $I$ ) was determined by integration of the central part of the corresponding peak to avoid mass overlaps and to increase accuracy simultaneously. For Kr and Xe, which are composed of several stable isotopes, the intensities were determined for the ion products  $^{86}\text{Kr}^+$ ,  $^{86}\text{KrH}^+$ ,  $^{134}\text{Xe}^+$ ,  $^{134}\text{XeH}^+$ ,  $^{136}\text{Xe}^+$ , and  $^{136}\text{XeH}^+$ .

It has to be noted that the mass-selected  $\text{CH}^{2+}$  reactant beam ( $m/z$  70) contained an isobaric impurity of  $\text{C}_3\text{H}_{10}^+$  due to hydrocarbon contaminants present as a background in the vacuum system. Likewise, the reactant beam of  $\text{CH}^{2+}$  ( $m/z$  16) may contain isobaric impurities of  $\text{O}^+$  and  $\text{O}_2^{2+}$ , potentially formed from residual air, although no evidence of the two latter ions was obtained.

All calculations were performed with a Gaussian 03 suite<sup>[10]</sup> using a coupled-cluster method CCSD(T)<sup>[11]</sup> in conjunction with a 6-311+G-(3df,3pd) triple-zeta basis set.<sup>[12]</sup> For all optimized structures, a frequency analysis at the same level of theory allows to assign the structures as genuine minima and to calculate the zero-point vibrational energies (ZPVEs). Relative energies ( $E_{\text{rel}}$ ) are given for 0 K, and thus include the ZPVEs. To determine energy balances for the reactions under study the experimentally known ionization energies and proton affinities of the rare gases (Ne, Ar, Kr, and Xe) and molecules ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{HCl}$ ) were employed.<sup>[13]</sup>

## Results and Discussion

**Structures and stability of the  $\text{CHX}^{2+}$  dications?** Detailed computational studies of the structure and reactivity of the  $\text{CHCl}^{2+}$  dication have been reported previously.<sup>[14]</sup>  $\text{CHCl}^{2+}$  can exist in two isomeric forms, with the hydrogen atom bonded either to the carbon ( $\text{H-C-Cl}^{2+}$ ) or to the chlorine atom ( $\text{C-Cl-H}^{2+}$ ). Although the former isomer is more stable by 3 eV, the less stable tautomer  $\text{C-Cl-H}^{2+}$  is formed in considerable amounts upon dissociative electron ionization of  $\text{CH}_3\text{Cl}$ . In contrast, the population and consequently the role of excited triplet states of either  $\text{H-C-Cl}^{2+}$  or  $\text{C-Cl-H}^{2+}$  were found to be negligible; the major reason is that there is a big energy gap between the singlet and the excited triplet states. The excited triplet state of  $\text{H-C-Cl}^{2+}$  lies 4.1 eV above the corresponding singlet ground state, and the

triplet state of  $\text{C-Cl-H}^{2+}$  is 1.9 eV higher in energy than the singlet state  $\text{C-Cl-H}^{2+}$ .<sup>[14a]</sup>

The CCSD(T) calculations reveal that two isomers, linear  $\text{H-C-X}^{2+}$  and bent  $\text{C-X-H}^{2+}$ , exist for  $X = \text{Cl, Br, and I}$  (Table 1). In contrast, the  $\text{C-F-H}^{2+}$  dication is unstable,<sup>[15]</sup>

Table 1. Relative energies ( $E_{\text{rel}}$ ) and structural parameters of CCSD(T)-optimized structures of  $\text{CHX}^{2+}$  dications. Energies are given at 0 K (including zero-point vibrational energy) and relative to the most stable isomer of the given derivative of  $\text{CHX}^{2+}$ .

$\text{CHX}^{2+}$	State	$E_{\text{rel}}$ [eV]	$R_{\text{C-X}}$ [Å]	$R_{\text{C-H}}/R_{\text{X-H}}$ [Å]	$\alpha$ [°]
$\text{H-C-F}^{2+[\text{a}]}$	$^1\text{A}_1$	0.00	1.123	1.202	180.0
$\text{C-F-H}^{2+}$	$^3\text{A}'$	5.42	1.296	1.075	124.5
$\text{H-C-Cl}^{2+}$	$^1\text{A}_1$	0.00	1.472	1.130	180.0
$\text{H-C-Cl}^{2+}$	$^3\text{A}'$	4.09	1.703	1.129	125.8
$\text{C-Cl-H}^{2+}$	$^1\text{A}'$	3.00	1.727	1.381	94.4
$\text{C-Cl-H}^{2+}$	$^3\text{A}'$	4.93	1.617	1.379	100.9
$\text{H-C-Br}^{2+}$	$^1\text{A}_1$	0.00	1.626	1.120	180.0
$\text{H-C-Br}^{2+}$	$^3\text{A}''$	3.66	1.913	1.124	129.7
$\text{C-Br-H}^{2+}$	$^1\text{A}'$	2.99	1.895	1.508	89.2
$\text{C-Br-H}^{2+}$	$^3\text{A}'$	4.66	1.784	1.507	97.0
$\text{H-C-I}^{2+}$	$^1\text{A}_1$	0.00	1.831	1.109	180.0
$\text{H-C-I}^{2+}$	$^3\text{A}''$	2.94	2.084	1.114	132.7
$\text{C-I-H}^{2+[\text{a}]}$	$^1\text{A}'$	3.09	2.114	1.675	84.7

[a] The corresponding triplet state is dissociative at the CCSD(T) level.

and all attempts of its localization led to Coulomb explosion into  $\text{CF}^+$  and  $\text{H}^+$ . Furthermore, even the computational localization of minima corresponding to the given isomers does not ensure that these ions can be observed experimentally. As pointed out earlier, such ions can be either thermodynamically stable or metastable, that is, kinetically stabilized.<sup>[2]</sup> For thermodynamically stable ions, all conceivable dissociations are endothermic. Thus, if there is a suitable method for their formation, they should be observable in the gas phase. On the other hand, the kinetically stabilized (metastable) dications have at least one exothermic dissociation pathway. It depends on the height of the corresponding barriers and the internal energy deposited in the ions in the course of their formation, as to whether the dications can be observed under the conditions of the experiment or whether the internal energy content is high enough to surmount the corresponding barriers, thus allowing only the resulting fragments to be observed.

Table 2 lists energy balances for all conceivable unimolecular fragmentations of  $\text{CHX}^{2+}$  ions, that is  $\text{CX}^+ + \text{H}^+$ ,  $\text{CH}^+ + \text{X}^+$ , and  $\text{C}^+ + \text{XH}^+$ . It can be seen that the less stable  $\text{C-X-H}^{2+}$  isomers—if they are accessible at all—are only kinetically stabilized towards Coulomb explosion. The dications  $\text{H-C-F}^{2+}$  and  $\text{H-C-Cl}^{2+}$  are lower in energy, but still metastable with respect to the expulsion of a proton, whereas the dications  $\text{H-C-Br}^{2+}$  and  $\text{H-C-I}^{2+}$  belong to the rather small family of di- and triatomic, thermodynamically stable dications.<sup>[2]</sup>

With regard to the excited states, the energy gap between the singlet ground state (Table 1) and the excited triplet state decreases from the fluorine to the iodine derivatives; note that the triplet state of  $\text{H-C-F}^{2+}$  is dissociative, whereas

Table 2. Reaction energies ( $\Delta_r H$ ) for the fragmentation of  $\text{CHX}^{2+}$  dications into two singly charged ions and adiabatic ionization energies (IE) of the corresponding  $\text{CHX}^+$  monocations calculated at the CCSD(T) level. Energies are given at 0 K (including zero-point vibrational energy); negative values correspond to exothermic fragmentations.

$\text{CHX}^{2+}$	$\text{CX}^+ + \text{H}^+$	$\Delta_r H^{0\text{K}}$ [eV]		IE( $\text{CHX}^+$ ) [eV]
		$\text{CH}^+ + \text{X}^+$	$\text{C}^+ + \text{XH}^+$	
H-C-F <sup>2+</sup>	-4.08	6.32	0.14	19.92
H-C-Cl <sup>2+</sup>	-0.83	2.60	1.24	17.39
C-Cl-H <sup>2+</sup>	-3.82	-0.40	-1.76	17.95
H-C-Br <sup>2+</sup>	0.04	1.69	0.21	16.63
C-Br-H <sup>2+</sup>	-2.96	-1.30	-2.79	17.30
H-C-I <sup>2+</sup>	1.34	1.33	0.65	15.49
C-I-H <sup>2+</sup>	-1.74	1.76	-2.44	16.58

the triplet state of C-F-H<sup>2+</sup> could be localized as a minimum. With regard to the ion–molecule reactions discussed below, it can be concluded that the excited states of the heavier dications have longer lifetimes and are therefore more likely to participate in bimolecular reactions of mass-selected ions.

For a comparison of proton and electron transfer between the dications and neutral reagents, the proton affinities (PAs) of  $\text{CX}^+$  and the ionization energies (IEs) of  $\text{CHX}^+$  play an important role and therefore need to be considered. The PAs correspond to the reaction energy of the dissociation channel given in the first column of Table 2, and the IEs are listed in the last column of Table 2. As expected, the IEs decrease from H-C-F<sup>+</sup> to H-C-I<sup>+</sup>. The largest energy gap between adjacent halogen congeners occurs between IE(H-C-F<sup>+</sup>) and IE(H-C-Cl<sup>+</sup>); for the heavier derivatives, the IEs decrease smoothly. Further, it should be emphasized that the difference between the IEs of the two isomers, H-C-X<sup>+</sup> and C-X-H<sup>+</sup>, is in general quite small (< 1 eV).

**Competition of proton and electron transfer:** As a quantitative measure for the competition between proton and electron transfer in the reactions of  $\text{CHX}^{2+}$  dications with rare gases (Rg), the branching ratios of  $\text{RgH}^+$  and  $\text{Rg}^+$  (Rg = Ne, Ar, Kr, and Xe) are considered. The complementary information obtainable from the  $I_{\text{CX}^+}/(I_{\text{CX}^+}+I_{\text{CHX}^+})$  ratio might be regarded as well; however, it is less reliable, because the latter inevitably includes several other contributions: 1) reactions with background gases cannot be prevented completely and may give rise to the same ions and 2) the  $I_{\text{CX}^+}/(I_{\text{CX}^+}+I_{\text{CHX}^+})$  ratio can be significantly affected by dissociative electron transfer, that is, the formation of excited  $\text{CHX}^{2+}$  by means of electron transfer followed by rapid unimolecular or collision-induced fragmentation to  $\text{CX}^+ + \text{H}^+$ .<sup>[16]</sup>

In principle, the ratio between proton and electron transfer can be further influenced by the collision energy of reactant partners  $\text{CHX}^{2+}$  and Rg and indirectly also by the pressure in the collision cell due to the occurrence of consecutive ion–molecule reactions. Figure 1 shows the dependence of the  $\text{ArH}^+$  and  $\text{Ar}^+$  ion yields in the reaction of  $\text{CHCl}^{2+}$  with Ar as a function of the potential applied to the octo-

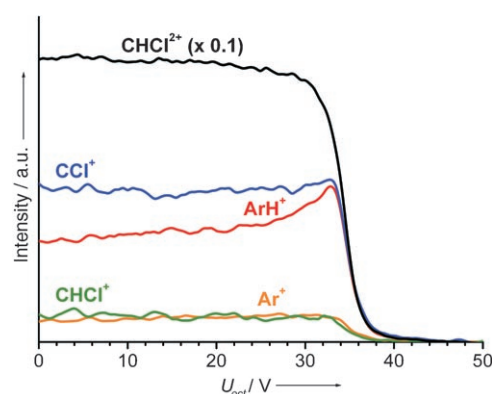


Figure 1. Relative abundance of  $\text{ArH}^+$  (red),  $\text{Ar}^+$  (orange),  $\text{CCl}^+$  (blue), and  $\text{CHCl}^+$  (green) in the reaction of  $\text{CHCl}^{2+}$  (relative intensity divided by ten, solid line) with Ar as a function of the potential of the octopole-collision cell ( $U_{\text{oct}}$ ).

pole collision cell ( $U_{\text{oct}}$ ). Within the energy range studied, the relative yields for the formation of the two product ions show only marginal dependences on the collision energy under the experimental conditions applied.<sup>[6a]</sup> This insensitivity is most likely due to 1) the impulsive mechanism<sup>[17]</sup> of electron and proton transfer operative in reactions of dications and 2) the considerable exothermicities associated with the processes studied here (see below). To probe the possible involvement of secondary reactions, the rare-gas pressure was varied in the  $10^{-4}$  mbar regime, but no significant changes in reactivity were observed under these conditions.

The branching ratios  $I_{\text{RgH}^+}/(I_{\text{RgH}^+}+I_{\text{Rg}^+})$  for the ion–molecule reactions between different  $\text{CHX}^{2+}$  dications and various rare gases are given in Table 3. The relative probability

Table 3. Normalized branching ratios of reaction products  $\text{RgH}^+$  defined as  $X(\text{RgH}^+) = I_{\text{RgH}^+}/(I_{\text{RgH}^+}+I_{\text{Rg}^+})$  for Rg = Ne, Ar, Kr, and Xe, in the reactions of  $\text{CHX}^{2+}$  (X = F, Cl, Br, and I).

	$X(\text{NeH}^+)$	$X(\text{ArH}^+)$	$X(\text{KrH}^+)$	$X(\text{XeH}^+)$
$\text{CHF}^{2+}$	– <sup>[a]</sup>	$0.06 \pm 0.02$	$0.13 \pm 0.05$	$0.06 \pm 0.03$
$\text{CHCl}^{2+}$	$0.98 \pm 0.02$	$0.83 \pm 0.01$	$0.13 \pm 0.01$	$0.04 \pm 0.01$
$\text{CHBr}^{2+}$	$0.99 \pm 0.01$	$0.94 \pm 0.01$	$0.18 \pm 0.04$	$0.02 \pm 0.01$
$\text{CHI}^{2+}$	$0.97 \pm 0.03$	– <sup>[b]</sup>	$0.34 \pm 0.02$	$0.06 \pm 0.01$

[a] Only traces of  $\text{NeH}^+$  were observed; quantification was impossible. [b] Not determined due to interfering fragments originating from isobaric  $\text{C}_5\text{H}_{10}^+$ , which was coselected together with  $\text{CHI}^{2+}$ .

of electron transfer can be estimated using the reaction-window concept based on the Landau–Zener formalism.<sup>[5]</sup> Briefly, this concept suggests that an electron-transfer process is favored, when the overall exothermicity ( $\Delta E_{\text{ET}}$ ) lies in an “energy window” of 2–6 eV. Such a widely applicable approximation including a corresponding range in values of  $\Delta E_{\text{PT}}$  has not yet been derived for proton transfer between molecular dications and neutral collision partners.<sup>[18]</sup>

The dication with the lightest halogen,  $\text{CHF}^{2+}$ , has a negative proton affinity, which suggests that it should be a powerful protonation agent. However, in the reaction with Ne, in which electron transfer is an endothermic process

Table 4. Exothermicities for electron ( $\Delta IE$ ) and proton transfer ( $\Delta PA$ ) between the H-C-X<sup>2+</sup> dication (X=F, Cl, Br, and I) and rare gases (Ne, Ar, Kr, and Xe).  $\Delta IE$  refers to  $IE(CHX^+) - IE(Rg)$  and  $\Delta PA$  corresponds to  $PA(Rg) - PA(CX^+)$ .

	Ne		Ar		Kr		Xe	
	$\Delta IE$ [eV]	$\Delta PA$ [eV]	$\Delta IE$ [eV]	$\Delta PA$ [eV]	$\Delta IE$ [eV]	$\Delta PA$ [eV]	$\Delta IE$ [eV]	$\Delta PA$ [eV]
CHF <sup>2+</sup>	-1.64	6.14	4.16	7.91	5.92	8.48	7.79	9.26
CHCl <sup>2+</sup>	-4.17	2.89	1.63	4.66	3.39	5.23	5.26	6.01
CHBr <sup>2+</sup>	-4.93	2.02	0.87	3.79	2.63	4.36	4.50	5.14
CHI <sup>2+</sup>	-6.07	0.72	-0.27	2.49	1.49	3.06	3.36	3.84

(Table 4) and thus predominant formation of NeH<sup>+</sup> is expected, only traces of NeH<sup>+</sup> could be detected; instead, a reaction with background water was observed. With Ar, Kr, and Xe, electron transfer to CHF<sup>2+</sup> dominates and the fraction of proton transfer only amounts to about 10%. These observations suggest that once the electron transfer falls in the reaction window, the proton-transfer reaction can no longer compete, even though it would lead to energetically more-favored products. This phenomenon points to the existence of a “barrier” in the proton-transfer process, and its origin has been precisely analyzed and described in detail.<sup>[19,20]</sup> In this respect, it is also worth mentioning that no reactions with background gases, water in particular, were detected in the reactions of CHF<sup>2+</sup> and Ar, Kr, and Xe, which implies that the proton transfer between CHF<sup>2+</sup> and Ne is most likely affected by a substantial energy barrier. However, a reaction between CHF<sup>2+</sup> and H<sub>2</sub>O (see below) is observed although water is present only as a residual gas.

The reactivity of the CHCl<sup>2+</sup> dication perfectly follows the outlined scenario. In the reaction with Ne, electron transfer is endothermic and accordingly only formation of NeH<sup>+</sup> is observed. Electron transfer with Ar is exothermic by 1.63 eV, but the exothermicity lies below the favored reaction window of 2–6 eV. In agreement, proton transfer still dominates and comprises 83% of the observed reactivity. For Kr and Xe, the exothermicities of electron transfer to CHCl<sup>2+</sup> fall into the favored energy range and, again, the fraction of the even more exothermic proton transfer decreases to 13% and 4%, most probably as a result of an intrinsic barrier.

Fully consistent with the relatively close ionization energies of CHCl<sup>+</sup> and CHBr<sup>+</sup>, 17.39 and 16.63 eV, respectively, as predicted by theory, similar reactivities of CHCl<sup>2+</sup> and CHBr<sup>2+</sup> are found in the experiment. Thus, in the reaction of CHBr<sup>2+</sup> with Ne, only proton transfer is detected. In the reaction with Ar, proton transfer forms an even larger fraction (94%). We note in passing that the small abundance of electron transfer between CHBr<sup>2+</sup> and Ar points to a small population of excited states in the dication. Electron transfer is again favored in the interaction of CHBr<sup>2+</sup> with Kr and Xe, for which proton transfer comprises only 18% and 2%, respectively.

The results obtained for the reactions of CHI<sup>2+</sup> further confirm the trends described above. In the reaction with Ne,

formation of NeH<sup>+</sup> is observed exclusively. Electron and proton transfer with Ar were not studied, because of interferences with fragments originating from the presence of an isobaric C<sub>5</sub>H<sub>10</sub><sup>+</sup> impurity. Nevertheless, electron transfer to CHI<sup>2+</sup> is endothermic with argon, so that only proton transfer is expected. The exothermicity of 1.49 eV for electron

transfer between CHI<sup>2+</sup> and Kr is below the reaction window of 2–6 eV.<sup>[21]</sup> However, the competition between proton and electron transfer turns out to be in favor of electron transfer (66%). Likewise, the reaction with Xe is, once more, dominated by electron transfer (94%).

In summary, even this simplified discussion suggests a rather general trend. For reactions, in which electron transfer between a dication and a rare-gas atom is endothermic or exothermic by less than 2 eV, proton transfer represents the main route of reaction. As soon as the exothermicity of electron transfer exceeds 2 eV, this channel predominates and proton transfer is suppressed, disregarding the actual exothermicity of the latter process. If the more energetic isomers and states are also included in the discussion, small numerical deviations from the above-mentioned trend can be accounted for, but no new qualitative features evolve. For example, electron transfer observed in the reaction of CHCl<sup>2+</sup> with Ar can be explained by the population of the more energetic isomer C-Cl-H<sup>2+</sup>.<sup>[14]</sup>

If this trend holds true in general, reactive intermediates proposed to be involved in important superacid-catalyzed reactions,<sup>[22]</sup> for example, NO<sub>2</sub>H<sup>+</sup> or CH<sub>3</sub>COH<sup>2+</sup>,<sup>[8]</sup> would be expected to undergo mostly electron transfer instead of the desired and actually observed proton transfer. Thus, the question arises: what is the origin of the major difference between interactions of CHX<sup>2+</sup> with rare gases and the dominant proton transfer in superacid-catalyzed reactions in solution? An evident and major difference is certainly the lack of any solvation in the gas-phase studies. However, the clear trend observed here may also reflect some intrinsic properties of the systems under study. With respect to the problem at hand, 1) the energy balances between proton and electron transfer can be different, and 2) the interactions of “bare” dications can fundamentally differ for neutral molecules versus atoms and may also be affected by other molecular features.

With regard to the energy balances, the calculated ionization energy of NO<sub>2</sub>H<sup>+</sup> is 19.1 eV,<sup>[8d]</sup> while that of CH<sub>3</sub>COH<sup>+</sup> is 15.4 eV;<sup>[23]</sup> the relevant proton affinities of NO<sub>2</sub><sup>+</sup> and CH<sub>3</sub>CO<sup>+</sup> are -3.5<sup>[8d]</sup> and -1.9 eV,<sup>[8b]</sup> respectively. These values are close to those calculated for CHF<sup>2+</sup> and CHI<sup>2+</sup>, and thus the halocarbene dications are expected to bear similar reactivity patterns, if only thermochemical aspects matter. The other difference (except solvation) may be due to the intrinsic character of the dication's interaction with

molecules, which can have significantly larger polarizabilities and even permanent dipole moments both leading to stronger interactions between the reaction partners and thus inter alia to significantly extended lifetimes of the initially formed encounter complexes between the dication and the neutral reagent. With an increasing lifetime of the reactant complex, the reaction can experience a switch from kinetic to thermodynamic control. In this study, this hypothesis is probed by investigating the reactions of mass-selected  $\text{CHX}^{2+}$  dications with a set of molecules, that is,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{HCl}$  (Table 5 and Table 6).

The reactions of  $\text{CHX}^{2+}$  with  $\text{N}_2$  can be compared to those with Ar, because  $\text{N}_2$  and Ar have similar ionization energies (15.58 and 15.76 eV, respectively) and also similar polarizabilities ( $1.74 \times 10^{-24}$  and  $1.64 \times 10^{-24}$  cm<sup>3</sup>, respectively).<sup>[24]</sup> The major difference that remains is a higher proton affinity of  $\text{N}_2$  compared to Ar (5.12 vs. 3.83 eV) and the fact that a diatomic molecule rather than an atom is involved. Inspection of Tables 3 and 5 reveals that the ratios of proton and electron transfer are qualitatively similar for Ar and  $\text{N}_2$ .  $\text{CHF}^{2+}$  gives only a little amount of proton transfer (6%

The situation changes completely, however, once polar molecules are involved.<sup>[25]</sup> Thus, the CO molecule ( $\mu = 0.11$  D) may be compared with Kr as their ionization energies are almost identical (14.01 and 14.00 eV, respectively). The polarity of CO leads to a higher proton affinity of 6.16 eV for protonation at C than that of Kr (4.40 eV), but the difference is comparable to that between  $\text{N}_2$  and Ar. The experimental data (Table 5) show that the relative probability of proton transfer from the dications to CO is significantly larger (2 to 3 times) than that for reactions with Kr. Particularly instructive in this respect is a consideration of  $\text{CHF}^{2+}$ , for which the amount of proton transfer is largest in reaction with CO compared to all neutral reactants discussed so far. This result points towards a fundamental difference in the competition of proton and electron transfer for nonpolar and polar molecules.

Changes in the competition between proton and electron transfer are even more pronounced when the more polar molecules,  $\text{H}_2\text{O}$  ( $\mu = 1.85$  D) and  $\text{HCl}$  ( $\mu = 1.08$  D), are taken as reaction partners. Both molecules can be compared to Xe, because the ionization energies of  $\text{H}_2\text{O}$  and  $\text{HCl}$  (12.62 and 12.74 eV, respectively) are close to that of Xe. Furthermore, the proton affinity of  $\text{HCl}$  (5.77 eV) is similar to that of Xe (5.18 eV), whereas  $\text{H}_2\text{O}$  has a somewhat larger proton affinity (7.16 eV). The experimental results (Table 5) demonstrate that the ratios between proton and electron transfer (ca. 1:1) in the reactions of all  $\text{CHX}^{2+}$  dications with both  $\text{H}_2\text{O}$  and  $\text{HCl}$  are similar. These results are in marked contrast with those obtained for the reactions with Xe, in which proton transfer comprises only about 5% of the reactivity for all  $\text{CHX}^{2+}$  dications. This result implies that the permanent dipole moment plays quite a decisive role in the proton transfer step from hydrogen-

Table 5. Normalized branching ratios of the reaction products  $\text{MH}^+$  defined as  $X(\text{MH}^+) = I_{\text{MH}^+} / (I_{\text{MH}^+} + I_{\text{M}^+})$  for  $\text{M} = \text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{HCl}$ , in the reactions of  $\text{CHX}^{2+}$  ( $\text{X} = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ ).

	$X(\text{N}_2\text{H}^+)$	$X(\text{O}_2\text{H}^+)$	$X(\text{COH}^+)$	$X(\text{H}_3\text{O}^+)$	$X(\text{H}_2\text{Cl}^+)$
$\text{CHF}^{2+}$	$0.16 \pm 0.01$	$0.02 \pm 0.01$	$0.22 \pm 0.01$	$0.56 \pm 0.02$	$0.54 \pm 0.03$
$\text{CHCl}^{2+}$	$0.75 \pm 0.01$	$0.07 \pm 0.01$	$0.39 \pm 0.01$	$0.49 \pm 0.02$	$0.56 \pm 0.01$
$\text{CHBr}^{2+}$	$0.96 \pm 0.01$	$0.06 \pm 0.01$	$0.51 \pm 0.02$	$0.50 \pm 0.03$	$0.38 \pm 0.06$
$\text{CHI}^{2+}$	– <sup>[a]</sup>	– <sup>[a]</sup>	$0.60 \pm 0.01$	$0.53 \pm 0.01$	$0.49 \pm 0.02$

[a] Not determined due to interfering fragments originating from isobaric  $\text{C}_3\text{H}_{10}^+$ , which is coselected together with  $\text{CHI}^{2+}$ .

Table 6. Exothermicities for electron ( $\Delta\text{IE}$ ) and proton transfer ( $\Delta\text{PA}$ ) between the H-C- $\text{X}^{2+}$  dication ( $\text{X} = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ ) and molecules M ( $\text{M} = \text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{HCl}$ ).  $\Delta\text{IE}$  refers to  $\text{IE}(\text{CHX}^+) - \text{IE}(\text{M})$  and  $\Delta\text{PA}$  corresponds to  $\text{PA}(\text{CX}^+) - \text{PA}(\text{M})$ .

	$\text{N}_2$		$\text{O}_2$		$\text{CO}$		$\text{H}_2\text{O}$		$\text{HCl}$	
	$\Delta\text{IE}$ [eV]	$\Delta\text{PA}$ [eV]	$\Delta\text{IE}$ [eV]	$\Delta\text{PA}$ [eV]	$\Delta\text{IE}$ [eV]	$\Delta\text{PA}$ [eV]	$\Delta\text{IE}$ [eV]	$\Delta\text{PA}$ [eV]	$\Delta\text{IE}$ [eV]	$\Delta\text{PA}$ [eV]
$\text{CHF}^{2+}$	4.34	9.20	7.85	8.44	5.91	10.24	7.30	11.24	7.18	9.85
$\text{CHCl}^{2+}$	1.81	5.95	5.32	5.19	3.38	6.99	4.77	7.99	4.65	6.60
$\text{CHBr}^{2+}$	1.05	5.08	4.56	4.32	2.62	6.12	4.01	7.12	3.89	5.73
$\text{CHI}^{2+}$	–0.09	3.78	3.42	3.02	1.48	4.82	2.87	5.82	2.75	4.43

with Ar and 16% with  $\text{N}_2$ ), proton transfer prevails for  $\text{CHCl}^{2+}$  (83% with Ar and 75% with  $\text{N}_2$ ), and  $\text{CHBr}^{2+}$  yields almost exclusively proton-transfer products (94% with Ar and 96% with  $\text{N}_2$ ).

Similarly, the reactions of the dications with  $\text{O}_2$  can be compared with those involving Xe. In this case,  $\text{O}_2$  and Xe have similar ionization energies (12.07 vs. 12.13 eV) and proton affinities (4.36 eV vs. 5.18 eV), but  $\text{O}_2$  has a significantly lower polarizability than Xe ( $1.58 \times 10^{-24}$  and  $4.04 \times 10^{-24}$  cm<sup>3</sup>, respectively). The experimental results are again very similar for both neutral reagents. In both cases, electron transfer predominates and accounts for more than 90% of the reactivity.

Based on these results it is expected that proton transfer would be more efficient with  $\text{H}_2\text{O}$  than with  $\text{HCl}$ , because water has a larger dipole moment; in addition there is also a greater difference in the exothermicities of proton and electron transfer for the reaction with  $\text{H}_2\text{O}$  and with  $\text{HCl}$  (Table 6). However, this trend is only modest; in the case of  $\text{CHCl}^{2+}$  proton transfer is even more efficient with  $\text{HCl}$  than with  $\text{H}_2\text{O}$ . It is supposed that the requirements for the arrangement of the transition structure for proton transfer from  $\text{CHX}^{2+}$  to triatomic  $\text{H}_2\text{O}$  are likely to be larger than those for proton transfer to diatomic  $\text{HCl}$ . Accordingly, the probability of proton transfer to  $\text{H}_2\text{O}$  may be smaller than to  $\text{HCl}$ . Moreover, the internuclear dis-

ces in the transition structure for proton transfer to H<sub>2</sub>O may be smaller than those for proton transfer to HCl, which possibly increases the barrier for proton transfer to H<sub>2</sub>O. The opposite trends of the structural demands on the transition structure on the one hand, and the dipole moments and exothermicities on the other hand can account for leveling out the results for reactions of CHX<sup>2+</sup> with HCl and H<sub>2</sub>O.

In summarizing the findings for the reactivity of CHX<sup>2+</sup> dications, a general rationale for the competition of proton and electron transfer is proposed in Figure 2. Electron trans-

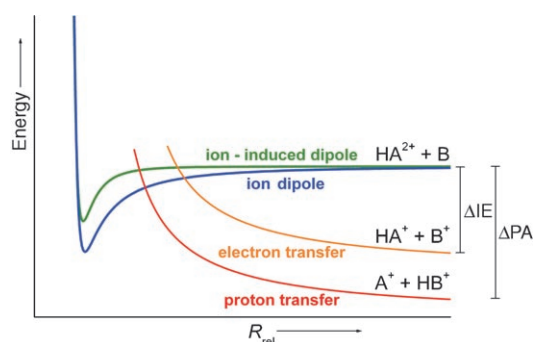


Figure 2. Schematic representation of the interaction between a hydrogen-containing dication HA<sup>2+</sup> with a neutral atom or molecule. The attractive potential between the dication and either a polar molecule (ion-dipole interaction,  $\sim 1/r^{12}-1/r^2$ ), a nonpolar molecule, or an atom (ion-induced-dipole interaction,  $\sim 1/r^{12}-1/r^4$ ) is crossed by repulsive potentials ( $\sim 1/r$ ) of pairs of cations: HA<sup>+</sup>+B<sup>+</sup> (electron transfer) and A<sup>+</sup>+HB<sup>+</sup> (proton transfer).

fer is the process that usually occurs at larger internuclear distances and is not associated with a geometrically well-ordered transition structure. On the other hand, proton transfer requires at least a minimal degree of orientation of the dication and the neutral reactant and is therefore likely to be associated with a relatively tight transition structure. As a consequence, electron transfer is kinetically favored compared to proton transfer; of course, the former must still be associated with an appropriate exothermicity according to the reaction-window concept. The difference between the interaction of a dication with a nonpolar molecule and that with a polar molecule can largely be attributed to the strengths of the attractive forces. In the interaction between an ion and the dipole of a polar molecule, the collision complex gives rise to a deeper energy minimum and the attractive forces operate at relatively larger internuclear distances than for the interaction of an ion with the induced dipole of a nonpolar molecule (or atom). This presumably results in the lowering of the barrier associated with proton transfer. Moreover, a deeper minimum of the encounter complex increases the slope of the attractive potential-energy curve in the regions where the curve intersects with the asymptote of electron transfer; thereby, the probability of electron transfer decreases.<sup>[5]</sup> Accordingly, the probability of the formation and the lifetime of the encounter complex increases for reactions between dications and polar molecules in compari-

son to analogous reactions between dications and nonpolar species. Extended lifetimes then favor thermodynamic control of the reaction and thus shift the branching ratio from the kinetically favored electron transfer to the thermochemically advantageous proton transfer.

## Conclusion

The ratios of proton and electron transfer in the reactions of CHX<sup>2+</sup> dications (X = F, Cl, Br, and I) with rare gases (Ne, Ar, Kr, and Xe) are predominantly determined by the energy balance of electron transfer. If this reaction is endothermic or exothermic by less than 2 eV, proton transfer predominates. When electron transfer is exothermic by more than 2 eV, the delivery of a proton is suppressed and the products of electron transfer are observed preferentially. The results are qualitatively similar for the reactions of the CHX<sup>2+</sup> dications with nonpolar molecules like N<sub>2</sub> or O<sub>2</sub>. However, the situation dramatically changes for the reactions of the dication CHX<sup>2+</sup> with polar molecules such as CO, H<sub>2</sub>O, and HCl, in that proton transfer becomes much more important. As a rationale, it is suggested that the lifetimes of the encounter complexes are significantly enhanced for polar reactants. Longer lifetimes then allow the formation of the thermodynamically favored products of proton transfer, whereas short lifetimes support kinetic control towards preferential electron transfer.

If these considerations are finally extrapolated to the chemistry of superacidic media, it is possible that the occurrence of electron transfer with dications such as NO<sub>2</sub>H<sup>2+</sup> or CH<sub>3</sub>COH<sup>2+</sup> is prevented by the presence of polar molecules in solution, which significantly stabilize the multiply charged species.<sup>[26]</sup> Thus, the effect of solvation on the stability of the dicationic species, which has so far mostly been studied for relatively easily accessible dications (e.g., multiply charged metal cations),<sup>[27]</sup> may be much more important for small, reactive dications, which have been suggested to play a crucial role in superacidic solutions.

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